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## 1. Description of task

The deliverable 3.6 “Development of modelling tools to predict release and transformation of NOAA “ is part of Task 3.6 “Development of modelling tools to predict release and transformation of NOAA”.

The goal of this task is to improve the current stochastic/probabilistic material flow analysis (PMFA) and apply the model algorithms for more realistic modelling of the release (EMPA) and the transportation/transformation kinetics of NOAA in natural and technical environments. By introducing such dynamics into the model our ambition is to run simulations that fully and simultaneously consider (i) time-dependent (ii) conceptual and (iii) parametric uncertainty and variability at different environmental exposure levels. Finally, the objective of this task is to link such probabilistic release and material flow modelling to the most updated knowledge of NOAA fate in natural and technical environments, focusing on short and long-term pollutant transport/transformation kinetics. By feeding such new experimental evidence on NOAA fate and behaviour – instead of lots of assumptive data – into the updated dynamic and stochastic material flow simulations, we aim at pushing risk assessment to a level beyond anything currently known. We will use and further develop an established approach to calculate predicted environmental concentrations (PECs). This stochastic method has been specifically designed to cope with large uncertainty and/or variability in the model input and output. EMPA will develop and parameterize new dynamic modelling approaches to describe release processes from products that feed into the materials flow analysis.

This deliverable report consists of four main parts. The first three parts have already been published as scientific papers and are available to the scientific community.

The first chapter is a review about the way that release data are incorporated into nanomaterials flow modeling. The second chapter presents a modeling of the fate of nanomaterials during waste incineration. In the third chapter the flows of nanomaterials through the recycling process are modeled.

The fourth chapter describes the R codes to calculate environmental exposure (PEC values, predicted environmental concentrations) and environmental toxicity (species sensitivity distributions).

### Literature references:

Caballero-Guzman, A.; Nowack, B. (2016) A critical review of engineered nanomaterial release data: are current data useful for material flow modeling? *Environ. Pollut.* **213**: 502-517.

Walser, T.; Gottschalk, F. (2014) Stochastic fate analysis of engineered nanoparticles in incineration plants. *Journal of Cleaner Production* 80: 241-251.

Caballero-Guzman, A.; Sun, T. Y.; Nowack, B. (2015) Flows of engineered nanomaterials through the recycling process in Switzerland. *Waste Management* 36: 33-43.

## 2. Description of work & main achievements

### 2.1. A critical review of engineered nanomaterial release data: Are current data useful for material flow modeling?

#### Abstract

Material flow analysis (MFA) is a useful tool to predict the flows of engineered nanomaterials (ENM) to the environment. The quantification of release factors is a crucial part of MFA modeling. In the last years an increasing amount of literature on release of ENM from materials and products has been published. The purpose of this review is to analyze the strategies implemented by MFA models to include these release data, in particular to derive transfer coefficients (TC). Our scope was focused on those articles that analyzed the release from applications readily available in the market in settings that resemble average use conditions. Current MFA studies rely to a large extent on extrapolations, authors' assumptions, expert opinions and other informal sources of data to parameterize the models. We were able to qualitatively assess the following aspects of the release literature: (i) the initial characterization of ENM provided, (ii) quantitative information on the mass of ENM released and its characterization, (iii) description of transformation reactions and (iv) assessment of the factors determining release. Although the literature on ENM release is growing, coverage of exposure scenarios is still limited; only 20% of the ENMs used industrially and 36% of the product categories involved have been investigated in release studies and only few relevant release scenarios have been described. Furthermore, the information provided is rather incomplete concerning descriptions and characterizations of ENMs and the released materials. Our results show that both the development of methods to define the TCs and of protocols to enhance assessment of ENM release from nano-applications will contribute to increase the exploitability of the data provided for MFA models. The suggestions we provide in this article will likely contribute to an improved exposure modeling by providing ENM release estimates closer to reality.

#### 2.1.1. Introduction

Nanotechnology research and the production of engineered nanomaterials (ENMs) have grown steadily, worldwide but particularly in developed countries (EC, 2013). Nano-products are increasingly available on the market (FM, 2014). Nanotechnology's applications include traditional products with improved performance, like coatings, paints, and cosmetics, and completely novel products, like next generation medicines, superconductors and high-performance ceramics and composites (FM, 2014). However, there is still some uncertainty about the effects that ENMs can have on organisms and the environment (Wiesner et al., 2006; Nowack and Bucheli, 2007; Klaine et al., 2012; Maynard, 2014), and warnings have been issued about their potential negative effects (Buzea et al., 2007; RIVM, 2015). The sustainable development of nanotechnology will require that the risks associated with ENMs are understood and managed. Risk levels are determined by a combination of exposure to nanomaterials and the hazards associated with them (Holden et al., 2014). Applying risk assessment methodologies and life-cycle concepts has been proposed as a realistic and holistic way of evaluating ENMs (Maynard, 2006; Nowack et al., 2012a). Hazard assessment of pristine nanomaterials is of limited value because they undergo transformations during their life cycle; the released ENM will behave in a different way to the pristine material (Nowack et al., 2012b).

ENMs can be incorporated into the surfaces of applications or into a material's matrix. They can be released from nano-products into the environment throughout their entire life cycle (Bauer et al., 2008; Nowack, et al., 2012a). The life cycle is understood to be the product's lifespan covering production, manufacturing of nano-products, use, and disposal of the nanomaterial and the nano-product. The main limitation facing researchers in the field of exposure assessment is the inability to detect and track ENM in the environment, except in a limited number of cases. There are several reasons for this, including the current low concentrations of ENMs and the complexity of the matrices in which they are found; this complicates the differentiation between natural and engineered nanomaterials (Nowack et al., 2015). Material flow analysis (MFA) models have been developed in order to overcome this gap, providing estimations of ENM concentrations in the environment. The first model to deal with environmental concentration was developed by Boxall et al. (2007). Since then, efforts to improve and develop models have never stopped; for example, they now incorporate dynamic and geographic dimensions (Gottschalk et al., 2009b; Sun et al., 2015a). Frequently, however, for many of their input parameters these models rely on an oversimplification of their assumptions or on data extrapolations. Descriptions of existing exposure models are available in Gottschalk et al. (2013b) and Hendren et al. (2013b).

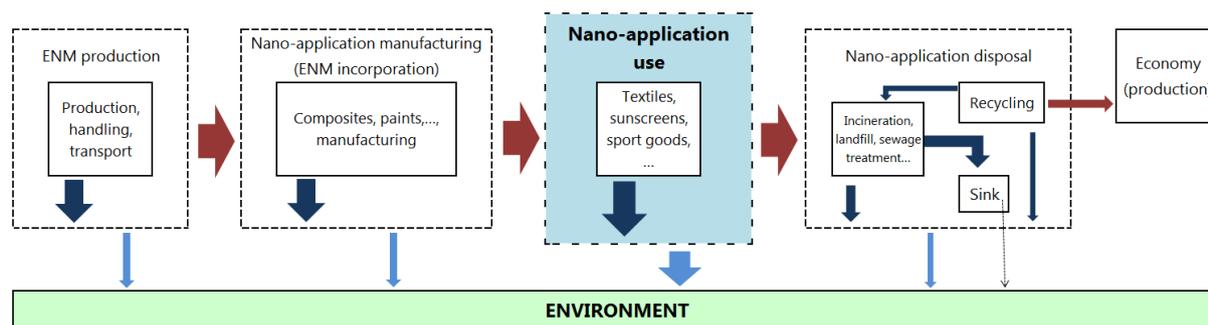
In the never ending process of modeling reality, there is always room for improvement or new developments. One area that has received insufficient treatment in ENM exposure modeling is the release of ENMs themselves. Although there is evermore literature available analyzing ENM release from nano-products, it is very limited when compared to the literature published in other fields of nanomaterial risk assessment (Froggett et al., 2014). The hypothesis for the present study was that the body of literature published in the last few years would provide useful elements with which to improve both the structure of environmental exposure models and their input parameters, particularly concerning the estimation of the transfer coefficients used by such models. The review's main goal was, therefore, to analyze the strategies implemented by MFA exposure models to estimate the ENM environmental concentrations and to evaluate the articles in the ENM release assessment field to determine whether or not their output can be used in MFA models, in particular, for the estimation of the transfer coefficients.

### 2.1.2. Release characteristics

This review defines **ENM release** as the liberation of ENM from its confinement and its subsequent transfer to a particular environment. This confinement may be a technical compartment or the material matrix into which the ENM is incorporated, embedded or contained, and which prevents the ENM mass from entering the natural environment. ENM release can occur at any point during the nanomaterial's life cycle. For example, during the production or manufacturing phase, release might occur during powder handling, storage, or transportation; during the use phase, release might occur during weathering or abrasion (e.g. painted walls); and during disposal, release might occur during any possible waste management activity (e.g. incineration or recycling) (Nowack et al., 2013a).

At the end of its life cycle, a nanomaterial may be stored in a technical or environmental compartment, as its final sink (e.g. landfill or sediments), or it may flow back to another economic production process if a material fraction containing the ENM is used further or recycled (Caballero-Guzman et al., 2015). For most nano-applications, it is expected that the largest likelihood for uncontrolled ENM release will occur during the use phase (**Figure 1**). In reality, ENM are most likely not released as single units, but rather embedded in product fragments such as the polymer of a composite (Froggett et al.,

2014). Therefore, release assessment does not focus only on the ENM particles released as single units, but also in the fragments where they are embedded, or the species they are transformed into.



**Figure 1.** ENM release during its life cycle, from ENM production to the nano-product disposal. The diagram highlights the fact that release may occur in two steps: the first step (dark blue arrows) occurs during the ENM or nano-product handling. The second step (light blue arrows) constitutes the final transfer to the environment. Dashed boxes represent materials or compartments that may impede final release to the environment. The release potential during the use phase may be higher because fewer control measures are adopted during this phase (as represented by the larger spaces between dashes), resulting in a bigger final transfer to the environment (as represented by a thicker light blue arrow). The flow from recycling does not connect to the production or manufacturing boxes to the left because most likely, the ENM entering the recycling system will either be disposed (landfilled or incinerated), or allocated in material fractions (e.g. plastics) used in the production of other type of applications, instead of ENMs or nano-applications (Caballero-Guzman, et al., 2015).

ENMs can be released into technical or environmental compartments (Bystrzejewska-Piotrowska et al., 2009; Gottschalk and Nowack, 2011; Smita et al., 2012; Ging et al., 2014; Yang and Westerhoff, 2014). Technical compartments include production and storage facilities, transport vehicles, shops, houses, offices, swimming pools, waste-management facilities and, in general, any man-made place structure where ENMs and nano-products are stored, used, or processed. Environmental compartments include the atmosphere, soils and sediments, and surface and groundwater.

Release to the environment may be indirect or direct. Indirect transfer occurs in two steps, first to a technical compartment and then to a natural one. Direct transfer occurs in one step, directly into the environment. Technical facilities may apply filtration techniques, thus reducing or eliminating the total transfer of ENMs to the environment (Nowack, et al., 2013a). An example of indirect transfer would be when nano-TiO<sub>2</sub> is released into a pool by a swimmer wearing sunscreen and later transferred to the sewage. An example of direct transfer would be when that swimmer prefers to bath in a river or lake. ENM release to the environment can be intentional or unintentional. Intentional release occurs when ENMs are deliberately deposited in a natural compartment for a specific reason, for example, remediation of water bodies, such as the use of nano-scale zerovalent iron (Mueller et al., 2012). Unintentional release occurs when ENM mass is liberated as a consequence of material handling (Nowack et al., 2014), the normal wear and tear on a nano-product during its life cycle, or simply because it is part of a product whose use implies 100% release, like aerosols or liquid applications.

The **release potential** of ENMs from applications to the environment is determined by both intrinsic and extrinsic factors. *Intrinsic factors* refer to the inherent properties of the

ENMs themselves and how the characteristics of the nano-products they are used in exert some influence on the amounts released (Hansen et al., 2008). *Extrinsic or systemic factors* refer to the characteristics of the system where ENMs and nano-applications are used or processed, including regulation, consumer preferences, economic development, the current state of technology, and others factors.

During production, release will be determined by the manufacturing procedures and the technology employed, the environmental regulations that companies need to abide by and the filtration technology available to avoid release from production facilities to the environment (Nowack, et al., 2013a). System variables that influence release amounts during production include economic and technological development, such as the innovation rate, economic growth, and the market penetration of nano-applications.

During the use phase, release will be determined by how the ENM is incorporated into the nano-product, e.g., suspended in liquids, airborne, surface-bound, or suspended in solids (Hansen et al., 2007). Users' decisions about how goods are used will define the processes a nano-product will be subject to. System variables that might influence the magnitude of release include the characteristics of the environment in which a nano-product is used (e.g. climatic parameters) and economic development (which will influence the demand for nano-products).

During disposal, ENM release will be determined by the waste-management regulations and technologies employed (Bystrzejewska-Piotrowska, et al., 2009; Musee, 2011; Asmatulu et al., 2012; Bouillard et al., 2013). Regulations will influence the processes nano-products are subject to (e.g. recycling, incineration, or landfill) and the technology available will define the characteristics of such processes, as well as which filtration technology can be implemented.

For any application type, the amount of nanomaterial released throughout its life cycle is usually quantified by the release fraction of the initial ENM content that is liberated during each phase of that life cycle. We call this the **release coefficient in period t**. Let  $Q_0$  be the initial amount of ENM mass allocated to one product. We define  $\Delta Q_t$  as the mass released in period  $t$  and the **release coefficient**  $r_t$  ( $\Delta Q_t/Q_0$ ) as the proportion, in percentage terms, of the initial ENM mass content that is liberated in period  $t$ . At the end of its life cycle, the ENM mass still bound in the nano-product is either released during the disposal process, permanently stored in a technical compartment ("sink"), or a combination of both. These concepts are illustrated in **Table 1**, where a hypothetical nano-application releases 20% of its original ENM before it goes into its final sink. A period may be defined as a year, a month, or any other relevant period, depending on the characteristics of the assessment.

	Life cycle phase				
	Production	Use			Disposal
Period (t)	1	2	3	4	5
ENM release coefficients $r_t$ (%)	1	10	5	1	3

**Table 1.** ENM release coefficients as a proportion of the initial mass content throughout the life cycle of a nano-product. This Table illustrates the case of a nano-product which releases 20% of the initial ENM content during its whole life cycle, 80% of the remaining ENM transferred to a technical compartment (e.g. landfill) at its end-of-life phase.

### 2.1.3. Review of approaches to model ENM release during the use phase

This section defines and evaluates the approaches and strategies used in environmental models to assess the release of ENMs during the use phase. The results are summarized in **Table 2**, which shows the reference, the main approaches used, whether the studies described the ENM transformations occurring during release, whether they characterized the mass released, and whether dynamics and uncertainty dimensions of modeling were considered.

The approaches and strategies implemented in the models were defined as worst-case assessment, qualitative assessment, applications of release scenarios, use of product categories and mechanistic assessment. In this section we describe them and analyze their advantages and disadvantages. We also discuss the incorporation of ENM transformations and the modeling dimensions of dynamics and uncertainty. We close the section with a general discussion on the data sources in this field.

**Table 2.** A table of release models and their characteristics showing a classification of the approaches used to describe release, the treatment of relevant aspects of release (transformation and characterization), and the treatment of relevant modeling dimensions (dynamics and uncertainty).

Model (reference)	Main approaches used	Transformation assessment	Characterization of the ENM mass released	Dynamics included	Uncertainty representation
(Boxall, et al., 2007)	Worst case Product categories	None	None	None	Scenarios for market penetration of nano-applications
Blaser et al. (2008)	Mechanistic: release as a function of the time in contact with water	Ag into silver ions	None	None	Scenarios for release coefficients
Mueller and Nowack (2008)	Product category and release scenario assessment	Silver dissolution	None	None	Scenarios for production amounts
Gottschalk, et al. (2009b)	Product category and release scenario assessment	Zinc and silver dissolution	None	ENM production	Probabilistic assessment of all parameters
O'Brien and Cummins (2011)	Product categories and release scenario assessment	None	None	None	Probabilistic assessment of all parameters
Tiede et al. (2011)	Product category assessment Qualitative	None	None	None	None
Keller et al. (2013)	Product category assessment	None	None	None	Scenarios for release coefficients
Keller and Lazareva (2013)	Product category assessment	None	None	None	Scenarios for release coefficients
Markus et al. (2013)	Worst case	None	None	ENM production	No
Arvidsson et al. (2014)	Mechanistic	None	None	None	Scenarios for concentration of silver in clothes

Model (reference)	Main approaches used	Transformation assessment	Characterization of the ENM mass released	Dynamics included	Uncertainty representation	
Keller et al. (2014)	Product category assessment	None	None	None	Probabilistic assessment	
Sun et al. (2014a)	Product category and release scenario assessment	Ag and sulfidation	ZnO	None	Probabilistic assessment of all model parameters	
Sun et al. (2015b)	Product category and release scenario assessment	Ag and sulfidation	ZnO	None	ENM production Probabilistic assessment	
Wigger et al. (2015)	Release scenario assessment	None	None	Release coefficients	Scenarios for release coefficients	
Gottschalk et al. (2015)	Product category and release scenario assessment	Ag and sulfidation, CeO <sub>2</sub> agglomeration	ZnO	None	None	Probabilistic assessment of all model parameters
Bornhoeft et al. (2016)	Product category and release dynamics	CNT burning	None	None	ENM production and release coefficients	Probabilistic assessment

**Worst-case assessment.** This approach takes a precautionary stance and assumes that all the ENMs in a product are released to the environment. It is commonly used for product categories that have a high potential for release, like cosmetics or liquid cleaning products. The total release into the environment is assumed to be equal to the amount of ENM produced and used. The main advantage of this approach is that it provides an insight to the maximum amounts of ENM that could reach the environment; its main limitation is that it may easily lead to misleading conclusions if the results are not adequately interpreted. Boxall, et al. (2007) used worst-case assessment to analyze ENM release to water. They determined the total emissions of ENM from consumer products to waste water, assuming specific market penetration levels of the nano-applications (by means of scenarios) and assuming specific ENM concentrations in the nano-applications, using information taken from patents. Worst-case assessments usually ignore transformations of ENMs during the use phase. Most authors use worst-case assumptions, to a greater or lesser extent, to estimate some of their models' parameters.

**Qualitative assessment.** A qualitative analysis evaluates non-measurable dimensions by defining certain relevant criteria using ordinal scales (scores or rankings). This approach's main advantage is obvious for the field of nanotechnology risk assessment, where a lack of measurements is generally the rule: it helps to systematically and meaningfully structure a framework incorporating all the relevant elements for which no information exists. Qualitative assessment can be complemented with quantitative or semi-quantitative approaches. The approach's disadvantages include its inability to provide numerical results based on measured data, the potential bias and incompleteness resulting from subjective knowledge, and the difficulty in replicating the assessment. Tiede, et al. (2011) used this approach to evaluate the potential of nano-applications to contaminate water. They qualitatively assessed the ENM concentrations in applications, the ENM's location within a product, frequency of use, and the potential for release in order to evaluate and rank their exposure levels in different water sources (drinking and non-drinking water sources). Their assessment was complemented by applying a quantitative method to estimate predicted concentrations of ENM in water.

**Release scenarios.** A scenario is defined as a projected sequence of events that describes a set of possibilities. Release scenarios are used to define the physicochemical

energies that interact with an application at a particular point during its life cycle. Some examples of release scenarios include “washing”, “weathering”, and “incineration”. Scenario characteristics are specific to each application’s expected life cycle. Its main advantage is the possibility to define realistic settings that are relevant from an environmental exposure assessment perspective, and the possibility to establish the amount of ENM released under such circumstances. The main disadvantage of this approach is that there is a reduced amount of sources and a lack of methods to derive the values of the mass released under such scenarios. One option that has been used by several modelers is the application of the release coefficients published by the European Union (EU) for the risk assessment of chemicals (ECHA, 2012). The exposure assessment module in this framework is based on environmental release categories (ERCs) that define the emission of chemicals into the environment based on aspects such as their life-cycle stages, intended use, level of containment, among others. ERCs are based on conservative and worst-case assumptions. Other alternatives used by modelers have been the refined release coefficients published by the OECD in its Emission Scenario Document (ESD), or the specific ERC (SPERC) which were developed by manufacturers and industrial participants.

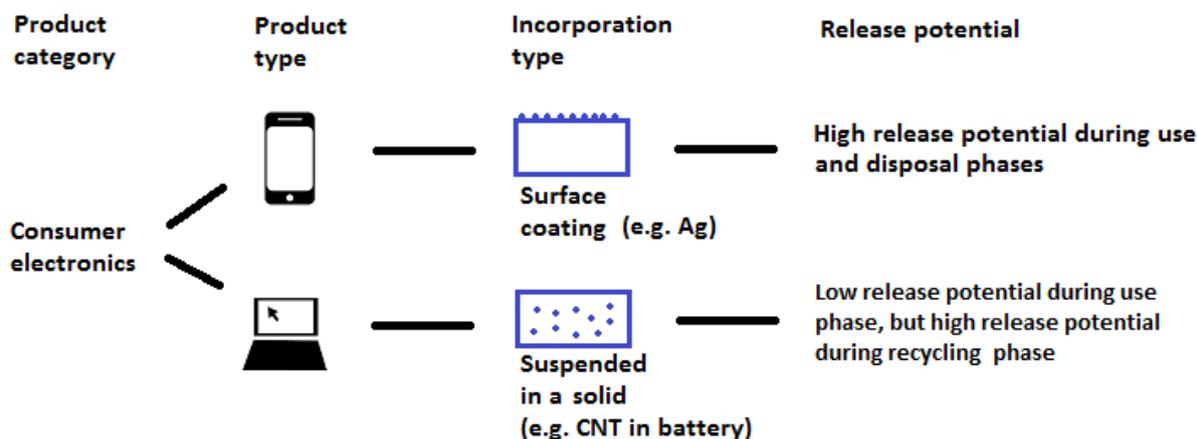
It remains an open question whether or not it is appropriate to extrapolate the release coefficients elaborated for chemicals to ENMs. Given their fundamentally different behavior, Westerhoff and Nowack (2013) discussed the need to develop ENM-specific indicators instead of using the traditional ones used for bulk chemicals. The same idea applies to release and emission assessment. Any ERCs based on the volatility of solvents is, of course, not applicable to solid materials. However, it should be remembered that the REACH framework – specifically its exposure assessment module – and the basic frameworks implemented by environmental models for ENMs, follow the same principles. Although they track the emission and release of fundamentally different materials, we do not expect that the release coefficients prepared for conservative scenarios will vary greatly between each other. More relevant are the refinement procedures that should be carried out as soon as more information is generated describing release or emissions under realistic conditions.

Most ENM environmental exposure studies have used release scenarios to implement their modeling strategies. The most comprehensive study analyzing a single application type was recently developed by Wigger, et al. (2015). These authors defined the release coefficients for all the relevant release scenarios during the life cycle of cotton and polyester textiles to predict the concentration of nano-Ag in the environment. The release scenarios analyzed by them include wearing, washing, drying and ironing for the use-phase, and recycling, incineration and landfill, for the disposal phase. It is reasonable that today the most comprehensive study of a single application focuses on textiles, as it is the product type for which a bigger amount of release assessment studies exists.

**Nano-application categorization.** In most models, release is strongly dependent on the use and definition of product categories. Product categories are used to group product types based on their physical and operational characteristics. Some examples of product categories are consumer electronics, textiles, paints, automotive products, cosmetics, and sensors (Lazareva and Keller, 2014; Sun, et al., 2014a). The categorization of products is particularly useful for the assessment of ENM release when the whole spectrum of existing applications is considered. The approach’s main drawback is that categorization is based on the physical and operational aspects of the applications, not on their potential for release. Thus, product types in the same category may have completely heterogeneous release behavior yet still be considered to have the same release.

This can be illustrated by taking a mobile phone and a computer as an example – two applications that can incorporate ENMs. Both belong to the consumer electronics

category and, using this approach, they would share the same fraction of nanomaterial release, independently of the initial allocation and type of ENMs, or the manufacturing processes. If we consider that a mobile phone might be coated with nano-Ag but that the nanomaterial in a computer could be incorporated into its battery (nano-TiO<sub>2</sub> or CNTs), then it is clear that these goods will release ENMs completely differently, at least during their use phase. One clear implication of this aspect is shown by the assessment of ENM release during recycling: the release and fate of the ENMs are clearly dependent on the material fraction, where it is incorporated and how (surface bound or matrix incorporated), and this is independent of the product category (Caballero-Guzman, et al., 2015) (Figure 2).



**Figure 2.** Release potential of a nano-application is not dependent on the product category it belongs to, as some environmental exposure models assume. Rather, it depends on the initial allocation of the ENM and how it is incorporated into the application (surface bound, suspended in liquids, bound in solids, or airborne).

The main reason for using such broad product categories is the absence of information on the characteristics of the applications that determine their release potential. The principal sources of data for real-world product assessments are public inventories, market reports, or manufacturers' information, which provide few relevant details for any evaluation of an application's release potential. Information on ENM types, quantities, allocations, and incorporation are hardly known because manufacturers are not obliged to reveal them. Neither the quantities of ENM in an application nor the distribution of ENMs in different product categories are known. Yet this information is critical to the application of release coefficients to these product categories in order to estimate ENM flows.

There is, however, a growing awareness of the relevance of this situation, and inventories are improving their descriptions, providing more details whenever they can: one example is The Danish Nanodatabase (Nanodatabase, 2015). Authors using the product-categories-based approach include Mueller and Nowack (2008) and Keller, et al. (2014). **Mechanistic assessment.** This approach is used when the mechanisms controlling the ENM release are well known. It is usually implemented through mathematical equations that outline the cause-effect relationship between dependent and independent variables. This approach's main advantage is the use of fundamental equations that describe the phenomena, its capacity to provide numerical estimations of the mass released and its potential to be used to describe other modeling aspects that are relevant too, like transformations and dynamics. However, currently there is still little understanding available on the actual mechanisms controlling release for most of the

nano-applications, considerably reducing the possibility of using this approach. Therefore, its application has been limited to a few studies, which oversimplify the release mechanisms description. Blaser, et al. (2008) assumed that silver from consumer products (plastics and textiles) was released as dissolved ions as a function of the time that an application remained in contact with water. Hendren et al. (2013a) developed a mechanistic model to estimate the release of silver into wastewater treatment plants effluents. However, due to the lack of information, the model applied was reduced to a simple two-term equation (amount of silver produced multiplied by the fraction released to the water), which in fact only describes the average amount of material released that is transferred to wastewater. Arvidsson, et al. (2014) defined the annual release of silver as population multiplied by the annual consumption rate of clothes, multiplied by the nanosilver concentration, multiplied by the fraction of silver released.

**Dynamic assessment.** The dynamic modeling of release intends to describe the evolution over time of the amounts of ENMs released to the environment. It requires to understand the changes of the variables that determine release over time, including the production or consumption volumes, the value of the transfer coefficients over the life cycle of an application or even the technological shifts. The first dynamic assessment was made by Gottschalk, et al. (2009b). The authors predicted the evolution of the environmental concentrations of five ENM in the US, Europe and Switzerland for a period of 11 years (2001-2012) by incorporating the evolution of the ENM production volumes in such regions. Sun, et al. (2015b) implemented a similar approach to predict the ENM concentrations in the relevant environmental compartments of the Greater Adelaide area (South Australia). Wigger, et al. (2015) modeled the release of nano-Ag from a textile garment during its life cycle, adjusting the transfer coefficient for wearing, washing, drying and ironing activities, along a period comprising 50 use cycles. Their model incorporates the release during disposal.

A comprehensive dynamic model was recently developed by Bornhoeft, et al. (2016), who created a model that integrates both the evolution of the production volumes and the transfer coefficients along the life cycle of the nano-applications. It includes a module that keeps track of the ENM stocks during the use phase and defines the ENM release amounts by mean of a set of rules (called *release strategy*) that determine the residence times of the ENM in the stocks. The method incorporates a Bayesian layer to account for uncertainty in the parameters.

**Transformations.** The most surprising revelation in this section of our review is that although the different models were able to deal with almost all the aspects related to ENM release (in one or another way), one key aspect has not been properly dealt with: the characterization of ENMs released during the use phase. As described previously, ENMs are transformed throughout their whole life cycle, yet only a limited number of current models incorporate transformations occurring during the use-phase. As a consequence of this, the ENM released amounts provided by the models are higher than the reality, delivering instead a picture which may not be accurate.

Although this situation was understandable during the early years of nanotechnology risk assessment, the growing body of experimental literature on release should be exploited to develop models that describe this very relevant aspect of release. Several new environmental fate models (Praetorius et al., 2012; Meesters et al., 2014; Dale et al., 2015; Liu et al., 2015) are currently using the results provided by the material flow studies listed in this section as input to analyze the fate and behavior of ENM once in the environment. Without any doubt, the fate models would benefit of receiving the picture of the complete range of materials actually released to the environment, leading to stronger conclusions for the whole ENM exposure assessment field.

**Uncertainty.** The parameters used by release models have a large uncertainty. To deal with this situation, the authors have implemented different scenarios for the definition of

their parameters. For example, Boxall, et al. (2007) used scenarios to describe different market penetration values of the nano-applications. Blaser, et al. (2008) and Keller, et al. (2013), among others, have also used scenarios to define the release coefficients. Another way to deal with the uncertainty inherent to the parameter values has been the application of probabilistic methods. Since Gottschalk et al. (2010b), numerous authors have implemented this method to describe the uncertainty using a probabilistic approach.

**Data sources.** The parameterization of the models reported in this section may vary from each other, but, in general, under the current modeling strategies, the estimates of the quantities of ENMs released rely on knowledge of the amount of ENMs used in a specific geographic region, the distribution between product categories, and products' potential for release, information which is not openly available or rather it is non-existent. Until recently, there were no official sources of information about the production and use of ENMs in any specific region. To tackle this issue, therefore, researchers had to make use of surveys, expert opinions, and the scarce information reported in some market reports. This helped them estimate global amounts of the ENMs produced, which were later extrapolated to specific regions using factors such as population, GDP, or the Human Developing Index. Although there is a difference between the amounts produced and used, authors have made no distinction between these variables. The only official source of information about the ENMs produced or imported into a particular geographic region was recently published by the French government (ANSES, 2013), and there is an ongoing debate as to whether or not this obligation should be extended to other countries (RPA and Bipro, 2014).

The chances of finding information regarding the amounts of ENMs used in specific categories is even lower. In some cases, this information had to be substituted by the relative weight of the product categories in public inventories (Mueller and Nowack, 2008), although authors are rarely transparent about how they distribute the amounts of ENMs produced between the categories. In general, the sources of information necessary for performing release assessments are rather limited, not only regarding the amounts of ENMs released from applications (**Section 4**) but also for the rest of the parameters. As a consequence of this, these assessments strongly rely on extrapolations of data, author's assumptions, and expert opinions.

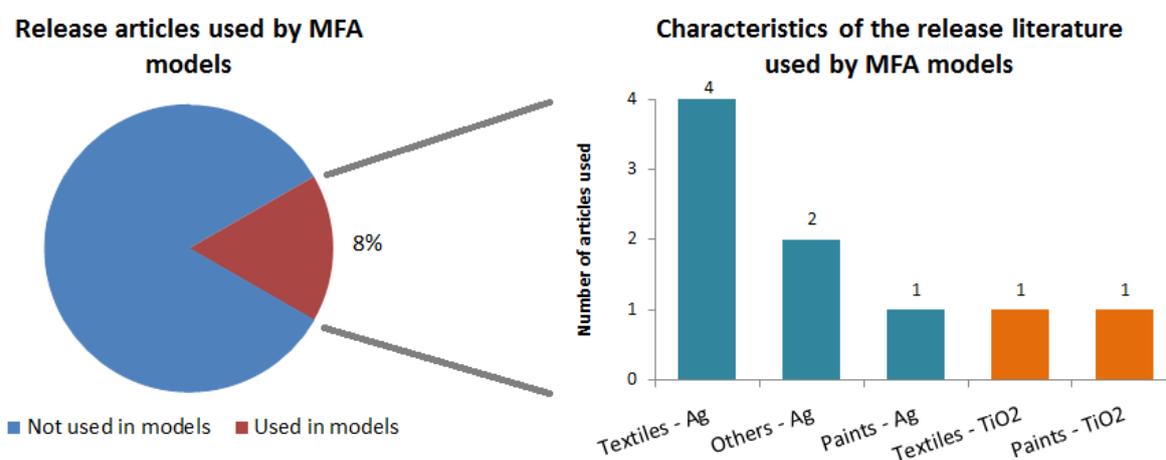
#### **2.1.4. Assessment of the usefulness of the ENM release literature for MFA modeling**

All the modeling studies presented in Table 2 are material flow analysis (MFA) models. Although most of them are not elaborated as standard MFA, the principle behind their design and application is the same which is to determine the mass flows of ENM from applications to technical and/or environmental compartments. The standard design of a MFA model requires the input of mass to the system as main input, together with the transfer coefficients that define the mass flows between compartments. The main flows from products to other compartments are defined by release coefficients.

In our view, the best source of data and information for the definition of the transfer coefficients should be the data provided by the experimental release literature. However, until recently, this type of literature was almost inexistent, leading the authors of modeling studies to rely on informal strategies to define the transfer coefficients of their models as presented in the previous section.

We reviewed the sources used by the scientists to define the transfer coefficients of their models. The sources include emission data for non-nanoapplications, author's assumptions, expert opinions, consumer surveys, technical reports, previously published

MFA models and only to a limited extent articles about release from nanoproducts. The results of this assessment for each of the published models is available in **Table S1** in the Supplementary Material. This assessment shows us that very little data has been taken from the release literature to define the transfer coefficients: only 8% of the total number of articles initially gathered for this review has been used by the release models (**Figure 3**). The used articles are mainly about nano-Ag release from textiles and other applications; only two nano-TiO<sub>2</sub> release articles have been used to derive a transfer coefficient.



**Figure 3.** Release articles used by ENM flow-models and its characteristics. Only 8% of the whole release articles gathered in this review has been used to estimate the transfer coefficients by MFA models (left panel). The 9 articles used are mainly dealing with nano-Ag and nano-TiO<sub>2</sub> in paints and textiles (right panel).

In the last few years, the number of articles that analyze the release of ENM from applications has increased a lot (Mackevica and Foss Hansen, 2016). The increasing size of this emerging literature presents opportunities for modelers. From our perspective, one important question is whether the data and information the studies provide can be exploited for the type of models described in the previous section. We performed a review of the literature to answer this question. We implemented a database search and gathered 106 release articles in total.

Because our scope is limited and focused on the models types presented in the last section, not all the release articles are suitable to be reviewed in depth. The data provided by all the articles might be exploited in some way to develop exposure models. However, in our case, we are interested in particular in data that can be directly used to define the transfer coefficients used by the MFA models to assess the ENM flows from nano-applications to the environment. In this section, anytime we refer to MFA models, it means the type of models described in the previous section.

Unfortunately, the models in **Table 2** do not provide any clear and formal method or procedure for the estimation of their transfer coefficients. This information would have been useful to define some objective criteria for the selection of the articles and to be able to evaluate with a solid basis the data provided by the literature. Nevertheless, from our assessment of the models, we defined the following features that we used as criteria for the selection of the articles to be reviewed:

- They assess the release from an existing application that is currently available in the market for the end-user.

- They assess release under conditions that resemble an average use of the application.
- They provide numerical data that can be used to define the transfer coefficients, namely:
  - The amount released over the whole life cycle of a nano-application.
  - The amount release per time unit.
- They provide information that can be used to understand the characteristics of the mass released.

We applied the previous criteria and selected 49 out of 106 articles. The full list of 106 articles, a short description of each, and the assessment of the type assigned to the studies is available in **Table S2** of the Supplementary Material. The studies not considered in this review are mainly about ENM release from composites made with CNTs (61%), and paints and coatings (12%). A review of the CNT-related articles by Kingston et al. (2014) provides further insight into the characteristics of the CNT-composites and their release potential. That work pointed out that the greatest potential for CNT release will occur towards their end-of-life phase, after weathering may have degraded the composite matrix in which they are embedded, and surface-exposed CNT networks can be detached. One methodological advantage in some of the articles not selected over the ones that we selected is that they are performed under controlled conditions based on ISO standards, minimizing unexpected interferences, as discussed by Wohlleben et al. (2014).

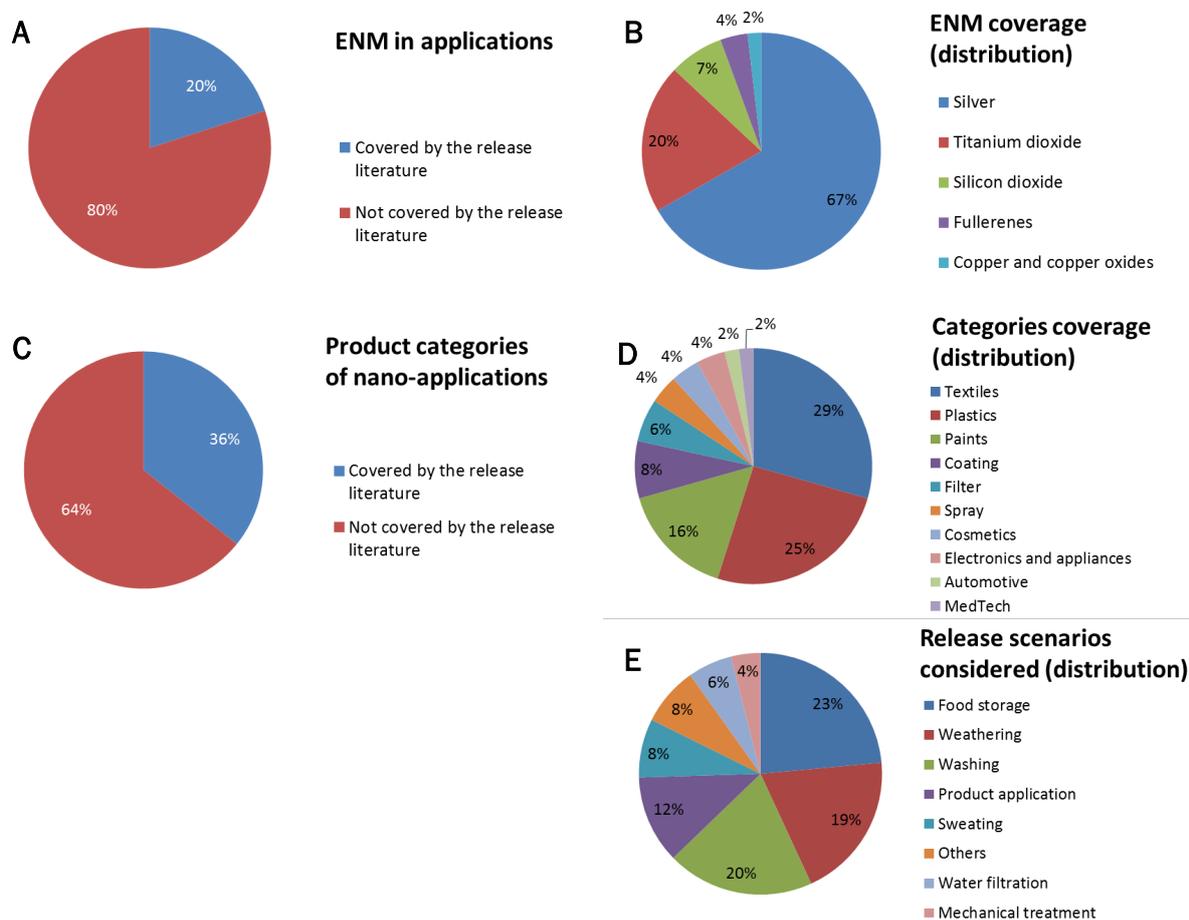
Several articles have previously reviewed the literature on ENM release (Froggett, et al., 2014; Kingston, et al., 2014; Noonan et al., 2014; Schlagenhauf et al., 2014; Duncan, 2015; Duncan and Pillai, 2015a). However, the present review distinguishes itself from them because of the specific focus and perspective it adopts. Kingston, et al. (2014) and Schlagenhauf, et al. (2014) focused only on the literature analyzing release from CNT composites. Noonan, et al. (2014), Duncan (2015), and Duncan and Pillai (2015a) focused on the literature that analyzed release from polymer nanocomposites, independently of the ENM incorporated. Froggett, et al. (2014) analyzed the whole spectrum of nano-applications. The perspective adopted by all these prior reviews was to summarize and evaluate the results found in the literature in a clear and systematic way, with a focus on understanding the processes resulting in release and characterization of the released materials.. On the other side, our study was not intended to summarize the results in the literature but rather to evaluate those aspects of release studies that we consider relevant for MFA models: (i) characterization of the nano-application and the incorporated ENM; (ii) quantitative information on the mass released and characterization of released materials; (iii) description of transformation reactions; and (iv) an assessment of the factors determining release.

A disadvantage faced by some of the selected studies are the low concentrations of ENMs actually available in the environment and the difficulty in distinguishing between natural, incidental, and engineered nanomaterials in the complex matrices of organic and inorganic materials found in the environment (Nowack, et al., 2015). To compensate for this limitation, in some cases ENM release is reinforced in such a way that the concentrations collected are enough to provide good measurements. One example of the former is Kaegi et al. (2008), who described the real-world release of nano-TiO<sub>2</sub> from façade paints. This article demonstrates that the release of nanoparticulate materials does indeed occur under realistic, relevant environmental conditions, and it provides some basic characteristics of the released materials. Meanwhile, an example of the latter is Al-Kattan et al. (2014), who assessed the release of nano-TiO<sub>2</sub> using milled, aged paint. Although, strictly speaking, this study did not examine a painted wall, it offers an approximation to the real size-distribution of the material that would be released under

real conditions.

### *ENMs, product categories and release scenarios covered by the current ENM release literature*

We analyzed the literature for its coverage of the range of: (i) nanomaterial types; (ii) product categories; and (iii) release scenarios. The results are presented in **Figure 4**. To evaluate the coverage of the range of ENMs, we referred to those ENMs listed in the DaNa 2.0 database (DaNa2.0, 2015). This source details 25 ENMs that currently have at least one application. The 49 studies selected from the literature on release covered only 20% of these ENMs. The majority of the studies dealt with silver (67%) and titanium dioxide (20%). The rest is distributed between silica, fullerenes, and copper. The literature's coverage of product categories was determined using those defined by Sun, et al. (2014a) for their complete material flow assessment of ENMs. The literature only assesses products belonging to 36% of those categories, and studies are concentrated mainly on textiles (29%), plastics (25%), and paints (16%). The rest relate to categories like "automotive", cosmetics, and electronics. With regard to release scenarios, the majority of the literature examined food storage (23%), washing (20%), and weathering (19%). Other scenarios included were sweating, water filtration, and mechanical treatments (mainly abrasion and stress tests). The assessments of all 106 articles are available in the Supplementary Material as **Figure S1**. It is clear from this analysis that the literature on ENM release that could be used for MFA modeling purposes only covers a small fraction of the existing nanomaterials, applications, and release scenarios.



**Figure 4.** How the literature on ENM release (model and real-world studies, excluding

mechanistic ones) covers the different types of ENM used currently in applications (top), the product categories of the whole spectrum of applications (middle), and different possible release scenarios (bottom). The top and middle charts on the left use as reference the number of ENMs according to DaNa2.0 (2015) and the product categories defined by Sun, et al. (2014a). Note that these numbers apply only to the 49 articles selected. The same assessment for the all the 106 studies is available in **Figure S1** of the Supplementary Material.

To further understand the data on release related to the product categories and types described in the literature, we developed **Table 3** using information in The Danish Nanodatabase (Nanodatabase, 2015) about the nano-applications currently available on the market. This table describes what is considered under each product category (product types available in the market and ENM types used) and what the literature on release has assessed in each of these categories (product types analyzed, release scenarios and references). The analysis showed that the product types used in the release studies represented only a limited number of the whole suite of current applications.

**Table 3.** How the literature on ENM release (model and real-world studies, excluding mechanistic ones) covers the existing applications and the ENM types. The studies are grouped by product category. The Table includes the release scenarios analyzed and, for comparison purposes, the product types available into the market and the ENM types actually incorporated into them. Sources: Product categories taken from Sun, et al. (2014a), product types available on the market from Nanodatabase (2015), and ENMs types from the latter reference and (ANSES, 2014). Notice that columns 2 and 3 are comprehensive examples and not exhaustive lists. The remaining columns are the results from this review.

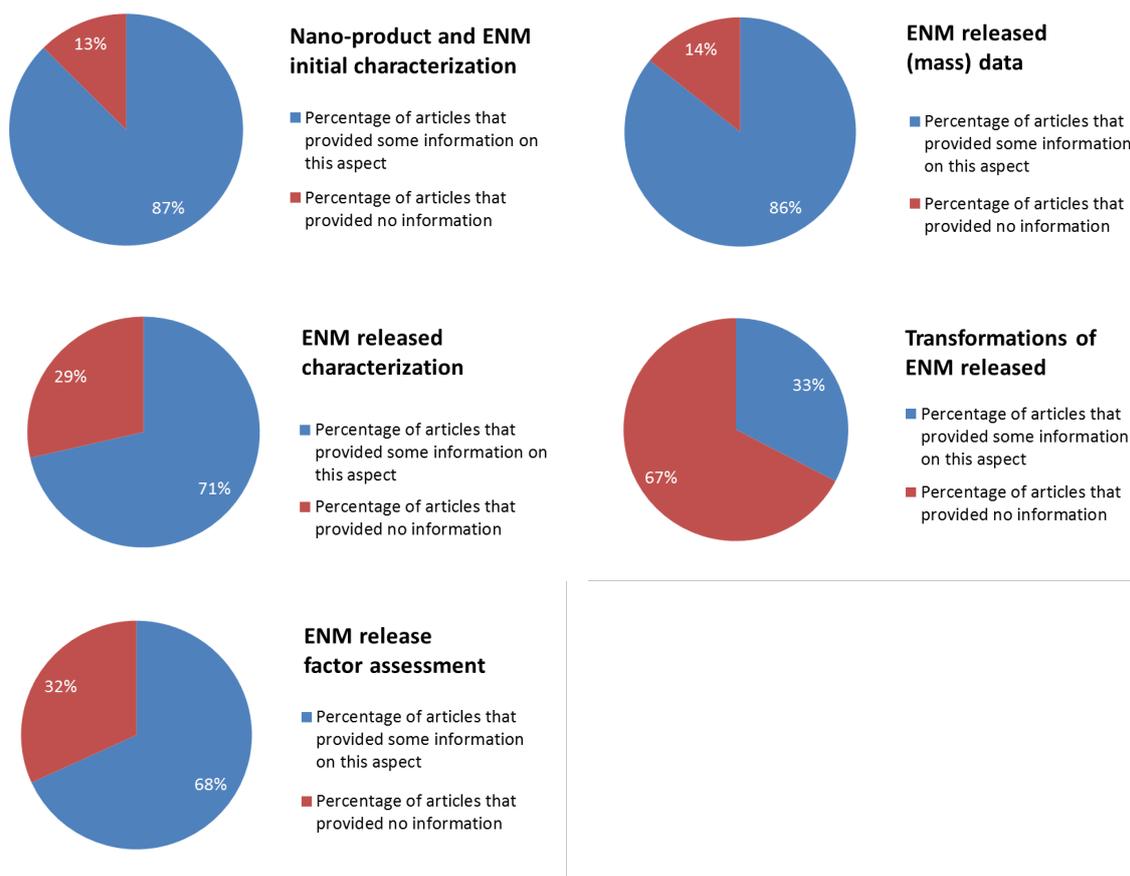
Product Category	Product types available on the market	ENMs types used	Product types and ENMs analyzed by the literature	Release scenarios analyzed by the release literature	References and total amount
Textiles	Gloves, jackets, jumpers, hoodies, diaper-changer mats, knickers, overalls, pants, pillow protector, shirts, shorts, , socks, sweaters, ties, towels, trousers, working uniforms, leg warmer and more.	Ag, Au, Bamboo charcoal, CaCO <sub>3</sub> , Carbon Black, CNT, Silica, TiO <sub>2</sub> , ZnO	Shirts, socks, teddy bears and plush toys (Ag and TiO <sub>2</sub> ).	Washing and sweating of clothes, leaching into saliva simulant.	(Benn and Westerhoff, 2008; Geranio et al., 2009; Impellitteri et al., 2009; Benn et al., 2010; Kulthong et al., 2010; Lorenz et al., 2012; Pasricha et al., 2012; Windler et al., 2012a; Yan et al., 2012; Quadros et al., 2013a; von Goetz et al., 2013b; Holbrook et al., 2014; Lombi et al., 2014; Mitrano et al., 2014; Stefaniak et al., 2014) TOTAL: 15
Plastics	Food storage bags, breast milk bags, baby milk bottles, cups, sandals, baby toys and more.	Ag, Ba, Bi, CaCO <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , Graphite, Iron hydroxide, Silica, TiO <sub>2</sub> , ZnO, (in)organic pigments.	Food containers (Ag and TiO <sub>2</sub> ).	Food storage (migration into food-simulating solutions).	(Hauri and Niece, 2011; Huang et al., 2011; Song et al., 2011; Cushen et al., 2013; Quadros, et al., 2013a; von Goetz et al., 2013a; Bott et al., 2014; Cushen et al., 2014a; b; Jokar and Abdul-Rahman, 2014; Lin et al., 2014; Artiaga et al., 2015) TOTAL: 12
Paints	Outdoor and indoor paints.	Ag, CaCO <sub>3</sub> , Kaolins, Carbon black, CeO <sub>2</sub> , CNT, Cu, SiO <sub>2</sub> , TiO <sub>2</sub> ,	Outdoor paints (Ag, SiO <sub>2</sub> , TiO <sub>2</sub> ).	Weathering, leaching and abrasion of painted walls.	(Kaegi, et al., 2008; Kaegi et al., 2010; Al-Kattan et al., 2013; Al-Kattan, et al., 2014; Zuin et al., 2014a; Zuin

Product Category	Product types available on the market	ENMs types used	Product types and ENMs analyzed by the literature	Release scenarios analyzed by the release literature	References and total amount
		ZnO, (in)organic pigments			et al., 2014b; Al-Kattan et al., 2015; Fiorentino et al., 2015) TOTAL: 8
Coatings	Coatings for: glass, metal, plastic, stone, textiles, windscreens and wood.	Ag, BaSO <sub>4</sub> , CaCO <sub>3</sub> , Carbon black, CeO <sub>2</sub> , CNT, Cu, Pd, SiO <sub>2</sub> , TiO <sub>2</sub> , ZnO, (in)organic pigments	Coatings for bricks, metals, plastics, tiles and wood (Ag and TiO <sub>2</sub> ).	Weathering of coated surfaces and immersion in salt water.	(Hsu and Chein, 2007; Zanna et al., 2010; Künniger et al., 2014; Shandilya et al., 2015) TOTAL: 4
Filters	Ceramic filters, membranes, filter cartridges.	Ag, TiO <sub>2</sub> , ZnO	Ceramic water filters (Ag).	Use of water filter	(Bielefeldt et al., 2013; Ren and Smith, 2013; Mittelman et al., 2015) TOTAL: 3
Cosmetics	Anti-age cream, skin regenerating cream, eyeliner, gloss, skin moisturizer, skin powder, lip serum, sunscreens and more.	Ag, Al <sub>2</sub> O <sub>3</sub> , Au, Bisocotrizole, Carbon Black, Fe <sub>2</sub> O <sub>3</sub> Magnesium salt, Silane, SiO <sub>2</sub> , TiO <sub>2</sub> , ZnO	Sunscreen (TiO <sub>2</sub> ).	Sunscreen application	(Botta et al., 2011; Holbrook et al., 2013) TOTAL: 2
Sprays	Air cleaner with aroma, deodorant, shoe protector, sprays to be used by people hunting and more.	Ag, CaO, Carbon Black, Mn, TiO <sub>2</sub> , W	Deodorant sprays, shoe protectors, plant supplements, (Ag).	Spray application	(Lorenz et al., 2011; Quadros and Marr, 2011) TOTAL: 2
Automotive	Car dashboards, bumpers, car wax, polymer polishing liquid, vinyl revitalizer, wheel protector liquid.	Al <sub>2</sub> O <sub>3</sub> , CaCO <sub>3</sub> , Carbon black, CeO <sub>2</sub> , CNT, SiO <sub>2</sub> , Ti, Fullereness Polytetra-fluoro-ethylene	Iron alloy coatings (shaft cap, C60).	Stress testing	(Le Bihan et al., 2013) TOTAL: 1
Electronics and electronic appliances	Fridges, stoves, irons, washing machines, mouse and keyboards, mobile phones, air purifiers, vacuum cleaners, air humidifiers and more	Ag, CaCO <sub>3</sub> , CeO <sub>2</sub> , CNT, Cu, Mn, Pd SiO <sub>2</sub> , TiO <sub>2</sub> , ZnO	Washing machines (Ag)	Machine operation	(Farkas et al., 2011) TOTAL: 1
MedTech	Bathing chair, mouth guard, accupunture set, water flosser (dental cleaner), burn wound dressings	Ag, Attapulgit, CaO, Si, Silane SiO <sub>2</sub> , TiO <sub>2</sub> ,	Burn wound dressings (Ag)	Leaching into pure water, serum substitute and saline solution	(Rigo et al., 2012) TOTAL: 1
Sanitary	Air masks, hand dryers, water purifiers, toothpaste, shampoo	Ag, Au, Calcium Peroxide, Bamboo charcoal, SiO <sub>2</sub>	Toothpaste and disinfecting spray (Ah)	Toothpaste and spray application	(Quadros, et al., 2013a) TOTAL: 1
Aerospace	Fuselage parts	CNT	None	-	-
Batteries	-	Carbon black, Graphene, CNT, SiO <sub>2</sub>	None	-	-
Cements	Cement, mortar	CNT, SiO <sub>2</sub> , TiO <sub>2</sub>	None	-	-
Cleaning agents	Deodorant bag, all purpose cleaner, liquid cleaner for bikes, floors, garments, refrigerators, stones, walls and more	Ag, Carbon black, TiO <sub>2</sub> , SiO <sub>2</sub> , ZnO	None	-	-

Product Category	Product types available on the market	ENMs types used	Product types and ENMs analyzed by the literature	Release scenarios analyzed by the release literature	References and total amount
Composites	Rackets, bicycles, bicycles components,	Al, Carbon black, CNT, Graphite, Iron hydroxide	None	-	-
Energy	Thermal insulators	CeO <sub>2</sub> , SiO <sub>2</sub> , CNT,	None	-	-
Food	Nutrition supplements	Ag, Ca, CaCO <sub>3</sub> , Mg, SiO <sub>2</sub> , TiO <sub>2</sub> , Zeolite	None	-	-
Glass and ceramics	Self-cleaning glass	Ag, TiO <sub>2</sub> , ZnO	None	-	-
Ink	Toners	CaCO <sub>3</sub> , Carbon black, TiO <sub>2</sub>	None	-	-
Light bulbs	-	TiO <sub>2</sub>	None	-	-
Metals	See coatings	Al <sub>2</sub> O <sub>3</sub> , Carbon black, Iron hydroxide, Silane, SiO <sub>2</sub>	None	-	-
Paper	-	Ag, CaCO <sub>3</sub> , SiO <sub>2</sub> , TiO <sub>2</sub> , ZnO, cellulose	None	-	-
Sensors	-	CNT	None	-	-
Soil remediation	-	Ag, Ba, Ca, Carbon black, Mesotrione, SiO <sub>2</sub> , TiO <sub>2</sub>	None	-	-
Sporting goods	Backpacks, sport bags, crampons, fishing hooks, hiking poles, badminton racket, squash racket, tennis racket, ski shoes, shoe cover, skies, hockey stick, sunglasses, tennis, bicycle tires	C, CNT, Graphite, Steel, Si, Ti, TiO <sub>2</sub>	None	-	-
Water treatment	-	Ag, SiO <sub>2</sub> , TiO <sub>2</sub> , Z nano- VI	None	-	-

### *Aspects of release described by the ENM release literature*

The summary of the results on this sub-section are described as **Figure 5**. We start the description of the aspects that we consider relevant for MFA modeling with a discussion about the initial characterization of the materials and products given in the literature. The present study defines *initial characterization* as the description of an application's characteristics and the ENMs incorporated in it before they are released. The description of the application can include information about the product type, manufacturer, model, picture, ENM location, and ENM mass concentration. The description of the ENM incorporated can include size distribution, shape, functionalization, surface area, surface chemistry and more. An extensive list of nanomaterial properties, all of which may be used for the characterization of ENMs, is found in Hischier (2014).



**Figure 5.** Percentage of the studies (model and real-world studies, excluding mechanistic ones) that provided at least basic information on the aspects that are considered relevant for environmental exposure modeling by this review. Details on what this review considers relevant under each aspect are to be found in the main text.

The most common information provided for initial characterization is the ENM size and shape, and the ENM mass concentration in the nano-application. Usually, the size and shape information is provided through scanning electron microscope (SEM) or transmission electron microscope (TEM) images. The identification of the ENM in the images is typically performed by energy-dispersive X-ray spectroscopy (EDX) elemental analysis. Although SEM/TEM images are useful for describing the shape and size of nanoparticles, they are normally not useful to generate statistical information, such as a size distribution.

Authors do not commonly include the initial size distribution of the nanomaterials in their studies. Pasricha, et al. (2012), however, assessed the release of nano-Ag from textile fabrics, offering size distribution, the processes for Ag synthesis and loading Ag onto the fabrics, and images showing the effects on the amount released from several incorporation procedures of the nanomaterial into the textile. Ren and Smith (2013) assessed the release of silver from a water filter application that they had fabricated themselves. They measured the ENM size using more than one analytical technique (dynamic light scattering or DLS, and TEM) and presented further details too, including the zeta potential and the capping agent. Mitrano, et al. (2014) evaluated the release of nano-Ag from textile fabrics. They performed a comprehensive initial characterization, including the ENM's trade name, its supplier, ENM mass concentration, particle size and, the fabric manufacturing process.

Although a wide range of analytical techniques is available for the initial characterization

of ENMs, we noticed that this aspect of release assessment is not carried out as completely as possible. We also noticed that authors working closely with commercial partners or who were developing an application by themselves, typically presented more comprehensive initial characterizations (e.g. (Al-Kattan, et al., 2013; Ren and Smith, 2013; Cushen, et al., 2014a; Jokar and Abdul-Rahman, 2014).

Traditionally, the *quantitative information on the ENM mass released* is reported either in absolute or relative terms (e.g. mass, mass per mass, mass per volume, mass per surface), depending on the media analyzed. Less frequently, authors provide release estimations as a percentage of the initial ENM content. Ideally, articles about ENM release would provide mass measurements in all three ways (absolute values, relative values, and as a percentage of the initial ENM content). However, it was noted that this seldom occurred in the literature examined. It would also be appropriate for studies to provide a full set of observations, in order to provide the elements to perform statistical analysis. Summary statistics (e.g. mean and standard deviation) are useful, but a full set of observations means that probability distributions can be generated. Artiaga, et al. (2015) assessed the release of nano-Ag from food containers; this is one of the few articles that provides a comprehensive set of data (ng/l, ng/dm<sup>2</sup>, ng/g, and % of Ag migrated), including the data for each experimental observation and the summary statistics. Other authors who provided more information than the norm were Cushen, et al. (2013) and Cushen, et al. (2014a).

An analysis of release dynamics can be enhanced by providing release observations as a function of time (release rates). This was done by some authors, including Lin, et al. (2014), who described the migration of silver once an hour throughout the duration of the experiment. This information can be complemented by including a set of images that help us to visualize the release process, as was done by Holbrook, et al. (2014); they applied an *in situ* imaging method to show the changes taking place. One problem noticed during the review was that some articles reported total material release in their mass observations, rather than specifically describing the ENM released.

Regarding the *characterization of the mass released*, an adequate characterization should describe the elements listed by Izak-Nau and Voetz (2014): the nanomaterial's appearance (size distribution, agglomeration/aggregation state, shape, and surface area), composition (chemical composition, crystal structure, impurities, and surface chemistry) and the properties that affect its interactions with its surroundings (surface charge, solubility, and dispersibility). A diverse range of analytical techniques is available for characterizing nanomaterials. The complete range of analytical techniques available, and some of their limitations, can be found in von der Kammer et al. (2012), and in the former reference as well. Many release studies include TEM/SEM images and EDX spectra also from the released material. Additional information beyond shape, size, and composition is still not common in the literature, although the review noted some exceptions which included a larger amount of information derived from a wider selection of analytical techniques. Hsu and Chein (2007) assessed the release of nanoparticles from a coating applied to wood, polymers, and tiles. Using a Scanning Mobility Particle Sizer (SMPS), the authors measured the diameter (nm, median), the particle number concentration (#/cm<sup>3</sup>), and the average emission rate (#/min). Botta, et al. (2011) assessed the characteristics and behavior of nano-TiO<sub>2</sub> released into water by sunscreens. Using inductively coupled plasma atomic emission spectroscopy (ICP-AES), the authors describe the mass balance between the colloidal and the non-dispersed fractions, which is useful for understanding the effect of UV light on the agglomeration of the nanomaterial. Pasricha, et al. (2012) assessed the release of nano-Ag from textiles and quantified the material that leached into the washing water using atomic absorption spectrometry (AAS). Al-Kattan, et al. (2014) analyzed the behavior and fate of aged, milled paint containing nano-TiO<sub>2</sub>. They gave the zeta potential and the DLS size as a

function of the pH and compared the pristine and aged materials. Liu and Cohen (2014) complemented their assessment of the material released from a plastic food container by studying its surface using atomic force microscopy (AFM).

As mentioned, it is not usual for researchers to provide the size characteristics of ENMs both before and after release. One interesting example is Holbrook, et al. (2014), who presented the particle size distribution of nano-TiO<sub>2</sub> both before and after release into swimming pool water; the size distribution clearly shifted to the right after release. Fiorentino, et al. (2015) analyzed the factors affecting the release of nano-SiO<sub>2</sub> from paints and described the particle number concentrations and size distributions using an electrical low pressure impactor (ELPI).

Although the selection of the analytical techniques used depends on several factors – including the research question, experimental design, instrument availability, and associated costs – researchers should apply as many methods as possible in order to provide significant amounts of data on the three important aspects discussed in the preceding paragraphs: (i) the appearance of the materials released; (ii) their composition; and (iii) the parameters that affect their interaction with the environment.

An assessment of whether the original ENMs contained in a product were *transformed* during release is important for determining whether new types of materials were formed. The literature on hazard and exposure focuses mainly on the assessment of pristine ENMs. However, once they have been released and reach the environment, they may have been significantly aged and transformed (Nowack, et al., 2012b). The assessment of transformation should, therefore, be given more weight in the literature on release. This information would help environmental models to describe and parameterize the different species generated and to avoid overestimation of concentrations of pristine ENMs. Mitrano et al. (2015b) reviewed the possible transformations that nanomaterials undergo during their life cycle. They considered a transformation to be any change or alteration to: (i) the primary particle; (ii) the nanomaterial's coating; or (iii) the configuration of the particles involved (agglomeration/aggregation). The processes producing those transformations depend on the type of nanomaterial, the type of application, and the release scenario, which defines the environmental parameters affecting the application and the ENM in it. It is important to consider that transformations may occur not only during the nano-product's use phase, but may start with the ENM's production itself. The most widely reported type of transformation in the literature on release is the state of aggregation or agglomeration of the nanoparticles released; this is to be expected when we examine the frequency with which SEM/TEM analysis is applied. The second most reported transformation is the dissolution of nanosilver. However, there was a general lack of transformation analysis. One exception was Mitrano, et al. (2014), who assessed the release of silver from textiles during household washing. The authors described the different species of silver generated during the washing process, applying their experimental protocol not only to nano-textiles but also to conventional silver textiles. They showed that nanosilver can be formed by washing textiles containing conventional silver. They also provided the transformation pathways leading to the formation of the new species. In a follow-up article, Mitrano et al. (2015a) analyzed the effect of the washing detergent on the transformations of the silver released from textiles. They assessed the effects of the detergent's chemical characteristics on the silver dissolution rate, changes in its surface chemistry, and the formation of new particles. Using TEM, EDX, and single-particle ICP-MS analysis, the authors showed that several transformations occur during washing, and they presented particle size-distributions over multiple time points. The presence and amount of oxidizing agents in the washing detergent, and whether it was used in powder or liquid form, played a key role in determining the speciation of silver during household washing. Any comprehensive transformation assessment should aim to detect all the subspecies of

ENM created as well as the factors producing them; this should include any data for identifying the mass fraction corresponding to each species and its characteristics.

To end this section, we discuss the assessment of the *determinants of release*. All the articles reviewed in the present study contained basic information about the determinants of release. It is clear that silver is released from textiles on contact with water or sweat and that titanium is released from painted outdoor surfaces during weathering. However, the detailed factors determining the release of ENMs are more complex than most current descriptions in the literature would suggest. Al-Kattan, et al. (2013) explicitly analyzed the effects that plaster type and age have on release, demonstrating that they may play a key role. Zuin, et al. (2014b) analyzed the effects of paint composition on the amount of silica released from outdoor paints, in one case varying the binder content and adding TiO<sub>2</sub>. Fiorentino, et al. (2015) performed a similar assessment improving our understanding of how paint manufacture affects release. In the analysis of release from plastics (food containers), most articles have analyzed the effects that temperature and exposure time to food simulants have on release. However, additional insight is found in Cushen, et al. (2013). They evaluated the effects of the particle diameter and the amount of ENM in the plastic on release. Jokar and Abdul-Rahman (2014) evaluated the effects of manufacturing methods. The articles on textiles by Geranio, et al. (2009), Kulthong, et al. (2010), von Goetz, et al. (2013b), and Mitrano, et al. (2014) improve our understanding by going beyond simple release assessments.. In general, in order to understand the complexity of the causes of release, in realistic use-scenarios, an assessment of the nature, extent, and interactions of those determinants is needed. Using statistical tools to evaluate the significance of the data on the factors affecting release, may improve the quality of that information, as it does in the articles by Cushen, et al. (2013) or Jokar and Abdul-Rahman (2014).

### 2.1.5. Recommendations, conclusions, and perspectives

In this review we looked at a selection of the literature on release of ENMs. Our purpose was to evaluate the type of information offered and qualitatively analyze its usefulness to parameterize the type of MFA models described in Section 3, in particular for the estimation of the transfer (release) coefficients used to describe the ENM flows from nano-applications to the environment. Based on our review of the modeling literature, we decided to select the release articles that assessed well defined nano-applications available in the market for the end-user under conditions that resembled normal average use. Regarding the characteristics of the data of the release literature to be analyzed, we focused on analyzing (i) the initial characterization of the nano-application, (ii) the quantitative data on the mass released and its characterization, (iii) the description of the transformation of the ENM during release, and (iv) the assessment of the factors determining release. Depending on the quality of the description given in the release articles, this information could be used to define the transfer coefficients of the models and improve other modeling dimensions, including description of transformations and release dynamics. Ideally, the amount of ENM released during the life cycle of a nano-application and its characteristics can be derived from this data.

Our review of the MFA models allowed us to make a description of the approaches and strategies implemented to reproduce the ENM flows from nano-applications to the environment. The main limitation faced by all modelers is that the information needed to feed those models is almost inexistent. One key missing point are methods and procedures for the definition of the transfer coefficients. This would render a better assessment and exploitability of the data available in the literature. We observed that the MFA models describe mainly the flows of pristine ENMs, that is, the physico-chemical

transformations undergone by ENMs between their production and their release are usually ignored. We noticed, too, that advanced characterization of the released ENM is usually unavailable and that the incorporation of dynamic assessments has only been used in a limited number of models. Uncertainty is dealt with using probabilistic frameworks, scenarios, or a combination of both. Below, based on our evaluation of the literature, we provide some recommendations for both modeling and release assessment, that could help MFA modeling advance towards a more realistic assessment of ENM release.

Our recommendations for MFA models start with the idea just mentioned previously: to provide a method or procedure for the definition of the transfer coefficients. This would facilitate the setting of objective criteria for the selection of the articles and the methods to exploit the data available in them. Most importantly, this would allow to interpret better the meaning of the transfer coefficients, to evaluate the quality of the results those models present, and to quantify with a stronger quantitative basis the uncertainty associated to their use. For the production amounts, modelers should closely track the changes in nanomaterial production in specific regions. This information is officially assessed nowhere but France (ANSES, 2013), which recently became the first country to oblige industry to report the amounts of nanomaterial produced or imported, as well as the types of application they are used for. While this information remains uncollected and unpublished, authors will have to continue relying on extrapolations of data that may introduce considerable uncertainty. Modelers should also keep track of the technological shifts that may affect the development of any specific application, by either increasing or reducing their manufactured amounts. One important focus should be tracking the amounts used, instead of the amounts produced, because international trade in ENMs separates the region of production from the region of use (and, therefore, release in a particular compartment).

Regarding the use of nanomaterials in specific applications, a more systematic assessment of the product categories should be done based on their release potential. Currently, the product categories defined to model release do not reflect this element, but rather common physical and operational characteristics. Other than in the work developed by Hansen, et al. (2008), efforts to improve the categorization of nano-applications have been limited. Nevertheless, this is very important as the release from applications in models should be consistent with the characteristics of the ENM and its type of incorporation into a product. Researchers in the exposure assessment field should strive to improve assessments of the release potential for today's ENM applications (Nowack et al., 2013a). There is a need for coherent evaluation of release across the whole spectrum of contemporary applications because that spectrum is set to expand significantly in the future.

Given the limited perspective of the literature on ENM release, it is clear that the coverage of other engineered nanomaterials and nano-product types has to increase. The concentration of the literature on nano-Ag in textiles and CNT in polymers considerably limits its usefulness for the systemic assessment that MFA models intend to perform. As long as the already large number of nano-products on the market continues to grow, investigations about their release should be prioritized based on criteria that increase the environmental relevance of the information provided for exposure assessment purposes. This should include the mass of ENM incorporated, the potential for release, expected toxicity, and the environmental compartments that would be most affected.

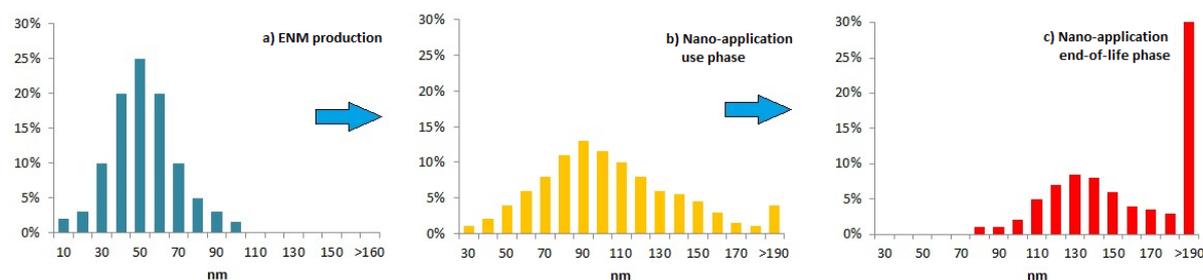
Arts et al. (2015) have developed a classification framework that goes some way towards this. They use intrinsic (nanomaterial properties) and system-dependent criteria to prioritize the assessment of ENMs and their applications for risk assessment. The development of standards or protocols may contribute to an improved characterization of the materials released, the definition and implementation of realistic scenarios, better

tracking of the transformations occurring during release and, particularly, better transferability of their information and results to environmental models. Cooperation with product manufacturers has rendered an improved understanding of the applications and an increased ability to improve the characterization of the material released. Therefore, cooperation with commercial partners should be encouraged.

The *initial characterization* provided by the literature should be extended in a way that a more complete description of the nano-applications and the ENM incorporated in it is offered. Which characterization measures are presented will depend on factors that consider the expected environmental exposure and toxicity that a specific ENM in a specific application may have. A bigger range of analytical techniques may be applied so that more data can be gathered and provided in order to perform probabilistic assessments. The *quantitative data on ENM mass released* should be presented as series of observations, which may prove useful for the implementation of dynamic and probabilistic assessment in models. In particular, it is important for MFA models to get these values as percentage of the initial ENM content in an application.

Regarding the *characterization of the nanomass released*, the assessment performed should go beyond size, shape and composition by TEM/SEM images and EDX analysis. More environmentally relevant measurements should be performed and reported. One measurement that we consider very relevant is the particle size distribution of the species generated during release. However, researchers should consider providing data about the ENM appearance, composition and the parameters that affect their interaction with the environment. A more systematic assessment of *transformations* should be performed to describe the relevant ENM sub-species that are generated during the average use of nano-applications. The *determinants of release* should go beyond basic assessment. An enhanced assessment could involve the development of improved protocols for release assessment (Wohleben, et al., 2014), that balance the control exerted to the factors affecting the experiment and the simulation of scenarios that resemble the average use of an application. The performance of statistical analysis for evaluating the significance of the data can help, too.

Although the specific improvements in MFA models that could be achieved if the recommendations in this review were followed depend on the future methodological developments, we envision that MFA models would be able to (i) provide flows of released ENM species that are environmentally relevant, not only for pristine nanomaterials as it is currently done; (ii) improve the description of the physico-chemical characteristics of the material released to the environment (**Figure 6**); (iii) be able to provide enhanced explanations of the ENM transformations; and (iv) be able to improve the dynamic modeling of release. Some ENM fate models developed recently rely on the results of MFA models (Praetorius, et al., 2012; Meesters, et al., 2014). The improvements proposed in this review may contribute that these models get improved inputs for their assessments.



**Figure 6.** Variation in the size distribution of engineered nanomaterials throughout their life cycle. (a) During production, the size distribution of the ENM powder will be largely

*within the nano-range. (b) During its incorporation into a nano-product, the ENM size can change due to agglomeration or functionalization reactions. (c) Once released from the application, most of the nanomaterial will be found agglomerated, aggregated, or attached to particles that are no longer in the nano-range.*

Recently developed fate models have used some of the material flow models described previously as input (Praetorius, et al., 2012; Meesters, et al., 2014). One important problem related to the lack of proper characterization of the ENMs released into the environment is that those models investigated the fate of pristine nanomaterials, those in **Figure 6** (a). However, they are more likely to be released transformed and with a size distribution that might resemble panel (c), that is, aggregated, agglomerated, or attached to bigger particles. As better-structured release experiments increase the availability of exploitable data, ENM release models will be able to improve the description of the released material and to supply more accurate information to fate models.

Providing a realistic description of ENM release using environmental models remains a very significant challenge, not only because of the general lack of information and data but also because the mechanisms producing release are not completely understood. The definition of mechanistic equations for systemic release assessment remains a challenge and probably limited to describe particular aspects of release, for example, the diffusion of nanoparticles from deep layers in a polymer composite to the surface (Duncan and Pillai, 2015b). Given the limited applicability of a mechanistic approach to describe and analyze the phenomena, probabilistic methods offer the most convenient way of dealing with all kinds of uncertainty and variability, from parametrical to epistemological uncertainties. Nevertheless, improving probabilistic methods remains also an important task.

As a general conclusion, advancing in both the release assessment field and MFA modeling as suggested in this review will likely render:

- ENM flows and concentrations closer to reality (relying less on worst-case scenarios),
- Improved parameterization of models (getting closer to mechanistic descriptions).
- Rely on measured data (and less on qualitative assessments).
- Reproduce release scenarios which are environmentally relevant.
- Improve the categorization of the nano-applications used in models, based on their potential for release rather than only on common physical and operational characteristics.
- Improve the dynamic description of release.
- Avoid the frequent use of extrapolations, authors' assumptions and expert opinions to define model parameters.

Despite their disadvantages, however, these models have been crucial in providing insight into the development and characteristics of potential ENM flows and concentrations in the environment. They have helped to tackle, in a creative way, the challenges resulting from scarce data and information and a lack of understanding of causal effects. Although not perfect, the results offered by those models have increased awareness of the problems that might arise from exposure to engineered nanomaterials and they have triggered the development of newer models that analyze both the behavior and fate of nanomaterials in the environment – models that will doubtless contribute to an improved understanding of the risks ultimately posed to humans and their environment.

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## 2.2. Stochastic fate analysis of engineered nanoparticles in incineration plants

### Abstract

Worldwide waste is increasing and can contain engineered nanoparticles (ENP) made from almost the entire spectrum of the periodic table. An increasing amount of waste (including nanowaste) is incinerated. A full-scale experiment in a modern waste incineration plant showed that even inert nanoparticles (nano-CeO<sub>2</sub>) are successfully removed from the flue gas and transferred to the solid incineration residues. Predicting the fate of nanomaterials in incineration plants with models based on real measurements would reduce the immense efforts (time and resources) for real-scale experiments. Here, we develop a model for the ENP fate in incineration plants, based on the data of the nanoCeO<sub>2</sub>-experiment. We investigated all possible transfers and sinks of ENP throughout the incineration by linking ENP concentration measurements to the nanomaterial flows and retention times. The model also delivers information on the associated uncertainties and how they propagate through the incineration system by using a fully probabilistic material flow analysis. The model can be generalized to other ENP and also to other incineration plants. We show that the output of the measurements was consistent albeit relying on multiple measurement methods, and that a one day sampling period is sufficient to obtain an overview on the fate of nanoparticles in incineration plants. In addition to the dynamic results, a generalized steady state mass flow with transfer factors is provided and can be used for modeling purposes of CeO<sub>2</sub> or other nano sized metals with similar physico-chemical properties.

### 2.2.1. Introduction

#### 2.2.1.1. Sustainable treatment of nanowaste is increasingly important

Nanoparticles from natural sources such as sea salt, soil dust or pollen lead to ambient concentrations of a few thousand particles per cm<sup>3</sup> (Shi et al., 2001). Anthropogenic sources such as traffic or heating further increase human exposure to nanoparticles. A new emission source is arising from the growing production and application of engineered nanoparticles (ENP) in industrial and consumer products (Gottschalk et al., 2010), which already represents a multiple billion USD industry (Becker, 2013). Various emission hotspots of ENP along their lifecycle in nanoenabled products have already been identified (Koehler et al., 2008), such as indoor emissions from nanopowder production and handling (Savolainen et al., 2010) or nanosilver release from textiles into wastewater (Lorenz et al., 2012). A further potential hotspot of accumulated and potentially re-emitted ENP are waste treatment systems (Musee, 2011), which have to deal with an increased amount of products containing ENP that have reached the end of their use. So-called nanowaste, i.e. discarded products that contain ENP, needs to be carefully evaluated with respect to sustainable waste management options. Increasingly important worldwide is incineration, which is a popular disposal option for conventional as well as for hazardous waste. Unfortunately, the amount and fate of nanoparticles in incineration plants is poorly understood because of virtually no experimental study and very simplistic modeling (Asmatulu et al., 2012; Bystrzejewska-Piotrowska et al., 2009; Mueller et al., 2013; Musee et al., 2011; Walser et al., 2012). Complicating aspects of nanoparticles are that they combine characteristics from gases (e.g. no sedimentation) and from larger particles (e.g. carrier for other compounds). Moreover, the complex chemical and physical conditions in real incineration plants make mechanistic fate modeling of ENP even more unrealistic. However, a real-scale experiment to test whether

incineration plants are a favorable solution for the disposal of nanowaste is a theoretical and practical challenge. Such studies have to deal with (i) the development of cutting-edge measurement capabilities, (ii) the extremely low nanoparticle concentrations on top of a commonly high elemental background concentration, and (iii) a complex large scale experimental setting. A recent study (Walser et al. 2012) showed that modern incineration plants can remove inert nanoparticles from the flue gas and deposit them in the solid incineration residues. This experimental study also showed that location, residence time and residence form of ENP during the waste treatment process cannot be modeled in detail without adding dynamics to the temporally and spatially resolved ENP fate parameters.

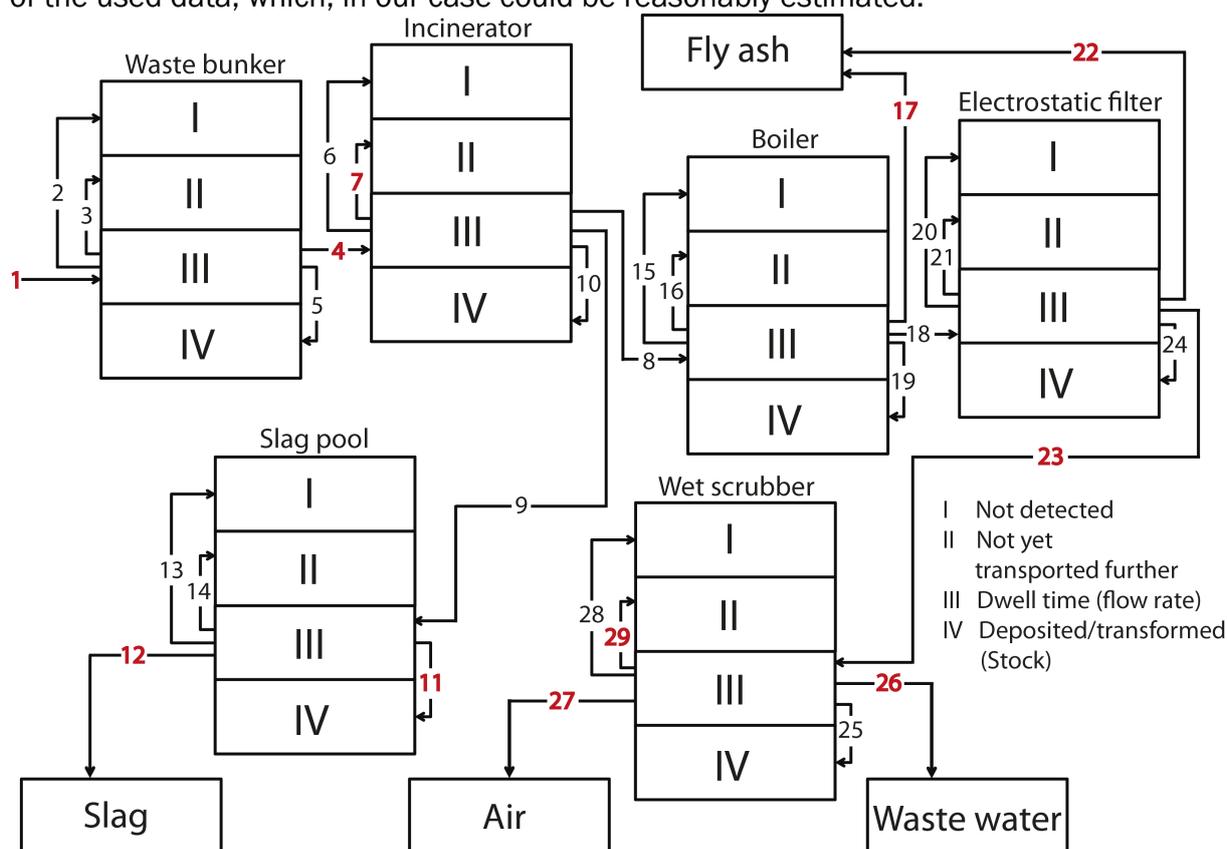
#### *2.2.1.2. Nanomaterial flow models can serve as complementary tools to measurement campaigns*

Aside from overcoming the scientific challenges, the financial burden of the previously mentioned large scale experiment had to be minimized and, therefore, only a limited number of samples were collected for analysis. A refined modeling of the nanomaterial fate through the incineration plant based on the abovementioned measurements would also provide valuable support to future studies. Until now, availability of data was limited to the output of simplistic material flow analyses (MFA) on some steady state particle mass fractions which were mainly deposited in the flue gas cleaning and slag (Mueller et al., 2013). Almost all these studies were conducted from a broad perspective of generic environmental release and/or exposure assessment for ENP without a closer look at the incineration and flue gas cleaning process (Gottschalk et al., 2013). A valuable extension of the classical MFA are probabilistic material flow analyses (PMFA), which extend the classical MFA with stochastic algorithms that may be linked to Bayesian statistics for computing non parametric (and parametric) probability distributions for model input and output. They are designed for covering substantial uncertainties of material flows and fates (Bornhöft et al., 2013) and programmed in R (R Development Core Team, 2012). Here we develop such a PMFA in order to improve the understanding of the fate of nanomaterials in incineration by adding dynamics and probabilistic information, and in order to highlight where more precise information on the incinerator under investigation is required. For this purpose, the measured nanomaterial flow of the experiment (Walser et al., 2012), however incomplete, can serve as the data provider for the model. The model allows for predicting the entire material transfer in the incineration plant and for evaluating and generalizing the ENP fate study described in Walser et al. (2012). The model described here has a higher architectural resolution than the reference analysis (Walser et al., 2012) because of a further division of the compartments and processes in the incineration plant. In addition, we extend the initially simplified steady state mass balance to having dynamic (time dependent) kinetics of nanomaterial ENP transfer, deposition and transformation. Moreover, the model is fed with measured evidence which reduces the usually large extent of assumed parameter values to a minimum. A further benefit of the model is that its logical structure can reveal potential inconsistencies in the measurement results.

Even the most sophisticated computations can neither compensate for missing measurement data nor improve available data of poor quality and low reliability. However, one advantage of modeling based on mass balances (in comparison to pure measurements) is that in the area of each input (or output) box of the system, one unknown output parameter can be computed as the difference of mass between the sum of the other outputs and 100% of the input. Such equalization generates additional knowledge and works in particular if the geometric structure of the material transfer

framework is exhaustively known (**Figure 7**). The application of this principle has also been shown for stochastic approaches (Gottschalk et al., 2010).

Based on this approach, we aim at considering the variability and uncertainty of measured input values as far as possible by directly following their empirical and analytical spread. We do not want to force the nanoparticle measurement data, which are often derived from completely different measurement approaches, into artificially derived theoretical probability distributions without any scientific basis. On quite the contrary, we limit ourselves to running the model as far as possible with the raw data in the form that they are available in **Table 4**. This is achieved by a random selection of input parameter values based on Monte Carlo (MC) computations that explore the entire possible input parameter space. Such a parameter space is only shaped by the spread and uncertainty of the used data, which, in our case could be reasonably estimated.



**Figure 7.** Model structure for the probabilistic nanoparticle fate and flow analysis through the waste incineration plant. Red: Measurement points for the nanoparticles. The numbered flows were modeled over time based on the measurement data, underlying mass flows, and known transfer coefficients between and in the compartments of the MSWI plant.

In contrast to earlier studies on ENP transport and the release of ENP (Gottschalk et al., 2013), we extend static ENP mass transfer modeling to dynamic ENP flow kinetics that vary as a function of the time. This allows insights into the ENP flow in the incineration plant, revealing the fate of the particles at any time. Moreover, for a generic ENP pollution control and quantification, our model allows deriving steady state values that reflect an overall nanomaterial fate and transport after the nanowaste treatment has been completed. Such steady state values are computed for environmental release and exposure assessments of CeO<sub>2</sub> that can also be used analogically for other metallic ENP.

**Table 4.** Data that was fed into the model, including the underlying uncertainties of the ENP flow calculation. The uncertainties propagate through the system. Flows with no uncertainty add no additional uncertainty to the inherited uncertainty range. Grey: measurement results; green: parameters from a logical combination of measurements and calculations; white: values which illustrate assumptive time dependent ENP mass flows that were either not measured (“nm”) and therefore extrapolated from the previous or subsequent period, or known to be (close to) zero (0); orange: flows that were unknown a priori and automatically generated by the model (flow number in bold).

## 6. ENMs flows by ENM type and product category

In this section we present the results shown in Section 3.3 of the main document disaggregated by product category. The category *Undefined* corresponds to the ENM mass that was not considered to any of the product categories selected in Section 3.1.1. Therefore, this outflow was not assigned to any of the receiving compartments.

**Table S10.** ENMs flows in 2012 from the recycling system to the seven compartments by ENM type and product category. Units: tons/year; mode values and percentiles 15<sup>th</sup> (P15) and 85<sup>th</sup> (P85)

Category	Percentile	WIP <sup>a</sup>	LF <sup>b</sup>	EXP <sup>c</sup>	PMC <sup>d</sup>	CK <sup>e</sup>	WW <sup>f</sup>	ELIM <sup>g</sup>	SUM
<b>TiO<sub>2</sub></b>									
Consumer electronics	P15	13.34	0	1.79	0	0	0.48	0	15.61
	Mode	19.79	0	2.58	0	0	0.69	0	23.06
	P85	36.57	0	5.51	0	0	1.51	0	43.59
Paints	P15	2.34	8.22	0	0.93	0.46	0	0	11.95
	Mode	3.44	12.71	0	1.27	0.69	0	0	18.12
	P85	7.28	23.47	0	2.94	1.47	0	0	35.17
Undefined <sup>h</sup>	P15	0	0	0	0	0	0	0	1.15
	Mode	0	0	0	0	0	0	0	1.72
	P85	0	0	0	0	0	0	0	3.45
Total	P15	15.68	8.22	1.79	0.93	0.46	0.48	0	28.70
	Mode	23.23	12.71	2.58	1.27	0.69	0.69	0	42.90
	P85	43.85	23.47	5.51	2.94	1.47	1.51	0	82.21
<b>ZnO</b>									
Paints	P15	0.59	2.04	0	0.23	0.12	0	0	2.98
	Mode	0.92	3.07	0	0.36	0.19	0	0	4.55
	P85	3.72	12.25	0	1.50	0.76	0	0	18.22
Undefined <sup>h</sup>	P15	0	0	0	0	0	0	0	0.10
	Mode	0	0	0	0	0	0	0	0.15
	P85	0	0	0	0	0	0	0	0.65
Total	P15	0.59	2.04	0	0.23	0.12	0	0	3.08
	Mode	0.92	3.07	0	0.36	0.19	0	0	4.70
	P85	3.72	12.25	0	1.50	0.76	0	0	18.87

<sup>a</sup> Waste Incineration Plant <sup>b</sup> Landfill <sup>c</sup> Exported <sup>d</sup> Production-Manufacture-Consumption sector of the economy <sup>e</sup> Cement Kiln <sup>f</sup> Waste Water <sup>g</sup> Eliminated <sup>h</sup> Undefined: it corresponds to the nanomass that was not assigned to any product category in Section 3.1.

**Table S10 Cont.** ENMs flows in 2012 from the recycling system to the seven compartments by ENM type and product category. Units: tons/year; mode values and percentiles 15<sup>th</sup> (P15) and 85<sup>th</sup> (P85)

Category	Percentile	WIP <sup>a</sup>	LF <sup>b</sup>	EXP <sup>c</sup>	PMC <sup>d</sup>	CK <sup>e</sup>	WW <sup>f</sup>	ELIM <sup>g</sup>	SUM
<b>Ag</b>									
Consumer electronics	P15	0.1768	0	0.0283	0	0	0.0284	0.0163	0.2498
	Mode	0.2221	0	0.0375	0	0	0.0371	0.0215	0.3182
	P85	0.2812	0	0.0547	0	0	0.0546	0.0321	0.4226
MedTech	P15	0.0134	0	0	0	0	0	0.0134	0.0268
	Mode	0.0180	0	0	0	0	0	0.0175	0.0355
	P85	0.0276	0	0	0	0	0	0.0276	0.0552
Textiles	P15	0	0	0.0206	0.0012	0	0	0	0.0217
	Mode	0	0	0.0267	0.0015	0	0	0	0.0282
	P85	0	0	0.0399	0.0027	0	0	0	0.0425
Metals	P15	0	0	0	0	0	0	0.0188	0.0188
	Mode	0	0	0	0	0	0	0.0240	0.0240
	P85	0	0	0	0	0	0	0.0365	0.0365
Paints	P15	0.0020	0.0071	0	0.0008	0.0004	0	0	0.0102
	Mode	0.0026	0.0094	0	0.0010	0.0005	0	0	0.0135
	P85	0.0045	0.0141	0	0.0018	0.0009	0	0	0.0213
Undefined <sup>h</sup>	P15	0	0	0	0	0	0	0	0.0005
	Mode	0	0	0	0	0	0	0	0.0006
	P85	0	0	0	0	0	0	0	0.0010
Total	P15	0.1922	0.0071	0.0489	0.0019	0.0004	0.0284	0.0486	0.33
	Mode	0.2427	0.0094	0.0642	0.0026	0.0005	0.0371	0.0629	0.42
	P85	0.3133	0.0141	0.0945	0.0045	0.0009	0.0546	0.0962	0.58
<b>CNT</b>									
Energy	P15	0	0	1.26	0	0	0	0	1.26
	Mode	0	0	1.75	0	0	0	0	1.75
	P85	0	0	2.97	0	0	0	0	2.97
Electronic	P15	0	0	0.41	0	0	0	0	0.41
	Mode	0	0	0.57	0	0	0	0	0.57
	P85	0	0	1.06	0	0	0	0	1.06
Coatings and Paints	P15	0	0	0.05	0	0	0	0.05	0.11
	Mode	0	0	0.07	0	0	0	0.08	0.15
	P85	0	0	0.15	0	0	0	0.15	0.30
Automotive	P15	0.04	0	0	0.04	0	0	0	0.09
	Mode	0.06	0	0	0.06	0	0	0	0.12
	P85	0.12	0	0	0.12	0	0	0	0.24
Undefined <sup>h</sup>	P15	0	0	0	0	0	0	0	0.12
	Mode	0	0	0	0	0	0	0	0.17
	P85	0	0	0	0	0	0	0	0.30
Total	P15	0.04	0	1.72	0.04	0	0	0.05	1.98
	Mode	0.06	0	2.39	0.06	0	0	0.08	2.75
	P85	0.12	0	4.17	0.12	0	0	0.15	4.87

<sup>a</sup> Waste Incineration Plant <sup>b</sup> Landfill <sup>c</sup> Exported <sup>d</sup> Production-Manufacture-Consumption sector of the economy <sup>e</sup> Cement Kiln <sup>f</sup> Waste Water <sup>g</sup> Eliminated <sup>h</sup> Undefined; it corresponds to the nanomass that was not assigned to any product category in Section 3.1.

## References

- EU, 2012. Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE). European Parliament.
- Goodship, V., Stevels, A., 2012. Waste Electrical and Electronic Equipment (WEEE) Handbook. Elsevier Science
- Sun, T.Y., Gottschalk, F., Hungerbuhler, K., Nowack, B., 2014. Comprehensive probabilistic modelling of environmental emissions of engineered nanomaterials. Environmental pollution 185, 69-76.

## 5.4. Supporting information for “Codes on environmental toxicity and release modeling for DSS”

### 1. R package on Probabilistic Species Sensitivity Distributions (PSSD)

Package: PSSD  
 Type: Package  
 Title: Probabilistic Species Sensitivity Distribution (PSSD) Package  
 Version: 1.0.0  
 Date: 2016-21-03  
 Author: Fadri Gottschalk [aut], Martin Schneider [initial support package management]  
 ETSS AG  
 Maintainer: Fadri Gottschalk <fadri.gottschalk@etss.ch>  
 Description: This is a package with functions used to perform PSSD (Probabilistic Species Sensitivity Distribution) modelling. The PSSD package is well-suited to run species sensitivity distribution simulations in cases of distinct ecotoxicological data scarcity and variability. Probability distributions of the uncertainty and variability of the target toxicological sensitivity are for the first time computed for each single species that are unified into a main PSSD simulation for considered ecosystems. The package allows the user also computing probability distributions of the predicted no effect concentrations (PNEC) derived from the PSSD model. Another purpose of using this PSSD package may be to run probabilistic environmental risk evaluation that combines the PSSD output with the probability distributions of the expected environmental exposure.  
 License: What license is it under?  
 LazyData: TRUE  
 NeedsCompilation: no  
 Packaged: 2016-21-03 13:09:44 UTC; fg

```
#####
#####
```

#### PackageManagement

```
#-----
#-----
```

```

# package management
library(devtools)
document("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-
Package/PSSD") # creates help files
build("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-Package/PSSD") #
erstellen von kompilierte
install.packages("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-
Package/PSSD_1.0.0.tar.gz",repos = NULL, type = "source") # installieren
library(PSSD) # laden des Pakets

```

```
#####
#####general management codes
```

```
.libPaths()
```

```
library(devtools)

document("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-
Package/PSSD") # creates help files
build("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-Package/PSSD") #
erstellen von kompiliertem Ordner

detach("package:PSSD")

install.packages("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-
Package/PSSD_1.0.0.tar.gz",repos = NULL, type = "source") # installieren

library(PSSD) # laden des Pakets

#####
#####
help(createPSSDModell)
help(plotCdf)
help(loadSpeciesDataFromExcel)
help(rawSpeciesData)

T_data <- rawSpeciesData(SpeciesA = c(20,123, 15), SpeciesB = c(25, 13, 19, 80), SpeciesC = c(5, 13,
17, 80))

setwd("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-
Package/PSSD/Extradata/")
getwd()

T_data<-loadSpeciesDataFromExcel('PSSD_Excel_Data.xlsx', xlsx = TRUE)

VPSSD_demonstration_2<-createPSSDModell(T_data, PSSD_simulations = 5, PSSD_length = 100,
species_length = 10^2, cv_factor1 = 0.5, cv_factor2 = 0.5,
cv_factor3 = 0, cv_low_end = 0.5, cv_high_end = 0.5,
interval_length = 10^2)

VPSSD_demonstration<-createPSSDModell(T_data, PSSD_simulations = 100, PSSD_length = 100,
species_length = 10^2, cv_factor1 = 0.5, cv_factor2 = 0.5,
cv_factor3 = 0, cv_low_end = 0.5, cv_high_end = 0.5,
interval_length = 10^2)

VPNEC_demonstration_2<-createPNECModell(VPSSD_demonstration_2)
VPNEC_demonstration<-createPNECModell(VPSSD_demonstration)

# plots

load("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-
Package/VPSSD_demonstration.R")
```

```
load("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PSSD_Model/R-
Package/TiO2_simulation_PEC_SSD Kopie.r")

plotCdf(PSSD_demonstration_2, T_data)

plotCdf(VPSSD_demonstration, T_data)

plotPdfPNEC(VPNEC)

plot(density(log(stpeffluent, base=10),from=-3, to=5.8),lty=3,lwd=1.4, col=4,main="")
lines(density(log(surfacewater, base=10),from=-3, to=5.8),lty=4,lwd=1.4,col=4, main="")

pdf <- density(log10(VPSSD_demonstration[,1]))

lines(pdf,lwd=2.0,col=2,main="Pdf of PSSD", xlab="log( $\mu\text{g/l}$ )", ylab="Density")#our PSSD

for (y in 2:ncol(VPSSD_demonstration)){

  lines(density(log10(VPSSD_demonstration[,y])),lwd=2.0,col=3)
  lines(pdf,lwd=2.0,col=2,main="Pdf of PSSD", xlab="log( $\mu\text{g/l}$ )", ylab="Density")#our PSSD
}

pdf <- density(VPNEC)

lines(pdf,xlim=c(-1,8),ylim=c(0,0.5), lwd=2.0,col=6,main="Pdf of PNEC", xlab="log( $\mu\text{g/l}$ )",
ylab="Density")#our PSSD

#####
#####

PSSDModell

#-----
#-----

#' createPSSDModell
#'
#' function to create a probabilistic species sensitivity distribution (PSSD) modell
#'
#' @param T_data A numeric matrix with nrow = 100 and ncol = 100
#' @param cv_data A numeric matrix with nrow = 100 and ncol = 100 (does not have to be
generated, the default is zero)
#' @param PSSD_simulations A number for the quantity of PSSDs to be computed
```

```
# @param PSSD_length A number for the quantity of the model output values for the PSSD
# @param species_length A number for the quantity of the model output values of the PSSD of one
single species
# @param cv_factor1 A fraction that reflects the uncertainty range (confidence interval) on both sides
of the first assessment factor (short to long term toxicity)
# @param cv_factor2 A fraction that reflects the uncertainty range (confidence interval) on both sides
of the second assessment factor (extrapolation from the observed effect concentrations into no effect
concentrations)
# @param cv_factor3 A fraction that reflects the uncertainty range (confidence interval) on both sides
of the third assessment factor (expected differences between lab based experimental conditions and
natural conditions)
# @param cv_low_end A fraction that reflects the uncertainty range (confidence interval) on the left
hand side of the lowest toxicological endpoint used for one single species
# @param cv_high_end A fraction that reflects the uncertainty range (confidence interval) on the right
hand side of the highest toxicological endpoint used for one single species
# @param interval_lenth A number for the quantity of the model output values of the interval
distributions that are the distributions between all the toxicological endpoints collected for a particular
species
#
# @return a matrix
#
# @export
#
createPSSDModell <- function(T_data, cv_data, PSSD_simulations = 1, PSSD_length = 100,
species_length = 10^2, cv_factor1 = 0.5,
                        cv_factor2 = 0.5, cv_factor3 = 0,
                        cv_low_end = 0.5, cv_high_end = 0.5, interval_length = 10^2){

#-----
#   Fraction of values (compared to full intervals) for border intervals
#-----

fraction_full_interval_for_low<-0.5

#-----
#   Fraction of values (compared to full intervals) for border intervals
#-----

fraction_full_interval_for_high<-0.5

#-----
#   Number of values left triangul
#-----

length_border_left<-interval_length*fraction_full_interval_for_low## number of values

#-----
#   Number of values right triangul
#-----
```

```

length_border_right<-interval_length*fraction_full_interval_for_high## number of values

# final input matrix
Vdata_raw <- T_data

#-----
#-----
#   Core algorithms
#-----
#-----

#-----
#   Iterative PSSD simulations
#-----

N <- PSSD_simulations

#Vp nec <- matrix(NA,1,N) #one value in each simulation
VPSSD <- matrix(NA,PSSD_length,N) #PSSD_length values in each simulation=rows, simulation
round = column

for (j in 1:N){

#-----
#   Start matrix for endpoint data randomization
#-----

Vdata_randomized<- matrix(0,10^2,10^2)  ## Read data, data in µg/L and names in first
Datavariationfactor<-matrix(1,10^2,10^2)#new with confidence values for data, given here in
order to have it ready by default

for (b in 1:10^4){

T_ran <- matrix(1,10^2,10^2)

n_sample<-rep(1:10^2,each=100, 1)
m_sample<-rep(1:10^2,each=1, 100)

n<-n_sample[b]#n equals species
m<-m_sample[b]#m equals species value of species

Datavariationfactor[n,m]<-runif(1,1-cv_data[n,m],1+cv_data[n,m])#In addition Data
variation given in the data input codes

Vdata_randomized[n,m]<-c(T_ran[n,m]*Datavariationfactor[n,m]*runif(1,1-
cv_factor1,1+cv_factor1)*runif(1,1-cv_factor2,1+cv_factor2)*runif(1,1-cv_factor3,1+cv_factor3) #
row = species, column=value,In addition Data variation
)

```

```
}  
  
#-----  
#   Endpoint data randomization  
#-----  
  
Vdata_unsorted<- Vdata_raw[,]*Vdata_randomized[,]  
  
#-----  
#   Endpoint data sorting sequences  
#-----  
Vdata_sortiert <- matrix(0,10^2,10^2)  
  
for (k in 1:10^2){  
  
  T_unsorted <- Vdata_unsorted  
  
  Vdata_sortiert[k,]<-sort(T_unsorted[k,])  
}  
  
#-----  
#   Endpoint data extremal values (border values)  
#-----  
  
Tmin <- matrix(0,1,10^2) # row = one value, column=species  
Tmax <- matrix(0,1,10^2) # row = one value, column=species  
  
for (z in 1:10^2){  
  
  Tmin[,z]<- min(Vdata_sortiert[z,])  
  Tmax[,z]<- max(Vdata_sortiert[z,])  
  
}  
  
#-----  
#   Endpoint distributions high end border values  
#-----  
  
triangular_right<-matrix(NA,length_border_right,10^2)# row = values, column=species  
  
for (u in 1:10^2){
```

```

if (Tmax[,u]>0) {
  a=Tmax[,u]
  b=Tmax[,u]
  c=Tmax[,u]*(1+cv_high_end)
  M <-
matrix(c(rep(a,length_border_right),rep(b,length_border_right),rep(c,length_border_right)),length_bor
der_right) # to see perhaps approx. 1/2 to avoid overestimating extremes at the borders
  triangular_right[,u]<- apply(M,1,triangulsimright)

} else {
  triangular_right[,u]<-matrix(0,1,length_border_right)
}

}

#-----
#   Endpoint distributions low end border values
#-----

triangular_left<-matrix(NA,length_border_left,10^2)# row = values, column=species

for (l in 1:10^2){

  if (Tmax[,l]<=0){

    triangular_left[,l]<-matrix(0,1,length_border_left)

  } else {

    a=min(Vdata_sortiert[l,][Vdata_sortiert[l,]>0])*(1-cv_low_end)
    b=min(Vdata_sortiert[l,][Vdata_sortiert[l,]>0])
    c=min(Vdata_sortiert[l,][Vdata_sortiert[l,]>0])

    M <-
matrix(c(rep(a,length_border_left),rep(b,length_border_left),rep(c,length_border_left)),length_border_
left) # to see perhaps approx. 1/2 to avoid overestimating extremes at the borders
    triangular_left[,l]<- apply(M,1,triangulsimleft)
  }

}

#-----
#   PSSD model
#-----

dim1<-c("Species 1", "Species 2","Species 3", "Species 4", "Species 5", "Species 6","Species 7",
"Species 8","Species 9", "Species 10","Species 11", "Species 12", "Species 13", "Species 14","Species
15", "Species 16", "Species 17", "Species 18","Species 19", "Species 20", "Species 21", "Species
22","Species 23", "Species 24","Species 25", "Species 26", "Species 27", "Species 28", "Species 29",

```

```
"Species 30","Species 31", "Species 32","Species 33", "Species 34","Species 35", "Species 36",
"Species 37", "Species 38","Species 39", "Species 40","Species 41", "Species 42","Species 43",
"Species 44", "Species 45", "Species 46", "Species 47", "Species 48", "Species 49", "Species
50","Species 51", "Species 52", "Species 53", "Species 54","Species 55", "Species 56","Species 57",
"Species 58","Species 59", "Species 60", "Species 61", "Species 62","Species 63", "Species
64","Species 65", "Species 66","Species 67", "Species 68", "Species 69", "Species 70","Species 71",
"Species 72", "Species 73", "Species 74","Species 75", "Species 76", "Species 77", "Species
78","Species 79", "Species 80","Species 81", "Species 82","Species 83", "Species 84", "Species 85",
"Species 86","Species 87", "Species 88","Species 89", "Species 90","Species 91", "Species 92",
"Species 93", "Species 94","Species 95", "Species 96", "Species 97", "Species 98","Species 99",
"Species 10^2")
```

```
dim2<-c("Interval 1", "Interval 2","Interval 3", "Interval 4", "Interval 5", "Interval 6","Interval 7",
"Interval 8","Interval 9", "Interval 10","Interval 11", "Interval 12", "Interval 13", "Interval
14","Interval 15", "Interval 16", "Interval 17", "Interval 18","Interval 19", "Interval 20", "Interval 21",
"Interval 22","Interval 23", "Interval 24","Interval 25", "Interval 26","Interval 27", "Interval 28",
"Interval 29", "Interval 30","Interval 31", "Interval 32","Interval 33", "Interval 34","Interval 35",
"Interval 36", "Interval 37", "Interval 38","Interval 39", "Interval 40","Interval 41", "Interval
42","Interval 43", "Interval 44", "Interval 45", "Interval 46","Interval 47", "Interval 48", "Interval 49",
"Interval 50","Interval 51", "Interval 52", "Interval 53", "Interval 54","Interval 55", "Interval
56","Interval 57", "Interval 58","Interval 59", "Interval 60", "Interval 61", "Interval 62","Interval 63",
"Interval 64","Interval 65", "Interval 66","Interval 67", "Interval 68", "Interval 69", "Interval
70","Interval 71", "Interval 72", "Interval 73", "Interval 74","Interval 75", "Interval 76", "Interval 77",
"Interval 78","Interval 79", "Interval 80","Interval 81", "Interval 82","Interval 83", "Interval 84",
"Interval 85","Interval 86","Interval 87", "Interval 88","Interval 89", "Interval 90","Interval 91",
"Interval 92", "Interval 93", "Interval 94","Interval 95", "Interval 96", "Interval 97", "Interval
98","Interval 99")
```

```
intervals_total_values=9900*interval_length#total amount of values (interval_length per interval,
9900 (99 intervals) times 100 (species)) intervals) computed in general
```

```
model_multidim_matrix<-array(rep(0,intervals_total_values), c(10^2,99,interval_length),
dimnames=list(dim1,dim2))# dim 1 = species, dim 2 = intervals, dim 3 = values in interval
```

```
p_sample<-rep(1:10^2,each=99, interval_length)#species: species 1, 99 times; species 2, 99 times
etc.
```

```
t_sample<-rep(1:99,10^2*interval_length)#intervals pro species:intervals 1 to 99,
10^2*interval_length times
```

```
l_sample<-rep(1:interval_length,each=9900)#number of matrix positions (value1_position,
value2_position, value3_position...) distributed equally to each interval
```

```
for (s in 1:intervals_total_values){
```

```
t<-t_sample[s]
p<-p_sample[s]
l<-l_sample[s]
```

```
if (Vdata_sortiert[p,t]>0){
  model_multidim_matrix[p,t,1] <- runif(1,Vdata_sortiert[p,t],Vdata_sortiert[p,t+1])
} else {
  model_multidim_matrix[p,t,1]<-c(0)
}
}

#-----
#-----
#   Single species evaluation only for a single PSSD without randomization of endpoint data
#-----
#-----

#-----
#   PSSD single species model ohne Border
#-----

single_species_PSSD_raw<-matrix(NA,99*interval_length,10^2)#row=values, column=species
for (s in 1:10^2){

  single_species_PSSD_raw[s]<- model_multidim_matrix[s,1:99,]

}

#-----
#   PSSD single species incl. Border
#-----

single_species_PSSD<-matrix(NA,species_length,10^2)#row=values, column=species
for (e in 1:10^2){
  if (max(single_species_PSSD_raw[,e])>0){
```

```
    single_species_PSSD[,e]<-
sample(c(single_species_PSSD_raw[,e][single_species_PSSD_raw[,e]>0],triangular_left[,e][triangular_
r_left[,e]>0],triangular_right[,e][triangular_right[,e]>0]),species_length)##achtung s angeben

  } else {

    single_species_PSSD[,e]<-
sample(c(triangular_left[,e],triangular_right[,e]),species_length)##achtung s angeben
  }

}

#-----
#   PSSD model cleaned
#-----

PSSD_total<-single_species_PSSD[,][single_species_PSSD[,]>0]

#-----
#   PSSD model cleaned
#-----

PSSD<-sample(PSSD_total,PSSD_length)

#-----
# Create HC5
#-----

#-----
# Create PSSD of single simulation rounds
#-----

#PNEC<-quantile(PSSD,0.05)

# Vp nec[j] <- PNEC
# VPSSD[j] <- PSSD

}

return(VPSSD)
```

```
}

#####
#####

PNECModell

#-----
#-----

#createPNECModell
#
#function to create a probabilistic predicted no effect concentration (PNEC) modell
#
#@param PSSD A probabilistic species sensitivity distribution (PSSD) modell output
#
#@return a numeric vector of the computed PNEC values
#
#@export
createPNECModell <- function(PSSD) {

  VPNEC <- vector()
  for (i in 1:ncol(PSSD)) {

    VPNEC[i] <- quantile(PSSD[, i], 0.05)
  }

  return(VPNEC)
}

#####
#####

loadModell_1

#-----
#-----

# loadSpeciesDataConfidenceFromExcel
#
# function to create a matrix with species data confidence from excel confidence data
#
#@param ... numeric Vectors named after species \code{speciesA = c(0.1,0.4, 0.5)}
#@return a numeric matrix with nrow = 100 and ncol = 100
#@examples
# cv_data<-loadSpeciesDataConfidenceFromExcel('PSSD_Excel_Data_Confidence.xlsx', xls =
TRUE)
#
#@importFrom openxlsx read.xlsx
```

```
##@export
loadSpeciesDataConfidenceFromExcel <- function(file, xlsx = TRUE) {

  cv_data <- matrix(0, 10 ^ 2, 10 ^ 2)

  row.names(cv_data) <- rep(NA, nrow(cv_data))

  #-----
  #   Read data tables excel (csv)
  #-----
  #-----

  if (!xlsx) {
    species_sensitivity_raw_data_confidence <- read.table(file, sep = ";", dec = ".")
  } else {
    species_sensitivity_raw_data_confidence <- openxlsx::read.xlsx(file, colNames = FALSE)
  }

  for (r in 1:100) {

    row.names(cv_data)[r] <- as.character(strsplit(gsub(" ", "", x =
species_sensitivity_raw_data_confidence[r+2, 2], ##Distribution values from excel table
fixed = TRUE), split = ",")[[1]])

    for (h in 1:100) {

      cv_data[r,h] <- as.numeric(strsplit(gsub(" ", "", x = species_sensitivity_raw_data_confidence[r + 2,
h + 2], ##Distribution values from excel table
fixed = TRUE), split = ",")[[1]])

    }
  }
  return(cv_data)
}

#####
#####

loadModell_2

#-----
#-----

#' loadSpeciesDataFromExcel
#'
#' function to create a matrix with species data from excel data
```

```

#
# @param ... numeric Vectors named after species \code{speciesA = c(20,123, 15)}
# @return a numeric matrix with nrow = 100 and ncol = 100
# @examples
# T_data<-loadSpeciesDataFromExcel('PSSD_Excel_Data.xlsx', xlsx = TRUE)
#
#@importFrom openxlsx read.xlsx
#@export
loadSpeciesDataFromExcel <- function(file, xlsx = TRUE) {

  T_data <- matrix(0, 10 ^ 2, 10 ^ 2)

  row.names(T_data) <- rep(NA, nrow(T_data))

  #-----
  #   Read data tables excel (csv)
  #-----

  if(!xlsx) {
    species_sensitivity_raw_data <- read.table(file, sep = ";", dec = ".")
  }else {
    species_sensitivity_raw_data <- openxlsx::read.xlsx(file, colNames = FALSE)
  }

  for (r in 1:100) {

    row.names(T_data)[r] <- as.character(strsplit(gsub(" ", "", x = species_sensitivity_raw_data[r+2, 2],
##Distribution values from excel table
              fixed = TRUE), split = ",")[[1]])

    for (h in 1:100) {

      T_data[r,h] <- as.numeric(strsplit(gsub(" ", "", x = species_sensitivity_raw_data[r + 2, h + 2],
##Distribution values from excel table
              fixed = TRUE), split = ",")[[1]])

    }
  }
  return(T_data)
}

#####
#####

rawSpeciesData Modell_1

```

```
#-----  
#-----  
  
# rawSpeciesData  
#  
# function to create a matrix with species data  
#  
# @param ... numeric Vectors named after species \code{speciesA = c(20,123, 15)}  
# @return a numeric matrix with nrow = 100 and ncol = 100  
# @examples  
# T_data <- rawSpeciesData(SpeciesA = c(20,123, 15), SpeciesB = c(25, 13, 19, 80), SpeciesC = c(5,  
13, 17, 80))  
#  
# @export  
rawSpeciesData <- function(...) {  
  
  inputData <- list(...)  
  
  T_data <- matrix(0,10^2,10^2)  
  
  row.names(T_data) <- rep(NA, nrow(T_data))  
  
  if (length(names(inputData)) > 0) {  
    row.names(T_data)[1:length(inputData)] <- names(inputData)  
  }  
  
  for (i in 1:length(inputData)) {  
    T_data[i, 1:length(inputData[[i]])] <- inputData[[i]]  
  }  
  
  return(T_data)  
}  
  
#####  
#####  
  
rawSpeciesData Modell_2  
  
#-----  
#-----  
  
# rawSpeciesDataConfidenceValues  
#  
# function to create a matrix with species data confidence values  
#  
# @param ... numeric Vectors named after species \code{speciesA = c(0.1,0.4, 0.5)}  
# @return a numeric matrix with nrow = 100 and ncol = 100  
# @examples  
# cv_data <- rawSpeciesDataConfidenceValues(SpeciesA = c(0.1,0.4, 0.5), SpeciesB = c(0, 0.2))  
#  
# @export  
rawSpeciesDataConfidenceValues <- function(...) {  
  
  inputDataConfidence <- list(...)
```

```
cv_data <- matrix(0,10^2,10^2)

row.names(cv_data) <- rep(NA, nrow(cv_data))

if (length(names(inputDataConfidence)) > 0) {
  row.names(cv_data)[1:length(inputDataConfidence)] <- names(inputDataConfidence)
}

for (i in 1:length(inputDataConfidence)) {
  cv_data[i, 1:length(inputDataConfidence)[i]] <- inputDataConfidence[[i]]
}

return(cv_data)
}

# triangulsimleft
#
# triangular distribution used for the probability distributions at the lower end of the PSSD of each
# single organism studied
#
# @param automatically generated vector data input from the createPSSDModell.R function
# @return a numeric vector (triangular distribution)
#
# @export
triangulsimleft <- function(vecabc) {

  min <- vecabc[1]
  mode <- vecabc[2]
  max <- vecabc[3]

  u <- runif(1,0,1)
  if (u <= (mode-min)/(max-min)) {
    r=min+sqrt(u*(max-min)*(mode-min)) }else{
    r=max-sqrt((1-u)*(max-min)*(max-mode))
  }
  r
}

# triangulsimright
#
# triangular distribution used for the probability distributions at the higher end of the PSSD of each
# single organism studied
#
# @param automatically generated vector data input from the createPSSDModell.R function
# @return a numeric vector (triangular distribution)
#
# @export
triangulsimright <- function(vecabc) {

  min <- vecabc[1]
```

```

mode <- vecabc[2]
max <- vecabc[3]

u <- runif(1,0,1)
if (u <= (mode-min)/(max-min) ){
  r=min+sqrt(u*(max-min)*(mode-min)) }else{
  r=max-sqrt((1-u)*(max-min)*(max-mode))
  }
r
}
#####
#####

plotModell

#-----
#-----

# plotCdf
#
# a function to plot a cumulative density function for the probabilistic species sensitivity distribution
(PSSD) modell
#
# @param VPSSD A vector of the probabilistic species sensitivity distribution (PSSD) modell output
# @param T_data A matrix with the species names and their endpoint values
#
# @return plot
#
# @export
plotCdf <- function(VPSSD, T_data) {

  nSpecies <- sum(!is.na(row.names(T_data)))

  height <- 1/(nSpecies + 1)

  #cdf of log sensitivity values
  cdf_selection<-sample(VPSSD,length(VPSSD[,1]))
  cdf <- ecdf(log10(cdf_selection))#cumulative illustration of sorted values
  #quartz("PSSD_xx_cdf.jpg")
  plot(cdf, main="Cdf of PSSD",xlim=c(log10(min(cdf_selection))-3,log10(max(cdf_selection))+5),
  col=2, lwd=1.3, lty=3, xlab="log( $\mu$ /l)", ylab="Density") #for the Risk graphs

  for (y in 1:ncol(VPSSD)){

    lines(ecdf(log10(VPSSD[,y])),lwd=2.0,col=3)
    lines(cdf,lwd=2.0,col=2)

  }
  for (specie in 1:nSpecies) {
    nPoints <- length(T_data[specie, T_data[specie, ] > 0])
    points(y = rep(height*specie, nPoints), x = log10(T_data[specie,1:nPoints]), cex = 1.5,pch = 21, bg
    = "black")
    text(y = height*specie, x = max(log10(T_data[specie,1:nPoints])) + 3, labels =
    row.names(T_data)[specie])
  }
}

```

```
}

# plotPdf
#
# a function to plot a probability density function for the probabilistic species sensitivity distribution
(PSSD) modell
#
# @param VPSSD A vector of the probabilistic species sensitivity distribution (PSSD) modell output
# @return plot
#
# @export
plotPdf <- function(VPSSD) {

  pdf_selection <- sample(VPSSD, length(VPSSD[, 1]))
  pdf_selection_density <- density(log10(pdf_selection))

  plot(pdf_selection_density, xlim=c(min(log10(pdf_selection)-
2), max(log10(pdf_selection)+2)), ylim=c(0, max(pdf_selection_density$y)*2),
lwd=2.0, col=2, main="Pdf of PSSD", xlab="log( $\mu\text{g/l}$ )", ylab="Density")#our PSSD

  for (y in 2:ncol(VPSSD)){

    lines(density(log10(VPSSD[, y])), lwd=2.0, col=3)

  }
  lines(pdf_selection_density, xlim=c(min(log10(pdf_selection)-
2), max(log10(pdf_selection)+2)), ylim=c(0, max(pdf_selection_density$y)*2),
lwd=2.0, col=2, main="Pdf of PSSD", xlab="log( $\mu\text{g/l}$ )", ylab="Density")#our PSSD

}

# plotPdfPNEC
#
# function to plot a probability density function for the probabilistic predicted no effect concentration
(PNEC) modell
#
# @param VPNEC A vector of the probabilistic predicted no effect concentration (PNEC) modell
#
# @return plot
#
# @export
plotPdfPNEC <- function(VPNEC) {
  pdf <- density(VPNEC)

  plot(pdf, xlim=c(-1, 8), ylim=c(0, 0.5), lwd=2.0, col=6, main="Pdf of PNEC", xlab=" $\mu\text{g/l}$ ",
ylab="Density")#our PSSD

}
```

```
#####  
#####  
  
create.Rd  
  
#-----  
#-----  
% Generated by roxygen2 (4.1.0): do not edit by hand  
% Please edit documentation in R/createPSSDModell.R  
\name{createPSSDModell}  
\alias{createPSSDModell}  
\title{createPSSDModell}  
\usage{  
createPSSDModell(T_data, cv_data, PSSD_simulations = 1, PSSD_length = 100,  
  species_length = 10^2, cv_factor1 = 0.5, cv_factor2 = 0.5,  
  cv_factor3 = 0, cv_low_end = 0.5, cv_high_end = 0.5,  
  interval_length = 10^2)  
}  
\arguments{  
\item{T_data}{A numeric matrix with nrow = 100 and ncol = 100}  
  
\item{cv_data}{A numeric matrix with nrow = 100 and ncol = 100 (does not have to be generated,  
the default is zero)}  
  
\item{PSSD_simulations}{A number for the quantity of PSSDs to be computed}  
  
\item{PSSD_length}{A number for the quantity of the model output values for the PSSD}  
  
\item{species_length}{A number for the quantity of the model output values of the PSSD of one  
single species}  
  
\item{cv_factor1}{A fraction that reflects the uncertainty range (confidence interval) on both sides of  
the first assessment factor (short to long term toxicity)}  
  
\item{cv_factor2}{A fraction that reflects the uncertainty range (confidence interval) on both sides of  
the second assessment factor (extrapolation from the observed effect concentrations into no effect  
concentrations)}  
  
\item{cv_factor3}{A fraction that reflects the uncertainty range (confidence interval) on both sides of  
the third assessment factor (expected differences between lab based experimental conditions and  
natural conditions)}  
  
\item{cv_low_end}{A fraction that reflects the uncertainty range (confidence interval) on the left hand  
side of the lowest toxicological endpoint used for one single species}  
  
\item{cv_high_end}{A fraction that reflects the uncertainty range (confidence interval) on the right  
hand side of the highest toxicological endpoint used for one single species}  
  
\item{interval_lenth}{A number for the quantity of the model output values of the interval  
distributions that are the distributions between all the toxicological endpoints collected for a particular  
species}  
}  
\value{  
a matrix  
}
```

```
\description{
function to create a probabilistic species sensitivity distribution (PSSD) model
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/createPNECModell.R
\name{createPNECModell}
\alias{createPNECModell}
\title{createPNECModell}
\usage{
createPNECModell(PSSD)
}
\arguments{
\item{PSSD}{A probabilistic species sensitivity distribution (PSSD) model output}
}
\value{
a numeric vector of the computed PNEC values
}
\description{
function to create a probabilistic predicted no effect concentration (PNEC) model
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/loadSpeciesDataConfidenceFromExcel.R
\name{loadSpeciesDataConfidenceFromExcel}
\alias{loadSpeciesDataConfidenceFromExcel}
\title{loadSpeciesDataConfidenceFromExcel}
\usage{
loadSpeciesDataConfidenceFromExcel(file, xlsx = TRUE)
}
\arguments{
\item{...}{numeric Vectors named after species \code{speciesA = c(0.1,0.4, 0.5)}}
}
\value{
a numeric matrix with nrow = 100 and ncol = 100
}
\description{
function to create a matrix with species data confidence from excel confidence data
}
\examples{
cv_data<-loadSpeciesDataConfidenceFromExcel('PSSD_Excel_Data_Confidence.xlsx', xlsx = TRUE)
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/loadSpeciesDataFromExcel.R
\name{loadSpeciesDataFromExcel}
\alias{loadSpeciesDataFromExcel}
\title{loadSpeciesDataFromExcel}
\usage{
loadSpeciesDataFromExcel(file, xlsx = TRUE)
}
\arguments{
\item{...}{numeric Vectors named after species \code{speciesA = c(20,123, 15)}}
}
\value{
```

```
a numeric matrix with nrow = 100 and ncol = 100
}
\description{
function to create a matrix with species data from excel data
}
\examples{
T_data<-loadSpeciesDataFromExcel('PSSD_Excel_Data.xlsx', xlsx = TRUE)
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/plotCdf.R
\name{plotCdf}
\alias{plotCdf}
\title{plotCdf}
\usage{
plotCdf(VPSSD, T_data)
}
\arguments{
\item{VPSSD}{A vector of the probabilistic species sensitivity distribution (PSSD) model output}

\item{T_data}{A matrix with the species names and their endpoint values}
}
\value{
plot
}
\description{
a function to plot a cumulative density function for the probabilistic species sensitivity distribution (PSSD) model
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/plotPdf.R
\name{plotPdf}
\alias{plotPdf}
\title{plotPdf}
\usage{
plotPdf(VPSSD)
}
\arguments{
\item{VPSSD}{A vector of the probabilistic species sensitivity distribution (PSSD) model output}
}
\value{
plot
}
\description{
a function to plot a probability density function for the probabilistic species sensitivity distribution (PSSD) model
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/plotPdfpNec.R
\name{plotPdfPNEC}
\alias{plotPdfPNEC}
\title{plotPdfPNEC}
\usage{
plotPdfPNEC(VPNEC)
```

```

}
\arguments{
\item{VPNEC}{A vector of the probabilistic predicted no effect concentration (PNEC) modell}
}
\value{
plot
}
\description{
function to plot a probability density function for the probabilistic predicted no effect concentration
(PNEC) modell
}

\name{PSSD-package}
\alias{PSSD-package}
\alias{PSSD}
\docType{package}
\title{
What the package does (short line)
~~ package title ~~
}
\description{
More about what it does (maybe more than one line)
~~ A concise (1-5 lines) description of the package ~~
}
\details{
\table{ll}{
Package: \tab PSSD\cr
Type: \tab Package\cr
Version: \tab 1.0\cr
Date: \tab 2016-03-21\cr
License: \tab What license is it under?\cr
}
~~ An overview of how to use the package, including the most important functions ~~
}
\author{
Who wrote it

Maintainer: Who to complain to <yourfault@somewhere.net>
~~ The author and/or maintainer of the package ~~
}
\references{
~~ Literature or other references for background information ~~
}
~~ Optionally other standard keywords, one per line, from file KEYWORDS in the R documentation
directory ~~
\keyword{ package }
\seealso{
~~ Optional links to other man pages, e.g. ~~
~~ \code{\link[<pkg>:<pkg>-package]{<pkg>}} ~~
}
\examples{
~~ simple examples of the most important functions ~~
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/rawSpeciesData.R

```

```
\name{rawSpeciesData}
\alias{rawSpeciesData}
\title{rawSpeciesData}
\usage{
rawSpeciesData(...)
}
\arguments{
\item{...}{numeric Vectors named after species \code{speciesA = c(20,123, 15)}}
}
\value{
a numeric matrix with nrow = 100 and ncol = 100
}
\description{
function to create a matrix with species data
}
\examples{
T_data <- rawSpeciesData(SpeciesA = c(20,123, 15), SpeciesB = c(25, 13, 19, 80), SpeciesC = c(5, 13,
17, 80))
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/rawSpeciesData Confidence.R
\name{rawSpeciesDataConfidenceValues}
\alias{rawSpeciesDataConfidenceValues}
\title{rawSpeciesDataConfidenceValues}
\usage{
rawSpeciesDataConfidenceValues(...)
}
\arguments{
\item{...}{numeric Vectors named after species \code{speciesA = c(0.1,0.4, 0.5)}}
}
\value{
a numeric matrix with nrow = 100 and ncol = 100
}
\description{
function to create a matrix with species data confidence values
}
\examples{
cv_data <- rawSpeciesDataConfidenceValues(SpeciesA = c(0.1,0.4, 0.5), SpeciesB = c(0, 0.2))
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/triangulsimleft.R
\name{triangulsimleft}
\alias{triangulsimleft}
\title{triangulsimleft}
\usage{
triangulsimleft(vecabc)
}
\arguments{
\item{automatically}{generated vector data input from the createPSSDModell.R function}
}
\value{
a numeric vector (triangular distribution)
}
\description{
```

```
triangular distribution used for the probability distributions at the lower end of the PSSD of each
single organism studied
}
% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/triangulsimright.R
\name{triangulsimright}
\alias{triangulsimright}
\title{triangulsimright}
\usage{
triangulsimright(vecabc)
}
\arguments{
\item{automatically}{generated vector data input from the createPSSDModell.R function}
}
\value{
a numeric vector (triangular distribution)
}
\description{
triangular distribution used for the probability distributions at the higher end of the PSSD of each
single organism studied
}
```

```
#####
#####
```

```
roxygen2Modell
```

```
#-----
#-----
```

```
# Generated by roxygen2 (4.1.0): do not edit by hand
```

```
export(createPNECModell)
export(createPSSDModell)
export(loadSpeciesDataConfidenceFromExcel)
export(loadSpeciesDataFromExcel)
export(plotCdf)
export(plotPdf)
export(plotPdfPNEC)
export(rawSpeciesData)
export(rawSpeciesDataConfidenceValues)
export(triangulsimleft)
export(triangulsimright)
importFrom(openxlsx,read.xlsx)
```

```
#####
#####
```

```
Read_files
```

```
#-----
#-----
```

```
* Edit the help file skeletons in 'man', possibly combining help files for multiple functions.
```

- \* Edit the exports in 'NAMESPACE', and add necessary imports.
- \* Put any C/C++/Fortran code in 'src'.
- \* If you have compiled code, add a useDynLib() directive to 'NAMESPACE'.
- \* Run R CMD build to build the package tarball.
- \* Run R CMD check to check the package tarball.

Read "Writing R Extensions" for more information.

## 2. R package on Probabilistic Material Flow Analysis (PMFA)

Package: PMFA  
Type: Package  
Title: Probabilistic Material Flow Analysis (PMFA) Package  
Version: 1.0.0  
Date: 2016-08-01  
Author: Fadri Gottschalk [aut], Martin Schneider [support package management]  
ETSS AG  
Maintainer: Fadri Gottschalk <fadri.gottschalk@etss.ch>  
Description: This is a package with functions used to perform Probabilistic Material Flow Analysis (PMFA).  
Dynamic material flow and material state simulations may be computed in cases of distinct data scarcity and variability. Probability distributions of the uncertainty and variability of the complete model input are generated. The package allows the user to combine empirical, experimental, analytical, expert and assumptive knowledge to construct the model. Another purpose of using this PMFA package may be to run probabilistic environmental risk evaluation that combines the PMFA output with the probability distributions of the ecotox modelling (e.g. PSSD, see PSSD package).  
License: What license is it under?  
LazyData: TRUE  
NeedsCompilation: no  
Packaged: 2016-08-01 13:09:44 UTC; fg

```
#####  
#####  
#Notifications from R
```

```
load("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PMFA_Model/R-  
package/simulation_demonstration.R")  
install.packages("beepr")#Then, at the bottom of your script, load the package and have it beep.
```

```
library(beepr)  
beep()#beepr comes with a bunch of different sounds (e.g., try beep("facebook")), or use a path to any  
wav file. I tried these cat sounds, but they came out (with my computer's speaker) sounding more like  
a really unhappy electronic lion...not very pleasant.  
beep("facebook")
```

```
install.packages("/Users/gfadri/Documents/2.Projects/SUN/Software_project/Messages/mailR_0.4.1.ta  
r.gz",repos = NULL, type = "source") # fourth step: installieren
```

```
library(PMFA) # laden des Pakets
```

```
setwd("/Users/gfadri/Documents/2.Projects/SUN/Software_project/Messages/mailR/")  
getwd()
```

```
install.packages("mailR")  
library(mailR)
```

```
install.packages("devtools", dep = T)  
library(devtools)
```

```
install_github("rpremrj/mailR")

library(mailR)
#####
#####

detach("package:PMFA")

#general management codes

.libPaths()

library(devtools) # first: creates help files

document("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PMFA_Model/R-
Package/PMFA") # second:creates help files
build("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PMFA_Model/R-Package/PMFA")
# third:erstellen von kompiliertem Ordner

install.packages("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PMFA_Model/R-
Package/PMFA_1.0.0.tar.gz",repos = NULL, type = "source") # fourth step: installieren

library(PMFA) # laden des Pakets
#####

setwd("/Users/gfadri/Documents/2.Projects/SUN/Software_project/PMFA_Model/R-
Package/PMFA/Extradata/")
getwd()

help(loadExcelData)

#Excel Variante

data_level_1<-loadExcelData('PMFA_Raw_Data_Kopie.xlsx', xlsx = TRUE, level = c("Input"))
data_level_1

data_level_2<-loadExcelData('PMFA_Raw_Data_Kopie.xlsx', xlsx = TRUE, level = c("Fate"))
data_level_2

data_level_3<-loadExcelData('PMFA_Raw_Data_Kopie.xlsx', xlsx = TRUE, level = c("Transfer"))
data_level_3

data_level_1[[50]]$values
max(data_level_1[[50]]$values)
min(data_level_1[[50]]$values)
```

```
data_level_2[[50]][paste0("values_state_", 4)]
max(unlist(data_level_2[[50]][paste0("values_state_", 4)]))
min(unlist(data_level_2[[50]][paste0("values_state_", 4)]))
```

```
data_level_3[[50]][paste0("values_targetbox_", 50)]
max(unlist(data_level_3[[50]][paste0("values_targetbox_", 50)]))
min(unlist(data_level_3[[50]][paste0("values_targetbox_", 50)]))
```

```
max(results)
```

```
data_level_1<-Input(list(box = 1, distribution = "Uniform", values = c(1:5)),list(box = 5, distribution =
"normal", values = c(2,5)),time=1)
```

```
data_level_2<-Fate(list(box = 49, distribution_state_1 = "Uniform", values_state_1 =
c(0.1,0.2,0.3),distribution_state_2 = "Uniform", values_state_2 = c(0.1,0.2,0.3),distribution_state_3 =
"Uniform",
      values_state_3 = c(0.1,0.2,0.3),distribution_state_4 = "Uniform", values_state_4 =
c(0.1,0.2,0.3)),
      list(box = 50,distribution_state_1 = "Uniform", values_state_1 = c(0.1,0.2,0.3),
      distribution_state_2 = "Uniform", values_state_2 = c(0.1,0.2,0.3),distribution_state_3 =
"Uniform", values_state_3 = c(0.1,0.2,0.3),distribution_state_4 = "Uniform", values_state_4 =
c(0.1,0.2,0.3)),time=1)
```

```
data_level_3<-Transfer(list(box = 49,
      distribution_targetbox_1= "Uniform",values_targetbox_1=c(0.1,0.2,0.3),
      distribution_targetbox_2= "Uniform",values_targetbox_2=c(0.1,0.2,0.3),
      distribution_targetbox_3= "Uniform",values_targetbox_3=c(0.1,0.2,0.3),
      distribution_targetbox_4 = "Uniform", values_targetbox_4 = 0,
      distribution_targetbox_5 = "Uniform", values_targetbox_5 = 0,
      distribution_targetbox_6 = "Uniform", values_targetbox_6 = 0,
      distribution_targetbox_7 = "Uniform", values_targetbox_7 = 0,
      distribution_targetbox_8 = "Uniform", values_targetbox_8 = 0,
      distribution_targetbox_9 = "Uniform", values_targetbox_9 = 0,
      distribution_targetbox_10 = "Uniform", values_targetbox_10 = 0,
      distribution_targetbox_11 = "Uniform", values_targetbox_11 = 0,
      distribution_targetbox_12 = "Uniform", values_targetbox_12 = 0,
      distribution_targetbox_13 = "Uniform", values_targetbox_13 = 0,
      distribution_targetbox_14 = "Uniform", values_targetbox_14 = 0,
      distribution_targetbox_15 = "Uniform", values_targetbox_15 = 0,
      distribution_targetbox_16 = "Uniform", values_targetbox_16 = 0,
      distribution_targetbox_17 = "Uniform", values_targetbox_17 = 0,
      distribution_targetbox_18 = "Uniform", values_targetbox_18 = 0,
      distribution_targetbox_19 = "Uniform", values_targetbox_19 = 0,
      distribution_targetbox_20 = "Uniform", values_targetbox_20 = 0,
      distribution_targetbox_21 = "Uniform", values_targetbox_21 = 0,
      distribution_targetbox_22 = "Uniform", values_targetbox_22 = 0,
      distribution_targetbox_23 = "Uniform", values_targetbox_23 = 0,
      distribution_targetbox_24 = "Uniform", values_targetbox_24 = 0,
      distribution_targetbox_25 = "Uniform", values_targetbox_25 = 0,
      distribution_targetbox_26 = "Uniform", values_targetbox_26 = 0,
```

```
distribution_targetbox_27 = "Uniform", values_targetbox_27 = 0,
distribution_targetbox_28 = "Uniform", values_targetbox_28 = 0,
distribution_targetbox_29 = "Uniform", values_targetbox_29 = 0,
distribution_targetbox_30 = "Uniform", values_targetbox_30 = 0,
distribution_targetbox_31 = "Uniform", values_targetbox_31 = 0,
distribution_targetbox_32 = "Uniform", values_targetbox_32 = 0,
distribution_targetbox_33 = "Uniform", values_targetbox_33 = 0,
distribution_targetbox_34 = "Uniform", values_targetbox_34 = 0,
distribution_targetbox_35 = "Uniform", values_targetbox_35 = 0,
distribution_targetbox_36 = "Uniform", values_targetbox_36 = 0,
distribution_targetbox_37 = "Uniform", values_targetbox_37 = 0,
distribution_targetbox_38 = "Uniform", values_targetbox_38 = 0,
distribution_targetbox_39 = "Uniform", values_targetbox_39 = 0,
distribution_targetbox_40 = "Uniform", values_targetbox_40 = 0,
distribution_targetbox_41 = "Uniform", values_targetbox_41 = 0,
distribution_targetbox_42 = "Uniform", values_targetbox_42 = 0,
distribution_targetbox_43 = "Uniform", values_targetbox_43 = 0,
distribution_targetbox_44 = "Uniform", values_targetbox_44 = 0,
distribution_targetbox_45 = "Uniform", values_targetbox_45 = 0,
distribution_targetbox_46 = "Uniform", values_targetbox_46 = 0,
distribution_targetbox_47 = "Uniform", values_targetbox_47 = 0,
distribution_targetbox_48 = "Uniform", values_targetbox_48 = 0,
distribution_targetbox_49 = "Uniform", values_targetbox_49 = 0,
distribution_targetbox_50 = "Uniform", values_targetbox_50 = c(0.1, 0.2, 0.3),
```

```
list(box = 50,
      distribution_targetbox_1 = "Uniform", values_targetbox_1 = c(0.1, 0.2, 0.3),
      distribution_targetbox_2 = "Uniform", values_targetbox_2 = c(0.1, 0.2, 0.3),
      distribution_targetbox_3 = "Uniform", values_targetbox_3 = c(0.1, 0.2, 0.3),
      distribution_targetbox_4 = "Uniform", values_targetbox_4 = 0,
      distribution_targetbox_5 = "Uniform", values_targetbox_5 = 0,
      distribution_targetbox_6 = "Uniform", values_targetbox_6 = 0,
      distribution_targetbox_7 = "Uniform", values_targetbox_7 = 0,
      distribution_targetbox_8 = "Uniform", values_targetbox_8 = 0,
      distribution_targetbox_9 = "Uniform", values_targetbox_9 = 0,
      distribution_targetbox_10 = "Uniform", values_targetbox_10 = 0,
      distribution_targetbox_11 = "Uniform", values_targetbox_11 = 0,
      distribution_targetbox_12 = "Uniform", values_targetbox_12 = 0,
      distribution_targetbox_13 = "Uniform", values_targetbox_13 = 0,
      distribution_targetbox_14 = "Uniform", values_targetbox_14 = 0,
      distribution_targetbox_15 = "Uniform", values_targetbox_15 = 0,
      distribution_targetbox_16 = "Uniform", values_targetbox_16 = 0,
      distribution_targetbox_17 = "Uniform", values_targetbox_17 = 0,
      distribution_targetbox_18 = "Uniform", values_targetbox_18 = 0,
      distribution_targetbox_19 = "Uniform", values_targetbox_19 = 0,
      distribution_targetbox_20 = "Uniform", values_targetbox_20 = 0,
      distribution_targetbox_21 = "Uniform", values_targetbox_21 = 0,
      distribution_targetbox_22 = "Uniform", values_targetbox_22 = 0,
      distribution_targetbox_23 = "Uniform", values_targetbox_23 = 0,
      distribution_targetbox_24 = "Uniform", values_targetbox_24 = 0,
      distribution_targetbox_25 = "Uniform", values_targetbox_25 = 0,
      distribution_targetbox_26 = "Uniform", values_targetbox_26 = 0,
      distribution_targetbox_27 = "Uniform", values_targetbox_27 = 0,
      distribution_targetbox_28 = "Uniform", values_targetbox_28 = 0,
      distribution_targetbox_29 = "Uniform", values_targetbox_29 = 0,
      distribution_targetbox_30 = "Uniform", values_targetbox_30 = 0,
```

```
distribution_targetbox_31 = "Uniform", values_targetbox_31 = 0,
distribution_targetbox_32 = "Uniform", values_targetbox_32 = 0,
distribution_targetbox_33 = "Uniform", values_targetbox_33 = 0,
distribution_targetbox_34 = "Uniform", values_targetbox_34 = 0,
distribution_targetbox_35 = "Uniform", values_targetbox_35 = 0,
distribution_targetbox_36 = "Uniform", values_targetbox_36 = 0,
distribution_targetbox_37 = "Uniform", values_targetbox_37 = 0,
distribution_targetbox_38 = "Uniform", values_targetbox_38 = 0,
distribution_targetbox_39 = "Uniform", values_targetbox_39 = 0,
distribution_targetbox_40 = "Uniform", values_targetbox_40 = 0,
distribution_targetbox_41 = "Uniform", values_targetbox_41 = 0,
distribution_targetbox_42 = "Uniform", values_targetbox_42 = 0,
distribution_targetbox_43 = "Uniform", values_targetbox_43 = 0,
distribution_targetbox_44 = "Uniform", values_targetbox_44 = 0,
distribution_targetbox_45 = "Uniform", values_targetbox_45 = 0,
distribution_targetbox_46 = "Uniform", values_targetbox_46 = 0,
distribution_targetbox_47 = "Uniform", values_targetbox_47 = 0,
distribution_targetbox_48 = "Uniform", values_targetbox_48 = 0,
distribution_targetbox_49 = "Uniform", values_targetbox_49 = 0,
distribution_targetbox_50 = "Uniform", values_targetbox_50 = c(0.1, 0.2, 0.3), time = 1)

simulation_demonstration_2 <- createPMFAModell(data_level_1, data_level_2, data_level_3, Number
= 2,
      t = 1)
beep("facebook")

Message("fadri.gottschalk@etss.ch", "fadri.gottschalk@etss.ch")

simulation_demonstration_2[5, 1:2, #][box, number of value, at time point]

PlotStatesVolumesTransfers(simulation_demonstration, 5, 1)
PlotStatesVolumesTransfers(simulation_demonstration, 1, 1)
PlotStatesVolumesTransfers(simulation_demonstration, 25, 1)

#Notifications from R

install.packages("beepr") #Then, at the bottom of your script, load the package and have it beep.

library(beepr)
beep() #beepr comes with a bunch of different sounds (e.g., try beep("facebook")), or use a path to any
wav file. I tried these cat sounds, but they came out (with my computer's speaker) sounding more like
a really unhappy electronic lion...not very pleasant.
beep("facebook")
```

```
install.packages("/Users/gfadri/Documents/2.Projects/SUN/Software_project/Messages/mailR_0.4.1.tar.gz", repos = NULL, type = "source") # fourth step: installieren
```

```
library(PMFA) # laden des Pakets
```

```
setwd("/Users/gfadri/Documents/2.Projects/SUN/Software_project/Messages/mailR/")  
getwd()
```

```
install.packages("mailR")  
library(mailR)
```

```
install.packages("devtools", dep = T)  
library(devtools)  
install_github("rpremraj/mailR")
```

```
library(mailR)
```

```
#####  
#####
```

```
PMFAModell
```

```
#-----  
#-----
```

```
##createPMFAModell
```

```
#  
#
```

```
##@export
```

```
createPMFAModell <- function(data_level_1, data_level_2, data_level_3, Number = 10, t = 1) {
```

```
#-----  
#-----  
#-----  
#-----
```

```
#-----  
#-----  
#   Data directory  
#-----  
#-----
```

```
# getwd()  
#  
# setwd("/Users/gfadri/")
```

---

#PMFA model for R-Package & internet-browser based graphical user interface tools that in certain circumstances might be run under real time (online) conditions\_Fadri Gottschalk\_2015

```
#-----  
#-----  
#-----  
#-----
```

```
#-----  
#-----  
#   Read data tables excel (csv)  
#-----  
#-----  
# data_level_1<-read.table("PMFA_Raw_Data_1_sonntag.csv", sep=";", dec=".")  
# data_level_2<-read.table("PMFA_Raw_Data_2_sonntag.csv", sep=";", dec=".")  
# data_level_3<-read.table("PMFA_Raw_Data_3_sonntag.csv", sep=";", dec=".")
```

```
#-----  
#-----  
#   General algorithms for model input data generation  
#-----  
#-----
```

```
#-----  
#   Number of Monte Carlo simulation rounds  
#-----
```

```
#Number<-10
```

```
#-----  
#   Number of time periods  
#-----
```

```
#t <- 1 ## Time (at time), # for R-pack default 1 and default 1 for r package
```

```
#
```

```
#-----  
#   Arrays for data that will be given into the core algorithm  
#-----
```

```
Values_level_1<-array(0,dim=c(50,1,Number,t))##values for material input into the system: for each  
main box one value for each Monte Carlo simulation at each time period
```

```
Values_level_2<-array(0,dim=c(50,4,Number,t))##values taken for subboxes: for each main box 4  
values for each Monte Carlo simulation at each time period
```

```
Values_level_3<-array(0,dim=c(50,50,Number,t))##values taken for connecting boxes: for each  
main box 50 values for each Monte Carlo simulation at each time period
```

```
#-----  
#   Arrays for raw data that will be normalized before given into the core algorithm  
#-----  
  
Values_level_1_raw<-array(0,dim=c(50,1,Number,t))##see remarks above  
Values_level_2_raw<-array(0,dim=c(50,4,Number,t))##values taken for subboxes  
Values_level_3_raw<-array(0,dim=c(50,50,Number,t))##values taken for connecting boxes  
  
#-----  
  
#-----  
#   Complete matrix  
#-----  
  
V_total<-array(NA,dim=c(2750,Number,t))##preparing an array for the model output: one value for  
each box and each Monte Carlo simulation at each time period  
  
#-----  
#   Material input into system  
#-----  
G <- c(rep(0,2750)) #preparing the G vector for material input  
  
#-----  
#   Zero and NA values as basis  
#-----  
  
V <- matrix(NA,2750,Number)## description of the output matrix  
  
T <- matrix(0,2750,2750) ## preparing model matrix with zero values as basis for 50 main boxes,  
200 (50 times 4) subboxes and 2500 connecting boxes (50 times 50)  
  
  
# 50 main boxes (with each 4 subboxes (elimination, accumulation, unknown fate, delay))  
# 200 subboxes (1 for elimination, 2 for accumulation, 3 for unknown fate, 4 for delay)  
# 2500 connecting boxes (50 times 50: from 1 to 2, 1 to 50, ...50 to 1, 50 to 2, ...)  
  
# Matrix structure: 1,2,3,4 (subboxes), 5 (main box), 6,7,8,9 (subboxes), 10 (main  
box)...246,247,248,249 (subboxes), 250 (main box), 251,252,253...2750 (connecting boxes)  
# organization 2500 connecting boxes: 251 = 5 to 5, 252 = 5 to 10... 300 = 5 to 250, thus initial box  
related packages 251-300, 301 to 350, 351 to 400 etc.  
  
#-----  
#-----  
#   PMFA algorithms  
#-----  
#-----  
  
#-----
```

```
# Iterative PMFA simulations first level
#-----

for (t in 1:t){# t=1 is default for r-package (R pack also another time periods for round of deposition
in a equilibrium model)

#-----
#-----
# Matrix general data
#-----
#-----

#-----
# Data for model input and data distributions
#-----

#-----
# Triangular distributions for use below
#-----

triangulsim <- function(vecabc) {

  min <- vecabc[1]
  mode <- vecabc[2]
  max <- vecabc[3]

  u <- runif(1,0,1)
  if (u <= (mode-min)/(max-min) ){
    r=min+sqrt(u*(max-min)*(mode-min)) }else{
    r=max-sqrt((1-u)*(max-min)*(max-mode))
  }
  r
}

#a=lowest value
#b=ideally modal value
#c=highest value

#M <- matrix(c(rep(a,Number),rep(b,Number),rep(c,Number)),Number)
#tri <- apply(M,1,triangulsim)

#-----
#-----
```

```

#-----
#   Input data with (or without time) dependency, for pack the time dependency covers the whole
range of indicated time periods, mean delay of transport during all time periods
#-----
#-----
#-----

#-----
#-----
#   Level 1 data
#
# (Material generation)
#-----
#-----

##Values_level_1 taken from raw data basis: [main box (usually only box 1 from 50 main boxes that
will become box 5),input into its virtual production box taht is always 1 , values from the
dsitributions,time periods] that is fixed at 1 for the r-pack, only for acumulation calculations used, this
principle applies alos for parts below

  for (r in 1:50){#50 main boxes

    pack_values_level_1 <- data_level_1[[r]]$values

    # pack_values_level_1<-as.numeric(strsplit(gsub(" ", "", x = data_level_1[[r]]$values, #values from
pack table settings
    #
    #           fixed = TRUE), split = ",")[[1]])

    distribution_selection_level_1<-as.character(data_level_1[[r]]$distribution)
#Verteilung aus settings!!!

    if (distribution_selection_level_1=="Uniform") {
      pack_values_distribution_level_1 <-
runif(Number,min(pack_values_level_1),max(pack_values_level_1)) ##into   degradation
    }

    else if (distribution_selection_level_1=="Triangular"){
      a=min(pack_values_level_1)
      b=median(pack_values_level_1)
      c=max(pack_values_level_1)
      M <- matrix(c(rep(a,Number),rep(b,Number),rep(c,Number)),Number)
      pack_values_distribution_level_1 <- apply(M,1,triangulsim)
    }

    else if (distribution_selection_level_1=="Normal"){
      normal_distribution_level_1 <- rnorm(Number,
mean=mean(pack_values_level_1),sd(pack_values_level_1))

```

```

        pack_values_distribution_level_1 <-
sample(normal_distribution_level_1[normal_distribution_level_1 >= 0], Number, replace =
      TRUE)
    }

    else if (distribution_selection_level_1 == "Bootrapping"){
      pack_values_distribution_level_1 <- sample(pack_values_level_1, Number,
replace = TRUE)
    }

    else {distribution_selection_level_1 == "Bayes Monte Carlo"
      pack_values_distribution_level_1 <-
sample(c(runif(Number, min(pack_values_level_1), max(pack_values_level_1)), rep(pack_values_level_1, Number/2)), Number)
    }
}

```

Values\_level\_1\_raw[r,1,,t] <- pack\_values\_distribution\_level\_1#[r,1,,t]; generation of material in each box (here only box 1 that will become box 5 in the indexing) one value (second 1), for each MC simulation that is Number as defined above, and for each time period that is one as default value and for r-package and pack: thus, could be [50,1,,t]

```

}

```

```

#-----
#-----
# Level 2 data

# (Data for transfer into subboxes: 1 degradation, 2 deposition, 3 unknown fate and 4 transport delay)
#-----
#-----

#-----
# Only used for one single Production and manufacturing box that is box 1
#-----

# into subbox for degradation from production and manufacturing box (first main box)

for (r in 1:50){#r = 1 is main box 1, from 1 to 50

for (h in 1:4){#h stands for 1 degradation, 2 deposition, 3 unknown fate and 4 transport delay

```

```

# pack_values_level_2<-as.numeric(strsplit(gsub(" ", "", x = data_level_2[r+2,2+2*h]), #the values
are just in the data level 1 table, however these are level 2 values
#
#           fixed = TRUE), split = ",")[[1]])
pack_values_level_2<- unlist(data_level_2[[r]][[paste0("values_state_", h)]]) #the values are just in
the data level 1 table, however these are level 2 values

```

```

distribution_selection_level_2<-unlist(data_level_2[[r]][[paste0("distribution_state_", h)]]) #the
values are just in the data level 1 table, however these are level 2 values

```

```

if (distribution_selection_level_2=="Uniform") {
  pack_values_distribution_level_2 <-
runif(Number,min(pack_values_level_2),max(pack_values_level_2)) ##into degradation
}

else if (distribution_selection_level_2=="Triangular"){
  a=min(pack_values_level_2)
  b=median(pack_values_level_2)
  c=max(pack_values_level_2)
  M <- matrix(c(rep(a,Number),rep(b,Number),rep(c,Number)),Number)
  pack_values_distribution_level_2 <- apply(M,1,triangulsim)
}

else if (distribution_selection_level_2=="Normal"){
  normal_distribution_level_2 <- rnorm(Number,
mean=mean(pack_values_level_2),sd(pack_values_level_2))
  pack_values_distribution_level_2<-
sample(normal_distribution_level_2[normal_distribution_level_2>=0]
[normal_distribution_level_2[normal_distribution_level_2>=0]<=1], Number, replace =
TRUE)
}

else if (distribution_selection_level_2=="Bootstrapping"){
  pack_values_distribution_level_2 <- sample(pack_values_level_2, Number,
replace = TRUE)
}

else {distribution_selection_level_2=="Bayes Monte Carlo"
  pack_values_distribution_level_2 <-
sample(c(runif(Number,0,1),rep(pack_values_level_2,Number/2)), Number)
}

Values_level_2_raw[r,h,t]<-pack_values_distribution_level_2#[r,h,t]:for each production box r
(here only one production box), transfer into boxes 1 for elimination, 2 for accumulation, 3 for
unknown fate, 4 for delay, Number of MC,time periods
}
}

```

```

#-----
#-----
#   Data for transfer into connecting boxes_level 3
#
#(Data for transfer compartment boxes into compartment boxes)
#-----
#-----

# r or h is the compartment (1 to 50)
for (h in 1:50){#h stands for all boxes(1 to 50)
  for (r in 1:50){#h stands for all boxes(1 to 50)

#           pack_values_level_3<-as.numeric(strsplit(gsub(" ", "", x = data_level_3[r+2,2+2*h],
#values from pack table
#           fixed = TRUE), split = ",")[[1]])

#           pack_values_level_3 <- unlist(data_level_3[[r]][[paste0("values_targetbox_", h)]] #the
values are just in the data level 1 table, however these are level 2 values
#           distribution_selection_level_3<-
unlist(data_level_3[[r]][[paste0("distribution_targetbox_",h)]] #the values are just in the data level 1
table, however these are level 2 values

#           distribution_selection_level_3<-as.character(data_level_3[r+2,1+2*h]) #hier anpassen

#           if (distribution_selection_level_3=="Uniform") {
#             pack_values_distribution_level_3 <-
runif(Number,min(pack_values_level_3),max(pack_values_level_3)) ##into degradation
#           }

#           else if (distribution_selection_level_3=="Triangular"){
#             a=min(pack_values_level_3)
#             b=median(pack_values_level_3)
#             c=max(pack_values_level_3)
#             M <- matrix(c(rep(a,Number),rep(b,Number),rep(c,Number)),Number)
#             pack_values_distribution_level_3 <- apply(M,1,triangulsim)
#           }

#           else if (distribution_selection_level_3=="Normal"){
#             normal_distribution_level_3 <- rnorm(Number,
#             mean=mean(pack_values_level_3),sd(pack_values_level_3))
#             pack_values_distribution_level_3<-
sample(normal_distribution_level_3[normal_distribution_level_3>=0]
[normal_distribution_level_3[normal_distribution_level_3>=0]<=1], Number, replace =
TRUE)
#           }

```

```

else if (distribution_selection_level_3=="Bootstrapping"){
    pack_values_distribution_level_3 <- sample(pack_values_level_3 , Number,
replace = TRUE)
    }

else {distribution_selection_level_3=="Bayes Monte Carlo"
    pack_values_distribution_level_3 <-
sample(c(runif(Number,0,1),rep(pack_values_level_3,Number/2)), Number) }

Values_level_3_raw[r,h,,t] <-pack_values_distribution_level_3#[r,h,,t]:for compartment box r,
transfer into compartment boxes, Number of MC,time periods

}

}

}

#-----
#-----
#   Normalizing process for all input data
#-----
#-----

#-----
#   level 1
#-----

Values_level_1<-Values_level_1_raw# no normalization due to numeric values that are not
percentages

#-----
#   level 2
#-----

## normalizing approach: each raw data transfer out of a box divided by the sum of all raw data
transfers out of this box

for(y in 1:Number){##for all MC simulations
for(z in 1:4){##for 4 subboxes
for(x in 1:50) {##for all main boxes
    if (Values_level_2_raw[x,z,y,t]>0) {
        Values_level_2[x,z,y,t]<-
Values_level_2_raw[x,z,y,t]/(sum(Values_level_2_raw[x,1:4,y,t])+sum(Values_level_3_raw[x,1:50,y,
t]))
    }

else

Values_level_2[x,z,y,t]=0

```

```
}  
}  
}
```

```
## check parameters  
check_parameters_sum_1<-matrix(0,50,Number)  
  
for(x in 1:50)  
{  
  for(y in 1:Number){check_parameters_sum_1[x,y]<-sum(Values_level_2[x,1:4,y,t])}  
}  
  
check_parameters_sum_1
```

```
#-----  
#   level 3  
#-----
```

```
## normalizing approach: each raw data transfer out of a box divided by the sum of all raw data  
transfers out of this box totally equivalent to what has been done above  
for(y in 1:Number){  
  for(z in 1:50){  
    for(x in 1:50) {  
      if(Values_level_3_raw[x,z,y,t]>0) {  
        Values_level_3[x,z,y,t]<-  
Values_level_3_raw[x,z,y,t]/(sum(Values_level_2_raw[x,1:4,y,t])+sum(Values_level_3_raw[x,1:50,y,  
t]))  
      }  
  
      else  
  
        Values_level_3[x,z,y,t]=0  
    }  
  }  
}
```

```
## check parameters  
check_parameters_sum_2<-matrix(0,50,Number)  
  
for(x in 1:50)  
{for(y in 1:Number)  
  {check_parameters_sum_2[x,y]<-sum(Values_level_3[x,1:50,y,t])}  
}  
  
check_parameters_sum_2
```

```
## check parameters
check_parameters_sum_1+check_parameters_sum_2

#-----
#-----
#   PMFA core algorithms
#-----
#-----

#-----
#   Data preparation
#-----

#-----
#   Main boxes outputflows into subboxes data to preparation for core algorithm
#-----

d_d_sample<-seq(from=5, to=250, by=5)##5,10,15,...250 ##that are the main boxes
d_sample<-rep(d_d_sample,each=4, 1)##5,5,5,5,10,10,10,10,15,15...

subfactor_subfactor<-seq(1:4)##1,2,3,4
subfactors<-rep(subfactor_subfactor,50)##1,2,3,4,1,2,3,4...1,2,3,4 (50 times)

##produced combinations: 5 to 1, 5 to 2, 5 to 3, 5 to 4, 10 to 1, 10 to 2, 10 to 3, 10 to 4, .....

#-----
#   Main boxes outputflows into connecting flows data to prepare for core algorithm
#-----

d_d_sample_cont<-seq(from=5, to=250, by=5)##5,10,15,...250 that are the main boxes
d_sample_cont<-rep(d_d_sample_cont,each=50, 1)##5,5,5,5,5,10,10,10 ...10,etc.

subfactor_subfactor_cont<-seq(1:50)##1,2,3,...50
subfactors_cont<-rep(subfactor_subfactor_cont,50)##1,2,3,...50 (50 times)

##produced combinations: 5 to 1, 5 to 2, 5 to 3, 5 to 4, ... 5 to 50, 10 to 1, 10 to 2, 10 to 3, 10 to
4, ..., 10 to 50.....
```

```
#-----  
#   Connection boxes output flows data to prepare for core algorithm  
#-----  
  
c_sample<-rep(seq(from=5, to=250, by=5),50)## c_sample stands for 50 times the following series:  
5, 10, 15,20,25,..250 (50 times all main boxes)  
  
for (b in 251:2750){## b stands for 2500 connecting boxes, 251 is the first connecting box  
  
  c<-c_sample[b-250]## c stands for 1,2,3..2500 values that have to be generated: as seen above 50  
times the following series: 5, 10, 15,20,25,..250 (50 times all main boxes)  
  
  T[c,b] <- 1*-1##flows of connecting receiving main boxes (100% for connecting box to its  
receiving box), 251 connects 5 and 5, 252 connects 5 and 10, 253 connects 5 and 15,..., 300 connects 5  
and 250; 301 connects 10 and 5, 302 connects 10 and 10, 303 connects 10 and 15 etc:thus, 251 goes  
into 5, 252 goes into 10, 253 goes into 15...300 goes into 250, 301 goes into 5 (connection for 10 to  
5)...2500 goes into 250 (connection for 250 and 250*)  
  
  }  
  
  ## *5 to 5, 10 to 10 etc. are also connected with connecting boxes, however, the raw data input into  
these connecting boxes is always zero, that is wrong following the PMFA approach, however, later in  
the model it will be changed to the +1 coefficient PMFA transfer for the flows into its own is not  
impacted later down in the model, see next section  
  
#-----  
#   Flows (theoretical) 1 to 1, 2 to 2 etc.  
#-----  
  
for (a in 1:2750){  
  
  T[a,a] <- 1 ## a stands for a box (all boxes, box flow into its own PMFA core idea)  
  
  }  
  
}
```

```

#-----
#   Linear PMFA model
#-----

for (time in 1:t){#time periods for pack always 1

for (k in 1:Number){#number of monte carlo iterations, see above

#-----
#   Material input into system
#-----

for (i in 1:50){

j<-i*5

G[j] <- c(Values_level_1[i,1,k,t]) ##[for each main box (only for box 1 that becomes in the
indexing box 5),one maerial input value ,number of monte carlo iterations,time periods]

}

#-----
#   Main boxes outputflows into subboxes (200 flows)
#-----

for (e in 1:200){

d<-d_sample[e]## d stands for main box: 5,5,5,5,10,10,10,10,15,15...
f<-d_sample[e]-subfactors[e]## f stands for subbox: 5-1,5-2,5-3,5-4,10-1,10-2,10-3,10-4...

dd<-d/5## 5/5, 10/5, 15/5... equals to 1,2,3...to 50: always 4 times 1,1,1,1,2,2,2,2,3,3,3,3... for the
50 to 4 matrix
ff<-5-subfactors[e] ##4,3,2,1,4,3,2,1,4,3,2,1.. (50 times)

T[f,d] <- c(Values_level_2[dd,ff,k,t])*-1 ##main boxes into subboxes, in Values_level_2[dd,ff,k,t])
from left to right and in T[f,d] from right to left as usual, k is the number of MC iteration, t is the time
that could be part of input data functions, thus f represents values 4,3,2,1,9,8,7,6,14,13,12,11..., d

```

represents 5,5,5,5,10,10,10,10,15,15... and dd represents 1,1,1,1,2,2,2,2,3,3,3,3,, ff represents 4,3,2,1,4,3,2,1,4,3,2,1

```
}

```

```
#-----
# Main boxes outputflows into connecting flows (2500 flows)
#-----

```

```
for (e_cont in 251:2750){

```

```
  d_cont<-d_sample_cont[e_cont-250]##5,5,5...,5,10,10,10 ...10,etc.(50 times 50 = 2500)
  f_cont<-e_cont# f_cont stands for connecting boxes: 251,252, 253 etc.

```

```
  dd_cont<-d_cont/5
  ff_cont<-subfactors_cont[e_cont-250] ##1,2,3,...50 (50 times=2500)

```

```
  T[f_cont,d_cont] <- c(Values_level_3[dd_cont,ff_cont, k,t])*-1 ##main boxes into connecting
boxes, k is the number of MC iteration, t is the time taht could be part of input data functions, t is the
time that could be part of input data functions, thus f_cont represents values 251,252,253, d_cont
represents 5,5,5,5.....,10,10,10,10.....,15,15... and dd_cont represents 1,1,1,1.....,2,2,2,2,3,3,3,3.....,
ff_cont represents 1,2,3,4,5,...50, 1,2,3,4,...50.....

```

```
  }

```

```
V[,k] <- solve(T,G)

```

```
## check Transfer quotients
max(T)##should be 1
min(T)##should be -1
T[T>0]##all values should be 1

```

```
}

```

```
V_total[,time]<-V[,]#[box,number of value,at time point]

```

```
}

return(V_total)

## check parameters PMC- all subboxes should be zero or extremely low due to digit errors

if( V_total[5]-V_total[1]-V_total[2]-V_total[3]-V_total[4]-V_total[6]-V_total[7]-V_total[8]-
V_total[9]-V_total[11]-V_total[12]-V_total[13]-V_total[14]-V_total[16]-V_total[17]-V_total[18]-
V_total[19]-V_total[21]-V_total[22]-V_total[23]-V_total[24]-V_total[26]-V_total[27]-V_total[28]-
V_total[29]-V_total[31]-V_total[32]-V_total[33]-V_total[34]-V_total[36]-V_total[37]-V_total[38]-
V_total[39]-V_total[41]-V_total[42]-V_total[43]-V_total[44]-V_total[46]-V_total[47]-V_total[48]-
V_total[49]-V_total[51]-V_total[52]-V_total[53]-V_total[54]-V_total[56]-V_total[57]-V_total[58]-
V_total[59]-
V_total[61]-V_total[62]-V_total[63]-V_total[64]-V_total[66]-V_total[67]-V_total[68]-V_total[69]-
V_total[71]-V_total[72]-V_total[73]-V_total[74]-V_total[76]-V_total[77]-V_total[78]-V_total[79]-
V_total[81]-V_total[82]-V_total[83]-V_total[84]-V_total[86]-V_total[87]-V_total[88]-V_total[89]-
V_total[91]-V_total[92]-V_total[93]-V_total[94]-V_total[96]-V_total[97]-V_total[98]-V_total[99]-
V_total[101]-V_total[102]-V_total[103]-V_total[104]-V_total[106]-V_total[107]-V_total[108]-
V_total[109]-
V_total[111]-V_total[112]-V_total[113]-V_total[114]-V_total[116]-V_total[117]-V_total[118]-
V_total[119]-
V_total[121]-V_total[122]-V_total[123]-V_total[124]-V_total[126]-V_total[127]-V_total[128]-
V_total[129]-
V_total[131]-V_total[132]-V_total[133]-V_total[134]-V_total[136]-V_total[137]-V_total[138]-
V_total[139]-
V_total[141]-V_total[142]-V_total[143]-V_total[144]-V_total[146]-V_total[147]-V_total[148]-
V_total[149]-
V_total[151]-V_total[152]-V_total[153]-V_total[154]-V_total[156]-V_total[157]-V_total[158]-
V_total[159]-
V_total[161]-V_total[162]-V_total[163]-V_total[164]-V_total[166]-V_total[167]-V_total[168]-
V_total[169]-
V_total[171]-V_total[172]-V_total[173]-V_total[174]-V_total[176]-V_total[177]-V_total[178]-
V_total[179]-
V_total[181]-V_total[182]-V_total[183]-V_total[184]-V_total[186]-V_total[187]-V_total[188]-
V_total[189]-
V_total[191]-V_total[192]-V_total[193]-V_total[194]-V_total[196]-V_total[197]-V_total[198]-
V_total[199]-
V_total[201]-V_total[202]-V_total[203]-V_total[204]-V_total[206]-V_total[207]-V_total[208]-
V_total[209]-
V_total[211]-V_total[212]-V_total[213]-V_total[214]-V_total[216]-V_total[217]-V_total[218]-
V_total[219]-
V_total[221]-V_total[222]-V_total[223]-V_total[224]-V_total[226]-V_total[227]-V_total[228]-
V_total[229]-
V_total[231]-V_total[232]-V_total[233]-V_total[234]-V_total[236]-V_total[237]-V_total[238]-
V_total[239]-
V_total[241]-V_total[242]-V_total[243]-V_total[244]-V_total[246]-V_total[247]-V_total[248]-
V_total[249] > 10^10){
  warning("Wrong modelling input data!")
}
}
```

```
#loadExcelData
#
#
#@importFrom openxlsx read.xlsx
#@export

loadExcelData <- function(file, xlsx = TRUE, level = c("Input", "Fate", "Transfer")) {

  #setwd("/Users/gfadri/")

  #setwd("Extradata")

  #-----
  #   Read data tables excel (csv)
  #-----
  #-----
  # data_level_1_from_excel<-read.table("PMFA_Raw_Data_Input.csv", sep=";", dec=".")
  # data_level_2_from_excel<-read.table("PMFA_Raw_Data_Fate.csv", sep=";", dec=".")
  # data_level_3_from_excel<-read.table("PMFA_Raw_Data_Transfer.csv", sep=";", dec=".")

  # check if correct level input
  stopifnot(level == c("Input", "Fate", "Transfer") | level == "Input" | level == "Fate" | level ==
"Transfer")

  # read either xlsx file or csv files
  if (xlsx != TRUE) {
    data_level <- read.table(file, sep = ";", dec = ".")
  } else {

    level_recode <- ifelse(level == "Input", 1, ifelse(level == "Fate", 2, 3))

    data_level <- openxlsx::read.xlsx(xlsxFile = file, sheet = level_recode[1], colNames = FALSE)

  }

  #-----
  #-----
  # Level 1 data
  #
  # (Material generation)
  #-----
  #-----

  if (level[1] == "Input") {

    data_level_1 <- list()

    for (i in 1:50) {
      data_level_1[[i]] <- list(box = i, distribution = "Uniform", values = 0)
    }

  }

}
```

```

for (r in 1:50) {#50 main boxes

  data_level_1[[r]]$values <- as.numeric(strsplit(gsub(" ", "", x = data_level[r + 1, 3], ##Distribution
values from excel table
                    fixed = TRUE), split = ",")[1])

  data_level_1[[r]]$distribution <- as.character(data_level[r + 1, 2]) #Distribution form from excel
table
}

return(data_level_1)

}

#-----
#-----
# Level 2 data taken from raw data basis in excel

# (Data for transfer into subboxes: 1 degradation, 2 deposition, 3 unknown fate and 4 transport delay)
#-----
#-----

#input_list <- list(...)

if (level == "Fate") {

  data_level_2 <- list()

  for (i in 1:50) {
    data_level_2[[i]] <- list(box = i, distribution_state_1 = "Uniform", values_state_1 = 0,
      distribution_state_2 = "Uniform", values_state_2 = 0,
      distribution_state_3 = "Uniform", values_state_3 = 0,
      distribution_state_4 = "Uniform", values_state_4 = 0)
  }

  for (r in 1:50) {#r =1 is main box 1, from 1 to 50

    for (h in 1:4) {#h stands for 1 degradation, 2 deposition, 3 unknown fate and 4 transport delay

      data_level_2[[r]][[paste0("values_state_", h)]] <- as.numeric(strsplit(gsub(" ", "", x = data_level[r
+ 2, 2 + 2 * h], ##Distribution values from excel table
                    fixed = TRUE), split = ",")[1])

      data_level_2[[r]][[paste0("distribution_state_", h)]] <- as.character(data_level[r + 2, 1 + 2 * h])
#Distribution form from excel table
    }
  }

  return(data_level_2)

}

#-----

```

```
#####
#####
LoadModell_1
#-----
#-----

# Data for transfer into connecting boxes_level 3 taken from raw data basis in excel
#
#(Data for transfer compartment boxes into compartment boxes)
#-----
#-----

#input_list <- list(...)

if (level == "Transfer") {

  data_level_3 <- list()

  for (i in 1:50) {
    data_level_3[[i]] <- list(box = i)#, distribution = "Uniform", values = 0)

    for (j in 1:50) {
      distribution_targetbox_j <- paste0("distribution_targetbox_", j)
      values_targetbox_j <- paste0("values_targetbox_", j)

      data_level_3[[i]][distribution_targetbox_j] <- "Uniform"
      data_level_3[[i]][values_targetbox_j] <- 0
    }
  }

  # r or h is the compartment (1 to 50)
  for (h in 1:50) {#h stands for all boxes(1 to 50)
    for (r in 1:50) {#h stands for all boxes(1 to 50)

      data_level_3[[r]][[paste0("values_targetbox_", h)]] <- as.numeric(strsplit(gsub(" ", "", x =
data_level[r + 2, 2 + 2 * h], ##Distribution values from excel table
      fixed = TRUE), split = ",")[[1]])

      data_level_3[[r]][[paste0("distribution_targetbox_", h)]] <- as.character(data_level[r + 2, 1 + 2 *
h]) #Distribution form from excel table
    }
  }

  return(data_level_3)

}

}
```

```
#####  
#####  
LoadModell_2  
#-----  
#-----  
#Input  
#  
#give input for Material  
#  
#@param ... list of elements list(box, distribution, values)  
#@param time  
#  
#@examples  
#Input(list(box = 1, distribution = "Uniform", values = c(1:5)),list(box = 5, distribution = "normal",  
values = c(2,5)),time=1)  
#  
#  
#@export  
Input <- function(..., time = 1) {  
#-----  
# Arrays for data that will be given into the core algorithm  
#-----  
  
input_list <- list(...)  
  
box_list <- list()  
  
for (i in 1:50){  
  box_list[[i]] <- list(box = i, distribution = "Uniform", values = 0)  
  
}  
  
boxes <- sapply(input_list, function(x){  
  x$box  
})  
  
for (i in 1:length(boxes)) {  
  box_list[[boxes[i]]]$distribution <- input_list[[i]]$distribution  
  box_list[[boxes[i]]]$values <- input_list[[i]]$values  
}  
  
for (i in 1:length(box_list)) {  
  box_list[[i]]$time <- time  
}  
  
negatives <- sapply(box_list, function(x)any(x$values < 0))  
if (any(negatives)) {  
  
  warning(paste0("unrealistic data, negative Values in boxes:", paste(which(negatives), collapse =  
", ")))  
}  
  
return(box_list)  
}
```

```
#createInputBox
#
#@export

createInputBox <- function(box, distribution = "Uniform", values = 0,
                           time = 1) {
  box_list <- list(box = box,
                  distribution = distribution,
                  values = values
                )
  #
  negatives <- any(box_list$values < 0 )
  if (any(negatives)) {
    warning("unrealistic data, in values")
  }

  return(box_list)
}
```

```

#####
#####
FateModell_1
#-----
#-----
#Fate
#
#*give input for Fate
#
#@param ... list of elements list(box, distribution, values)
#@param time
#
#@examples
#Fate(list(box = 49, distribution_state_1 = "Uniform", values_state_1 =
c(0.1,0.2,0.3),distribution_state_2 = "Uniform", values_state_2 = c(0.1,0.2,0.3),distribution_state_3 =
"Uniform", values_state_3 = c(0.1,0.2,0.3),distribution_state_4 = "Uniform", values_state_4 =
c(0.1,0.2,0.3)),list(box = 50,distribution_state_1 = "Uniform", values_state_1 =
c(0.1,0.2,0.3),distribution_state_2 = "Uniform", values_state_2 = c(0.1,0.2,0.3),distribution_state_3 =
"Uniform", values_state_3 = c(0.1,0.2,0.3),distribution_state_4 = "Uniform", values_state_4 =
c(0.1,0.2,0.3)),time=1)
#
#
#@export
Fate <- function(..., time = 1) {

  input_list <- list(...)

  box_list <- list()

  for (i in 1:50) {
    box_list[[i]] <- list(box = i, distribution_state_1 = "Uniform", values_state_1 = 0,
      distribution_state_2 = "Uniform", values_state_2 = 0,
      distribution_state_3 = "Uniform", values_state_3 = 0,
      distribution_state_4 = "Uniform", values_state_4 = 0)
  }

  boxes <- sapply(input_list, function(x){
    x$box
  })

  for (i in 1:length(boxes)) {
    box_list[[boxes[i]]]$distribution_state_1 <- input_list[[i]]$distribution_state_1
    box_list[[boxes[i]]]$values_state_1 <- input_list[[i]]$values_state_1
    box_list[[boxes[i]]]$distribution_state_2 <- input_list[[i]]$distribution_state_2
    box_list[[boxes[i]]]$values_state_2 <- input_list[[i]]$values_state_2
    box_list[[boxes[i]]]$distribution_state_3 <- input_list[[i]]$distribution_state_3
    box_list[[boxes[i]]]$values_state_3 <- input_list[[i]]$values_state_3
    box_list[[boxes[i]]]$distribution_state_4 <- input_list[[i]]$distribution_state_4
    box_list[[boxes[i]]]$values_state_4 <- input_list[[i]]$values_state_4
  }
}

```

```
for (i in 1:length(box_list)) {
  box_list[[i]]$time <- time
}

return(box_list)
}

#####
#####
FateModell_2
#-----
#-----

#createFateBox
#
#@export

createFateBox <- function(box, distribution_state_1 = "Uniform", values_state_1 = 0,
  distribution_state_2 = "Uniform", values_state_2 = 0,
  distribution_state_3 = "Uniform", values_state_3 = 0,
  distribution_state_4 = "Uniform", values_state_4 = 0,
  time = 1) {
  box_list <- list(box = box,
    distribution_state_1 = distribution_state_1,
    values_state_1 = values_state_1,
    distribution_state_2 = distribution_state_2,
    values_state_2 = values_state_2,
    distribution_state_3 = distribution_state_3,
    values_state_3 = values_state_3,
    distribution_state_4 = distribution_state_4,
    values_state_4 = values_state_4
  )
  #
  negatives <- any(box_list$values_state_1 < 0 | box_list$values_state_1 > 1)
  if (any(negatives)) {
    warning("unrealistic data, in state 1")
  }
  negatives <- any(box_list$values_state_2 < 0 | box_list$values_state_2 > 1)
  if (any(negatives)) {
    warning("unrealistic data, in state 2")
  }
  negatives <- any(box_list$values_state_3 < 0 | box_list$values_state_3 > 1)
  if (any(negatives)) {
    warning("unrealistic data, in state 3")
  }
}
```

```

negatives <- any(box_list$values_state_4 < 0 | box_list$values_state_4 > 1)
if (any(negatives)) {

  warning("unrealistic data, in state 4")
}

return(box_list)
}

#####
#####
TransferModell_1
#-----
#-----

#Transfer
#
#give input for Material Transfer
#
#@param ... list of elements list(box, distribution, values)
#@param time
#
#@examples
#Transfer(list(box = 49, distribution_targetbox_1=
"Uniform",values_targetbox_1=c(0.1,0.2,0.3),distribution_targetbox_2=
"Uniform",values_targetbox_2=c(0.1,0.2,0.3),distribution_targetbox_3=
"Uniform",values_targetbox_3=c(0.1,0.2,0.3),distribution_targetbox_4 = "Uniform",
values_targetbox_4 = 0,distribution_targetbox_5 = "Uniform", values_targetbox_5 = 0,...
distribution_targetbox_50= "Uniform",values_targetbox_50=c(0.1,0.2,0.3)),list(box = 50,
distribution_targetbox_1= "Uniform",values_targetbox_1=c(0.1,0.2,0.3),distribution_targetbox_2=
"Uniform",values_targetbox_2=c(0.1,0.2,0.3),distribution_targetbox_3=
"Uniform",values_targetbox_3=c(0.1,0.2,0.3),distribution_targetbox_4 = "Uniform",
values_targetbox_4 = 0,distribution_targetbox_50= "Uniform",values_targetbox_50=c(0.1,0.2,0.3)),
time=1)
#
#@export
Transfer <- function(..., time = 1) {

  input_list <- list(...)

  box_list <- list()

  for (i in 1:50){
    box_list[[i]] <- list(box = i)#, distribution = "Uniform", values = 0)

    for (j in 1:50) {
      distribution_targetbox_j <- paste0("distribution_targetbox_", j)
      values_targetbox_j <- paste0("values_targetbox_", j)

      box_list[[i]][distribution_targetbox_j] <- "Uniform"
      box_list[[i]][values_targetbox_j] <- 0
    }
  }
}

```

```
boxes <- sapply(input_list, function(x){
  x$box
})

for (i in 1:length(boxes)) {
  for (j in 1:50) {
    distribution_targetbox_j <- paste0("distribution_targetbox_", j)
    values_targetbox_j <- paste0("values_targetbox_", j)

    box_list[[boxes[i]][distribution_targetbox_j] <- input_list[[i]][distribution_targetbox_j]
    box_list[[boxes[i]][values_targetbox_j] <- input_list[[i]][values_targetbox_j]
  }
}

for (i in 1:length(box_list)) {
  box_list[[i]]$time <- time
}

return(box_list)
}

#createTransferBox
#
#@export
createTransferBox <- function(box, distribution_targetbox_1 = "Uniform", values_targetbox_1 = 0,
  distribution_targetbox_2 = "Uniform", values_targetbox_2 = 0,
  distribution_targetbox_3 = "Uniform", values_targetbox_3 = 0,
  distribution_targetbox_4 = "Uniform", values_targetbox_4 = 0,
  distribution_targetbox_5 = "Uniform", values_targetbox_5 = 0,
  distribution_targetbox_6 = "Uniform", values_targetbox_6 = 0,
  distribution_targetbox_7 = "Uniform", values_targetbox_7 = 0,
  distribution_targetbox_8 = "Uniform", values_targetbox_8 = 0,
  distribution_targetbox_9 = "Uniform", values_targetbox_9 = 0,
  distribution_targetbox_10 = "Uniform", values_targetbox_10 = 0,
  distribution_targetbox_11 = "Uniform", values_targetbox_11 = 0,
  distribution_targetbox_12 = "Uniform", values_targetbox_12 = 0,
  distribution_targetbox_13 = "Uniform", values_targetbox_13 = 0,
  distribution_targetbox_14 = "Uniform", values_targetbox_14 = 0,
  distribution_targetbox_15 = "Uniform", values_targetbox_15 = 0,
  distribution_targetbox_16 = "Uniform", values_targetbox_16 = 0,
  distribution_targetbox_17 = "Uniform", values_targetbox_17 = 0,
  distribution_targetbox_18 = "Uniform", values_targetbox_18 = 0,
  distribution_targetbox_19 = "Uniform", values_targetbox_19 = 0,
  distribution_targetbox_20 = "Uniform", values_targetbox_20 = 0,
  distribution_targetbox_21 = "Uniform", values_targetbox_21 = 0,
  distribution_targetbox_22 = "Uniform", values_targetbox_22 = 0,
  distribution_targetbox_23 = "Uniform", values_targetbox_23 = 0,
  distribution_targetbox_24 = "Uniform", values_targetbox_24 = 0,
  distribution_targetbox_25 = "Uniform", values_targetbox_25 = 0,
  distribution_targetbox_26 = "Uniform", values_targetbox_26 = 0,
  distribution_targetbox_27 = "Uniform", values_targetbox_27 = 0,
  distribution_targetbox_28 = "Uniform", values_targetbox_28 = 0,
  distribution_targetbox_29 = "Uniform", values_targetbox_29 = 0,
```

```
distribution_targetbox_30 = "Uniform", values_targetbox_30 = 0,
distribution_targetbox_31 = "Uniform", values_targetbox_31 = 0,
distribution_targetbox_32 = "Uniform", values_targetbox_32 = 0,
distribution_targetbox_33 = "Uniform", values_targetbox_33 = 0,
distribution_targetbox_34 = "Uniform", values_targetbox_34 = 0,
distribution_targetbox_35 = "Uniform", values_targetbox_35 = 0,
distribution_targetbox_36 = "Uniform", values_targetbox_36 = 0,
distribution_targetbox_37 = "Uniform", values_targetbox_37 = 0,
distribution_targetbox_38 = "Uniform", values_targetbox_38 = 0,
distribution_targetbox_39 = "Uniform", values_targetbox_39 = 0,
distribution_targetbox_40 = "Uniform", values_targetbox_40 = 0,
distribution_targetbox_41 = "Uniform", values_targetbox_41 = 0,
distribution_targetbox_42 = "Uniform", values_targetbox_42 = 0,
distribution_targetbox_43 = "Uniform", values_targetbox_43 = 0,
distribution_targetbox_44 = "Uniform", values_targetbox_44 = 0,
distribution_targetbox_45 = "Uniform", values_targetbox_45 = 0,
distribution_targetbox_46 = "Uniform", values_targetbox_46 = 0,
distribution_targetbox_47 = "Uniform", values_targetbox_47 = 0,
distribution_targetbox_48 = "Uniform", values_targetbox_48 = 0,
distribution_targetbox_49 = "Uniform", values_targetbox_49 = 0,
distribution_targetbox_50 = "Uniform", values_targetbox_50 = 0,
time = 1
) {
  box_list <- list(box = box,
    distribution_targetbox_1=
distribution_targetbox_1,values_targetbox_1=values_targetbox_1,
    distribution_targetbox_2=
distribution_targetbox_2,values_targetbox_2=values_targetbox_2,
    distribution_targetbox_3=
distribution_targetbox_3,values_targetbox_3=values_targetbox_3,
    distribution_targetbox_4=
distribution_targetbox_4,values_targetbox_4=values_targetbox_4,
    distribution_targetbox_5=
distribution_targetbox_5,values_targetbox_5=values_targetbox_5,
    distribution_targetbox_6=
distribution_targetbox_6,values_targetbox_6=values_targetbox_6,
    distribution_targetbox_7=
distribution_targetbox_7,values_targetbox_7=values_targetbox_7,
    distribution_targetbox_8=
distribution_targetbox_8,values_targetbox_8=values_targetbox_8,
    distribution_targetbox_9=
distribution_targetbox_9,values_targetbox_9=values_targetbox_9,
    distribution_targetbox_10=
distribution_targetbox_10,values_targetbox_10=values_targetbox_10,
    distribution_targetbox_11=
distribution_targetbox_11,values_targetbox_11=values_targetbox_11,
    distribution_targetbox_12=
distribution_targetbox_12,values_targetbox_12=values_targetbox_12,
    distribution_targetbox_13=
distribution_targetbox_13,values_targetbox_13=values_targetbox_13,
    distribution_targetbox_14=
distribution_targetbox_14,values_targetbox_14=values_targetbox_14,
    distribution_targetbox_15=
distribution_targetbox_15,values_targetbox_15=values_targetbox_15,
    distribution_targetbox_16=
distribution_targetbox_16,values_targetbox_16=values_targetbox_16,
```

distribution\_targetbox\_17=  
distribution\_targetbox\_17,values\_targetbox\_17=values\_targetbox\_17,  
distribution\_targetbox\_18=  
distribution\_targetbox\_18,values\_targetbox\_18=values\_targetbox\_18,  
distribution\_targetbox\_19=  
distribution\_targetbox\_19,values\_targetbox\_19=values\_targetbox\_19,  
distribution\_targetbox\_20=  
distribution\_targetbox\_20,values\_targetbox\_20=values\_targetbox\_20,  
distribution\_targetbox\_21=  
distribution\_targetbox\_21,values\_targetbox\_21=values\_targetbox\_21,  
distribution\_targetbox\_22=  
distribution\_targetbox\_22,values\_targetbox\_22=values\_targetbox\_22,  
distribution\_targetbox\_23=  
distribution\_targetbox\_23,values\_targetbox\_23=values\_targetbox\_23,  
distribution\_targetbox\_24=  
distribution\_targetbox\_24,values\_targetbox\_24=values\_targetbox\_24,  
distribution\_targetbox\_25=  
distribution\_targetbox\_25,values\_targetbox\_25=values\_targetbox\_25,  
distribution\_targetbox\_26=  
distribution\_targetbox\_26,values\_targetbox\_26=values\_targetbox\_26,  
distribution\_targetbox\_27=  
distribution\_targetbox\_27,values\_targetbox\_27=values\_targetbox\_27,  
distribution\_targetbox\_28=  
distribution\_targetbox\_28,values\_targetbox\_28=values\_targetbox\_28,  
distribution\_targetbox\_29=  
distribution\_targetbox\_29,values\_targetbox\_29=values\_targetbox\_29,  
distribution\_targetbox\_30=  
distribution\_targetbox\_30,values\_targetbox\_30=values\_targetbox\_30,  
distribution\_targetbox\_31=  
distribution\_targetbox\_31,values\_targetbox\_31=values\_targetbox\_31,  
distribution\_targetbox\_32=  
distribution\_targetbox\_32,values\_targetbox\_32=values\_targetbox\_32,  
distribution\_targetbox\_33=  
distribution\_targetbox\_33,values\_targetbox\_33=values\_targetbox\_33,  
distribution\_targetbox\_34=  
distribution\_targetbox\_34,values\_targetbox\_34=values\_targetbox\_34,  
distribution\_targetbox\_35=  
distribution\_targetbox\_35,values\_targetbox\_35=values\_targetbox\_35,  
distribution\_targetbox\_36=  
distribution\_targetbox\_36,values\_targetbox\_36=values\_targetbox\_36,  
distribution\_targetbox\_37=  
distribution\_targetbox\_37,values\_targetbox\_37=values\_targetbox\_37,  
distribution\_targetbox\_38=  
distribution\_targetbox\_38,values\_targetbox\_38=values\_targetbox\_38,  
distribution\_targetbox\_39=  
distribution\_targetbox\_39,values\_targetbox\_39=values\_targetbox\_39,  
distribution\_targetbox\_40=  
distribution\_targetbox\_40,values\_targetbox\_40=values\_targetbox\_40,  
distribution\_targetbox\_41=  
distribution\_targetbox\_41,values\_targetbox\_41=values\_targetbox\_41,  
distribution\_targetbox\_42=  
distribution\_targetbox\_42,values\_targetbox\_42=values\_targetbox\_42,  
distribution\_targetbox\_43=  
distribution\_targetbox\_43,values\_targetbox\_43=values\_targetbox\_43,  
distribution\_targetbox\_44=  
distribution\_targetbox\_44,values\_targetbox\_44=values\_targetbox\_44,

```
      distribution_targetbox_45=
distribution_targetbox_45,values_targetbox_45=values_targetbox_45,
      distribution_targetbox_46=
distribution_targetbox_46,values_targetbox_46=values_targetbox_46,
      distribution_targetbox_47=
distribution_targetbox_47,values_targetbox_47=values_targetbox_47,
      distribution_targetbox_48=
distribution_targetbox_48,values_targetbox_48=values_targetbox_48,
      distribution_targetbox_49=
distribution_targetbox_49,values_targetbox_49=values_targetbox_49,
      distribution_targetbox_50=
distribution_targetbox_50,values_targetbox_50=values_targetbox_50)

for(i in 1:50) {
  box2check <- paste0("values_targetbox_", i)
  negatives <- any(unlist(box_list[box2check]) < 0 | unlist(box_list[box2check]) > 1)
  if (any(negatives)) {

    warning(paste0("unrealistic data, for targetbox",i))
  }
}

return(box_list)

}

#####
#####
MessageModell
#-----
#-----

#Message State of Simulation
#
#send a message
#
#@param ... list of elements list(sender, recipients)
#@param addresses
#
#@examples
#Message(sender,recipients)
#
#
#@export
Message <- function(sender=sender, recipients=recipients) {
  email <-send.mail(from = sender,
    to = recipients,
    subject="PMFA simulation done",
    body = "Your PMFA simulation is ready!",
    smtp = list(host.name = "login-137.hoststar.ch", port = 587),
```

```
        authenticate = FALSE,
        send = TRUE)
    }
#####
#####
PlotModell_draft
#-----
#-----

#PlotStatesVolumesTransfers
#
#*plot results
#
#@param ... boxes for States, Volumes and Transfers
#@param time
#
#
#
#@export
PlotStatesVolumesTransfers <- function(V_total, box, time) {

  plot(density(V_total[box,, ]))

}

#####
#####
create.Rd
#-----
#-----

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/createPMFAModell.R
\name{createPMFAModell}
\alias{createPMFAModell}
\title{createPMFAModell}
\usage{
createPMFAModell(data_level_1, data_level_2, data_level_3, Number = 10,
  t = 1)
}
\description{
createPMFAModell
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/Input.R
\name{Input}
\alias{Input}
\title{Input}
\usage{
Input(..., time = 1)
}
\arguments{
\item{...}{list of elements list(box, distribution, values)}
```

```
\item{time}{}
}
\description{
give input for Material
}
\examples{
Input(list(box = 1, distribution = "Uniform", values = c(1:5)),list(box = 5, distribution = "normal",
values = c(2,5)),time=1)
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/createInputBox.R
\name{createInputBox}
\alias{createInputBox}
\title{createInputBox}
\usage{
createInputBox(box, distribution = "Uniform", values = 0, time = 1)
}
\description{
createInputBox
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/createFateBox.R
\name{createFateBox}
\alias{createFateBox}
\title{createFateBox}
\usage{
createFateBox(box, distribution_state_1 = "Uniform", values_state_1 = 0,
distribution_state_2 = "Uniform", values_state_2 = 0,
distribution_state_3 = "Uniform", values_state_3 = 0,
distribution_state_4 = "Uniform", values_state_4 = 0, time = 1)
}
\description{
createFateBox
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/Fate.R
\name{Fate}
\alias{Fate}
\title{Fate}
\usage{
Fate(..., time = 1)
}
\arguments{
\item{...} {list of elements list(box, distribution, values)}

\item{time}{}
}
\description{
give input for Fate
}
\examples{
Fate(list(box = 49, distribution_state_1 = "Uniform", values_state_1 =
c(0.1,0.2,0.3),distribution_state_2 = "Uniform", values_state_2 = c(0.1,0.2,0.3),distribution_state_3 =
```

```
distribution_targetbox_50="Uniform",values_targetbox_50=c(0.1,0.2,0.3)),list(box = 50,
distribution_targetbox_1="Uniform",values_targetbox_1=c(0.1,0.2,0.3),distribution_targetbox_2=
"Uniform",values_targetbox_2=c(0.1,0.2,0.3),distribution_targetbox_3=
"Uniform",values_targetbox_3=c(0.1,0.2,0.3),distribution_targetbox_4="Uniform",
values_targetbox_4=0,distribution_targetbox_50="Uniform",values_targetbox_50=c(0.1,0.2,0.3)),
time=1)
}
```

```
% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/createTransferBox.R
```

```
\name{createTransferBox}
```

```
\alias{createTransferBox}
```

```
\title{createTransferBox}
```

```
\usage{
```

```
createTransferBox(box, distribution_targetbox_1="Uniform",
values_targetbox_1=0, distribution_targetbox_2="Uniform",
values_targetbox_2=0, distribution_targetbox_3="Uniform",
values_targetbox_3=0, distribution_targetbox_4="Uniform",
values_targetbox_4=0, distribution_targetbox_5="Uniform",
values_targetbox_5=0, distribution_targetbox_6="Uniform",
values_targetbox_6=0, distribution_targetbox_7="Uniform",
values_targetbox_7=0, distribution_targetbox_8="Uniform",
values_targetbox_8=0, distribution_targetbox_9="Uniform",
values_targetbox_9=0, distribution_targetbox_10="Uniform",
values_targetbox_10=0, distribution_targetbox_11="Uniform",
values_targetbox_11=0, distribution_targetbox_12="Uniform",
values_targetbox_12=0, distribution_targetbox_13="Uniform",
values_targetbox_13=0, distribution_targetbox_14="Uniform",
values_targetbox_14=0, distribution_targetbox_15="Uniform",
values_targetbox_15=0, distribution_targetbox_16="Uniform",
values_targetbox_16=0, distribution_targetbox_17="Uniform",
values_targetbox_17=0, distribution_targetbox_18="Uniform",
values_targetbox_18=0, distribution_targetbox_19="Uniform",
values_targetbox_19=0, distribution_targetbox_20="Uniform",
values_targetbox_20=0, distribution_targetbox_21="Uniform",
values_targetbox_21=0, distribution_targetbox_22="Uniform",
values_targetbox_22=0, distribution_targetbox_23="Uniform",
values_targetbox_23=0, distribution_targetbox_24="Uniform",
values_targetbox_24=0, distribution_targetbox_25="Uniform",
values_targetbox_25=0, distribution_targetbox_26="Uniform",
values_targetbox_26=0, distribution_targetbox_27="Uniform",
values_targetbox_27=0, distribution_targetbox_28="Uniform",
values_targetbox_28=0, distribution_targetbox_29="Uniform",
values_targetbox_29=0, distribution_targetbox_30="Uniform",
values_targetbox_30=0, distribution_targetbox_31="Uniform",
values_targetbox_31=0, distribution_targetbox_32="Uniform",
values_targetbox_32=0, distribution_targetbox_33="Uniform",
values_targetbox_33=0, distribution_targetbox_34="Uniform",
values_targetbox_34=0, distribution_targetbox_35="Uniform",
values_targetbox_35=0, distribution_targetbox_36="Uniform",
values_targetbox_36=0, distribution_targetbox_37="Uniform",
values_targetbox_37=0, distribution_targetbox_38="Uniform",
values_targetbox_38=0, distribution_targetbox_39="Uniform",
values_targetbox_39=0, distribution_targetbox_40="Uniform",
values_targetbox_40=0, distribution_targetbox_41="Uniform",
values_targetbox_41=0, distribution_targetbox_42="Uniform",
```

```
"Uniform", values_state_3 = c(0.1,0.2,0.3),distribution_state_4 = "Uniform", values_state_4 =  
c(0.1,0.2,0.3)),list(box = 50,distribution_state_1 = "Uniform", values_state_1 =  
c(0.1,0.2,0.3),distribution_state_2 = "Uniform", values_state_2 = c(0.1,0.2,0.3),distribution_state_3 =  
"Uniform", values_state_3 = c(0.1,0.2,0.3),distribution_state_4 = "Uniform", values_state_4 =  
c(0.1,0.2,0.3)),time=1)  
}
```

```
% Generated by roxygen2 (4.1.0): do not edit by hand  
% Please edit documentation in R/createFateBox.R  
\name{createFateBox}  
\alias{createFateBox}  
\title{createFateBox}  
\usage{  
createFateBox(box, distribution_state_1 = "Uniform", values_state_1 = 0,  
  distribution_state_2 = "Uniform", values_state_2 = 0,  
  distribution_state_3 = "Uniform", values_state_3 = 0,  
  distribution_state_4 = "Uniform", values_state_4 = 0, time = 1)  
}  
\description{  
createFateBox  
}
```

```
% Generated by roxygen2 (4.1.0): do not edit by hand  
% Please edit documentation in R/loadExcelData.R  
\name{loadExcelData}  
\alias{loadExcelData}  
\title{loadExcelData}  
\usage{  
loadExcelData(file, xlsx = TRUE, level = c("Input", "Fate", "Transfer"))  
}  
\description{  
loadExcelData  
}
```

```
% Generated by roxygen2 (4.1.0): do not edit by hand  
% Please edit documentation in R/Transfer.R  
\name{Transfer}  
\alias{Transfer}  
\title{Transfer}  
\usage{  
Transfer(..., time = 1)  
}  
\arguments{  
item{...} {list of elements list(box, distribution, values)}  
  
item{time} {}  
}  
\description{  
give input for Material Transfer  
}  
\examples{  
Transfer(list(box = 49, distribution_targetbox_1=  
"Uniform",values_targetbox_1=c(0.1,0.2,0.3),distribution_targetbox_2=  
"Uniform",values_targetbox_2=c(0.1,0.2,0.3),distribution_targetbox_3=  
"Uniform",values_targetbox_3=c(0.1,0.2,0.3),distribution_targetbox_4 = "Uniform",  
values_targetbox_4 = 0,distribution_targetbox_5 = "Uniform", values_targetbox_5 = 0,...
```

```
values_targetbox_42 = 0, distribution_targetbox_43 = "Uniform",
values_targetbox_43 = 0, distribution_targetbox_44 = "Uniform",
values_targetbox_44 = 0, distribution_targetbox_45 = "Uniform",
values_targetbox_45 = 0, distribution_targetbox_46 = "Uniform",
values_targetbox_46 = 0, distribution_targetbox_47 = "Uniform",
values_targetbox_47 = 0, distribution_targetbox_48 = "Uniform",
values_targetbox_48 = 0, distribution_targetbox_49 = "Uniform",
values_targetbox_49 = 0, distribution_targetbox_50 = "Uniform",
values_targetbox_50 = 0, time = 1)
}
\description{
createTransferBox
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/PlotStatesVolumesTransfers.R
\name{PlotStatesVolumesTransfers}
\alias{PlotStatesVolumesTransfers}
\title{PlotStatesVolumesTransfers}
\usage{
PlotStatesVolumesTransfers(V_total, box, time)
}
\arguments{
\item{time}{{}}

\item{...}{{boxes for States, Volumes and Transfers}}
}
\description{
plot results
}

% Generated by roxygen2 (4.1.0): do not edit by hand
% Please edit documentation in R/Message.R
\name{Message}
\alias{Message}
\title{Message State of Simulation}
\usage{
Message(sender = sender, recipients = recipients)
}
\arguments{
\item{...}{{list of elements list(sender, recipients)}}

\item{adresses}{{}}
}
\description{
send a message
}
\examples{
Message(sender,recipients)
}

#####
#####
Read_files
#-----
```

- \* Edit the help file skeletons in 'man', possibly combining help files for multiple functions.
- \* Edit the exports in 'NAMESPACE', and add necessary imports.
- \* Put any C/C++/Fortran code in 'src'.
- \* If you have compiled code, add a useDynLib() directive to 'NAMESPACE'.
- \* Run R CMD build to build the package tarball.
- \* Run R CMD check to check the package tarball.

Read "Writing R Extensions" for more information.

### 5. Material fate assessment

In this section the results of the flow assessment for each material fraction containing the nanomaterial are presented (*Table S9*).

**Table S9.** Flow assessment of the material fraction containing nanomaterial within the recycling system.

ENM	Recycling process	Material type	Product examples	Flow assessment				
TiO <sub>2</sub>	e-waste	ceramics	flat irons, curling irons, hot rollers	Detox	Shredding	Magnetic separation	Eddy current separation	Waste washing
				Hazardous material		Ferrous metal	Non-ferrous metal	Plastics and other residues
	e-waste	plastics	computer mice and keyboards	Detox	Shredding	Magnetic separation	Eddy current separation	Waste washing
				Hazardous material		Ferrous metal	Non-ferrous metal	Plastics and other residues
cooling devices	filter components	fridges and conditioners	air	Dismantling	Shredding	Drying and PUR foam separation	Magnetic separation	Eddy current separation
				Glass and plastics		CFC and foam	Non-ferrous metal	Non-ferrous metals, plastics and others
concrete	concrete	demolition and waste concrete, bricks	Cleaning	Crushing and conditioning	Screening	Sorting	Aggregates	
			Metals and plastics					

ENM	Recycling process	Material type	Product examples	Flow assessment				
CNT	cars	batteries anode	Li-ion batteries	Removal Reusable parts	Detox Hazardous material	Shredding Cfc and foam	Magnetic separation Ferrous metal	Sorting Non-ferrous metals, plastics and others
	cars	composites	car boards and bumpers	Removal Reusable parts	Detox Hazardous material	Shredding Cfc and foam	Magnetic separation Ferrous metal	Sorting Non-ferrous metals, plastics and others
	cars	plastics	fuel components system	Removal Reusable parts	Detox Hazardous material	Shredding Cfc and foam	Magnetic separation Ferrous metal	Sorting Non-ferrous metals, plastics and others
Ag	e-waste	ceramics, plastics, filter components	flat iron, curling iron, hot rollers	Detox Hazardous material	Shredding	Magnetic separation Ferrous metal	Eddy current separation Non-ferrous metal	Waste washing Plastics and other residues
	e-waste	ferrous metal	electric shavers	Detox Hazardous material	Shredding	Magnetic separation Ferrous metal	Eddy current separation Non-ferrous metal	Waste washing Plastics and other residues

ENM	Recycling process	Material type	Product examples	Flow assessment				
	cooling devices	plastics and filter components	fridges and conditioners	Dismantling	Shredding	Drying and PUR foam separation	Magnetic separation	Eddy current separation
			air	Glass and plastics		CFC and foam	Non-ferrous metal	Non-ferrous metals, plastics and others

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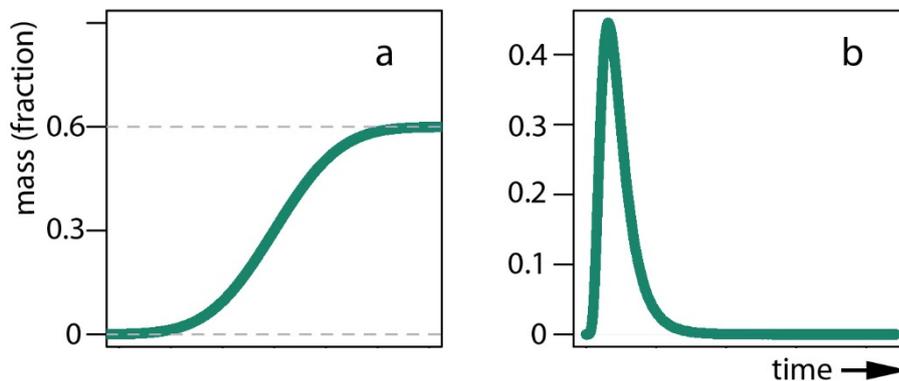
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## 5.2. Supporting information for “Stochastic fate analysis of engineered nanoparticles in incineration plants”.

### Appendix A: Figures



**Fig. A.1.**

*Didactical examples of transfer coefficient functions showing time dependent mass transfer values (e.g. median or other central values from the probability distributions) of detected as well as not detected nanoparticles (mass) up to a certain time point: a) for flow rates, transfers into deposition and/or transformation processes as well as for transfers into boxes reflecting not detected or not transported further mass (cumulative) and b) for transfers into boxes for not yet detected or not yet transported material.*

```

N <- 10000
V_t <- matrix(NA,n,N)
for (k in 1:N){
  I_t <- c(discharge mass[k]_t, rep(0,n-1))
  A_t <- matrix(0,n,n)
  A [2,1]_t <- -(mf1,2[k]_t)
  ...
  A [n,1]_t <- -(1- mf1,2[k]_t - mf1,3[k]_t - mf1,4[k]_t -...
  - mf1,n-1[k]_t)
  ...
  V [,k]_t <- solve(A_t,I_t)}

```

N: number of iterations for the point in time t

n: total number of boxes

mf<sub>1,2</sub>: mass fraction transferred from box 1 to box 2

**Fig. A.2.** Conceptual R Code for Monte Carlo Simulations of the ENP mass flows in the MSWI plant.

**Appendix B: Tables****Table B.1** *Travel time of ENP across the incinerator compartments.*

Compartments	Seconds
Waste bunker → Incinerator	20
Incinerator → Boiler	10
Incinerator → Slag pool	60
Boiler → Bunker for fly ash	2
Boiler → Electrostatic filter	2
Slag pool → Bunker for slag	120
Electrostatic filter → Bunker for fly ash	5
Electrostatic filter → Wet scrubber	10
Wet scrubber → Waste water	300
Wet scrubber → Cleaned exhaust	10

**Table B.2** Transfer factors for all mass transfer paths in a waste incineration system as shown in Fig. 1 and derived from the results (at the quasi steady state after 16 h) of the Monte Carlo simulations for nano-CeO<sub>2</sub>. These factors depict the steady state mass transport/transformation for all significant paths reached after 16 hours (see also Fig. 2 and Fig. 4b). This means that they represent values that illustrate how much nano-CeO<sub>2</sub> has been deposited, transformed or not detected after 16 hours. These factors may be used for mass flow in other plants which deal with constant nano-CeO<sub>2</sub> transfer/transformation (see also Table B.3); in comparison the factors might also be applicable for studies on other metal nanoparticles.

Transfer path	Transfer factors		
	5% quantiles	medians	95 % quantiles
1.	1.000E+00	1.000E+00	1.000E+00
2.	2.524E-03	2.478E-02	4.757E-02
3.	1.293E-37	9.098E-33	5.973E-28
4.	9.524E-01	9.752E-01	9.975E-01
5.	1.228E-13	1.229E-13	1.230E-13
6.	3.879E-01	4.481E-01	5.062E-01
7.	3.825E-05	3.913E-05	4.006E-05
8.	1.179E-01	1.359E-01	1.536E-01
9.	3.625E-01	4.164E-01	4.718E-01
10.	1.232E-13	1.260E-13	1.290E-13
11.	2.679E-28	3.029E-28	3.476E-28
12.	8.962E-01	9.416E-01	9.853E-01
13.	1.473E-02	5.845E-02	1.038E-01
14.	2.763E-07	3.141E-07	3.624E-07
15.	1.847E-03	1.777E-02	3.348E-02
16.	9.999E-05	1.000E-04	1.100E-04
17.	3.165E-01	3.322E-01	3.482E-01
18.	6.498E-01	6.499E-01	6.500E-01
19.	8.224E-13	9.281E-13	1.068E-12
20.	5.789E-03	5.099E-02	9.574E-02
21.	3.571E-05	3.572E-05	3.573E-05
22.	9.039E-01	9.487E-01	9.939E-01
23.	2.023E-04	3.157E-04	4.463E-04
24.	1.265E-12	1.428E-12	1.643E-12
25.	3.352E-09	4.519E-09	6.945E-09
26.	2.999E-01	3.000E-01	3.001E-01
27.	3.352E-09	4.519E-09	6.945E-09
28.	6.633E-01	6.803E-01	6.901E-01
29.	9.880E-03	1.973E-02	3.674E-02

\*The same marked transfer categories do not necessarily exactly add up to 1 in a particular column of quantiles, for mass balance computations one value has to be derived in dependence of the others.

**Table B.3** Transfer factors for all mass transfer paths in a waste incineration system as shown in Fig. 1 and derived from the results of the Monte Carlo simulations for nano-CeO<sub>2</sub>. These factors depict the steady state mass transport/transformation for all significant paths reached after steady state mode (infinite time scale) (see also Fig. 2 and Fig. 4a). Analytically not detected and not yet transported material has been assigned to the subsequent further transport and/or to the subsequent deposition/transformation because the stochastic parameters in the model cover the entire range of possibilities. The values show the fraction of nano-CeO<sub>2</sub> that has been deposited or transformed in the incineration system in analogy to the results of Table B.2. These factors may be used for mass flow in other plants that deal with constant nano-CeO<sub>2</sub> transfer/transformation. In analogy the factors might also be applicable for studies on other metal nanoparticles.

Transfer path	Transfer factors		
	5% quantiles	medians	95 % quantiles
1.	1.000E+00	1.000E+00	1.000E+00
2.	<i>Considered either in path 4 or path 5</i>		
3.	<i>Considered either in path 4 or path 5</i>		
4.	9.524E-01	9.762E-01	1.000E+00
5.	1.228E-13	2.379E-02	4.757E-02
6.	<i>Considered either in path 8, 9 or path 10</i>		
7.	<i>Considered either in path 8, 9 or path 10</i>		
8.	1.179E-01	1.817E-01	2.455E-01
9.	3.625E-01	5.585E-01	7.545E-01
10.	1.232E-13	2.598E-01	5.195E-01
11.	2.679E-28	5.189E-02	1.038E-01
12.	8.962E-01	9.481E-01	1.000E+00
13.	<i>Considered either in path 11 or path 12</i>		
14.	<i>Considered either in path 11 or path 12</i>		
15.	<i>Considered either in path 17, 18 or path 19</i>		
16.	<i>Considered either in path 17, 18 or path 19</i>		
17.	3.165E-01	3.328E-01	3.490E-01
18.	6.498E-01	6.504E-01	6.510E-01
19.	4.107E-14	1.683E-02	3.367E-02
20.	<i>Considered either in path 22, 23 or path 24</i>		
21.	<i>Considered either in path 22, 23 or path 24</i>		
22.	9.039E-01	9.517E-01	9.995E-01
23.	2.023E-04	3.680E-04	5.337E-04
24.	1.265E-12	4.794E-02	9.587E-02
25.	3.352E-09	3.501E-01	7.001E-01
26.	2.999E-01	6.499E-01	1.000E+00
27.	3.352E-09	7.264E-09	1.118E-08
28.	<i>Considered either in path 25, 26 or path 27</i>		
29.	<i>Considered either in path 25, 26 or path 27</i>		

\*The same marked transfer categories do not necessarily exactly add up to one in a particular column of quantiles, for mass balance computations one value has to be derived in dependence of the others.

### 5.3. Supporting information for “Flows of engineered nanomaterials through the recycling process”

#### 1. Product categories, ENM share and nanomass entering the recycling system

In this section the nanomass content and the recycling rate by product category is presented. This information was used to estimate the relative importance of each category within the recycling system and being able to select the most relevant ones for the overall modeling.

**Table S1.** Product categories where engineered nanomaterials are found. It includes the nanomass share by product category (A), the recycling rate of the product category (B), the nanomass share by product category that enters the recycling system (C), the weight of the nanomass in the product category as a percentage of the total nanomass that enters the recycling system (D), and the accumulative nanomass that enters the recycling system. All units are percentages. Source of product categories, A and B: Sun, et al. (2014b). Source of C-E: author's calculations.

ENM	#	Product category	A	B	C	D	E
TiO <sub>2</sub>	1	Consumer electronics	6.9	75	5.18	53.56	53.56
	2	Paints	8.9	46	4.09	42.37	95.93
	3	Batteries and capacitors	0.4	33	0.10	1.37	97.30
	4	Metals	0.1	90	0.09	0.93	98.23
	5	Cement	0.1	80	0.08	0.83	99.06
	6	Glass and ceramics	1.7	3	1.34	0.53	99.59
	7	Light bulbs	0.2	20	0.04	0.41	100
	8	Plastics	3.6	0	0	0	100
	9	Cosmetics	59.4	0	0	0	100
	10	Coating	3.7	0	0	0	100
	11	Filter	5.8	0	0	0	100
	12	Textiles	0.3	0	0	0	100
	13	Dietary supplements	0.4	0	0	0	100
	14	Ink	0.0	0	0	0	100
	15	Cleaning agents	6.2	0	0	0	100
	16	Spray	0.2	0	0	0	100
	17	Paper	0.0	80	0	0	100
	18	Sport goods	1.5	0	0	0	100
	19	WWTP	0.7	0	0	0	100
		TOTAL	100	-	10.95	-	-
ZnO	1	Paints	14.3	41	5.86	97.17	97.17
	2	Consumer Electronics	0.2	75	0.15	2.49	99.65
	3	Glass and ceramics	0.7	3	0.02	0.35	100
	4	Plastics	2.0	0	0	0	100
	5	Cosmetics	82.6	0	0	0	100
	6	Cleaning agent	0.1	0	0	0	100
	7	Foods	0.0	0	0	0	100
	8	Textiles	0.0	0	0	0	100
	9	Metals	0.0	90	0	0	100
	10	Woods	0.0	0	0	0	100
	11	Filter	0.1	0	0	0	100
	12	Paper	0.0	70	0	0	100
		TOTAL	100	-	6.53	-	-
CNT	1	Energy	9.1	75	6.83	62.19	62.19
	2	Consumer Electronics	3.1	75	2.33	21.19	83.38

	3	Paint	1.4	46	0.64	5.87	89.25
	4	Automotive	1.3	40	0.50	4.74	93.99
	5	Aerospace	0.6	60	0.36	3.28	97.27
	6	Sensor	0.4	75	0.30	2.73	100
	7	Composites	84.1	0	0	0	100
		TOTAL	100	-	10.97	-	-
Ag	1	Consumer Electronics	38.1	75	28.58	75.75	75.75
	2	MedTech	3.6	90	3.24	8.59	84.32
	3	Textiles	25.1	10	2.51	6.65	90.97
	4	Metals	2.4	90	2.16	5.72	96.69
	5	Paints	3.0	41	1.23	3.26	99.95
	6	Glass and ceramics	0.6	3	0.02	0.05	100
	7	Plastics	3.3	0	0	0	100
	8	Cosmetics	10.2	0	0	0	100
	9	Coatings & cleaning ag.	6.0	0	0	0	100
	10	Filter aggregates	0.3	0	0	0	100
	11	Additive to soil	0.6	0	0	0	100
	12	Sanitary	0.2	0	0	0	100
	13	Dietary supplements	6.6	0	0	0	100
		TOTAL	100	-	38.16	-	-

## 2. Elements of the inventory by ENM type

In this section a table with products belonging to each product category is presented. Its content is non-exhaustive and the idea is to show a glimpse to the inventory used during the modeling. The purpose of creating an inventory was mainly to understand the composition of the product categories and being able to detect the material fraction (metal, plastics,...) where the ENM is allocated.

**Table S2.** Elements of the inventory of products within each product category, including information on the manufacturer or model, the expected material fraction where the ENM is allocated and the product category it belongs to.

ENM	Product	Manufacturer/Model <sup>a</sup>	ENM allocation	Product category
TiO <sub>2</sub>	Flat iron (hair straightener)	BaByLiss	Ceramic plates	Consumer electronics
	Hair dryer	FHI Heat Nano Salon Pro 2000	Unclear	Consumer electronics
	Curling irons	BaByliss Pro 180 Curling Iron	Ceramic plates	Consumer electronics
	Fridges	Hitachi R550ET5X	Filter component	Consumer electronics
	Computer mice	IOGEAR Germ Free Wireless Laser Mouse	Plastic	Consumer electronics
	Computer keyboard	IOGEAR Long range wireless keyboard/mouse (combo)	Plastic	Consumer electronics
	Interior walls paint	Caparol – CapaSan Innenwandfarbe	Solution	Paints
ZnO	Exterior wall paints	Unknown	Solution	Paints
CNT	Energy storage devices	Unknown	Battery	Energy

	Semiconductor devices	Unknown	Printed circuit boards (PCB)	Electronics
	RAM	Unknown	PCB	Electronics
	CMOS (chips)	Unknown	PCB	Electronics
	Anti-fouling coating	Unknown	Ship hull	Coatings and Paints
	Fuel system components (connectors, pumps, o-rings)	Unknown	Plastics	Automotive
Ag	Curling iron	Jibere nano silver curling iron	Ceramic plates	Consumer electronics
	Flat iron (hair straightener)	Jilbere Nano Silver Ultra-Thin Flat Iron	Ceramic plates	Consumer electronics
	Deep waver	Helix AdjustaWave Deep Waver - 2175	Unclear	Consumer electronics
	Hair dryer	Remington Nano Silver Hair Dryer	Handle Ceramic grill	Consumer electronics
	Woman shaver	Remington Smooth & Silky	Blades coating	Consumer electronics
	Man shaver	Remington Nano Silver Personal Groomer	Blades coating	Consumer electronics
	Hot rollers	Conair Infiniti Nano Silver	Roller ceramics	Consumer electronics
	Washing machine	Samsung's SILVER WASH	Filter components	Consumer electronics
	Air conditioner	Samsung	Filter components	Consumer electronics
	Refrigerator	Samsung	Inner plastic walls	Consumer electronics
	Toothbrush sterilizer	Chungpung Co. Ltd	Unclear	Consumer electronics
	Multipurpose sanitizer	Klenz	Unclear	Consumer electronics
	Vacuum cleaner	Daewoo	Plastic coating	Consumer electronics
	Humidifier	Pure Guardian H2000	Unclear	Consumer electronics
	Hand dryer	o3 solutions ltd	Plastic coating	Consumer electronics
	Coffee machine	Saeco United States Co	Unclear	Consumer electronics
	Keyboards and mice	logear	Plastic coating	Consumer electronics
	Mobile phone	LG F2300	Plastic coating	Consumer electronics
	Notebooks	Samsung Q40 and R20	Plastic coating	Consumer electronics
	Air purifiers	AiroKorea	Plastic coating	Consumer electronics
	Operating table	Unknown	Metal coating	MedTech
	Door lock	Unknown	Metal coating	Metals
	Pet food bowls	Nano Care Technology	Metal coating	Metals
	Watch chains	Nano Care Technology	Metal coating	Metals
	Water tap	Nano Care Technology	Metal coating	Metals
	Kitchenware	Nano Care Technology	Metal coating	Metals
	Shirts	-	Textile matrix	Textiles

Socks	-	Textile matrix	Textiles
Blankets	-	Textile matrix	Textiles
Sport wear	-	Textile matrix	Textiles
Gloves	-	Textile matrix	Textiles
Interior wall paint	Mr. Paint Man Superwash Hygienic Coating	Solution	Paint



Figure 1S. Pictures of products included in the inventory. Note: the images were taken

directly from the public inventories consulted or through the Internet using the model description available in them.

### 3. Recycling processes description

In this section a more detailed description of the following recycling systems is provided: electronic waste (*Table S3*), cooling devices (*Table S4*), metals (*Table S5*), cars (*Table S6*), concrete (*Table S7*), textiles. This information was necessary to achieve a better understanding of the relevant recycling process to be able to model the flow of ENM within the system. At the end of the section the different sources consulted are presented.

#### *Electronic waste*

**Table S3.** *Electronic waste recycling process description.*

STEP	DESCRIPTION
1 Dismantling and depollution	Manual sorting of WEEE and removal of hazardous materials (ink cartridges, batteries).
2 Main shredding	Reduction of material to pieces of 100mm approximately. Different types of shredding technologies can be used: grinders, chippers, hammermills, shear shredders, all-purpose shredders and speciality shredders. This is a very abrasive process that could reach temperatures around 600°C due to kinetic energy. Dust absorbed with very strong ventilation systems (10,000m <sup>3</sup> /hour).
3 Sorting	The material is dropped into a large shaking hopper. This spaces the material out so it moves evenly onto the conveyor system. Big material is removed from the conveyor.
4 Secondary shredding	The material then proceeds through a secondary size reduction process. Dust extracted at this stage is sent for sound environmental disposal.
5 Magnetic separation	By means of a strong magnetic field, the overband magnet separates the ferrous (iron and steel) metals from those non-ferrous elements in the waste mix. This material is then collected in large storage containers ready for sale.
6 Eddy current separation	Electroconductive material is separated from non-electroconductive ones using Eddy Current Separators (ECS), including small particles (10mm). The ECS includes first and second hubs coupled to opposite ends of a magnet support tube. Magnets are coupled to the magnet support tube, substantially between the hubs. A motor coupled to one or both of the hubs rotates the magnet support tube and magnets to generate an eddy current in electroconductive material conveyed proximate the separator. The material in which the eddy current is created is repelled and projected away from the ECS along a predictable trajectory. An eddy current is not generated in nonconductive material conveyed proximate the separator, and thus is not projected away.
7 Waste washing	Additional steps can include waste washing. Here the granulated waste could be passed through a washing tank where the waste is cleaned to remove adhesive residues from labels and dirt debris. Water and surfactant are typically used to remove inks and organic contaminants of waste plastics. The waste is then sieved, where the polymer is recovered and fine debris are removed. Water used in the process is normally reused repeatedly and waste materials are thoroughly rinsed and passed through to the separation method.

Hazardous material removed in the first step includes batteries, printed circuit boards, print cartridges, polychlorinated biphenyls containing capacitors, mercury containing components, liquid crystal displays (LCD), cathode ray tubes, asbestos waste, plastics containing brominated flame retardants, components containing radioactive substances, and others EU (2012). They are taken apart during the first steps and sent to different specialized facilities where they can be treated under controlled environments.

#### *Cooling devices*

A Nitrogen rich atmosphere is maintained throughout the entire plant serving two purposes: (i) condensing and collection of CFC gases, and (ii), reducing the risk of explosions. The proportion of oxygen in the load rock and the following stages remains at a controlled 5%.

**Table S4.** *Cooling devices recycling process description.*

STEP	DESCRIPTION
1 Preparation (disassembly, drain-off and decontamination)	Disassembly of different components such as, glass, wood, cables and mercury switches. Heating of the compressor and cooling circuit to aid the flow of coolants. The liquid coolant, a mixture of refrigerants and oils is then drawn off and the compressor removed from the unit.
2 Shredding	After preparation, refrigerators are fed-in on roller conveyors in loads of 5-11 fridges. These then are sealed to allow emission free processing, passing over time and microwave sensors. Horizontal flexible accelerating tools create an enclosed tornado. The metal and aluminum will cut the plastics and the foam up to the required sizes, dependent on properties of the materials. Grain sizes range from 0.1mm to 100mm. This is a very abrasive process that could reach temperatures around 600 °C due to kinetic energy. Dust absorbed with very strong ventilation systems (10,000m <sup>3</sup> /hour).
3 Drying	The shredded material is heated up to 80 °C to reduce moisture in the material in an enclosed drying stage.
4 PUR foam separation	A sieving technique is used to extract the PUR (Polyurethane) foam from the other materials. The typical size of the foam particles is less than 2mm. The foam is then heated to 120 °C, which allows the CFC's to be extracted as a vapor, which is then passed to the Cryocondensation equipment for liquefaction in a temperature range of minus 100 °C to minus 160 °C. Once gathered and removed, ODS are shipped in canisters for sound environmental destruction by heating them to 2000 °C, temperature at which the gasses are broken down into gas and ash.
5 Overband magnet	Ferrous metal separation. Iron and steel (ferrous) metals are removed from the mixture of grained/sieved material using electro magnets. This material is then collected in large storage containers.
6 Eddy currents	Aluminum / copper (non-ferrous) metals are then separated from the plastics using Eddy currents (created by rapidly alternating magnetic fields). The non-ferrous material is stored in a container and the plastics are stored in a large bag.

#### *Metals*

**Table S5.** *Metal generic recycling process description.*

STEP	DESCRIPTION
1 Sorting	Different type of metals are sorted according to their characteristics, mainly into ferrous and non-ferrous metals. This can be done manually

	or mechanically by means of magnetic separation, eddy currents or others. Radiation tests can also be applied in this step.
2 Shredding	Metals are shredded and crushed so they can be processed.
3 Separation	Resulting material is sorted again according to their composition or their properties. Some methods include X-ray and IR technology, electrical currents, high-pressure air flow (cyclonic separation and liquid floating systems).
4 Baling	Once the different metals have been sorted and shredded, they are compressed into cubes or bales, which make it easier for them to be transported to smelting facilities. When the metals reach the smelting facilities, the bales are fed into a furnace where they are heated until they become molten metal.
5 Recovery-refining	The methods applied are generically described as hydro or pyrometallurgical processes and their specific characteristics depend on the properties of the metals to be recycled.

### Cars

**Table S6.** Cars recycling process description.

STEP	DESCRIPTION
1 Collecting	End-of-life vehicles are accepted in the recycling process. Only roadworthy and minimally damaged or functioning replacement parts qualify as used goods, which can be reused for their original purpose. These may be exported in accordance with the procedures applicable to the normal movements of goods.
2 Removal	Functioning parts are removed and sold to be used as replacement parts. Larger parts made from uniform materials (e.g. bumpers) can undergo separate material recovery.
3 Detox and dismantling	Licensed disposal companies drain vehicles that have been withdrawn from circulation and strip them of pollutants. They remove the petrol/diesel, oil and other operating fluids, batteries, tyres and catalysts. Particular attention is paid to components that contain known pollutants such as asbestos, mercury and PCBs: these must be disposed of separately.
4 Shredding	Around two thirds of a car consists of metals which can be recovered as raw materials through shredding and separating. The remaining shredder light fraction mostly consists of plastics, textiles, rubber, glass and metals. This is referred to by waste specialists as RESH (residue + shredder) and usually undergoes thermal utilization.
5 Sorting	Recyclable material is sorted and undergoes further recycling processes. The main recyclable waste fraction is metallic scrap, while the rest is mostly plastics, textiles, rubber and glass, which usually undergoes thermal utilization.
6 Metal recovery	Ferrous metal is usually melted in electric arc furnaces, where impurities are removed and new steel is produced for the car industry (or others).

### Concrete

**Table S7.** Concrete recycling process.

STEP	DESCRIPTION
1 Collecting	Construction and Demolition Waste (CDW) is collected in construction sites and transported to recycling facilities. CDW could be either mixed waste or only demolition concrete. Mixed waste includes concrete, bricks, tiles, gypsum, rubble and plastics. Additional input for concrete

	recycling includes gravel and concrete waste (concrete leftover in construction sites).
2 Cleaning	Metallic components and material like plastics and textiles, or any other material which is usually not used as aggregate are retired in this step.
3 Crushing	The material is crushed in pieces of several sizes. Some additives can be added in this step.
4 Screening and sorting	Resulting aggregate is screened and sorted according to their size and their composition (concrete waste or mixed waste), and stored.

### Textiles

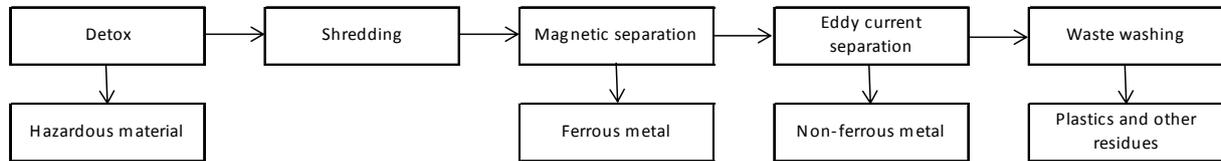
There are 2 companies that recycle textiles in Switzerland: one is TexAid, which covers 75% of the market, and the other is Tell-Tex. Tex-Aid is the result of the merging of TexAid and Contex, while Tell-Tex is the result of the merging of Solitex and Satex/TextaAg. TexAid export all the material that is collected, while Tell-Tex export the vast majority of it and only a minor fraction is distributed among social organizations in Switzerland. The main destinies of exported textiles are Eastern European countries, Russia, Africa and Middle East. The material that is sent abroad is used for different purposes: it can be resold as rewearable clothes, used to produce cleaning rags used by the car and mechanical engineering industries, used to produce recycled wool for the production of new clothes or blankets, or as insulating material.

### Sources

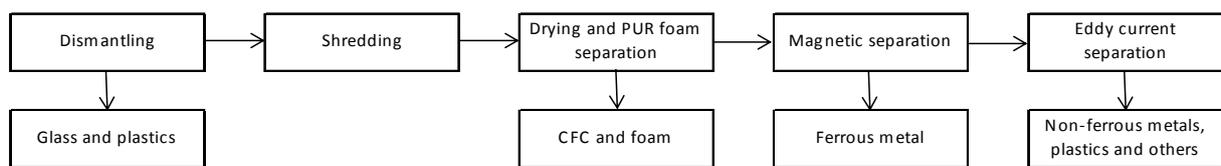
Electronic waste	SIMS WEEE recycling process <a href="http://www.simsrecycling.co.uk/Resources/WEEE-recycling-process">http://www.simsrecycling.co.uk/Resources/WEEE-recycling-process</a> Retrieved on 19.03.2013. ERP. "How is WEEE Recycled?" Retrieved on 11.03.2013 ( <a href="http://www.erp-recycling.co.uk/get_document.php?id=406">http://www.erp-recycling.co.uk/get_document.php?id=406</a> ) BAFU webpage: <a href="http://www.bafu.admin.ch/abfall/01472/01478/index.html?lang=en">http://www.bafu.admin.ch/abfall/01472/01478/index.html?lang=en</a> EMPA expert Goodship and Stevels (2012)
Cooling devices	SIMS WEEE recycling process <a href="http://www.simsrecycling.co.uk/Resources/Fridge-recycling-process">http://www.simsrecycling.co.uk/Resources/Fridge-recycling-process</a> . Retrieved on 20.03.2013. ERP. "How is WEEE Recycled?" Retrieved on 11.03.2013 ( <a href="http://www.erp-recycling.co.uk/get_document.php?id=406">http://www.erp-recycling.co.uk/get_document.php?id=406</a> ) FOEN webpage: <a href="http://www.bafu.admin.ch/abfall/01472/01482/index.html?lang=en">http://www.bafu.admin.ch/abfall/01472/01482/index.html?lang=en</a> Goodship and Stevels (2012)
Metals	Conserve Energy Future website: <a href="http://www.conserve-energy-future.com/RecyclingMetal.php">http://www.conserve-energy-future.com/RecyclingMetal.php</a> FOEN website, section Metals: <a href="http://www.bafu.admin.ch/abfall/01472/01486/index.html?lang=en">http://www.bafu.admin.ch/abfall/01472/01486/index.html?lang=en</a>
Cars	FOEN website, section End-of-life vehicles: <a href="http://www.bafu.admin.ch/abfall/01472/12810/index.html?lang=en">http://www.bafu.admin.ch/abfall/01472/12810/index.html?lang=en</a>
Concrete	Eberhard Recycling. Recycling facility in Kloten, Zurich, was visited on July 2013.
Textiles	TexAid website: <a href="http://www.texaid.ch/en-us/textilerecycling">http://www.texaid.ch/en-us/textilerecycling</a> Tell-Tex website: <a href="http://www.tell-tex.ch/verwertung/index.php">http://www.tell-tex.ch/verwertung/index.php</a> FOEN website, section Clothing ans Shoes: <a href="http://www.bafu.admin.ch/abfall/01472/01860/index.html?lang=en">http://www.bafu.admin.ch/abfall/01472/01860/index.html?lang=en</a> Telephone conference with TexAid Media Officer on 09.07.2013.

#### 4. Recycling processes flow diagrams

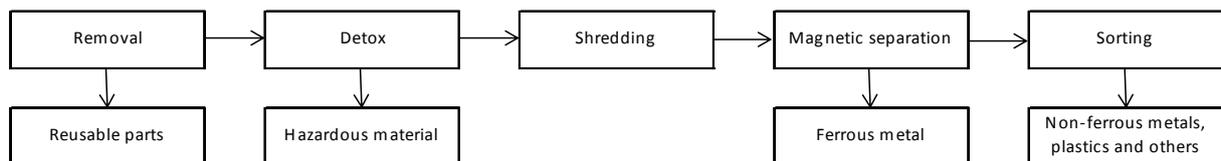
In this section the flow diagrams of the recycling processes created to perform the flow assessment of the nanomaterials are presented. The diagrams include specific material fractions and the step where they are expected to be retired. The diagrams were designed using the information provided in the former section.



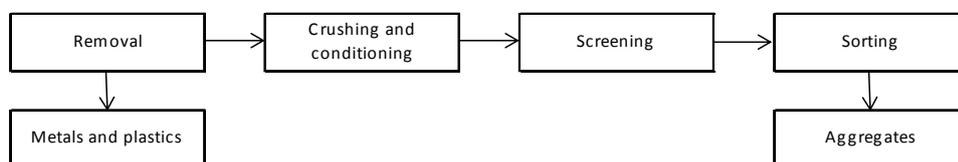
**Figure 2S.** Flow diagram of the electronic waste recycling process.



**Figure 3S.** Flow diagram of the cooling devices recycling process.



**Figure 4S.** Flow diagram of the car recycling process.



**Figure 5S.** Flow diagram of the concrete recycling process.

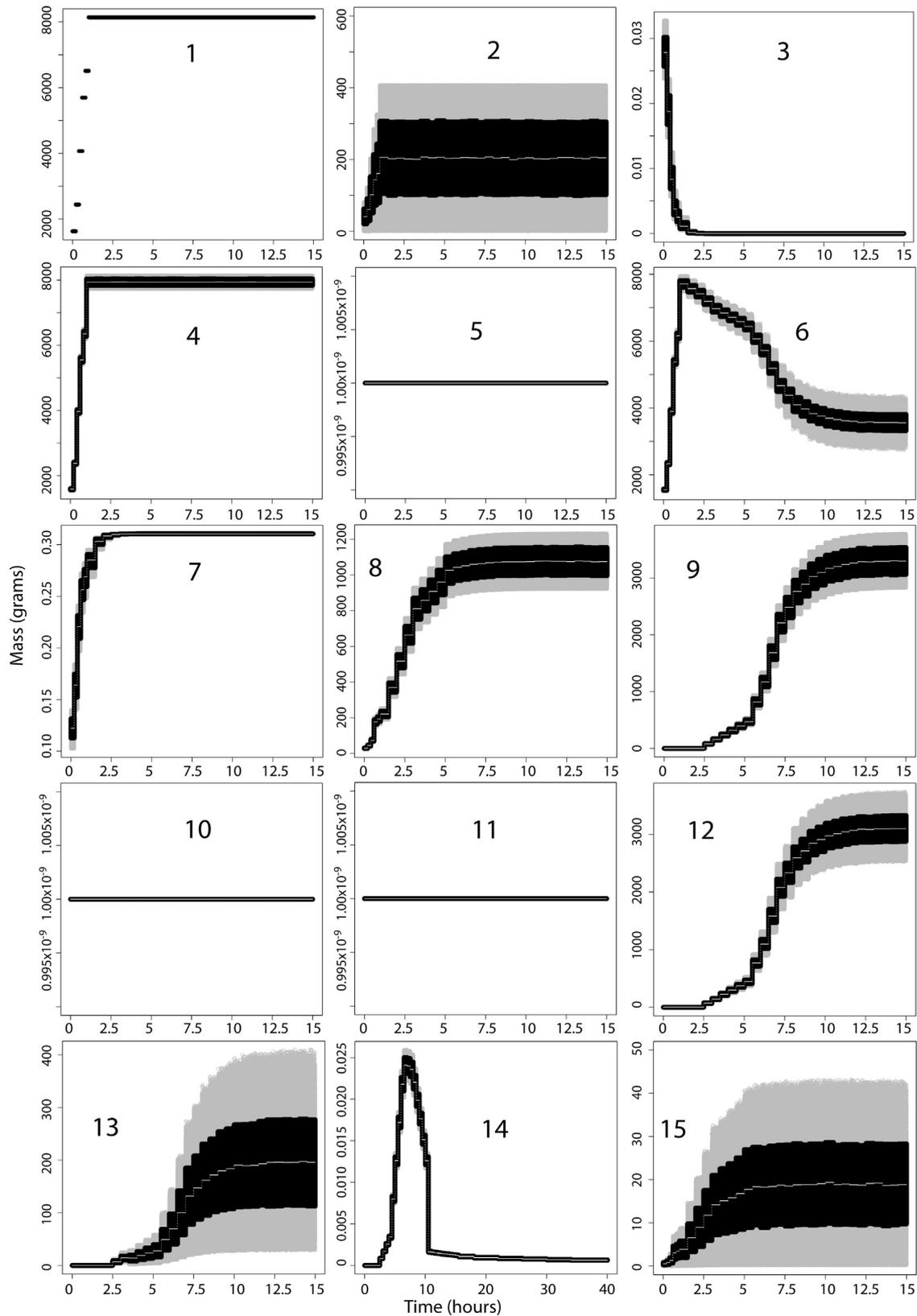
**Table S3.** General description and release data provided by the release literature selected. The general description included product category, nanomaterial, study type (model or real-world), product type and scenario. The release data columns only describes whether an specific article provides or not data related to relevant aspects for environmental modeling that were reviewed in the current work.

General description						Release data					
Product category	ENM	Study	Type	Product type	Scenario	Initial characterization	Mass-related info		Release characteristics		Release factors assessment
							Mass released	Release %	Characterization	Transformations	
Textiles	Ag	Benn and Westerhoff (2008)	Model	Socks	Washing	Yes	Yes	No	Yes	No	No
		Geranio et al. (2009)	Model	Shirts	Washing	Yes	Yes	Yes	Yes	Yes	Yes
		Holbrook et al. (2014)	Model	Wound dressing	Leaching	Yes	No	No	Yes	No	Yes
		Impelletieri et al. (2009)	Model	Socks	Washing	No	No	No	No	Yes	No
		Kulthong et al. (2010)	Model	Lab-produced and commercial fabrics	Sweating	Yes	Yes	No	No	No	Yes
		Lorenz et al. (2012)	Model	Socks, shirts, trousers	Washing	Yes	Yes	Yes	Yes	Yes	No
		Lombi et al. (2014)	Real world	Shirts	Washing	Yes	Yes	Yes	No	Yes	No
		Mitrano et al. (2014)	Real world	Socks	Washing	Yes	Yes	Yes	Yes	Yes	No
		Pasricha et al. (2012)	Model	Cotton, nylon and wool fabrics	Washing	Yes	Yes	Yes	Yes	No	No
		Stefaniak et al. (2014)	Model	Polyester fabrics	Sweating	Yes	No	Yes	Yes	Yes	Yes
	Yan et al. (2012)	Model	Socks, shirts, trousers, pants	Sweating	No	Yes	Yes	Yes	Yes	Yes	
	Ag, TiO <sub>2</sub>	von Goetz et al. (2013)	Model	Socks, shirts and trousers	Sweating + Physical stress	Yes	Yes	No	Yes	Yes	Yes
	TiO <sub>2</sub>	Windler et al. (2012)	Model	T-shirts, pants, reference material	Washing	Yes	Yes	Yes	Yes	No	No
Plastics	Ag	Artiaga et al (2015)	Model	Food container	Food storage	Yes	Yes	Yes	Yes	No	No
		Bott et al. (2011)	Model	Food container	Food storage	Yes	Yes	No	No	Yes	Yes

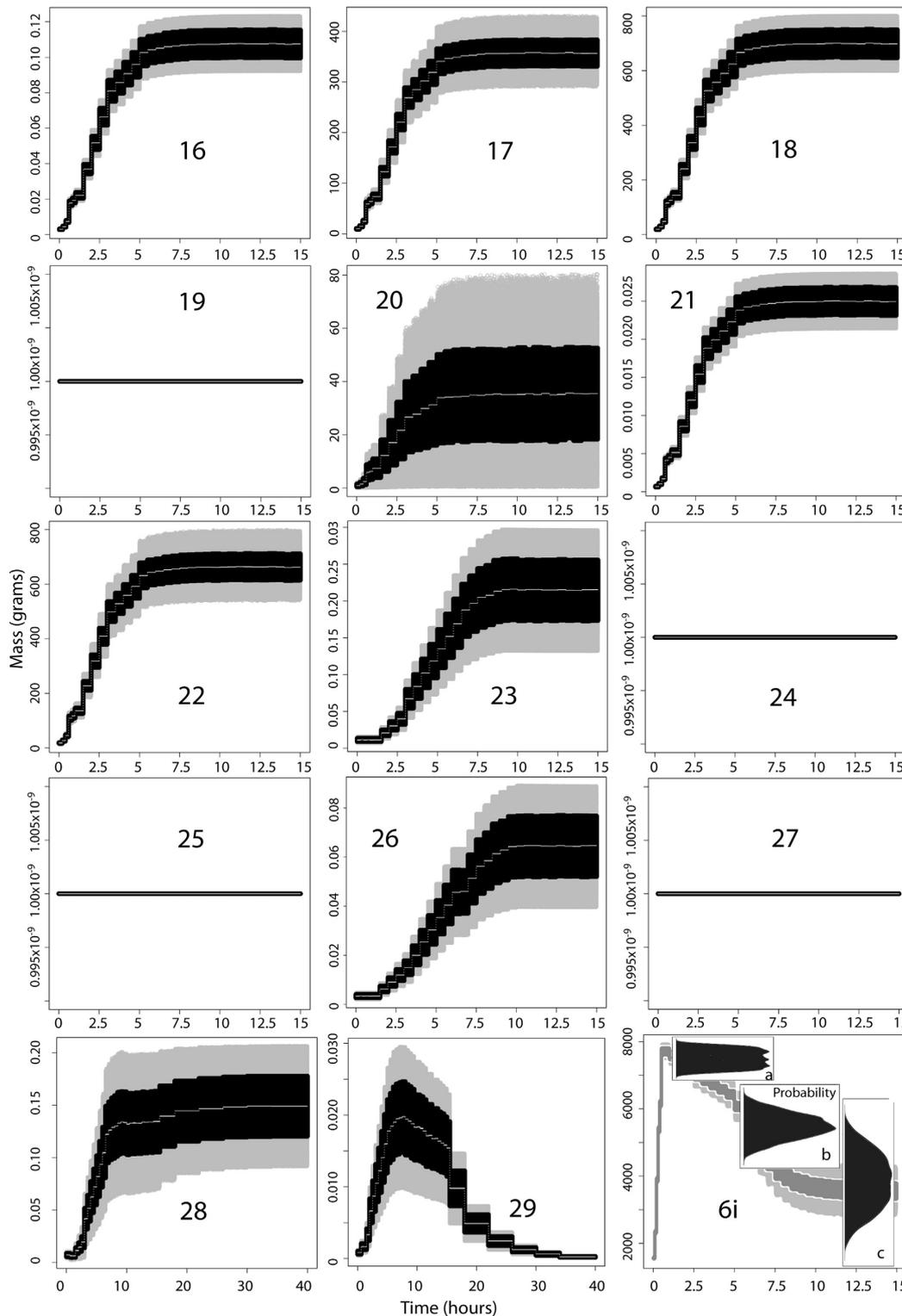
General description						Release data					
Product category	ENM	Study	Type	Product type	Scenario	Initial characterization	Mass-related info		Release characteristics		Release factors assessment
							Mass released	Release %	Characterization	Transformations	
Paint		Cushen et al. (2013)	Real world	Food container	Food storage	Yes	Yes	Yes	No	No	Yes
		Cushen et al. (2014)	Real world	Food container	Food storage	Yes	Yes	No	No	No	Yes
		Cushen et al. (2014)	Model	Food container	Food storage	Yes	Yes	No	No	Yes	Yes
		Echegoyen and Nerin (2013)	Model	Food container	Food storage	Yes	Yes	No	Yes	No	Yes
		Hauri and Niece (2011)	Model	Food container	Food storage	No	Yes	No	No	No	Yes
		Huang et al. (2011)	Model	Food container	Food storage	Yes	Yes	No	Yes	No	Yes
		Jokar and Abdul-Rahman (2014)	Model	Food container	Food storage	Yes	Yes	No	No	No	Yes
		Song et al. 2011)	Model	Food container	Food storage	Yes	Yes	Yes	No	No	Yes
		von Goetz et al. (2013)	Model	Food container	Food storage	Yes	Yes	No	Yes	No	Yes
		TiO <sub>2</sub> Lin et al. (2014)	Model	Food container	Food storage	Yes	Yes	No	Yes	No	Yes
		TiO <sub>2</sub> Al-Kattan et al. (2013)	Model	Outdoor paint	Weathering	Yes	Yes	No	Yes	No	Yes
		Al-Kattan et al. (2014)		Outdoor paint	Weathering	Yes	No	No	Yes	No	No
		SiO <sub>2</sub> Kaegi et al. (2008)	Real world	Outdoor paint	Weathering	No	Yes	No	Yes	No	No
		Al-Kattan et al. (2015)	Model	Outdoor paint	Weathering	Yes	Yes	Yes	Yes	No	No
	Coating		Fiorentino et al. (2015)	Model	Paint	Weathering plus abrasion	Yes	Yes	No	Yes	No
		Zuin et al. (2014)	Model	Paint	Leaching	Yes	Yes	No	Yes	No	Yes
		Ag Kaegi et al. (2010)	Real world	Outdoor paint	Weathering	No	Yes	No	Yes	Yes	No
		TiO <sub>2</sub> . Ag, SiO <sub>2</sub> Zuin et al. (2014)	Model	Paint	UV exposure and water immersion	Yes	Yes	No	Yes	No	No
		Ag Kunniger et al.	Real world	Wood coating	Weathering	Yes	Yes	No	No	No	Yes

General description						Release data					
Product category	ENM	Study	Type	Product type	Scenario	Initial characterization	Mass-related info		Release characteristics		Release factors assessment
							Mass released	Release %	Characterization	Transformations	
		(2014) Zanna et al. (2010)	Model	Anti-fouling coating	Inmersion into salt water	Yes	No	Yes	No	Yes	Yes
	TiO <sub>2</sub>	Hsu and Chein (2007)	Model	Wood, polymer and tile coating	Weathering, human contact	Yes	No	No	Yes	No	Yes
		Shandilya et al. (2015)	Model	Bricks coating	Weathering	Yes	Yes	No	Yes	No	Yes
Filter	Ag	Bielefeldt et al. (2013)	Model	Ceramic water filter	Water filtration	Yes	Yes	No	Yes	No	Yes
		Mittelman et al. (2015)	Real world	Ceramic water filter	Water filtration	Yes	Yes	No	Yes	No	Yes
		Ren and Smith (2013)	Model	Ceramic water filter	Water filtration	Yes	Yes	Yes	No	No	Yes
Cosmetics	TiO <sub>2</sub>	Botta et al. (2011)	Model	Sunscreens	Sunscreen application	Yes	Yes	N.A.	Yes	Yes	N.A.
		Holbrook et al. (2013)	Real world	Sunscreens	Sunscreen application	N.A.	Yes	N.A.	Yes	Yes	N.A.
Spray	Ag	Lorenz et al. (2011)	Real world	Spray	Spray application	Yes	Yes	No	Yes	No	N.A.
		Quadros and Marr (2011)			Spray application	Yes	Yes	No	Yes	Yes	N.A.
Automotive	C60	Le Bihan et al. (2013)	Model	Shaft cap	Several stress tests	No	No	No	Yes	No	Yes
Electronics	Ag	Farkas et al. (2011)	Real world	Washing machine	Normal machine operation	Yes	Yes	No	Yes	No	N.A.
MedTech	Ag	Rigo et al. (2012)	Model	Burn wounds dressing	Leaching	Yes	Yes	No	Yes	Yes	Yes
Textiles, MedTech, Sanitary,	Ag	Benn et al. (2010)	Model	Shirts, medical cloths, shampoo,	Washing (textiles), average use	Yes	Yes	No	Yes	No	No

General description						Release data					
Product category	ENM	Study	Type	Product type	Scenario	Initial characterization	Mass-related info		Release characteristics		Release factors assessment
							Mass released	Release %	Characterization	Transformations	
Electronics				toothpaste, teddy bear, humidifier	(sanitary and electronics)						
Textiles, Plastics, Sanitary, Electronics	Ag	Quadros et al. (2013)	Model	Plush toy, blanket, wipes, humidifier	Leaching	Yes	Yes	Yes	No	No	Yes
N.A. Not applicable											



**Figure 8.** Probabilistic mass flow of the nano-CeO<sub>2</sub> in the modeled sub-boxes and sinks. Numbers correspond to the boxes and sinks in Fig. 7. The white line indicates the median value, the black area the 50% confidence interval, and the grey area the entire possible space. The x-axis covers the time until quasi steady state mode is reached, and the y-axis varies on a linear scale.



**Figure 8 cont.** Probabilistic mass flow of the nano-CeO<sub>2</sub> in the modeled sub-boxes and sinks. Numbers correspond to the boxes and sinks in Fig. 7. The white line indicates the median value, the black area the 50% confidence interval, and the grey area the entire possible space. The x-axis covers the time until quasi steady state mode is reached, and the y-axis varies on a linear scale. 6i shows how the uncertainty can be read: each flow has an underlying uncertainty distribution that changes shape and becomes wider over time. The three inlets a-c have equal scales and equal sample sizes with the y-axis describing probability (absolute scale is not relevant in this didactical example). They are snapshot distributions for results after 1 hour, 5 hours, and 14 hours.

### 2.2.1.3. Aim of the study

In this study, we address following questions:

- What is the model structure of a mass transfer based fate analysis for ENP in Municipal Solid Waste Incineration (MSWI) plants?
- What are the associated uncertainties, and how do they propagate through the incineration system?
- Can the developed model framework provide evidence for the consistency of the measurement results?
- How can future experiments of ENP in incineration plants benefit from such model results?
- If case specific steady state parameters for the ENP fate in incineration can be obtained, how can generic environmental release values be computed for use in environmental exposure assessment?

## 2.2.2. Method

### 2.2.2.1. The nanoparticle experiment in the incineration plant

The basis for the probabilistic fate model was set by the aforementioned study, in which 10 kg of dispersed CeO<sub>2</sub> nanoparticles were sprayed over 1 hour onto municipal waste that was then incinerated in a modern MSWI plant (renewed in 1998). The MSWI plant consists of the incinerator, a flue gas cleaning system with an electrostatic precipitator and a wet scrubber, a boiler for the use of the excessive heat, and various bunkers for the incineration residues. In this plant, 0.14 tons of fly ash and nearly 2 tons of slag are generated from the more than 8 tons of treated waste per hour. The slag is quenched with 140 kg water per hour. Samples of all solid and fluid residues were collected up to 10 times each during the 7 hour experiment and then analyzed for their cerium concentration and nanoparticle morphology. Despite the exhaust gas leaving the stack, cerium concentrations were always above the quantification limit and exceeded the background concentrations. For the calculation of the cerium flows, the concentrations in the residues were multiplied with the underlying mass flows after the background concentration of the cerium in the residues from the conventional waste was subtracted. This background was measured prior to the experiment and served as control value in each type of residues. The values were 30.2 µg/g in the slag, 41.5 µg/g in the fly ash, and much lower in the waste water (0.6 ng/ml), where 0.02% of the recovered nanoparticles was found. The main fraction of the recovered engineered nanoparticles was found unaltered in the slag (81%) and the fly ash (19%). The overall recovery rate of cerium was approximately 40%.

### 2.2.2.2. Conversion of the real plant into a model

In order to be able to compute the nanomaterial dispersion into the different residues, the model was set up to reflect the structure of the real MSWI plant (**Figure 7**) and to convert the tracer experiment into a dynamic and probabilistic nanoparticle fate analysis. Each compartment in the plant is divided into four boxes that are connected by nanoparticle flows. The four boxes illustrate the minimal model architecture on the state of the ENP at a certain point in time from a researcher's perspective. The rationale of the underlying concept is the need to distinguish between the uncertainty of the precision of the measurements of the discovered material and the uncertainty of the fate of the

undetected material at any stage of the waste treatment. In addition, differences between delayed and immediate ENP mass transport are resulting from varying retention times in the different compartments of the incineration plant. They also need to be included in the model. Finally, deposition/transformation must also be considered in the model. In order to account for all of these requirements, each compartment in the incineration plant was converted into four boxes (boxes I, II, III, IV in **Figure 7**). Nanoparticles in box I were not detected because of missing or limited measurement capabilities causing missing or fuzzy information on material flows. Nanoparticle flows of box I reach steady state after a certain time. However, in case of a dynamic interaction between mass transport and the discovery process, an interim mass decrease is possible (see e.g. Flow 6 in **Figure 8**). Box II contains nanoparticles that are present in the compartment at a certain point in time but will eventually continue travelling to the next compartment. Such flows are bidirectional due to the complex interplay between mass increase (mass not transported further) and decrease (mass transported further). In certain cases, the decrease kinetics dominate after a certain time, which results in an overall non-cumulative behavior and hence a fading of the ENP transportation (Flows 3, 14, 29). The instantaneous flow rate is captured by box III and hence reflects together with box II the mass travelling in the incineration plant. The travel times are shown in **Table B.1 (Appendix)**. Finally, box IV captures all nanoparticles that are either transformed or finally deposited.

We investigated all mass transfers and stocks of ENP throughout the incineration by linking ENP concentration measurements to the modeled mass flows and retention times. We obtained new data in comparison to Walser et al. (2012) directly from the operator of the same MSWI plant as described in Walser et al. (2012). Residence and travel times of the nano-CeO<sub>2</sub> in and between the different compartments were refined, and detailed uncertainty and variability was added (**Table 4 and Table B.1**). Data on the slag pool were amended. The deposited fractions in the incinerator, boiler, electrostatic precipitator, and wet scrubber have been estimated and are now an inherent part of the model. For example, five tons of solid residues accumulate in the incinerator during one maintenance cycle of 10 weeks. Hence, 0.4‰ of the ENP (and of any inert material) is assumed to be deposited in box IV, based on the total waste flow of 8.5 tons per hour. Transfer factors from the boiler and the electrostatic filter to the bunker for the fly ash (Flows 17, 22 in **Figure 7**) were empirically determined. In this case, 30-40% of all detected ENP in the fly ash directly comes from the boiler, while a further 60-70% of the ENP makes the detour via the electrostatic precipitator.

### 2.2.2.3. From a static to a dynamic, probabilistic approach

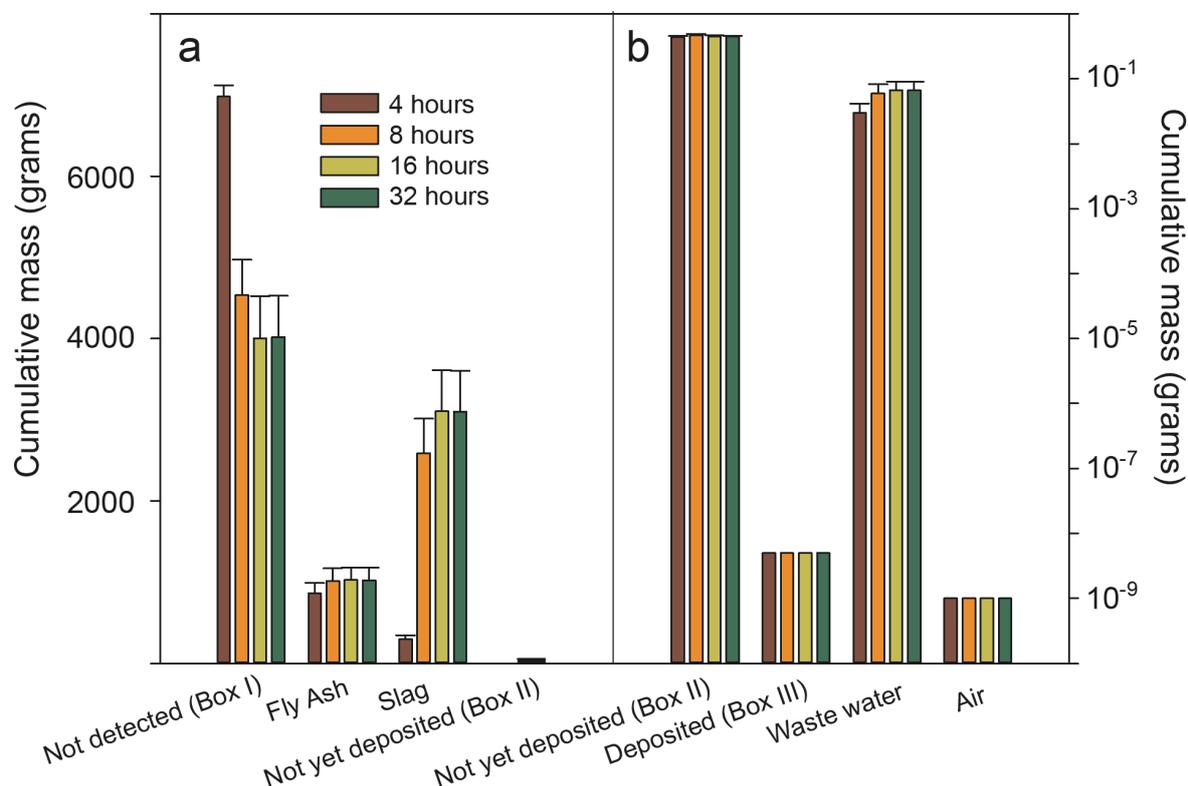
We then carried out a quantitative analysis on flows and concentrations of nano-CeO<sub>2</sub> in the MSWI plant. The PMFA, which was specifically developed for environmental exposure analysis (Gottschalk et al., 2010), was adapted for dynamic material transfer computations. Hence, the entire uncertainty and variability propagation of the ENP transfer through the incineration system has been approached by extending a fully stochastic/probabilistic material flow analysis for time dependent computations. The applied Monte Carlo (MC) algorithms, employed to stochastically solve systems of linear mass transfer and transformation equations by randomly calculating model input parameters and model output, allow selecting values from a variety of probability distributions. The input data needed here includes the ranges of ENP mass flow into the waste incineration system and their further distribution in the waste incineration system. The mass balance algorithms embedded in matrix algebra are programmed in R (R Development Core Team, 2012) with a conceptual code in **Figure A.1**. The computed input distributions for the model – in this study varying over time – reflect empirical and experimental evidence (non-parametric distributions) and expert and/or theoretical knowledge. They allow capturing of the missing precision and the entire possible value spectrum, i.e. the uncertainty and variability of all model parameters. The wider these spectra are the smaller becomes the probability of missed events in the MC results.

First, we randomized and combined for each time point possible parameter values out of the value range – determined by all the model input distributions – in order to feed these values into the mass balance equations and to solve them. Additionally, our algorithms performed this procedure iteratively by generating 10,000 possible parameterizations of the material flow system. In contrast to static calculations, we did not only compute such a number of systems for one point in time but on a continuous time scale (**Figure A.1**). Such a system variation ensured that the complete spectrum of time dependent uncertainty propagation was considered as much as required. It also includes any known variability in the operational processes of the MSWI plant (**Table 4**).

As outlined before, the ENP fate calculations can be kept simple by reducing them to the quantification of nanoparticles sprayed onto the municipal waste in the MSWI plant (nanomaterial input, in grams) and to nanomaterial transfer (modeled as transfer coefficient (TC), from 0 to 1) between the established boxes of the incineration system. We quantified such material input and transfer in the MSWI plant as a function of time and location. TCs to feed the model were derived from the mass flow data (**Table 1**) by dividing a particular ENP output flow value at a particular point in time and space by the total ENP input at that time into the corresponding box. The resulting simulated mass flows were then computed as a cumulative ENP mass reflecting the measured and detected ENP, as well as the ENP not detected up to a certain time point. This time point can be set arbitrarily. Half-hourly intervals were used to illustrate the results (**Fig. 8**) with a higher temporal resolution in the first hour (and larger ones after 15 hours) of the continuous input of the nano-CeO<sub>2</sub>. An input of 10 kg ENP was chosen for the generic TC (**Figure 10**).

**Table 4** shows all the raw data used and distinguishes between (i) pure measurement results (ii) parameters from logical combination of measurements and calculations, (iii) values that illustrate assumptive time dependent ENP mass flows that were either not measured and therefore extrapolated from the previous or subsequent period, or known to be (virtually) zero, and (iv) flows that were unknown a priori and automatically generated by the model. All measured and calculated values in **Table 1** are shown for the

measurement period only while the model can extend this period infinitely. These data points were the source for the MC randomization process that consists of a bootstrap re-sampling of the observed data that vary in time and location. The MC algorithms directly draw model input numbers and uncertainties from the distributions derived from the primary data in **Table 4**. Three examples of the generated MC distributions can be seen in **Figure. 8 (6i)**.



**Figure 9.** Cumulative recovery of engineered nanoparticles (8.14 kg pure cerium added to the system). Temporally differentiated nanoparticle mass (median value) in the final flows and the modeled sub-boxes. Uncertainty bars cover the 95% confidentiality interval. a) shows the main fractions of ENP on an absolute scale. b) shows the smaller fractions of ENP on a logarithmic scale.

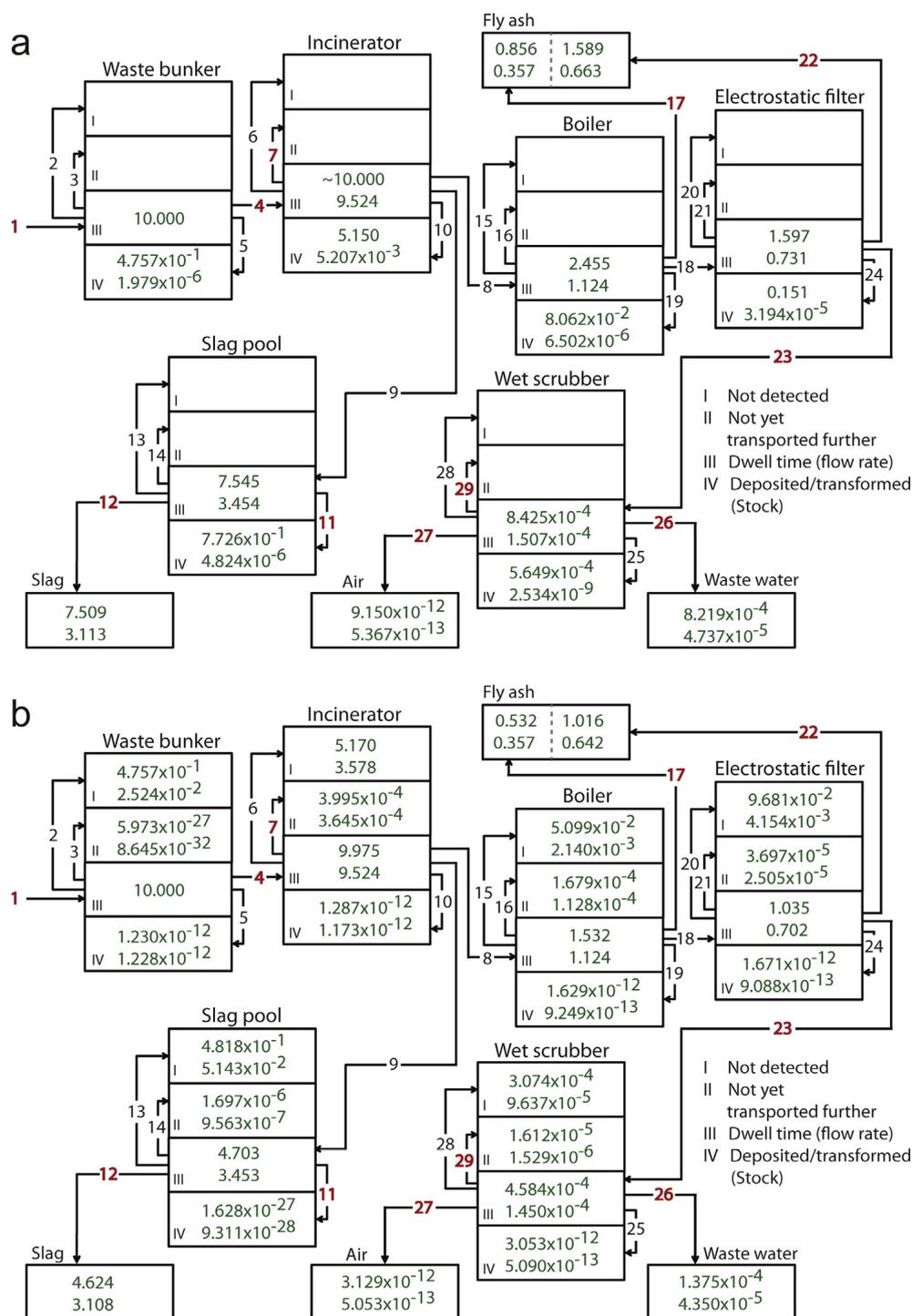
#### 2.2.2.4. Feeding the model with data: Measurements, variability, and uncertainties

Once the structure of the analyzed system was set, the travel behavior of the ENP through the boxes was determined: the simulated real scale experiment started with the continuous input of 10 kg nano-CeO<sub>2</sub> onto the waste for one hour (shown as 8.14 kg pure cerium in **Table 4**, Fig. 8-9). The transfer of the ENP from the waste to the incinerator is close to 100%. The incinerator transfers the ENP either to the slag pool or to the boiler. A minor part of the ENP is deposited in the incinerator. The ENP then travel through the flue gas cleaning compartments and become increasingly diluted until they end up in the different residue streams that eventually leave the waste incineration plant (**Figure. 7**).

Ideally, the measurement data are consistent with the logical structure of the model, i.e. the cumulative ENP inflow would never be higher than the cumulative ENP outflow. This consistency was challenged by (i) the various measurement techniques that are required

for the ENP quantification in the different incineration residues, (ii) miniscule ENP flows on top of the gigantic solid and gaseous waste residue flows, (iii) the limited amount of measurement points in comparison to the 29 estimated flows, (iv) a variable background concentration of the investigated elements assumed to be constant, and (iv) the limited frequency of sample collection.

The uncertainty ranges for the individual flows were quantified based on empirically derived material flow variability (e.g. slag and fly ash flows), calculated measurement uncertainties (e.g. from ICP-MS measurements), and estimated mass flow fractions in the system (e.g. from the contribution of the electrostatic precipitator and the boiler to the total amount of fly ash). The uncertainty ranges are found in Table 1, which also provide mass values for detected nanomaterial for measurement periods of 30 minutes in the ideal case. For some incineration residues, the measurement periods were extended to one or two hours. Values for periods with no measurements (nm) were derived from scaling the preceding and/or following measured results based on individual assumptions on the expected time dependent tendency (mathematical details in **Table 4**). Time dependent cumulative functions were derived from the calculated concentrations and underlying flows by summing up all the detected material until a certain point in time. As a consequence, semi- or non-cumulative functions emerged after the accumulation of nanoparticle mass was complemented with the expected mass loss (flows into box I: flow 6, and box II: flows 3, 14, 29). In case only starting conditions were known, the continuations of mass flows were derived from exponential curves (flows 3 and 7). We extrapolated the measurement results over time only if a significant trend was found, and we skipped any extrapolations that would have been based on weak assumptions. Hence, for the case study, the modeled total recovery rate did reach 100% on an infinite time scale with the unrecovered part labeled as “not detected”.



**Figure 10.** a. ENP mass that is transported through the different compartments in steady state mode (infinite time scale). The assumed input is 10 kg ENP. Upper values and lower values represent the entire spectrum of possible results. The results are shown for a scenario with all ENP being detected and ending up deposited/transformed at their final destination. b. ENP mass that is transported through the different compartments after 16 h (quasi steady state). The assumed input is 10 kg ENP. Upper values and lower values represent the entire spectrum of possible results. The results are shown for the real scale experiment (Walser et al., 2012) on an infinite time scale with approximately a 40% recovery rate with the remaining approximately 60% probabilistically allocated to the boxes I and II.

### 2.2.3. Results and Discussion

#### 2.2.3.1. Consistency of the measurement results

The ENP measurements have lower uncertainties (<20%) than the underlying mass flows and therefore contribute to the overall uncertainties to a smaller degree. The measurement data showed a sufficient consistency to set a solid basis for the flow model, which was later reconfirmed by the model output. Consistency means that at a certain point in time, the cumulative mass of detected ENP in a specific sub-box could never be higher than the cumulative mass of detected ENP in the previous sub-boxes. Only the third measurement in the waste water was classified as an outlier and was therefore excluded (see also Fig. 2 in Walser et al., 2012). No reason was found for this extreme value. Fig. 8 shows the results of the cumulative flow model. The Figures present a condensed form of many subsequent uncertainty distributions spanning over at least 15 hours. Generally, the curve of the cumulative ENP mass in boxes II and III has a sigmoidal or exponential shape with a saturation after approximately 7.5 hours for ENP in solid residues, 5 hours for ENP in liquid residues, or less than 2.5 hours for ENP in the flue gas. The wet scrubber (1/20 mass loss per hour) and the slag pool (1/10 mass loss per hour) have longer retention times, which results in a longer period until the ENP flow stabilizes (Flows 14, 28, 29 in Fig. 8 with the x-axis spanned up to 40 hours). The uncertainty of the ENP fate in the incineration plant increases with increasing traversed compartments. The model reflects this aspect with a widening of the confidence intervals. In addition to the highly dynamic ENP flow in the first few hours of the experiment presented in **Figure 8**, **Figure 9** shows four snapshots of the evolution of the cumulative mass in the major compartments of the MSWI plant.

#### 2.2.3.2. Fate analysis of the ENP from the incinerator to the slag

Flow 1 in **Figure 8** shows that the ENP transfer rate from the waste bunker to the incinerator is close to 100% with low uncertainty. A prerequisite for this result is a well characterized ENP suspension (or powder) which is homogeneously sprayed onto the waste. Flow 2 steeply increases but stabilizes immediately after the ENP input is stopped. The cumulative mass of approximately 200 grams has a large uncertainty with  $\pm 50\%$  of this value falling into the 50% confidence interval around the average value. Reason for this is the large input variability of the conventional waste. The relatively long residence time of the waste in the incinerator keeps the nanoparticles from being transferred to the slag. Hence, the initial amount of not detected ENP is large and decreases over time (flow 6). The unrecovered fraction (box I) is assumed to mainly remain in the incinerator because any other destination would have been speculative. The quantified ENP are then travelling through the slag pool into the slag (flows 9 and 12), with a small loss in the slag pool (flow 11 and 14). The slag pool does not act as a substantial sink for the ENP because the slag water evaporates, and the ENP eventually end up in the slag again. The slag pool is modeled similarly to the wet scrubber: with the decreasing concentration of ENP in the slag (7 hours after the experiment started), the inflow into the slag pool decreases as well. The retention time is only a few minutes, which minimizes the reaction time of the outflow to any changes in the inflow.

#### 2.2.3.3. ENP flow in the flue gas

More than 99% of the ENP that are transferred from the solid waste to the flue gas are captured in the boiler and electric filter and subsequently end up in the fly ash. The model follows the measurement results very closely without model-fitting and does not

show any inconsistency. The ENP not being found in the fly ash or slag are either transferred to the wet scrubber or remain as caking in the boiler (<1 ‰, flow 16) or in the electric filter (<1 ‰, flow 21). The ENP in the boiler and electrostatic filter are removed during the regular maintenance activities. These caked (albeit not agglomerated in the case of CeO<sub>2</sub>) nanoparticles from the modeled boxes II are transferred at a later stage to the incineration residues or the cleaning residues during the regular maintenance work in the MSWI plant. Therefore, the ENP are unlikely to be ultimately deposited in the system, and hence the boxes IV in boiler, electrostatic filter, and wet scrubber do not accumulate ENP over the long term. However, the known tendency of ENP to stick to any available surface (Kittelson, 1998) can still result in an accumulation of ENP in the incineration system with high (nano)particle concentrations and on a large amount of surfaces (walls), as can be seen in the sub-boxes I, II, and IV. This phenomena could indicate that the ENP generally show a slightly lower mobility in comparison to other incineration residues in this particular MSWI plant.

#### *2.2.3.4. ENP in the wet scrubber and clean gas*

The wet scrubber is modeled differently in comparison to the other compartments. The ENP inflow is homogeneously distributed in the water, and the captured ENP are pulse-released to the waste water. The known residence time of 11 hours was implemented into a one-box model with known outflow. Flow 26 shows the ENP outflow that first increases rapidly and then slows down as the ENP inflow stops. Flow 29 captures the long residence time of the ENP in the wet scrubber with a slow decrease of the ENP concentration after the inflow has stopped. The quantification limit of the ENP in the clean gas was never surpassed, which is reflected in the virtually zero amount of ENP in flow 27.

#### *2.2.3.5. Transfer coefficients and underlying uncertainties*

If more knowledge on physic-chemical changes of ENP in relation to specific compartments in the incineration plants becomes available, an estimation or a mechanistic prediction of the location of the not recovered part of the ENP will become possible. With the gained experience from small scale and large scale experiments (both can be found in Walser et al 2012) and the model results from the steady state analysis (numeric values are found in Fig. 10a-b), we estimate that the transfer coefficients will not change significantly in other MSWI plants, meaning that approximately 99% of the ENP can be found in the slag or fly ash. However, in order to obtain a complete mass balance in practice, the exact underlining material flows (waste, slag, fly ash, flue gas) have to be known with a high temporal resolution. To support modelers in their work, we went beyond the case study and probabilistically calculated transfer factors for a generalized case with a closed mass balance (Fig. 10a-b and Tables B.2-3). The results are still based on the available measurement results, but they were combined with the probabilistic model, which allowed us to estimate the fate of the not detected fraction and the respective transfer factors. The presented transfer factors were derived for all pathways in the incinerator 16 hours after the start of the experiment when the cumulative nanoparticle mass did not change anymore (Fig. 10a-b). Hence, the numeric values in Fig. 10a-b provide an overview on how much nanomaterial has been accumulated/transformed in total (Fig. 10a) and on how much has not been detected (Fig. 10b) in the various compartments during the analyzed time period. These results may be used for mass flow studies that need to incorporate constant ENP transfer and transformation in similar incineration plants, and they might also be applicable for nanomaterials with similar physic-chemical behavior.

#### *2.2.3.6. Practical challenges in the experiment and implications for the model*

Increasing the sampling frequency and prolonging the sampling period in future experiments would also improve and refine the quantification of nanoparticle flows. Moreover, the sampling strategy must be reliable and representative. For example, the flue gas that is drawn through the measurement filters must be carefully extrapolated to the total flue gas flow, and a representative amount of ENP has to be quantified on the filters, which requires knowledge on the expected concentrations in order to reach measurable concentrations. The fly ash and the slag must be homogeneously covered with the ENP in order to allow the collection of a representative sample. While this prerequisite is not too much of a challenge in the laboratory, it is difficult to achieve in a full scale incineration plant. In addition, details on the temporal variability of the elemental background concentration for the ENP under investigation would also improve the ENP fate analysis in a MSWI plant. Another practical challenge is the modeling of the wet scrubber. Working like a shower, the wet scrubber captures corrosive gases and particles by spraying water into the flue gas. The resulting liquid fraction is then reused until the salt concentration reaches a predefined threshold value. Surpassing this threshold value results in a pulse release of the wastewater and an inflow of freshwater. The discharge frequency depends, among other factors, on the composition of the flue gas and is therefore fluctuating. This frequency is not always known, although we can handle an exact specification of the discharge frequency in the model. The actual water volume also varies, and the volume of 12 m<sup>3</sup>, assumed constant in our case, is a simplification. However, our computations can be adjusted to any additional available information, which adds further specificity to the output of the model.

#### *2.2.3.7. Low recovery potential for engineered nanoparticles*

As long as the ENP remain stable in the incineration residues, their commercial recovery will unlikely become economically attractive. However, new technologies that would allow ENP enrichment in the solid residues and/or enforce an aggregation of the ENP into larger particles may change this perspective. Surprisingly, the wet quenching of the slag does not lead to aggregation of the investigated nanoparticles. Regardless, the main mass flow is into the solid fraction and, hence, any focus on the wet or gaseous outflows does not seem to be promising for ENP recovery activities in future. The commercial recovery of ENP after the wet scrubber is further complicated by the use of the alkaline fly ash to neutralize the acidic waste water in irregular periods. Therefore, a prediction for the amount of nanoparticles in the waste water after incineration of nanowaste remains vague. Hence, the main purpose of the wet scrubber will likely remain the minimization of any toxic ENP release to the waste water or the atmosphere rather than a recovery of the ENP.

#### 2.2.3.8. Model performance

The combination of theoretical flow analysis and measurement data instead of pure modeling supports experimenters and modelers in creating an optimal experimental setup and in the estimation of nanoparticle loads in the different waste incineration compartments. The model used can be generalized and adapted to other MSWI plants. For instance, we estimated recovery rates under various conditions, which allows the simulation of a variety of nanoparticle flows in different MSWI plants. Adaptations usually require minor adjustments at the level of the MSWI plant geometry. This can be done for box and flow based systems by refining existing boxes with further sub-units and/or extending them with additional boxes and related flows. This also implies eliminating unnecessary flows and boxes. In addition to these pure geometrical adaptations of MSWI plants, specific MSWI performance properties such as residence time of waste material in the different areas of the plant may be conducted by adjusting the material transfer coefficients at any point in time. For instance, this can be the case for the wet scrubber where the waste water is released in irregular pulses. Transfer coefficients are likely to be material dependent: besides the expansion of the measured time, similarly designed studies for various nanomaterials would be crucial to improve the generic data basis for the transfer coefficients and would reduce the necessity of falling back to assumptive data. However, analogies between materials could possibly replace some use of assumptive values.

A sensitivity analysis that evaluates the influence of each model input parameter to the complete model output would be a complementary step in the study of ENP (and other compounds) in MSWI plants. In a stochastic context, the uncertainty of the data used to feed the MC algorithms would also be evaluated (Gottschalk et al., 2010). This kind of sensitivity would reveal, for instance, whether the most influential parameters are the least available in terms of measurement data. In such a case, the explanatory power of the modeling would be significantly and adversely affected. As long as the number of parameters for MSWI processes remains manageable (for example for generalized plants), such sensitivity tests may be conducted with reasonable effort. The analysis of the results could give researchers some guidance on the right locations for measurements and on reasonable time periods.

#### 2.2.3.9. Further improvements of nanoparticle flow experiments and modeling

A temporally resolved background concentration of the investigated chemical compounds would provide a more accurate flow estimation of the engineered nanoparticles consisting of the same elements. This is of particular importance if either the background concentration is high (in comparison to the ENP) or if the distinction between background elemental concentration and the elemental concentration from the ENP are difficult to distinguish. A possible way around this would be isotope labeling of the ENP or the design of stable nanoparticles with a very rare elemental composition. For future nanoenabled applications, however, unstable (e.g. tendency to form agglomerates) engineered nanoparticles should be promoted because of an anticipated reduction of toxic properties and therefore less impact on the environment and human health.

### 2.2.4. Conclusion

Our model demonstrated the overall consistency of the measurement data. Particular strengths of the model are the evaluation capability for the uncertainty (variability) of

each single material transport/sink by means of probability estimations at any stage (time and location) of the MSWI process. Although the precise quantification of these amounts still remains difficult, this type of modeling provides an idea of the possible and most likely range of results. A potential extension of the model could be the inclusion of non-rhythmic material transfer, or in other words a variability of travel times. Irregular pulse releases of fly ash from the boiler or the varying emission of waste water from the wet scrubber are such candidates. These varying releases could be considered with an extension to non-linear computations that go beyond our cumulative perspective, which is for now limited to examining what is discovered (or not) in the ENP flows and sinks up to a certain point in time and under average conditions.

Further studies on the behavior of other ENP in incineration plants could take into account how changing waste compositions could affect the reactivity of ENP less stable than CeO<sub>2</sub>. Our analysis can be easily extended to the fate of other ENP, including potential release to the atmosphere. An additional application of the method might be the investigation of pollutants that are carried by ENP through the incineration plant. In such a case, depending on the chemical bonding between the ENP and the other compounds, the modeling may follow a similar structure as used with solely ENP.

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## 2.3. Flows of engineered nanomaterials through the recycling process

### Abstract

The use of engineered nanomaterials (ENMs) in diverse applications has increased during the last years and this will likely continue in the near future. As the number of applications increase, more and more waste with nanomaterials will be generated. A portion of this waste will enter the recycling system, for example, in electronic products, textiles and construction materials. The fate of these materials during and after the waste management and recycling operations is poorly understood. The aim of this work is to model the flows of nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag and CNT in the recycling system in Switzerland. The basis for this study is published information on the ENMs flows on the Swiss system. We developed a method to assess their flow after recycling. To incorporate the uncertainties inherent to the limited information available, we applied a probabilistic material flow analysis approach. The results show that the recycling processes does not result in significant further propagation of nanomaterials into new products. Instead, the largest proportion will flow as waste that can subsequently be properly handled in incineration plants or landfills. Smaller fractions of ENMs will be eliminated or end up in materials that are sent abroad to undergo further recovery processes. Only a reduced amount of ENMs will flow back to the productive process of the economy in a limited number of sectors. Overall, the results suggest that risk assessment during recycling should focus on occupational exposure, release of ENMs in landfills and incineration plants, and toxicity assessment in a small number of recycled inputs.

### 2.3.1. Introduction

The use of nanomaterials in consumer products and industrial applications is growing and this fact will not change in the coming years. Extensive resources are invested by both industries and governments to boost nanotechnology development and promote economic growth (Shapira and Youtie, 2012). However, understanding the effects that engineered nanomaterials (ENMs) have on human and environmental health through these applications is still limited (Klaine, et al., 2012).

Nanomaterials can be released to the environment throughout their entire life cycle (Gottschalk and Nowack, 2011). “Life cycle” is generally understood as the life-span covering production, use, and disposal of a material, chemical or product (Som et al., 2010). Risk assessment and life cycle paradigms are currently used together to achieve a comprehensive and realistic assessment of the effects of ENMs when they interact with the environment (Grieger et al., 2012).

As the number of nanotechnology applications grows, more nanoproducts will enter into the waste stream during the end-of-life stage (EoL) of their life cycle. That influx raises concerns related to the appropriate management of waste. At EoL, a nanoproduct may enter the recycling system, be incinerated or landfilled. The scarce knowledge on the fate and behavior of ENMs during recycling limits our ability to assess the risks they may represent. Indeed, the current legal and technological frameworks may not be suitable to adequately handle *nanowaste*, that is, waste containing nanomaterials (Bystrzejewska-Piotrowska, et al., 2009). Some authors consider ENMs as an emerging pollutant which should be properly tracked during waste treatment (Marcoux et al., 2013). The risks posed by nanowaste to humans in technical and environmental compartments range from very low hazard and exposure, to extremely harmful with a high level of exposition (Musee, 2011).

Only few experimental studies about ENM fate during EoL are available. Walser et al. (2012) studied the behavior of nano-CeO<sub>2</sub> in a municipal waste incineration plant in Switzerland. They found that the major fraction of ENMs is attached to the bottom or fly ash without being transformed at all. According to them, the nanomaterials in the fly ash are efficiently removed by the filters. A growing amount of literature models environmental exposure of nanomaterials (Gottschalk, et al., 2013b). Mueller et al. (2013) modeled the mass flows of nano-Ag, nano-ZnO, nano-TiO<sub>2</sub> and CNT during incineration. They identified that in most cases the nanomaterials flow to the landfill through the bottom ash, except for the CNT, which primarily is burned. Other studies provide a wider picture of the flow of nanomaterials and the paths they may follow to reach environmental compartments (air, soil, water), for instance, Gottschalk et al. (2009c). They modeled the environmental concentrations of five nanomaterials (TiO<sub>2</sub>, ZnO, Ag, CNT and Fullerenes) in air, soil, surface water and other compartments. Sun et al. (2014b) provided an update of the concentrations of the same nanomaterials in the EU and Switzerland for 2012. They found an increasing transfer and concentration of ENMs in environmental compartments compared to the older studies.

However, there are no studies that assess the flows of nanomaterials during the recycling processes, which may be the most likely EoL fate for nanoproducts, at least for some developed economies (Asmatulu, et al., 2012). Gottschalk, et al. (2009c) and Sun, et al. (2014b) included the total flows of ENMs into the recycling system, but did not model the dissipation after recycling. From the risk assessment perspective, recycling is relevant for three reasons: 1) as a source of occupational exposure to ENM, 2) as a source of nanomaterial release to the environment, and 3) as a source of recirculation of raw material with potentially hazardous content (Marcoux, et al., 2013). In a release scenario analysis, Nowack et al. (2013b) suggested that recycling activities may represent a source of occupational exposure and environmental release of ENMs. However, the relative importance of exposure levels is largely dictated by the waste management infrastructure and the legal framework that each country has.

The goal of the current work is to model and quantify the flows of ENMs out of recycling operations in Switzerland. Our basis is the aforementioned work by Sun, et al. (2014b). The approach used is the probabilistic material flow modeling parameterized with detailed knowledge on the types of products that contain ENMs, and the existing information on recycling operations in the Swiss system.

### 2.3.2. Materials and Methods

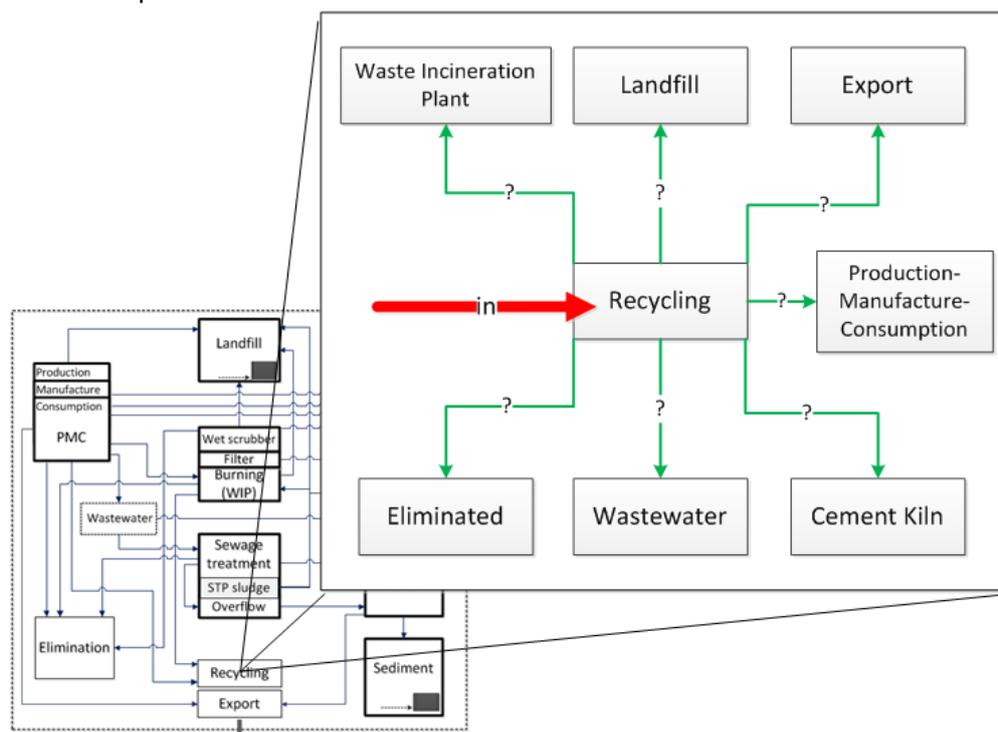
#### 2.3.2.1. System definition and input information

The system considered in this work is based on the definition of recycling outlined in the material flow model used by Sun, et al. (2014b), with additional characteristics of the Swiss recycling system introduced for this specific model. Recycling is defined as any recovery operation of which waste materials are reprocessed into products, materials or substances whether for the original or other purposes (EU, 2008). It is important to stress that this work models the flows of nanomaterials after the products containing them enter the recycling system, not the recycling of ENMs themselves. The components included in this system are, in alphabetical order, Cement Kiln, Elimination, Export out of the system boundaries (Switzerland), Landfills, Production-Manufacturing-Consumption Sector, Waste Incineration Plants and Wastewater (**Figure 11**). These components represent the potential destination of the materials after leaving the recycling system and are defined as follow:

- Cement Kiln (CK). Swiss cement kilns recycle mineral and general waste. A nanomaterial flows to a cement kiln in materials used as alternative fuel or

mineral substitutes for the production of cement, like treated wood, tires and gypsum (SAEFL (2005)).

- Elimination (ELIM). A nanomaterial is considered eliminated if it loses its nano-properties, either due to chemical or physical changes/transformations, e.g. particle dissolution and combustion.
- Export (EXP). The system boundary of our model is Switzerland. For economic reasons, some materials are not recycled in Switzerland but abroad. Therefore, a nanomaterial is exported if it is part of a material fraction that is sent abroad to undergo a recycling process. Materials exported for recycling purposes include non-ferrous metals, batteries and textiles (Boeni et al., 2012).
- Landfill (LF). A fraction with ENMs flows to a landfill if it is not recovered during the recycling process and it is not suitable for incineration. The characteristics of the different types of landfills in Switzerland, and the materials they receive, is described by Mueller, et al. (2013) in the context of nanomaterial flow modeling of wastes.
- Production-Manufacturing-Consumption (PMC). This compartment synthesizes the general production and consumption processes of commodities in the economy. A nanomaterial is transferred to PMC if it is allocated in the recovered raw material fraction that flows back into the productive process of the economy.
- Waste Incineration Plant (WIP). A nanomaterial flows to an incineration plant if the material fraction with ENM is not further processed for recovery purposes but rather disposed of. All combustible waste in Switzerland must be incinerated prior to landfilling.
- Wastewater (WW). A nanomaterial flows to the wastewater if the recycling process includes a washing step and a fraction of nanomaterial is expected to flow into the disposed water.



**Figure 11.** Mass flows of ENM considered in this work (right) and entire Swiss system (left). The small panel, used in Sun, et al. (2014b) model, depicts the entire material flow diagram for ENMs that they investigated. The flows out of the recycling box that are considered in this work are shown in the right panel.

The input information for our modeling was taken from Sun, et al. (2014b) and includes (i) the mass flows of nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag and CNT in tons per year that are transferred to the recycling system; (ii) the product categories used to characterize the products available in the existing inventories; and (iii) the share of the total ENM mass in each product category (in percentages). The aforementioned model includes release during use stage and transfer to technical compartment such as waste incineration. The total mass of nano-TiO<sub>2</sub>, nano-ZnO, nano-Ag and CNT that enters the recycling system in Switzerland is 42.89, 4.75, 0.42 and 2.75 tons/y respectively (notice that these amounts represent the mode values of the resulting flow distributions to Recycling from that reference; in our modeling we used the complete probability distributions. We considered 33 different product categories, which span the range of nano-enhanced products. Products with nano-TiO<sub>2</sub> are grouped into 19 categories, with nano-ZnO in 12, CNT in 9, and nano-Ag in 13 categories. A list with all the product categories is available in the *Section 1* of the supplementary material.

### 2.3.2.2. Recycling system characterization

The steps that we followed to identify only the relevant information about the recycling processes are:

1. *Creation of an inventory.* Based on publicly available information, we created an inventory, including the product types, the nanomaterial types used, their allocation within the product and the model and manufacturer, whenever this information was available.
2. *Selection of relevant recycling processes.* We used the inventory to identify which products are processed in Switzerland and which abroad. For example, Li-ion batteries are processed abroad, even though the majority of batteries are recycled within the country.
3. *Description of relevant information to assess nanomaterial flows.* The details for each recycling process were evaluated only to the extent as was necessary to assess nanomaterial behavior. We therefore focused on the key aspects, such as the general steps along the recycling process and the parameters that might specifically affect the nanomaterials, like the temperature expected to be reached, or the liquid media that may be used during the washing steps.

### 2.3.2.3. Transfer vector calculation

The method used through this research is based on the material flow assessment principles and on basic linear algebra. We defined a *transfer vector* for each product category  $i$  ( $TV_i$ ) with seven *transfer coefficients* ( $TC_j$ ) as components, each one representing the partition of the nanomaterial mass into each of the seven system components, that is,  $TV_i = (TC_1, \dots, TC_7)$ ,  $TC_j \in [0,1]$ ,  $j \in \{1, \dots, 7\}$  and  $\sum_j TC_j = 1$ . To estimate a category transfer vector we divide the category into product subcategories with homogenous characteristics. If a product category  $i$  can be partitioned in  $n$  mutually exclusive subcategories, then the transfer vector is calculated as the linear combination of the transfer vectors of the product subcategories ( $TV_{ik}$ ):

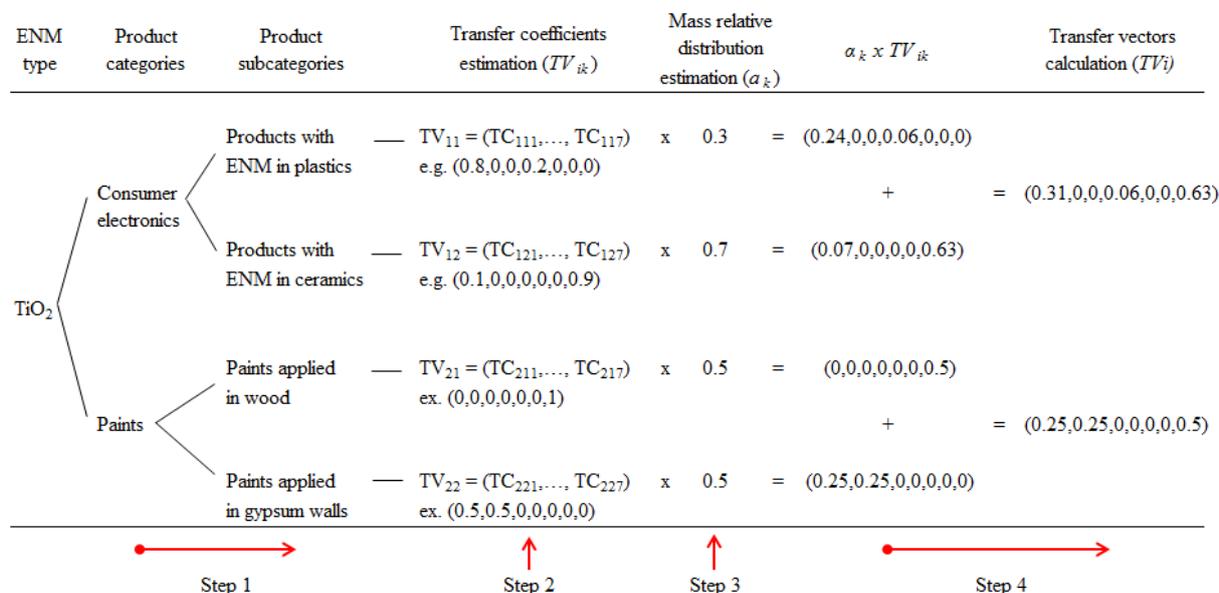
$$TV_i = \alpha_1 TV_{i1} + \dots + \alpha_n TV_{in} \quad (1)$$

With  $n \in \{1, 2, \dots\}$ . The numbers  $\alpha_k \in [0,1]$  represent the nanomass distribution between subcategories, where  $k \in \{1, n\}$  and  $\sum_k \alpha_k = 1$ . The amount of subcategories  $n$  is determined by the number of different material types where the nanomaterials are

allocated. The 4-step process to calculate the transfer vectors for the categories is:

1. *Partition of a product category  $i$  into subcategories.* The number  $n$  of subcategories is equal to the different materials where the ENMs are allocated in a product category. A material type can be metal, plastic or any other material with a homogeneous composition.
2. *Estimation of the value of the transfer vector of each subcategory.* The values of the transfer coefficients to the seven compartments are determined by the recycling process, the characteristics of the nanoproduct, mainly the material fraction that allocates the ENM, and the ENM characteristics.
3. *Estimation of the ENM mass distribution among subcategories.* We define the relative ENM mass content in each subcategory  $\alpha_k$  as the quotient between the ENM mass content in the product subcategory and the ENM mass content in the product category.
4. *Calculation of the transfer vector of each product category.* The transfer vector for each product category is calculated as the linear combination described in **Equation (1)**.

This process is depicted graphically in **Figure 12**:



**Figure 12.** Schematic illustration of the process to calculate the transfer vectors of the product categories: (1) partition of the product categories into subcategories; (2) estimation of the transfer coefficients of the subcategories vectors; (3) estimation of the ENM mass distribution among subcategories; and (4) calculation of the transfer vectors for every single product category.

#### 2.3.2.4. Flow assessment

We used material flow modeling as a simple way to allocate the total ENM mass entering the recycling system to the seven receiving compartments. The distribution of each ENM is determined by the incoming flow and the resulting transfer coefficients. However, in every step described in the last section there may exist important uncertainties which were not taken into consideration in the point estimations. For example, the information on the mass content within a nanoproduct is almost non-existent. To incorporate the inherent uncertainty in our results, we used the probabilistic methodology developed by

Gottschalk, et al. (2010b). The key idea behind their methodology is to treat the transfer coefficients as stochastic parameters, instead of point values, producing outflow distributions instead of point value estimations.

According to Gottschalk, et al. (2010b), a triangular distribution is a proper distribution when a single value of the transfer coefficient is available. A triangular distribution is completely defined by the lower and upper bounds, and the mode value. The mode of the distribution was set as the point value of the transfer coefficient, while the lower and the upper bounds were set as 50% and 150% of the same point value respectively. Using these parameters, 10,000 random values of the distribution were drawn. There were two special cases which needed to be considered in finer detail: i) when the point value estimation is 0, and ii), when 150% of the point value is larger than 1. In the first case, no distribution was generated and thus the resulting mass transfer was zero. For the second case, the maximum was set at 1, and the minimum and the mode are set as stated before.

Our model is embedded in the system analyzed by Sun, et al. (2014b). The assumptions of the former work related to the flow modeling, which apply to our model as well, are:

- The model tracks total nanomaterial mass irrespective of the actual form (e.g. agglomeration state).
- Nanomaterials are conserved in their original form or eliminated during their flow through the recycling system. No other transformation reactions than elimination are considered.
- Nanomaterial-specific parameters like particle size distribution, shape or functionalization do not influence the nanomaterial fate within the recycling system.
- The model is static: All flows are considered to take place in one period.
- All ENM are allocated into consumer products. No use of ENM in intermediate production is considered.

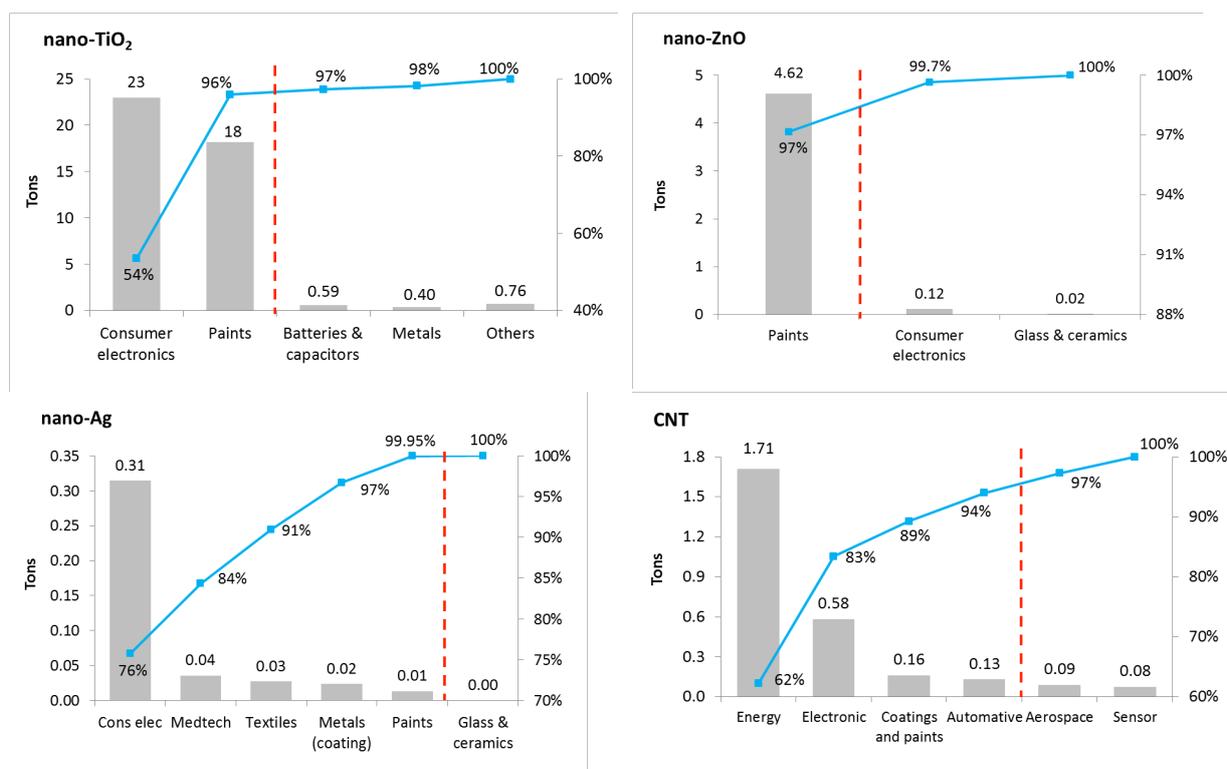
Besides, in our case we also needed to assume that all the product categories can be partitioned in mutually exclusive subcategories with homogeneous characteristics, as stated in the previous section.

### 2.3.3. Results

#### 2.3.3.1 Modeling framework development

##### *a) Identification and analysis of the relevant product categories*

We identified the relevant categories by selecting those that collectively accounted for at least 90% of the total ENM mass transferred to the recycling system for each nanomaterial type. The results are shown in **Figure 13**. For nano-TiO<sub>2</sub>, the product categories “Consumer Electronics” and “Paints” accounted for at least 96% of the total mass transferred to the recycling system. In the case of nano-ZnO, we included only the “Paints” category, where 97% of the total mass was transferred. For nano-Ag the categories “Consumer Electronics”, “MedTech”, “Textiles”, “Metals (coating)” and “Paints” are considered (99% of the total mass transferred). Finally, for CNT, we included the categories “Energy”, “Electronics”, “Coatings and Paints” and “Automotive” (94% of the total mass transferred collectively). The input data and the calculations to get this numbers are available on *Table S1* of the supplementary material.



**Figure 13.** ENM mass transferred to the recycling system in tons/y by product category (grey bars, left axis), cumulative mass transferred into recycling in percentage (blue curve, right axis), and product categories considered in this study (left of the red dotted line). Source: Author's calculations with info from Sun, et al. (2014b). See Table S1 of the Supplementary Information.

The next step was to identify typical and representative products that belong to each product category. For most materials, we used the information provided by the Project on Emerging Nanotechnologies (PEN, 2013), the European Consumers' Organization (ANEC/BEUC, 2013), Friends of Earth Germany (BUND, 2013) and Beyond Pesticides (ICTA, 2013). For CNT we used the information in Future\_Markets (2012) and De Volder et al. (2013). Asmatulu, et al. (2012) provide a comprehensive description of the PEN inventory, which was our primary source of information for the identification of the products. A simplified description of the products belonging to each product category is shown in **Table 5**, with a more comprehensive version in Section 2 of the supplementary information.

**Table 5.** Summarized description of the product categories content, separated by ENM.

ENM	Product category	Product examples
TiO <sub>2</sub>	Consumer electronics	Flat irons, hair dryers, keyboards, mice, refrigerators
	Paints	Exterior wall paints
ZnO	Paints	Exterior wall paints
Ag	Consumer electronics	Hair dryers, shavers, refrigerators, mobile phones
	MedTech	Operating tables
	Textiles	Shirts, socks, blankets, sportswear, gloves
	Metal (coatings)	Door locks, pet food bowls, watch chains

	Paints	Interior wall paints
CNT	Energy	Li-ion batteries
	Electronics	RAM, computer chips
	Coatings and Paints	Anti-fouling coatings
	Automotive	Dashboards, fuel system components (connectors, pumps, o-rings)

### b) Recycling system characterization

We characterized the recycling processes to understand how they work and to be able to assess the fate of the material fraction containing ENMs. The recycling processes that we analyzed were those that process cars, cooling devices, electronic waste (e-waste), metals and batteries, mineral material coming from the construction and demolition waste, textiles and wood. In this section, we present the information in a way that is meaningful for the assessment of nanomaterial flows, rather than providing a detailed description of the processes involved (a more comprehensive description is available in the *Section 3* of the supplementary material). The main sources used to characterize the recycling processes are Goodship and Stevels (2012), SAEFL (2005) and the information available in the webpages of the Swiss Federal Office of the Environment (BAFU, 2013), Swiss e-waste competence (E-waste, 2013), SWICO Recycling (SWICO, 2013), TexAid (TexAid, 2013), SIMS Recycling Solutions (SIMS, 2013) and ERP Recycling the European Recycling Platform (ERP, 2013)

The characterization of each recycling process was complemented with information provided by experts from EMPA (R. Hischer, P. Wäger and R. Widmer), Eberhard Bau AG and TexAid Textilverwertungs AG. The following results highlight the fate of the different waste fractions during recycling:

- *Cars*. The main fraction recovered during car recycling is ferrous metal. Reusable components are dismantled at the beginning of the process and hazardous components are removed before shredding. After shredding and sorting ferrous metals are sent to a smelter and the rest undergoes thermal utilization. A more detailed description of the car recycling process in Switzerland may be found in Blaser et al. (2012).
- *Cooling devices*. The steps within the recycling process are dismantling, shredding, drying and polyurethane foam separation, magnetic separation and eddy current separation. The main fractions that are recovered are plastics and metals. As in the e-waste process, the shredding step can become very hot and efficient ventilation systems are used to filter the dust produced.
- *E-waste*. The steps of the recycling process include dismantling and depollution, shredding, magnetic separation and eddy current separation. Water-based washing steps may also be used in some circumstances. Hazardous materials (e.g. batteries, printed circuit boards or ink cartridges) are separated in the initial step and sent for further recovery process or disposed of in an environmentally sound way. The main material fractions that are recovered are metals and plastics and the rest is sent to incineration. Recovered plastics are transferred abroad for further recycling processes, and metals are exported (non-ferrous) or sent to smelters (ferrous). Shredding is done in an encapsulated environment which efficiently filters the dust produced. It can reach several hundreds of degrees centigrade. A detailed description of the Swiss e-waste take back system from a

material flow point of view may be found in Waeger et al. (2011) and Waeger et al. (2012).

- *Metals and batteries.* The recovery principles for both materials are the same. In Switzerland, only ferrous metals and non Li-ion batteries are processed, while non-ferrous metals and Li-ion batteries are exported to undergo further recovery processes elsewhere. Here, we only model ferrous metals, which undergo pyrometallurgical process. Smelters of ferrous metals should reach temperatures above the melting point of iron, that is, above 1,100°C.
- *Construction and demolition waste* includes concrete, bricks and mineral material like plaster. Concrete and bricks are used to produce aggregates (used in the concrete production) while plaster is either landfilled or used as corrective material during the production of cement. This material is collected from construction sites and is known as mixed construction and demolition waste. The recycling process of concrete includes the following steps: collection, leaning, crushing, treatment and sorting.
- *Textiles.* Clothes (including leather), shoes and household linens are all included in this category. The vast majority (95%) of the textiles collected in Switzerland is sent abroad and only a minor fraction remains in the country to either be sold at reduced prices or donated as secondhand clothes.
- *Wood.* Treated wood should be disposed in waste incineration or cement plants equipped with appropriate filters. Only natural wood or wood with low pollutant content may be reused in the manufacturing of new products.

### c) Material fate analysis

In this section we determine the fate within the Swiss system of the different materials that allocate ENMs (**Table 6**). For this purpose we used the preceding results and the flow diagrams displayed in *Section 4* of the supplementary material. According to information gathered from the inventories, the material types hosting nanomaterials are: ceramics, concrete, gypsum, filter components, Li-ion batteries, metals, plastics, textiles and wood.

**Table 6.** Fate of the materials with ENM in nanoproducts within the Swiss recycling system.

Material fraction	Related Process	Recycling	Fate
Ceramics	E-waste		Waste Incineration Plant
Concrete	CDW <sup>a</sup>		Aggregates production (PMC)
Gypsum	CDW		Landfill or Cement Kiln
Ferrous metals	Metals		Eliminated
Filter components	E-waste, Cooling Devices		Waste Incineration Plant
Li-Ion Batteries	Batteries		Exported
Non-ferrous metals	E-waste, Metals		Exported
Plastics	E-waste, Cooling Devices		Waste Incineration Plant or Exported
Printed circuit boards	E-waste		Exported
Textiles	Textiles		Exported or Reused (PMC)

Material fraction	Related Process	Recycling	Fate
Wood	Wood		Waste Incineration Plant or Cement Kiln

<sup>a</sup> CDW refers to the processes that recycle construction and demolition waste.

### 2.3.3.2 Transfer vectors assessment

In this section we present the results of the assessment of the transfer vectors. The information is first presented by ENM and product subcategory (**Tables 7-9**), and later, the resulting vectors are displayed by product category (**Table 6**). We describe the coefficients using the notation  $TC_i$ , where  $i$  can be any of the abbreviations used in **Section 2.1** to define the system compartments, that is CK, ELIM, EXP, LF, PMC, WIP or WW. **Section 5** of the Supplementary Material shows the flow diagrams we used as supporting tools, which describe the flow of the fraction with ENM within the recycling processes, for each ENM type and product category.

#### *nano-TiO<sub>2</sub>*

The transfer coefficients and the ENM mass content in each product subcategory are shown in **Table 7**.

- Consumer Electronics.** Nano-TiO<sub>2</sub> is allocated in materials like ceramics, filter components and plastics. Ceramics and filter components are disposed of at the end of the recycling process and sent to an incineration plant, so the  $TC_{WIP}$  is set to 1.00. Plastics are either incinerated or recycled. According to Boeni, et al. (2012) approximately half of the plastics originating from e-waste is incinerated and the other half is exported for further recovery process and so both  $TC_{WIP}$  and  $TC_{EXP}$  are set to 0.50. Our model of the e-waste recycling process includes a washing step, so it is important to assess the effect this could have on the ENM. Windler et al. (2012b) and Al-Kattan, et al. (2013) studied the release of nano-TiO<sub>2</sub> from textiles and paints and report a release between 0.01 and 4% of the ENM mass content in the products analyzed. The amount of ENM released strongly depends on how it is incorporated into a product (e.g. as coating or within a solid matrix) and the washing or weathering process it is subject to. Because of this, it is difficult to set a specific percentage value to satisfy “general” circumstances. However, we do expect releases of nanomaterials during the washing step and therefore set release to waste water as the upper bound found in those studies, that is,  $TC_{WW}$  is set to 0.04. Refrigerators follow a slightly different recycling process. ENMs are allocated into filter components, which are disposed of at the end of the recycling process. Because the process for cooling devices does not include washing steps, no ENMs are released to the waste water, but rather, completely transferred to the incineration plant and so  $TC_{WIP}$  is set to 1.00. It was impossible to determine the nanomass content by product subcategory, as this information is non-existent. However, to define the nanomass distribution among subcategories ( $\alpha$  coefficients in **Equation (1)**), we used as proxy the distribution in our inventory of the products within each subcategory. We used the quotient of the number of products belonging to a subcategory divided by the total amount of products in the category.

- *Paints.* We focus on paints in construction and demolition waste. We assume that paints are mainly applied on plaster which is collected as a waste fraction during recycling of mixed construction waste and that a small fraction is applied on concrete (Hischier et al., 2014). The transfer coefficients for ENM are set therefore as  $TC_{LF}$  to 0.85,  $TC_{PMC}$  to 0.10 and  $TP_{CK}$  to 0.05. Based on BUWAL (2001) and Wüst\_&\_Partner (2008), we know that 87% of wood is incinerated and the rest is recycled or landfilled. However, since only wood which is not treated with coatings or paint is recycled, we concluded that 100% is incinerated and therefore  $TC_{WIP}$  is set to 1.00. The distribution of nanomass among the subcategories was approximated using the distribution of the materials where paint is applied, information which was surveyed among EMPA experts during personal communications.

**Table 7** Transfer coefficients of nano-TiO<sub>2</sub> to the seven compartments of the system for each product subcategory, and distribution of ENM mass between subcategories.

Product Category	Material Fraction <sup>a</sup>	Dist <sup>b</sup>	Transfer Coefficients						
			WIP <sup>c</sup>	LF <sup>d</sup>	EXP <sup>e</sup>	PMC <sup>f</sup>	CK <sup>g</sup>	WW <sup>h</sup>	ELIM <sup>i</sup>
Consumer electronics	Ceramics	74	0.96	0.00	0.00	0.00	0.00	0.04	0.00
	Plastics	22	0.48	0.00	0.48	0.00	0.00	0.04	0.00
	Filter Components	4	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Paints	Mixed material	80	0.00	0.85	0.00	0.10	0.05	0.00	0.00
	Wood	20	1.00	0.00	0.00	0.00	0.00	0.00	0.00

<sup>a</sup> A product subcategory is defined for each material type where the ENM is allocated within the products of a category. <sup>b</sup> Distribution of the ENM mass between product subcategories (in percentages). <sup>c</sup> Waste Incineration Plant <sup>d</sup> Landfill <sup>e</sup> Exported <sup>f</sup> Production-Manufacture-Consumption sector of the economy <sup>g</sup> Cement Kiln <sup>h</sup> Waste Water <sup>i</sup> Eliminated.

Note: Paints coefficients apply to nano-ZnO and nano-Ag as well.

### *nano-ZnO*

Only Paints category belongs to nano-ZnO assessment. The transfer vectors for the subcategories are the same as for nano-TiO<sub>2</sub> (**Table 7**) because the recycling processes and the fate of nanomaterials do not depend on the ENM type, but on the material where it is applied to or incorporated in.

### *nano-Ag*

The transfer coefficients and ENM mass content in each product subcategory are shown in **Table 8**.

- *Consumer Electronics.* Nano-Ag in consumer electronics is allocated in ceramics, plastics, metals and materials in filtering systems. Ceramics used in personal care devices are not recovered, but rather incinerated, so we set  $TC_{WIP}$  to 1.00. If the nanomaterial is in plastics we already know that typically half could be disposed of and half could be sent abroad to be recycled, so  $TC_{WIP}$  is set to 0.50 and  $TC_{EXP}$  to

0.50. Washing machines, vacuum cleaners and water purifiers have ENMs in filter components, which are incinerated so  $TC_{WIP}$  is set to 1.00. We assumed a washing step so some release to water may be expected. Geranio, et al. (2009), Benn, et al. (2010) and Quadros et al. (2013b) studied the release of nano-Ag from different products when subject to different liquid media. They report releases between 0.01% and 44% of the total nanosilver mass content. As mentioned previously, the amount released is strongly dependent on the way in which ENMs are applied and the washing process it is subject to. We have therefore assigned a value between the bounds reported in those studies (18%), and so  $TC_{WW}$  is 0.18. ENM in metals (e.g. electric shavers) are processed in smelters. In this case we can clearly assume that the nanomaterial is eliminated, when comparing its boiling point with the temperature reached within the smelters (above 1,100°C). The boiling point of nano-silver is between 530° and 930° (Hu et al., 2010), so  $TC_{ELIM}$  is set to 1.00. ENM in cooling devices are allocated in plastics or filter components. In the former case,  $TC_{WIP}$  is 0.50 and  $TC_{EXP}$  is 0.50, and in the latter,  $TC_{WIP}$  is 1.00. Once more, the distribution of the nanomass among subcategories was determined using the distribution of the products in the inventory by subcategory as proxy.

- *MedTech*. Nano-Ag in metals is eliminated during the smelting process so  $TC_{ELIM}$  is set to 1.00. If allocated to plastics, the materials are incinerated, so  $TC_{WIP}$  is set to 1.00. The distribution between metals and the other materials is unknown. Therefore we set a uniform distribution between both as a proxy.
- *Textiles*. 95% of the material collected in Switzerland is sent abroad and the remainder is distributed among social organizations within the country, so  $TC_{EXP}$  is set to 0.95 and  $TC_{PMC}$  to 0.05.
- *Metals*. We assumed that only ferrous metals are used in the corresponding applications. Nano-Ag coating metallic applications is eliminated during the smelting process, so  $TC_{ELIM}$  is set to 1.00
- *Paints*. The transfer vectors for this subcategory are the same as for nano-TiO<sub>2</sub> and nano-ZnO (**Table 3**), for the reasons expressed during nano-ZnO assessment.

**Table 8.** Transfer coefficients of nano-Ag to the seven compartments of the system for each product subcategory, and distribution of the ENM mass between subcategories.

Product Category	Material Fraction <sup>a</sup>	Dist <sup>b</sup>	Transfer Coefficients						
			WIP <sup>c</sup>	LF <sup>d</sup>	EXP <sup>e</sup>	PMC <sup>f</sup>	CK <sup>g</sup>	WW <sup>h</sup>	ELIM <sup>i</sup>
Consumer Electronics	Ceramics	32	0.82	0.00	0.00	0.00	0.00	0.18	0.00
	Filter Components	31	0.82	0.00	0.00	0.00	0.00	0.18	0.00
	Plastics	24	0.41	0.00	0.41	0.00	0.00	0.18	0.00
	Ferrous Metals	7	0.00	0.00	0.00	0.00	0.00	0.00	1.00
	Plastics <sup>j</sup>	4	0.50	0.00	0.50	0.00	0.00	0.00	0.00
	Filter Components <sup>j</sup>	2	1.00	0.00	0.00	0.00	0.00	0.00	0.00
MedTech	Ferrous metals	50	0.00	0.00	0.00	0.00	0.00	0.00	1.00

	Plastics	50	1.00	0.00	0.00	0.00	0.00	0.00	0.00
Textiles	Textiles	100	0.00	0.00	0.95	0.05	0.00	0.00	0.00
Metals	Ferrous metals	100	0.00	0.00	0.00	0.00	0.00	0.00	1.00

<sup>a</sup> A product subcategory is defined for each material type where the ENM is allocated within the products of a category. <sup>b</sup> Distribution of the ENM mass between product subcategories (in percentages). <sup>c</sup> Waste Incineration Plant <sup>d</sup> Landfill <sup>e</sup> Exported <sup>f</sup> Production-Manufacture-Consumption sector of the economy <sup>g</sup> Cement Kiln <sup>h</sup> Waste Water <sup>i</sup> Eliminated <sup>j</sup> Fractions in cooling devices, whose recycling process differ from the rest of the e-waste, although they still belong to the consumer electronics category.

### CNT

The resulting transfer coefficients and the ENM mass content in each product subcategory are shown in **Table 9**.

- *Energy*. Li-ion batteries are exported, so  $TC_{EXP}$  is set to 1.00.
- *Electronics*. Printed circuit boards (PCBs) are exported to be recycled. This includes the electronic chips bound to them, like RAM memories, so  $TC_{EXP}$  is set to 1.00.
- *Coatings and Paints*. Strictly speaking, only coatings with CNT are commercially available. They are mainly used for their anti-fouling properties by the ship industry to keep hulls free of marine organisms. We assumed that ship hulls are made of steel or aluminum alloys. CNTs ignite in the presence of oxygen at 830°C, according to Volotskova et al. (2010). Because the smelters used in the metal recycling process reach a temperature above 1,100°C, the CNTs are destroyed, so we set  $TC_{ELIM}$  to 1.00. In the case of hulls made of aluminum alloys, we set  $TC_{EXP}$  to 1.00, because non-ferrous metals are not recycled in Switzerland but abroad. A uniform distribution between both metal types was assumed as a proxy as well.
- *Automotive*. We assume that all car composites with CNT are reused, so  $TC_{PMC}$  is set to 1.00. Polymer-based components with CNT are used in the fuel system due to their anti-static properties. These products are incinerated so  $TC_{WIP}$  is set to 1.00. A uniform distribution between both materials was assumed as a proxy as well.

**Table 9.** Transfer coefficients of CNTs to the seven compartments of the system for each product subcategory, and distribution of the ENM mass between subcategories.

Product Category	Material Fraction <sup>a</sup>	Dist <sup>b</sup>	Transfer Coefficients						
			WIP <sup>c</sup>	LF <sup>d</sup>	EXP <sup>e</sup>	PMC <sup>f</sup>	CK <sup>g</sup>	WW <sup>h</sup>	ELIM <sup>i</sup>
Energy	Li-ion Batteries	100	0.00	0.00	1.00	0.00	0.00	0.00	0.00
Electronics	PCBs <sup>j</sup>	100	0.00	0.00	1.00	0.00	0.00	0.00	0.00
Coatings and Paints	Non-Fe Metals	50	0.00	0.00	1.00	0.00	0.00	0.00	0.00
	Fe Metals	50	0.00	0.00	0.00	0.00	0.00	0.00	1.00

Automotive	Composites	50	0.00	0.00	0.00	1.00	0.00	0.00	0.00
	Plastics	50	1.00	0.00	0.00	0.00	0.00	0.00	0.00

<sup>a</sup> A product subcategory is defined for each material type where the ENM is allocated within the products of a category. <sup>b</sup> Distribution of the ENM mass between product subcategories (in percentages). <sup>c</sup> Waste Incineration Plant <sup>d</sup> Landfill <sup>e</sup> Exported <sup>f</sup> Production-Manufacture-Consumption sector of the economy <sup>g</sup> Cement Kiln <sup>h</sup> Waste Water <sup>i</sup> Eliminated <sup>j</sup> Printed Circuit Boards

### Transfer vector calculation

The final step was the calculation of the transfer vectors of the product categories using Equation (1). The results are available in **Table 10**, which displays the final vectors by ENM type. This table was the main input used for the probabilistic assessment of the nanomaterials flows coming out of the recycling system, as described in Section 2.4.

**Table 10.** Transfer coefficients of the four ENMs by product category.

ENM	Product category	Transfer coefficients							
		WIP <sup>a</sup>	LF <sup>b</sup>	EXP <sup>c</sup>	PMC <sup>d</sup>	CK <sup>e</sup>	WW <sup>f</sup>	ELIM <sup>g</sup>	SUM
TiO <sub>2</sub>	Consumer Electronics	0.85	0.00	0.11	0.00	0.00	0.04	0.00	1.00
	Paint	0.20	0.68	0.00	0.08	0.04	0.00	0.00	1.00
ZnO	Paint	0.20	0.68	0.00	0.08	0.04	0.00	0.00	1.00
Ag	Consumer Electronics	0.65	0.00	0.12	0.00	0.00	0.16	0.07	1.00
	MedTech	0.50	0.00	0.00	0.00	0.00	0.00	0.50	1.00
	Textiles	0.00	0.00	0.95	0.05	0.00	0.00	0.00	1.00
	Metals	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00
	Paints	0.20	0.68	0.00	0.08	0.04	0.00	0.00	1.00
CNT	Energy	0.00	0.00	1.00	0.00	0.00	0.00	0.00	1.00
	Consumer Electronics	0.00	0.00	1.00	0.00	0.00	0.00	0.00	1.00
	Coating and Paints	0.00	0.00	0.50	0.00	0.00	0.00	0.50	1.00
	Automotive	0.50	0.00	0.00	0.50	0.00	0.00	0.00	1.00

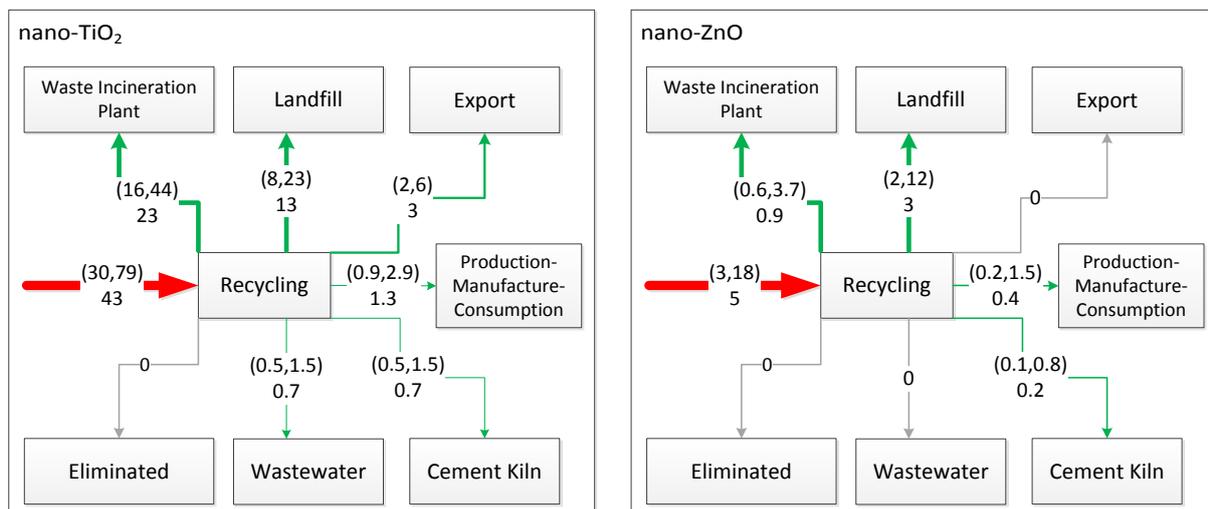
<sup>a</sup> Waste Incineration Plant <sup>b</sup> Landfill <sup>c</sup> Exported <sup>d</sup> Production-Manufacture-Consumption sector of the economy <sup>e</sup> Cement Kiln <sup>f</sup> Waste Water <sup>g</sup> Eliminated

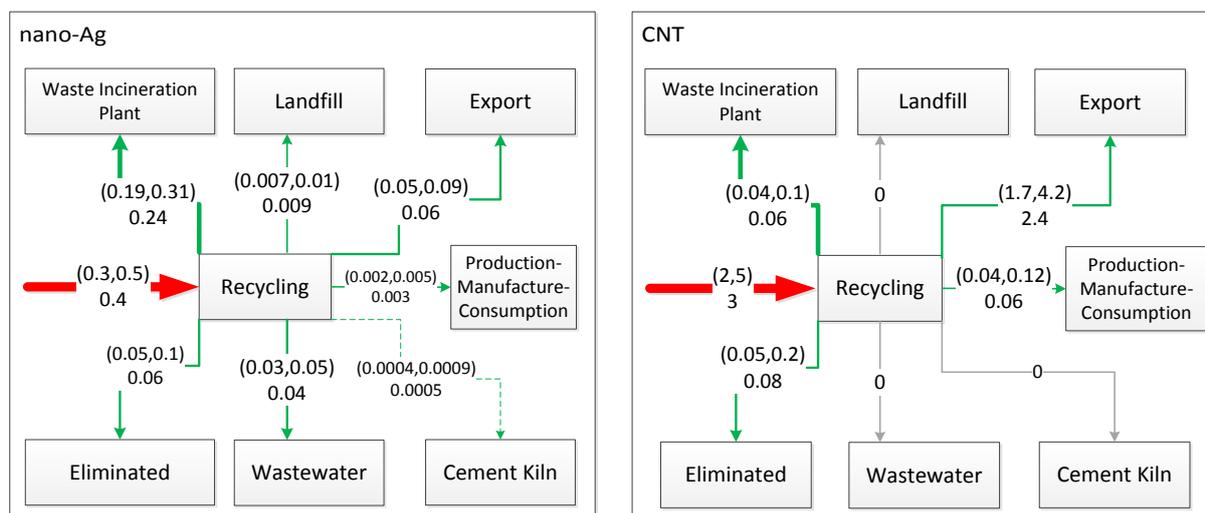
### 2.3.3.3 ENM mass flows

Our main results are the ENMs outflow distributions in tons per year (tons/y) by ENM type. From those distributions we drew the mode values and the percentiles 15<sup>th</sup> and 85<sup>th</sup>, which are shown in **Figure 14** over the green arrows. That figure includes the same values for the incoming flows as well. The results disaggregated by product categories are available in Section 6 of the *Supplementary Material*.

The description of the outflows by ENM type using the mode values of the distributions is the following:

- $\text{TiO}_2$ : Of the 43 tons/y that enters the recycling system, 23 tons/y end up in WIPs, followed by 13 tons/y that end up in a landfill. The former case occurs when plastics, treated wood or ceramics are incinerated, and the latter when the mineral material with paint coming from the construction waste is disposed of. The remaining outflow is sent abroad in the plastics that will be recycled (3 tons/y) or destined for the production of cement and concrete aggregates (2 tons/y). Less than 2% of the total ENMs (0.7 tons/y) are expected to be transferred to wastewater.
- Nano-ZnO: most of the mass (3 tons/y) flows to a landfill in the mineral construction waste. The rest flows to WIP in painted wood (1 ton/y) or to the production of cement and concrete aggregates (0.6 tons/y).
- Nano-Ag: 0.2 tons/y in plastics, filter components or treated wood are incinerated, 0.06 tons/y in plastics and textiles are exported and 0.06 tons/y in ferrous metals are eliminated. Approximately 0.04 tons/y are released to the waste water and 0.01 tons/y in mineral waste with paint is landfilled. Less than 0.01 tons/y would be used in the production of cement or concrete aggregates, or distributed within the textiles collected by social organizations.
- CNT: The largest mass fraction is exported (2.4 tons/y) in Li-ion batteries, chips in printed circuit boards or aluminum alloys of ship hulls. The remaining amount is either destroyed (0.08 tons/y), re-used as second-hand car composites (0.06 tons/y) or incinerated in polymer-based car components which are not recovered (0.06 tons/y).





**Figure 14.** Mass flow diagrams for each ENM type from the recycling system to other compartments. The red arrows represent the inflows to the recycling system while the green ones represent the outflows. The numbers in parenthesis above the arrows correspond to the 70% confidence intervals of the flow distributions in 2012 (tons/y). Below the intervals the modes are displayed.

#### 2.3.4. Discussion

In this work we combined the scarce knowledge available about the presence of ENMs in products, the mass flows into the recycling system, and information about the recycling processes to estimate the flows of ENM out of recycling based on a probabilistic approach. The results show that the largest amounts of nanomaterials flow to incineration plants and landfills. This occurs because ENMs are mostly allocated in materials with low economic value which are usually not recovered.

The main economic sectors to foster transfer of ENMs from recycling to new products are cement and aggregates production, which use recycled inputs like gypsum as corrective material in the former case, and demolished concrete in the latter. In these instances, workers and, less likely, consumers, could be directly exposed to nanomaterials. This is the case at least for nano-TiO<sub>2</sub>, nano-ZnO and nano-Ag in paints. Other recycled materials that can reach consumers in Switzerland are second-hand car composites with CNT and textiles with nano-Ag. In the field of recycling, an important topic is the quality of the recycled material, particularly to avoid reinsertion of contaminated inputs into the production chain. Although the recycled inputs were not identified as hazardous material, it is important to recognize the products that may host them, until a better understanding of their toxicity is achieved. A framework that could be used for this purpose was proposed by Hansen, et al. (2007).

A percentage of the ENMs is exported to undergo further recovery processes. Exported materials include plastics, non-ferrous metals, textiles and printed circuit boards. While our model identifies that the nanomaterials leave Switzerland, it does not identify any specific destination countries, though France, Germany, Italy, Sweden, and Japan have all received material in the past (Boeni, et al., 2012). It should also be mentioned that while small amounts of waste are imported to be recycled, these inputs were not accounted for in our model.

The flows of ENM out of recycling investigated here should be considered in future updates of ENM flow modeling. However, these flows are small compared to the overall flows in the whole system analyzed by Sun, et al. (2014b). The main contribution of our

new results in the comprehensive model is recognizing an increase of the mass deposited in landfills (directly or as bottom and fly ash coming from the waste incineration plants). Based on previous modeling on ENMs flows from landfill and incineration plants (Mueller, et al. (2013)), we can expect limited transfer to soil and water compartments as a consequence.

This work constitutes the first assessment of ENMs during the recycling processes, and as such faces important uncertainties. These are associated to the absence of hard data, mainly on the way ENMs are used in applications, and the limited studies available on the behavior of nanomaterials in real systems. Broadly speaking, recycling a product means to split its components and recovering or disposing of the different fractions according to their economic value and the technology available. Once split, valuable materials are retired into successive stages according to their properties and transformed into raw material. Waste transformation may occur either during the initial processing or in other facilities where the recovered material is collected. For the analysis of the ENM mass flows it is paramount to understand the allocation of the ENMs (into which fraction, i.e., plastic, metals or other), the way it is integrated into the material (into the surface or into the volume of the material) and the quantities used. However, this information is not available in the inventories surveyed, which mainly compile the commercial information publicly provided by the manufacturers. The knowledge on the nanomaterials properties including their functionalities was key to improve this input information and the accuracy of our assessment.

The distribution of the ENMs mass among the product subcategories was another major challenge in the method we designed. One way to get this information is to know the ENMs mass content within the applications and to know also their market size (quantities sold). In most cases this information is non-existent. We consider that the distribution of the products within the inventories provides a good indication of the allocation of the mass between subcategories. In the worst case, where no information was available to distribute the mass, a uniform distribution between the subcategories was used. Similar approaches have been applied by Mueller and Nowack (2008), Gottschalk, et al. (2009c) and Sun, et al. (2014b), which constitute the background for this research.

Whereas we consider it to be relatively straightforward to predict in which fraction the ENM will end up during recycling, it is less clear if and how much release during these operations will occur. ENMs released during recycling operations may be an important source of occupational exposure to workers, but little information is available (Struwe et al., 2012). During any shredding or dismantling operations, release of particulates into the air is likely, but no data is available (Froggett, et al., 2014). Release of materials from nanoproducts into water has been observed for textiles, paints and coatings during the use phase (Nowack, 2014), so it is reasonable to assume that also during recycling operations a certain fraction will be released into water. The mechanical actions on materials during recycling may also form unintentional nanomaterials, e.g. by abrasive water jet machining, grinding or cutting (Goehler et al., 2010; Ling and Pui, 2013). It has been shown that during recycling of concrete, ultrafine particles (i.e., incidental nanoparticles) are formed for different mechanical processes such as crushing, demolition and processing (Kumar et al., 2012; Kumar and Morawska, 2014). Hence, further research is needed to understand release within the recycling processes, and their fate and behavior once released, including any transformation or speciation of the nanomaterial. This is critical to evaluate workers exposure and ENM transfer to environmental compartments.

In view of the uncertainties discussed, providing point estimation of the mass flows of nanomaterials would have been misleading. The probabilistic material flow methodology developed by Gottschalk, et al. (2010b) is an efficient way to deal with limited or incomplete information, using probability distributions of the flows rather than point

estimations. Furthermore, the input values that we used already are the result of the application of the same approach (Sun et al. 2014), thus the uncertainties about ENMs production amounts and uses are already incorporated in this exercise. The limitation of this approach have already been discussed by Gottschalk et al. (2010d).

Our research highlights the necessity to improve the quality and amount of information available on the uses and applications of ENMs. Current inventories and scientific literature are a limited source of information when actual applications are analyzed. Industry has to arise its awareness on the key role they play to achieve long-term success of nanotechnology. They can do so disclosing more detailed information, for instance, quantities used, nanomaterial allocation, surface/volume application, particle size and functionalization. This information should be provided at least for a scientific-based risk assessment. Mass-based approaches are a good starting point to evaluate nanotechnology risk, but there are other parameters that become more relevant in the nano-scale, for example, particle size. Regulators may also play an important role providing the right incentives and the platforms to gather and disseminate in an efficient way this information, as recently shown by the French government through ANSES (2013), which reports the production amounts and uses of ENMs in France. Science will benefit with more information to validate its models and providing accurate risk assessments of nanotechnology. At the end, society and industry will be the ultimate winners. The former by increasing its acceptance for those applications that have been proved to be safe and by improving its welfare, while the latter by increasing the chances to achieve positive returns to their investments for sustained periods.

### 2.3.5. Conclusions

Recycling products containing ENMs does not result in significant dissipation of nanomaterials to other (new) products. Rather, a large proportion of nanomaterials will very likely end-up in waste fractions that can be properly handled. Our research shows that nano-TiO<sub>2</sub>, nano-ZnO and nano-Ag, in consumer products are mainly associated with fractions that are not recovered during the recycling processes and that are subsequently incinerated or landfilled. For CNTs, the largest fraction is exported from Switzerland as material fractions that undergo further recovery processes (batteries, printed circuit boards and non-ferrous metals). Smaller quantities of the four ENMs covered in this work are expected to flow back to the productive process of the economy, mainly through recycling of construction waste and plastics. Some minor releases of nano-TiO<sub>2</sub> and nano-Ag to waste water are likely to happen. Our results suggest that the risk assessment of ENMs during recycling should focus on occupational exposure, the release of nanomaterials to the environment in waste incineration plants and landfills, and the evaluation of hazards in a small number of sectors that use inputs containing nanomaterials.

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## 2.4. Codes on environmental toxicity and release modeling for DSS

### 2.4.1. Introduction, workflow and concept

#### 2.4.1.1. Introduction

The R package development work replaced the initially intended ETSS research on improving landfill modeling, which included the compartment where most of the ENM probably end up. The particular challenge in the landfill work would have been to understand and also model the fate of nanomaterials from a long-term perspective, based on a very thin data base. Thus, developing a model for long-term ENM release modeling and monitoring would have been an essential part of this work.

However, the work on landfill release modeling was not started as required by the SUN coordinators. Hence, ETSS focused, under high pressure, on the development of probabilistic software for environmental exposure and effects (along with risk analysis). The tools should be linked to the SUN DSS (decision support system). This deviation from the work plan occurred with the approval of the coordinator and work package leader.

The workload required for the tools' development has been (and continues to be) much higher than what would have been required for the above mentioned, initially planned study.

#### 2.4.1.2. Workflow

The Package development work phases are presented in the next section. I followed the recommendations given by Wickham (2015). The key elements of creating R packages can be described and listed as follows (for generic details on package development and good coding style, see Wickham):

- A) Package metadata
- B) R-Code
- C) Compiled code
- D) Namespaces
- E) Object documentation
- F) Vignettes
- G) Testing
- H) Data
- I) Installed files

A) Package metadata: The DESCRIPTION files are produced in order to store all the metadata of a particular R package. These files are based on DCF (Debian control format) files. DCF packages represent Unix ar (archiver) archives as well as tar archives (computer software that collects different files into a single file).

B-C) R-Code and compiled code: The R code work is the main part of a package development and, in principle, creates generic R functions (on a script and package level). These functions include, in short code algorithms, the usually page-long and often complex code for specific software applications. Those functions are stored in their own files, and follow the standard and current style of R-coding.

R represents what is called a high-level, expressive programming language (R Development Core Team, 2012; Wickham, 2015). Unfortunately, such expressivity may cause some speed problems when running complex stochastic and other computer-based simulations. One way to avoid such speed problems is to use low-level compiled software in R scripts. However, we did not incorporate a so-called low-level compiled software such as C++ that may complement the R code. We spent some time clarifying the possibilities of speeding up the packages and came to the conclusion that including and extending our software to a C++ (or other) complement was not necessary and would go beyond the temporal and financial possibilities of this SUN task.

D) Namespaces: The namespace has, in principle, been programmed in a way such that the packages could be submitted to the CRAN (comprehensive R archive network) for public use. However, such publication is not in our scope and would need some additional testing efforts on improving the Namespace files, as well as the package documentation. The CRAN requires that R packages can fully interact with all other existing CRAN packages. The namespace allows values of an object associated with a particular name to be connected, and shows (using simple words) how functions in our package may be connected to functions in other packages.

E) Object documentation: In order to document the objects, I created what are called “.Rd files.” We used Roxygen2 for automatically transforming the documentation into such files. These belong to the “man/” directory and are based on a LaTeX syntax. They can be visualized in HTML, PDF and other text formats. The R functions and their documentation are combined in the sense that, during the development stage of updating the package code, we also need to modify the corresponding documentation.

F) Vignettes: The extended form of function documentation is called a vignette. Such documentation clips deep technical aspects of the algorithms/functions and is used when experts need to understand the functions in detail. For a pure application of such packages, vignettes are not useful. Such comprehensive documentation discriminates between algorithms and functions in different problem solving categories that are not needed for pure application purposes.

G) Testing is a fundamental step. It is a very time-consuming (and in principle non-productive) phase of software development. I have performed such testing in a very rigorous and comprehensive way, based on different approaches:

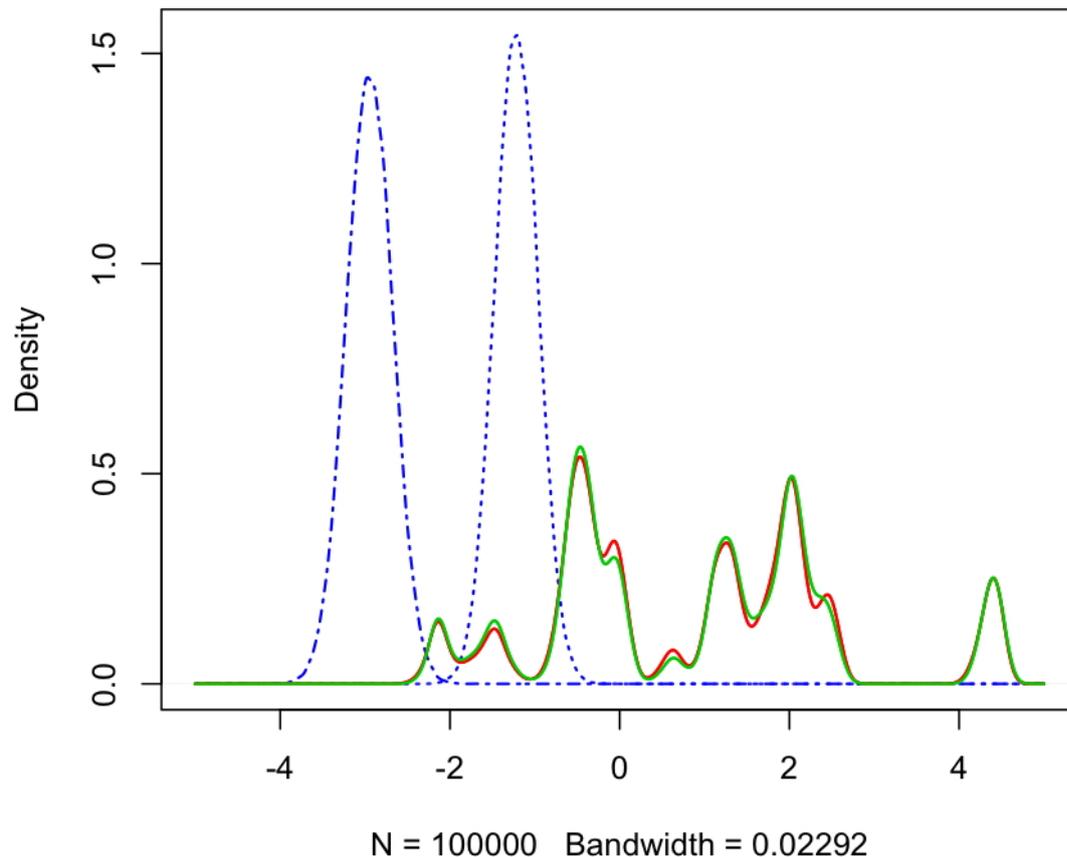
- 1) Visual check (theoretical analysis) of construction and consistency of coding (not finished for PMFA);
- 2) Computational check of all single parts of construction and consistency of coding (not finished for PMFA);
- 3) Modeling of theoretical studies, including some extreme scenarios that can also be checked visually (not finished for PMFA);
- 4) Re-modeling (a) one to one (see **Figure 15**) and b) with full and new parameter variance (as suggested by Prof. Nowack (EMPA) at the Empa meeting) of Gottschalk et al., 2013 (nano-Ag), Coll et al., 2015 (nano-Ag) (not yet done for PMFA, other reference work to be used).

H) Data: I designed the package in such a way to allow integration of Excel data that can be load into the R functions. This simplifies the use of tools for available data that are rarely stored in R-based data sets.

I) Installed files: The top-level package directory and the subdirectory has to be programmed and organized in a robust way that guarantees reliable software use without crashing. Simply put, this means one needs to write (for example) “inst/” and “.Rbuildignore” files, where “inst/” is the opposite of “.Rbuildignore.” The latter allows for removing files and directories, while the former allows for installing them. Other files programmed in this context are *build*, *data*, *demo*, *exec*, *help* and other.

The software has been presented in oral presentations (including discussion) at Empa St. Gallen (February 2016), Basel joint event EU NMP projects eNanoMapper, NanoFASE, GUIDEnano, SUN (March 2016), Hands-On Workshop, Technology Park, Basel. South African Statistical Association (SASA) 2015 conference, University of Pretoria. Pretoria, (South Africa).

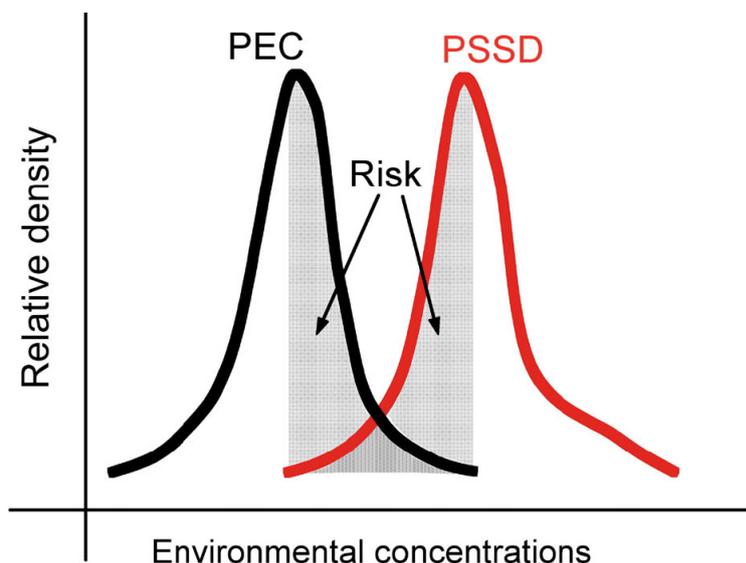
The SUN workshop (but open for a wider audience) organized and moderated by Prof. Nowack at Empa (February 2016) was very helpful. In this workshop the participants provided important stimulation to the package development. Especially the data uncertainty management could be improved based on potential user needs and comments. Such needs reflect in the PSSD modeling – to give an example – the possibility to integrate the variability and uncertainty of each single NOEC (no observed effect concentration) or NOEC equivalent values taken from the ecotox literature. Those values represent the main input for such modeling.



**Figure 15.** R package based reproduction (green line) of probabilistic species sensitivity distribution (PSSD) of the nanosilver case as shown in (Gottschalk et al., 2013a) reflecting the no-observed-effect concentration curve (red line) compared with the probability distributions of predicted environmental concentrations (PEC) of engineered nanomaterials for aquatic compartments (surfacewater and sewage treatment effluents (blue line on the left)

#### 2.4.1.3. Concept and purpose of the tools

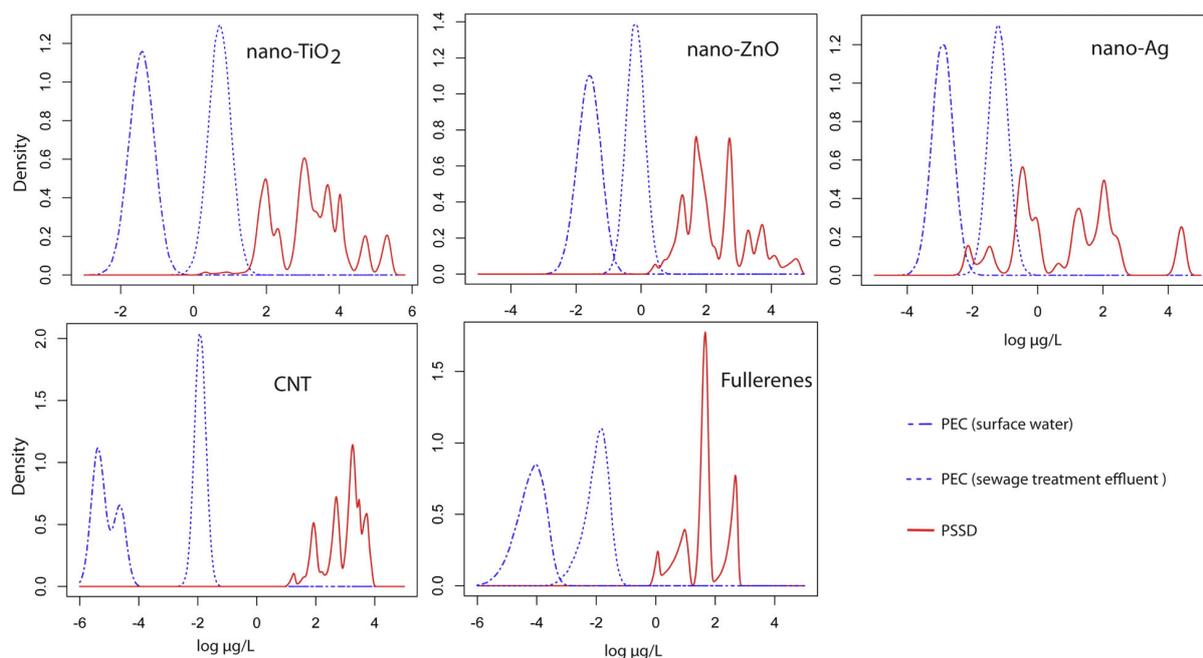
As mentioned above, the R packages have been conceptualized and programmed following a comprehensive technical guide given by Wickham (2015): a PSSD R package (probabilistic species sensitivity distribution), a PMFA R package (probabilistic material flow analysis) and an R package for risk modeling that combines the two other modules (see also **Figure 16**). Such software is based on stochastic methodologies used in different contexts in the nanotech research of probabilistic/stochastic flow and ecotoxicological effects and risk models developed by ETSS and Empa (Gottschalk, et al., 2013a).



**Figure 16.** Probabilistic species sensitivity distributions (PSSD) and predicted environmental concentration (PEC) fuse together into environmental risk. The degree of risk is represented by the extent of the predicted environmental concentration (PEC) values overlapping the probabilistic species sensitivity distribution values and vice versa; shaded areas indicate where risk may occur. Adapted from (Gottschalk, et al., 2013a).

These software tools are designed to potentially be the basis for a continuously administrated European environmental risk database (and its attached institution/company). The database would have global relevance, as such a resource does not yet exist for assessing the risk of emerging chemicals/nanomaterials and other potential contaminants.

As exemplary presented in **Figure 17** (simulation results), such software will also allow non-experts in programming in industry and academia to conduct stochastic environmental risk assessment projects. It will allow the user to predict concentrations of potential contaminants in various environments and produce species sensitivity distribution models that can be compared to exposure predictions in order to quantify and predict the expected risks. All three software modules will run fully probabilistically and can also be used in cases of data scarcity with a large variability spectrum.



**Figure 17.** Probabilistic species sensitivity distribution (PSSD) reflecting the no-observed-effect concentration data compared with the probability distributions of predicted environmental concentrations (PEC) of engineered nanomaterials for aquatic compartments. Environmental risk is observed where the predicted environmental concentrations distributions overlap the probabilistic species sensitivity distribution or vice versa. CNT = carbon nanotube. (Gottschalk, et al., 2013a).

## 2.4.2. Software structure and concept

### 2.4.2.1 The PSSD R package

This is a package with functions used to perform PSSD (probabilistic species sensitivity distribution) modeling. The PSSD package is well-suited to run species sensitivity distribution simulations in cases of distinct ecotoxicological data scarcity and variability. Probability distributions of the uncertainty and variability of the target toxicological sensitivity are, for the first time, computed for each single species and unified into a main PSSD simulation for considered ecosystems. The package also allows the user to compute probability distributions of the predicted no-effect concentrations (PNEC) derived from the PSSD model. The package may also be used to run probabilistic environmental risk evaluations that combine the PSSD output with the probability distributions of the expected environmental exposure.

The main advantages and innovations of this approach are:

- First approach that considers and computes its own models of sensitivity distributions for each single species
- These single species models are combined into a total model for a target ecosystem
- Full stochastic and probabilistic treatment for all model parameters

- No need to follow theoretical (often not validated) functions for the Species Sensitivity Distributions (SSD)
- Use of different endpoint data that can be derived to, for example, no observed effect concentrations (NOEC)
- Large event spectrum analysis based on an advanced Monte Carlo approach

The R package is structured as shown in **Figure 18** and aims at simplifying the standard R-based coding procedure in ecotox modeling. Thus, the code is much shorter than the one used in full R-code programming procedures for specific research studies. The package-based software versions allow a more efficient use of these approaches, including for non-programmers. Appendix 5.3 shows the elemental parts of the R-coding work phase.

The package is organized in a way (see **Figure 18**) that allows the different elemental modeling areas to easily be combined into the total PSSD simulation.

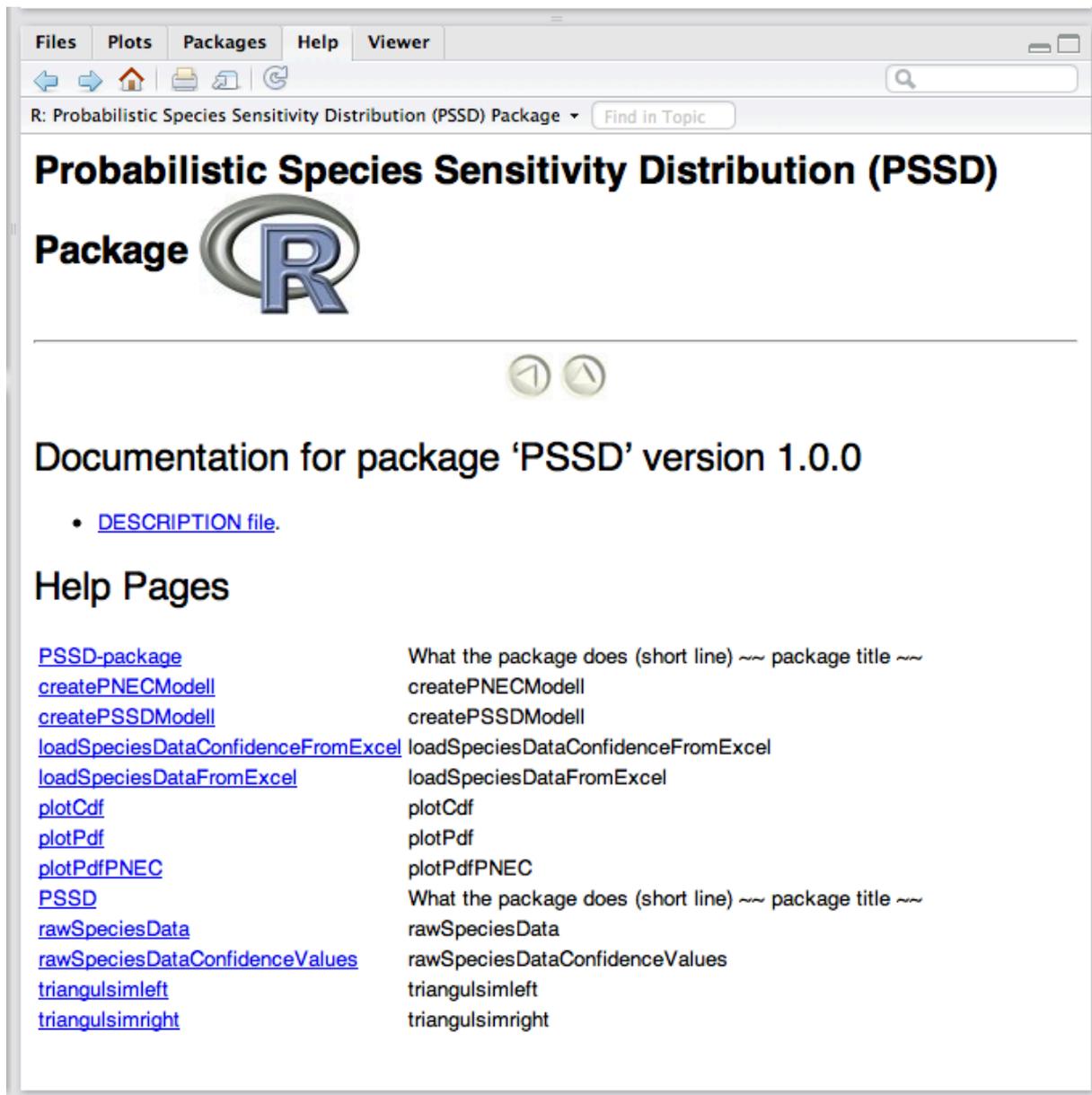
Those fundamental parts reflect:

- Data loading, modeling (PSSD and PNEC [predicted no effect concentrations]) and plotting scripts;
- E-mail message scripts for informing the user of the actual state of the computer simulations;
- Scripts on raw data management; and
- Scripts on shaping probability distributions (not relevant for the standard user).

As shown in **Figure 19**, the elemental parameters to run the PSSD are:

- The numeric matrix with endpoint values and the corresponding matrix with the uncertainty range of such data;
- The number of the quantity of PSSDs to be computed;
- PSSD length: the number for the quantity of the model output values for the PSSD;
- Species length: the quantity of the model output values of the PSSD of one single species;
- The fraction that reflects the uncertainty range (confidence interval) on both sides of the first assessment factor (short- to long-term toxicity);

- The fraction that reflects the uncertainty range (confidence interval) on both sides of the second assessment factor (extrapolation from the observed effect concentrations into no-effect concentrations);
- The fraction that reflects the uncertainty range (confidence interval) on both sides of the third assessment factor (expected differences between lab-based experimental conditions and natural conditions);
- The fraction that reflects the uncertainty range (confidence interval) on the left-hand side of the lowest toxicological endpoint used for one single species;
- The fraction that reflects the uncertainty range (confidence interval) on the right-hand side of the highest toxicological endpoint used for one single species; and
- Interval length: the number for the quantity of model output values of the interval distributions that are the distributions between all the toxicological endpoints collected for a particular species.



**Figure 18.** R package version 1.0.0 for Probabilistic species sensitivity distribution (PSSD) modeling as shown in RStudio.

R: createPSSDModell

## createPSSDModell

### Description

function to create a probabilistic species sensitivity distribution (PSSD) modell

### Usage

```
createPSSDModell(T_data, cv_data, PSSD_simulations = 1, PSSD_length = 100,
  species_length = 10^2, cv_factor1 = 0.5, cv_factor2 = 0.5,
  cv_factor3 = 0, cv_low_end = 0.5, cv_high_end = 0.5,
  interval_length = 10^2)
```

### Arguments

<b>T_data</b>	A numeric matrix with nrow = 100 and ncol = 100
<b>cv_data</b>	A numeric matrix with nrow = 100 and ncol = 100 (does not have to be generated, the default is zero)
<b>PSSD_simulations</b>	A number for the quantity of PSSDs to be computed
<b>PSSD_length</b>	A number for the quantity of the model output values for the PSSD
<b>species_length</b>	A number for the quantity of the model output values of the PSSD of one single species
<b>cv_factor1</b>	A fraction that reflects the uncertainty range (confidence interval) on both sides of the first assessment factor (short to long term toxicity)
<b>cv_factor2</b>	A fraction that reflects the uncertainty range (confidence interval) on both sides of the second assessment factor (extrapolation from the observed effect concentrations into no effect concentrations)
<b>cv_factor3</b>	A fraction that reflects the uncertainty range (confidence interval) on both sides of the third assessment factor (expected differences between lab based experimental conditions and natural conditions)
<b>cv_low_end</b>	A fraction that reflects the uncertainty range (confidence interval) on the left hand side of the lowest toxicological endpoint used for one single species
<b>cv_high_end</b>	A fraction that reflects the uncertainty range (confidence interval) on the right hand side of the highest toxicological endpoint used for one single species
<b>interval_lenth</b>	A number for the quantity of the model output values of the interval distributions that are the distributions between all the toxicological endpoints collected for a particular species

### Value

a matrix

[Package PSSD version 1.0.0 [Index](#)]

**Figure 19.** Package use template of the R package version 1.0.0 for running the actual PSSD (probabilistic species sensitivity distribution).

#### 2.4.2.2 The PMFA R package

This is a package with functions used to perform probabilistic material flow analysis (PMFA). Material flow and material state simulations may be computed in cases of distinct data scarcity and variability. Probability distributions of the uncertainty and variability of the complete model input are generated. The package allows the user to combine empirical, experimental, analytical, expert and assumptive knowledge to construct the model. The package may also be used to run a probabilistic environmental risk evaluation that combines the PMFA output with the probability distributions of the ecotox modeling (e.g., PSSD; see PSSD package).

The main advantages and innovations of this approach are:

- Full stochastic and probabilistic treatment for all model parameters (model input and output);
- No need to follow theoretical functions in order to compute probability distributions (for data management instructions, see the following sections on data management);
- Use of (and the possibility to combine) any kind of data (experimental, analytic, assumptive information, etc.); and
- Full event spectrum analysis based on an advanced Monte Carlo approach.

The R package is designed as shown in **Figure 20**, and aims at simplifying the standard R-based coding procedure used in environmental modeling. Thus, the code is much shorter than standard code manuscripts for environmental research purposes and allows a more efficient use of these approaches, including for non-programmers. (Please see the second part of appendix 5.3 for further information.)

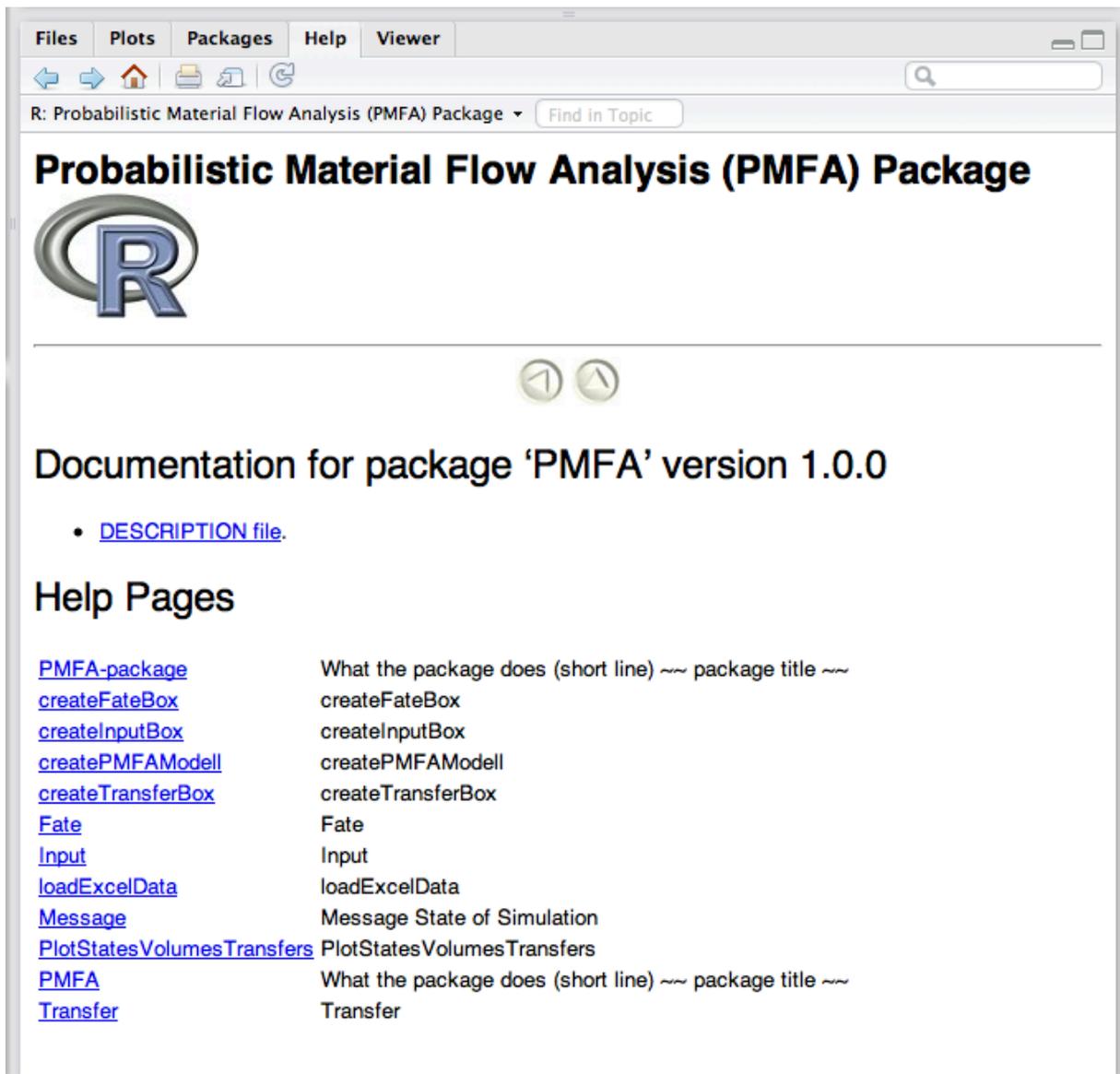
The package is organized (see **Figure 20**) to make the different modeling areas clearly visible; however, they are automatically combined to produce the total model.

Those *modeling areas* reflect:

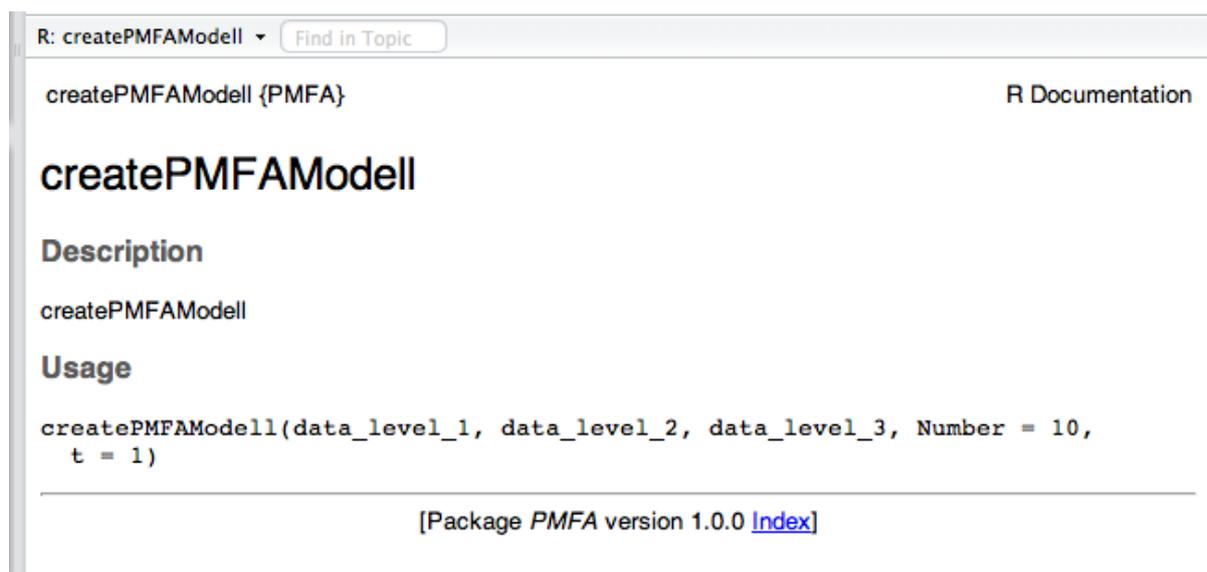
- Data loading, modeling and plotting scripts;
- E-mail message scripts for informing the user of the actual state of the computer simulations;
- Scripts on material input into a target system; and
- Scripts on material transfer and fate (deposition, elimination, transport delay, unknown fate) in particular compartments of a target system.

As shown in **Figure 21**, after the data input preparation, there are only very few parameters needed to run the final PMFA:

- Data level **one** values for material input into the system, production, import etc.
- Data level **two** values for material fate in compartments (deposition, elimination, unknown fate, transfer delay)
- Data level **three** values for material fate (transfer between compartments)
- Number of Monte Carlo iterations
- Time-based data for dynamic modeling (to be used by experienced users and in cases of significant amounts of feedback loops, only after a thorough analysis and interpretation of those loops)



*Figure 20. R package version 1.0.0 for Probabilistic material flow analysis (PMFA) as shown in RStudio.*



**Figure 21.** Package use template of the R package version 1.0.0 for running the actual PMFA simulation (probabilistic material flow analysis).

#### 2.4.2.3 ENM Data Management for stochastic modeling (PSSD R package)

The PSSD (probabilistic species sensitivity distribution) model output reflects generally spoken modeling results that are based on no observed effect concentrations (NOEC). Such values stand, in the PSSD modeling, for the highest test concentrations where a potential toxicant does not show any negative effects on organisms when exposed to it under labor conditions.

##### *Types of model input data*

###### Data situation A

In the best case, we feed the model with as many NOEC values, for as many different species, and run it with them. In this case, no assessment factors (AFs) have to be used, and the NOECs are directly fed into the model. However, also for such a situation the model allows to consider confidence intervals for each endpoint used. Such intervals can be loaded for example from an Excel database.

###### Data situation B

Very often, such NOECs are not available and have to be derived from other well-established toxic endpoints. As recently described (Gottschalk, et al., 2013a; Gottschalk and Nowack, 2013; Coll et al., Accepted), the model input data used to feed the PSSD model can be derived from a large spectrum of different toxicity data. However, in order to exclude the possibility that a modeler will operate with toxic values that are too weak (weak data, in the sense that no significant toxic effects were observed), one should only use standardized endpoints that revealed or excluded lethality or significant growth and/or reproduction inhibition, as well as significant negative effects on metabolic processes (for example, photosynthesis). Small effects observed on the organism's behavior, body color, enzyme regulations or biochemical adjustments were not

considered in earlier case studies (Gottschalk and Nowack, 2013; Coll, et al., Accepted).

#### *Derivation of NOECs from other ecotoxicological endpoints*

The derivation of NOECs from other ecotoxicological endpoints is conducted by using three AFs that allow the modeler to consider three basic epistemological uncertainties. First, such uncertainties may stem from possible differences between (known) short and (unknown) long-term effects. Second, the transformation of observed effects into knowledge for no observed effect concentrations brings insecurity as well. Third – more from a theoretical point of view, and until now merely neglected – differences between lab and natural exposure and effect conditions that are mostly unknown could also significantly influence the examined potential negative effects of a toxicant.

This use of the AFs for transformation can be done following REACH guidance principles first presented in 2008 (ECHA, 2008). As described above, in establishing the AF values, it is a balancing act to evaluate uncertainties that link single-species laboratory knowledge to evidence for a multi-species ecosystem. This implies that the modeler has to balance between, according to (ECHA, 2008):

- Intra- and inter-laboratory variation of toxicity data;
- Intra- and inter-species variations (biological variance);
- Short-term to long-term toxicity extrapolation; and
- Laboratory data to field impact extrapolation.

### *Fix the Assessment Factors (AF)*

The guidelines mentioned above do not give any kind of specific decision tree-based guide for the use of AFs. It states that “long-term tests (expressed as EC10 or NOEC for a sublethal parameter) are preferred to those [results] of short-term tests (EC/LC50), because such results give a more realistic picture of effects on the organisms during their entire life cycle (ECHA, 2008).”

Nevertheless, these guidelines propose the use of a maximal total factor of 1000, for example, in the aquatic context of PNEC (predicted no effect concentrations) derivations (Table R.10-4). This maximal total factor of 1000 reflects three maximal factors of 10 for toxicity data with unfavorable conditions regarding the three main areas of uncertainty mentioned above: short-long term differences, observed/no observed effects and lab-natural conditions. The lab-natural conditions are (as far as we currently know) not considered; thus, in the PSSD studies that have been conducted, a maximal factor of 100 has been used.

### *Transformation from observed effects into not-observed effects*

Coll, et al. (Accepted) recently proposed, for transforming observed effect values into no-effect values, a factor of 10 for LC/EC<sub>25-50</sub>, and a factor 2 for LC/EC<sub>10-20</sub>, as well as a factor of 1 (no factor) for LED, MIC, LOEC and HONEC.

### *Transformation of short-long term studies*

Regarding extrapolation of short-long term studies, these authors used a factor of 1 for long-term ones and a factor 10 for short-term ones. The categorization as long-term depends on the species and taxonomic group; Gottschalk and Nowack (2013) followed European recommendations (European Commission, 2011) in defining long-term toxicity (for the aquatic) when observed from exposure that reflects at least one complete life cycle of the tested organisms. They indicated, for cases of fish exposure, that up to 7 days was acute (short term), and 14 days was acute, but prolonged. An algae exposure time of 72 hours has a long-term limit: 7 days for the minimal long-term of daphnids (*Ceriodaphnia dubia*) or 21 days for *Daphnia magna*. For algal chronic exposure, 72 hours or more was used as a limit. Experiments with vertebrates as well as invertebrates were classified as chronic (long term) experiments when lasting at least 21 days.

For soils, the limits on short-long term followed some other references (OECD, 2000). Long-term toxicity for earthworms was set at 28 days (reproduction) and 21 days (cocoon reproduction). In cases of unicellular species that may multiply under favorable environments within hours, a conservative value of 24 hours was used for the short-chronic distinction.

### *Abbreviations*

Effective concentration of adverse effects in 50% of the organisms (EC50)  
Half maximal inhibitory concentration (IC50)  
Highest observed no effect concentration (HONEC)  
Lethal concentrations for 50% of the organisms (LC50)  
Lowest observed effect concentration/level (LOEC/LOEL)  
Minimum inhibitory concentration (MIC)  
No observed effect concentrations (NOEC)  
Predicted no effect concentration (PNEC)

### *2.3.2.4 ENM Data Management for stochastic modeling (PMFA R package)*

#### *The PMFA (probabilistic material flow analysis)*

In the context of environmental exposure, the PMFA aims to track the release of potential contaminants into natural and technical compartments, as well as to quantify their quantities in those environments. A methodical and study-based overview is given elsewhere (Gottschalk et al., 2009a; Gottschalk et al., 2010a; Gottschalk et al., 2010c; Walser and Gottschalk, 2014).

#### *Types of model input data*

Basically, the software developed for general users needs only two different types of model input data. Material input into the system and transfer inside the system.

##### *A) Material input into the system*

First, the periodical material input (in the form of a mass per period) has to be known (for example, tons per year). This material input usually takes place in one single box – the initial main box. The indexing of all boxes is explained below. Material input comprises material synthesis as well as material import from outside of the system. Such import may also occur as material ingredients of imported use products/articles.

##### *B) Transfer inside the system.*

Transfer inside the system involves transport from one box into another one or a transfer into four sub-boxes of each main box. These sub-boxes represent 1) material degradation, 2) material deposition, 3) transport delay (material not transported further in the target time period) and 4) unknown material fate.

All the transfer parameters are quantified as a fraction that lies between 0 and 1 including the borders.

#### *General user interface structure for Excel based modeling*

The general user interface for environmental exposure contexts is organized in a three-level framework.

### *Level 1*

Level 1 comprises the material input into the system as well as 1) material degradation, 2) material deposition, 3) transport delay (material not transported further in the target time period) and 4) unknown material fate.

### *Level 2*

Level 2 reflects the transfer of the target material from the material synthesizing process (including, again, material import from outside the system) into a general environmental compartment, and the transfer of the synthesized material into use products/articles as part (ingredients) of these use products. Second, for all these receiving compartments, the further transfer of data into specific environmental and technical compartments is required and computed. In each of those (intermediate) receiving boxes (boxes between material synthesizing and target final [material life cycle] environmental or technical box), a transfer into sub-boxes is again possible: 1) material degradation, 2) material deposition, 3) transport delay (material not transported further in the target time period) and 4) unknown material fate.

### *Level 3*

Level 3 involves first the transfer between all main boxes (all environmental and technical compartments). Second, transfer into the sub-boxes (1) material degradation, 2) material deposition, 3) transport delay (material not transported further in the target time period) and 4) unknown material fate) is possible for all the main boxes as in level 1 and level 2.

## *Computing of model input data*

### A) Deterministic modeling

In the case of deterministic modeling, the single model input parameter values are fed into the model, and in each case, the default probability distribution “Uniform” is used to run the computer simulations.

### B) Probabilistic modeling (Monte Carlo [MC] Modeling)

For the probabilistic approach, all the parameters are usually computed based on probability distributions. The user can fit their data for each parameter into five different distributions: uniform, triangular, normal, bootstrapping and a simple type of Bayes Monte Carlo.

#### Uniform

The minimal and the maximal values are taken as extremes of the distribution, and other values are ignored.

#### Triangular

The minimal and the maximal value are taken as extremes of the distribution, and the median value is computed as the peak (most frequent) value of the distribution.

#### Normal

Mean and standard deviation are computed by using the raw values and fed as standard arguments into the distribution.

#### Bootstrapping

The raw values fed into the model are randomly, equally and repetitively taken to compute an empirical distribution.

### Bayes Monte Carlo

What we have until now (see footnotes) called "Bayes Monte Carlo" is a mix of the uniform and bootstrapping approaches. As a kind of prior distribution for transfer parameters, the full spectrum from zero to one (for the material input, the minimal and maximal value form the borders) is used as a uniform distribution and linked to the bootstrapping procedure explained above. Half of the values (which could be changed and adapted) come from a full spectrum, uniform distribution and are randomly linked to the other half (could be changed and adapted), which come from the bootstrapping.

### *Rough decision guide for the use of the different probability distributions*

#### Uniform

Chose uniform if only two values are known that represent the extremes of the full parameter spectrum. Or, if a few values in between the extremes do not represent any tendency regarding raw values with higher probability or plausibility, that means you should more or less trust the border values. Use a full spectrum uniform (0 to 1) if you know that such a transfer occurs but data and knowledge (also assumptive expert knowledge) is completely missing.

#### Triangular

Chose triangular if there are two values known that represent the extremes of the full parameter spectrum. If one or a few values in between the extremes somehow represent a tendency regarding raw values with higher probability or plausibility, this means you should trust them (in the sense that they show a higher probability/plausibility than the border values).

#### Normal

Chose normal if you have some data and/or if you assume that the data samples (shapes) so far represent the target parameter distribution but you do not know the extremes. However, even if you do not know the extremes you still need to account for very high and very low values at the borders of the target distribution, e.g., high value data with low probability (that however cannot be excluded) for the material production/use.

#### Bootstrapping

Basically, bootstrapping makes sense if you have large sample sizes and/or you assume the data samples (shapes) so far represent the target parameter distribution. Thus, choose bootstrapping if you have a sufficient amount of data values and the impression that they cover extremal values (low probability values) as well as modal values (high probability values). This means that you trust your data without the need to fit them into a parametrical distribution, and you have no other knowledge on possible values in between and beyond these data.

#### Bayes Monte Carlo

Choose Bayes Monte Carlo if, on one side, you know the (theoretical) possible (full) parameter spectrum and you have, on the other side, some data that samples (shapes) to some extent (in the trend but not to the full extent) the target parameter distribution as described above for the bootstrapping approach. This is only a working name – it could also be called Bayesian bootstrapping.

*Indexing of boxes (also called compartments, sometimes also processes)*

The material states and transfer system covers 50 main boxes representing residence compartments of a target material (production, manufacturing, consumption areas, technical and natural compartments). Second in each main box 4 sub-boxes (a total of 200 boxes) are modeled that reflect different material states (material degradation, deposition, unknown fate and transport delay), see **Figure 22**. Third, 2500 transport paths boxes connect all the main boxes (unidirectional connection), see **Figure 23**.

*Main Boxes (50 boxes)*

The following main boxes were used in testing phase.

- 1 Category production (synthesizing) and manufacturing (including import from outside)
  - 2 Category 1=General Environmental Box (general box for further transport into specific technical or natural environments)
  - 3 Category 2 = Use Product 1(intermediate boxes for further transport into specific technical or natural environments)
  
  - 4 Category 3 = Use Product 2
  - 5 Category 4 = Use Product 3
  - 6 Category 5 = Use Product 4
  - 7 Category 6 = Use Product 5
  - 8 Category 7 = Use Product 6
  - 9 Category 8 = Use Product 7
  - 10 Category 9 = Use Product 8
  - 11 Category 10 = Use Product 9
  - 12 Category 11 = Use Product 10
  - 13 Category 12 = Use Product 11
  - 14 Category 13 = Use Product 12
  - 15 Category 14 = Use Product 13
  - 16 Category 15 = Use Product 14
  - 17 Category 16 = Use Product 15
  - 18 Category 17 = Use Product 16
  - 19 Category 18 = Use Product 17
  - 20 Category 19 = Use Product 18
  - 21 Category 20 = Use Product 19
  - 22 Category 21 = Use Product 20
  - 23 Category 22 = Use Product 21
  - 24 Category 23 = Use Product 22
  - 25 Category 24 = Use Product 23
  - 26 Category 25 = Use Product 24
  - 27 Category 26 = Use Product 25
  - 28 Category 27 = Use Product 26
  - 29 Category 28 = Use Product 27
  - 30 Category 29 = Use Product 28
  - 31 Category 30 = Use Product 29
  - 32 Waste water
  - 33 Sewage treatment plant
  - 34 Sludge
  - 35 Overflow
  - 36 Waste incineration plant
-

37	Landfill
38	Recycling
39	Export
40	Freshwater
41	Seawater
42	Freshwatersediment
43	Seawatersediment
44	Soils
45	Atmosphere
46	Not defined
47	Not defined
48	Not defined
49	Not defined
50	Not defined

*Sub-boxes (200 boxes)*

1	"-4 degradation"
2	"-3 deposition"
3	"-2 unknown"
4	"-1 delay"
<b>5</b>	<b>Production and manufacturing (first main box)</b>
6	"-4 degradation"
7	"-3 deposition"
8	"-2 unknown"
9	"-1 delay"
<b>10</b>	<b>Category 1 (second main box)</b>
11	"-4 degradation"
12	"-3 deposition"
13	"-2 unknown"
14	"-1 delay"
<b>15</b>	<b>Category 2 (third main box)</b>
16	"-4 degradation"
17	"-3 deposition"
18	"-2 unknown"
19	"-1 delay"
<b>20</b>	<b>Category 3</b>
...	

*Figure 22. Sub-boxes reflecting the material states.*

Transfer-boxes (2500 boxes)

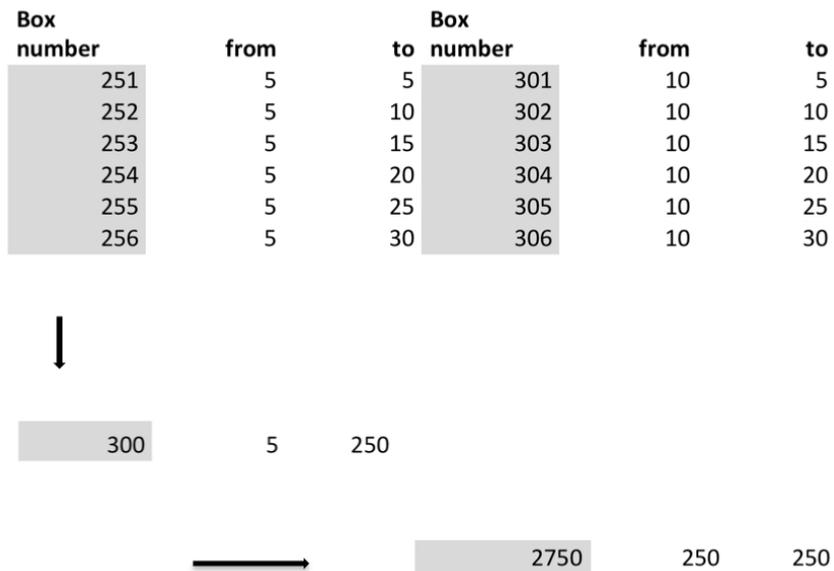


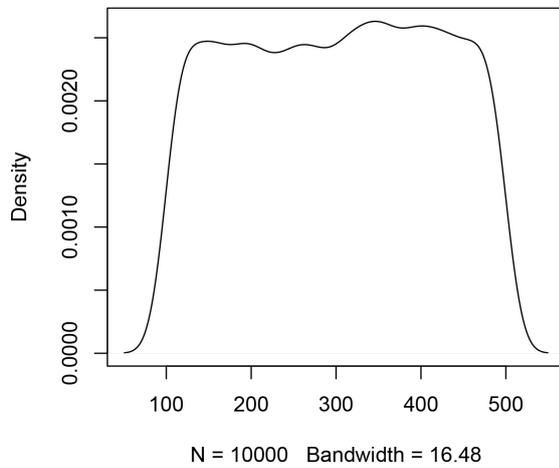
Figure 23. Sub-boxes reflecting the material transfer.

### Examples of distributions

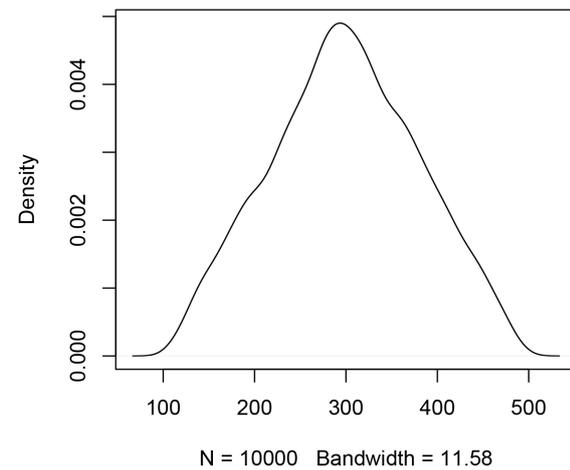
#### A) Material input

Probability distributions based each time on some didactical raw values 100, 200, 300, 400 and 500 and shown in non-indexed image impressions.

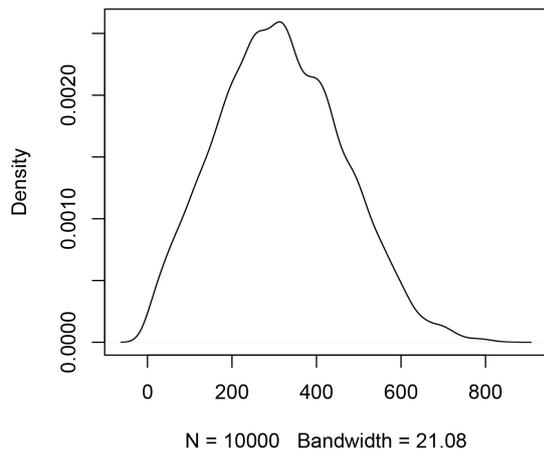
#### Uniform



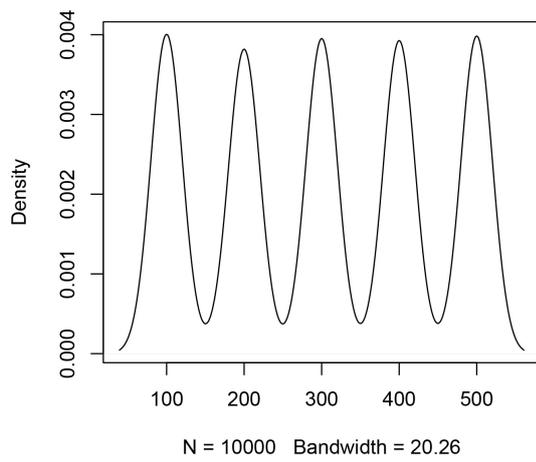
#### Triangular



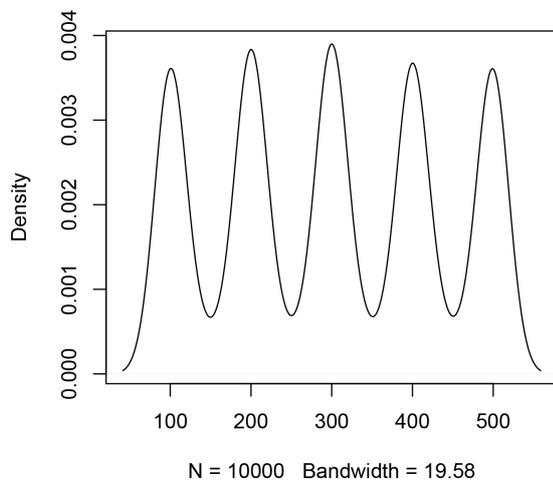
Normal



Bootstrapping



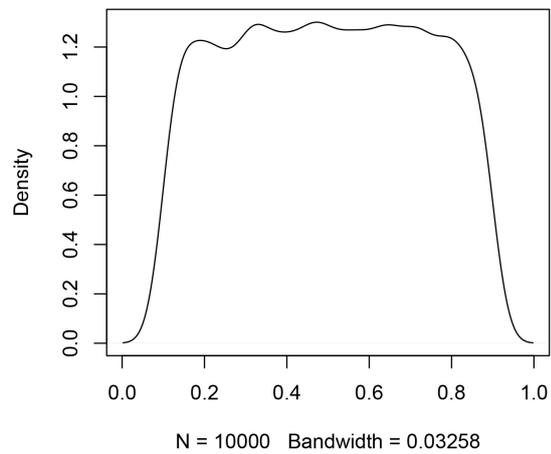
Bayes Monte Carlo



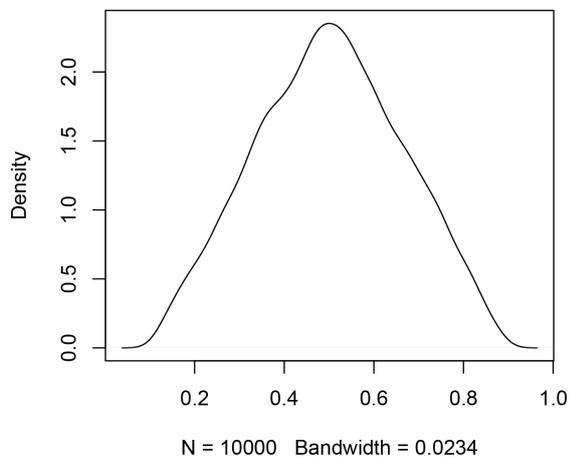
## B) Material transfer

Probability distributions based each time on the raw values 0.1, 0.4, 0.5, 0.6 and 0.9

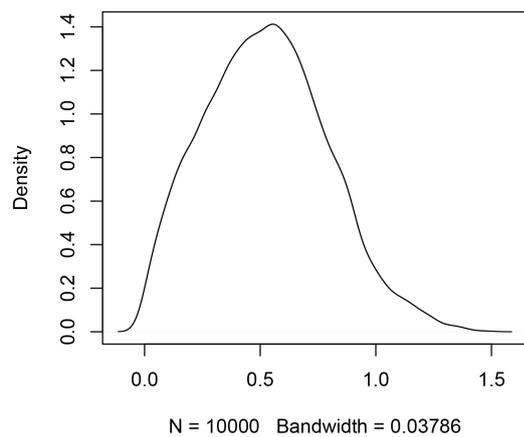
## Uniform



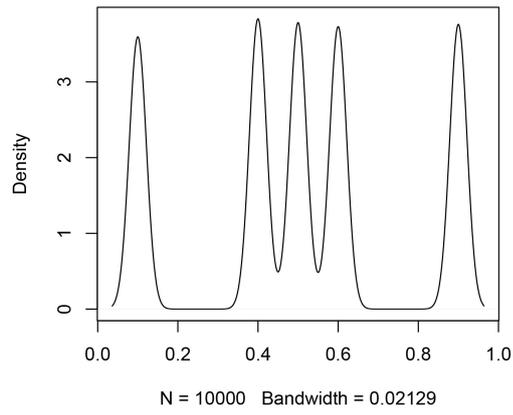
## Triangular



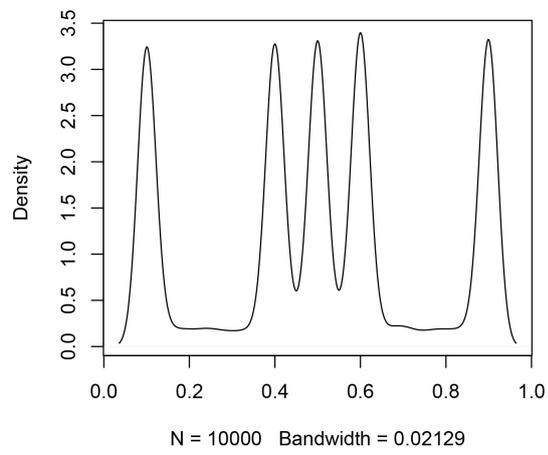
## Normal



### Bootstrapping



### Bayes Monte Carlo



### 2.4.3. Conclusion, current state of development and use conditions

The software development for general use in science and in consultation differs fundamentally from very specific modeling and programming for research studies. Instead of using scientifically based problem solving from computer models for specific questions, one has to develop a software for general use contexts. Such contexts require that the programmer retain a large use context and user skills spectrum in their focus that represents a much higher programming challenge than specific problem solving software.

The developed software packages represent elemental units of reproducible R modeling that are based on reusable R functions. R code scripts are shown in Appendix 5.3.

The work steps presented above were:

- A) Package metadata
- B) R-Code
- C) Compiled code
- D) Namespaces
- E) Object documentation
- F) Vignettes
- G) Testing
- H) Data
- I) Installed files

For the PSSD R package, the parts A through I (with the exception F) have been conducted. For the PMFA R package, parts A through E, H and I have been performed. Part G should be finished this month.

The presently available R packages are designed and implemented so that they can also be used by inexperienced academics and consultants, in principle, after a brief introduction.

The risk tool will soon be realized. It links the two existing packages and creates a risk quantification from the stochastic exposure and effect modeling.

The developed software is for the SUN DSS, additional terms of use will be agreed upon in detail with interested partners.

#### 2.4.4. References

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### 3. Deviations from the Workplan

There was one deviation from the workplan as explained in the introduction to part: The R package development work replaced the initially intended ETSS research on improving landfill modeling, which included the compartment where most of the ENM probably end up. The particular challenge in the landfill work would have been to understand and also model the fate of nanomaterials from a long-term perspective, based on a very thin data base. Thus, developing a model for long-term ENM release modeling and monitoring would have been an essential part of this work.

However, the work on landfill release modeling was not started as required by the SUN coordinators. Hence, ETSS focused, under high pressure, on the development of probabilistic software for environmental exposure and effects (along with risk analysis). The tools should be linked to the SUN DSS (decision support system). This deviation from the work plan occurred with the approval of the coordinator and work package leader.

The workload required for the tools' development has been (and continues to be) much higher than what would have been required for the above mentioned, initially planned study.

## 4. Conclusions

### 4.1. Overall Conclusions

The work performed in this task has improved the material flow modeling of ENM significantly, both for the flows to the environment as well as the fate in technical systems. Dynamic processes were for example included in the waste incineration modeling. The probabilistic release and material flow modeling performed for recycling and waste incineration plants fully considers the uncertainty and variability of all model parameters, enabling to make use of all data and information that are available. The modeling of the waste stage has been shown to be very important as most ENM will end up in these compartments at the end of their life cycle. SUN has played a seminal part in this assessment of the waste flows.

The provision of user-friendly R-codes that were further developed based on existing flow, hazard and risk models available at Empa and ETSS constitutes another important step forward in our ability to model the risks of ENM. The stochastic method used in the codes has been specifically designed to cope with large uncertainty and/or variability in the model input and output.

### 4.2. General review of release data

The review of the MFA models allowed us to make a description of the approaches and strategies implemented to reproduce the ENM flows from nano-applications to the environment. The main limitation faced by all modelers is that the information needed to feed those models is almost inexistent. One key missing point are methods and procedures for the definition of the transfer coefficients. This would render a better assessment and exploitability of the data available in the literature. We observed that the MFA models describe mainly the flows of pristine ENMs, that is, the physico-chemical transformations undergone by ENMs between their production and their release are

usually ignored. We noticed, too, that advanced characterization of the released ENM is usually unavailable and that the incorporation of dynamic assessments has only been used in a limited number of models. Uncertainty is dealt with using probabilistic frameworks, scenarios, or a combination of both. Below, based on our evaluation of the literature, we provide some recommendations for both modeling and release assessment, that could help MFA modeling advance towards a more realistic assessment of ENM release.

Our recommendations for MFA models start with the idea to provide a method or procedure for the definition of the transfer coefficients. This would facilitate the setting of objective criteria for the selection of the articles and the methods to exploit the data available in them. Most importantly, this would allow to interpret better the meaning of the transfer coefficients, to evaluate the quality of the results those models present, and to quantify with a stronger quantitative basis the uncertainty associated to their use. One important focus should be tracking the amounts used, instead of the amounts produced, because international trade in ENMs separates the region of production from the region of use (and, therefore, release in a particular compartment).

Regarding the use of nanomaterials in specific applications, a more systematic assessment of the product categories should be done based on their release potential. Researchers in the exposure assessment field should strive to improve assessments of the release potential for today's ENM applications. There is a need for coherent evaluation of release across the whole spectrum of contemporary applications because that spectrum is set to expand significantly in the future.

Regarding the characterization of the nanomass released, the assessment performed should go beyond size, shape and composition by TEM/SEM images and EDX analysis. More environmentally relevant measurements should be performed and reported. One measurement that we consider very relevant is the particle size distribution of the species generated during release. However, researchers should consider providing data about the ENM appearance, composition and the parameters that affect their interaction with the environment. A more systematic assessment of transformations should be performed to describe the relevant ENM sub-species that are generated during the average use of nano-applications. The determinants of release should go beyond basic assessment. An enhanced assessment could involve the development of improved protocols for release assessment that balance the control exerted to the factors affecting the experiment and the simulation of scenarios that resemble the average use of an application.

### **4.3. Stochastic modeling of waste incineration**

Our model demonstrated the overall consistency of the measurement data. Particular strengths of the model are the evaluation capability for the uncertainty (variability) of each single material transport/sink by means of probability estimations at any stage (time and location) of the MSWI process. Although the precise quantification of these amounts still remains difficult, this type of modeling provides an idea of the possible and most likely range of results. A potential extension of the model could be the inclusion of non-rhythmic material transfer, or in other words a variability of travel times. Irregular pulse releases of fly ash from the boiler or the varying emission of waste water from the wet scrubber are such candidates. These varying releases could be considered with an extension to non-linear computations that go beyond our cumulative perspective, which is for now limited to examining what is discovered (or not) in the ENP flows and sinks up to a certain point in time and under average conditions.

Further studies on the behavior of other ENP in incineration plants could take into account how changing waste compositions could affect the reactivity of ENP less stable

than CeO<sub>2</sub>. Our analysis can be easily extended to the fate of other ENP, including potential release to the atmosphere. An additional application of the method might be the investigation of pollutants that are carried by ENP through the incineration plant. In such a case, depending on the chemical bonding between the ENP and the other compounds, the modeling may follow a similar structure as used with solely ENP.

#### 4.4. ENM flows in recycling

Recycling products containing ENMs does not result in significant dissipation of nanomaterials to other (new) products. Rather, a large proportion of nanomaterials will very likely end-up in waste fractions that can be properly handled. Our research shows that nano-TiO<sub>2</sub>, nano-ZnO and nano-Ag, in consumer products are mainly associated with fractions that are not recovered during the recycling processes and that are subsequently incinerated or landfilled. For CNTs, the largest fraction is exported from Switzerland as material fractions that undergo further recovery processes (batteries, printed circuit boards and non-ferrous metals). Smaller quantities of the four ENMs covered in this work are expected to flow back to the productive process of the economy, mainly through recycling of construction waste and plastics. Some minor releases of nano-TiO<sub>2</sub> and nano-Ag to waste water are likely to happen. Our results suggest that the risk assessment of ENMs during recycling should focus on occupational exposure, the release of nanomaterials to the environment in waste incineration plants and landfills, and the evaluation of hazards in a small number of sectors that use inputs containing nanomaterials.

#### 4.5. R codes

The software development for general use in science and in consultation differs fundamentally from very specific modeling and programming for research studies. Instead of using scientifically based problem solving from computer models for specific questions, one has to develop a software for general use contexts. Such contexts require that the programmer retain a large use context and user skills spectrum in their focus that represents a much higher programming challenge than specific problem solving software.

The developed software packages represent elemental units of reproducible R modeling that are based on reusable R functions. The presently available R packages are designed and implemented so that they can also be used by inexperienced academics and consultants, in principle, after a brief introduction. The developed software is for the SUN DSS, additional terms of use will be agreed upon in detail with interested partners.

## 5. Annex

### 5.1. Supporting information for “A critical review of engineered nanomaterial release data: Are current data useful for material flow modeling?”

**Table S1.** Assessment of the sources for the definition of the transfer coefficients (TCs) used in MFA model articles (only during use-phase assessment). The table shows how many release literature articles were used in each model, the respective references (second and third columns), as well as the complementary sources used to define the TCs (last column).

Model	Release literature articles used as source for the TCs definition		Complementary sources
	Number	References	
Boxall et al. (2007)	0	-	Emission data of not nano-applications taken from scientific publications.
Blaser et al. (2008)	1	Kumar et al. (2005)	-
Mueller and Nowack (2008)	0	-	“Information on product life-cycles and disposal in Switzerland” Authors’ assumptions/Expert knowledge
Gottschalk et al. (2009)	1	Benn and Westerhoff (2008)	Previous model studies (Blaser et al. (2008)) Authors’ assumptions/Expert knowledge
O’Brien and Cummins (2011)	0	-	Previous model studies (Mueller and Nowack (2008)) Authors’ assumptions/Expert knowledge
Tiede et al. (2011)	0	-	EU technical guidance document Author’s estimations
Keller et al. (2013)	3	Benn and Westerhoff (2008) Kaegi et al. (2008) Windler et al. (2012)	Previous model studies (Boxall et al. (2007), Blaser et al. (2008), Mueller and Nowack (2008), Gottschalk et al. (2010), O’Brien and Cummins (2010))
Keller and Lazareva (2013)	0	-	“Estimated releases during use were based on available studies”. The sources seem to be the same as Keller et al. (2013)
Markus et al. (2013)	3	Benn and Westerhoff (2008) Lorenz et al. (2012) Kaegi et al. (2010)	Model studies (Boxall et al. (2007), Lorenz (2011))
Arvidsson et al. (2014)	4	Benn and Westerhoff (2008) Geranio et al. (2009) Benn et al. (2010) Hjärtnäs and Blom (2009)	-
Keller et al. (2014)	0	-	Consumer survey
Sun et al. (2014)	4	Geranio et al. (2009) Lorenz et al. (2012) Kaegi et al. (2008) Kaegi et al. (2010)	Authors’ assumptions/Expert knowledge
Bornhoeft et al. (2016)	0	-	Model studies (Sun et al. (2014)) Technical reports Authors’ assumptions/Expert knowledge
Sun et al. (2015)	0	-	Model studies (Sun et al. (2014))
Wigger et al. (2015)	5	Yan et al. (2012) Kulthong et al. (2010) Benn and Westerhoff (2008) Geranio et al. (2009) Lorenz et al. (2012)	Release studies Other scientific literature and reports
Gottschalk et al. (2015)	2	Park et al (2008) Johnson and Park (2012)	Model studies (Sun et al. (2014)) Authors’ assumptions/Expert knowledge Other scientific literature and reports

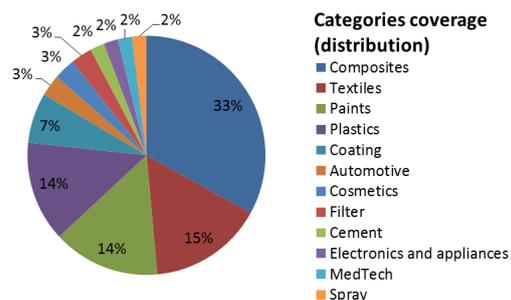
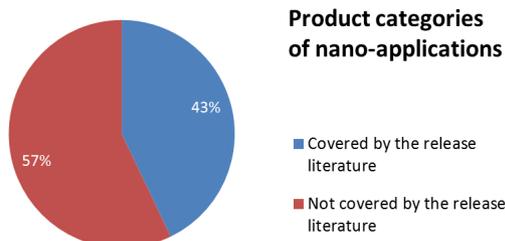
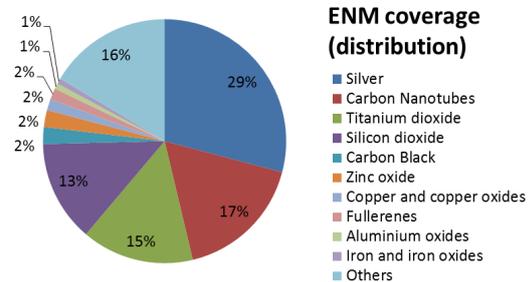
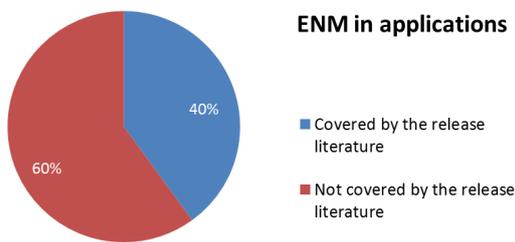
**Table S2.** Complete list of literature on release of ENM from applications. The column *SEL* describes whether the article was selected or not for our review.

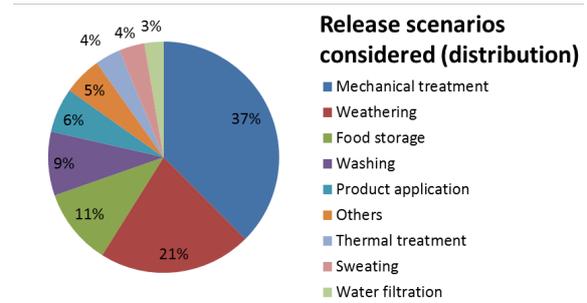
#	Study	Application	ENM	Description	Sel
1	Al-Kattan et al. (2013)	Paint	TiO <sub>2</sub>	Release of ENM on weathering chamber	Yes
2	Al-Kattan et al. (2014)	Paint	TiO <sub>2</sub>	Behavior of ENM in aged and milled paint	Yes
3	Al-Kattan et al. (2015)	Paint	SiO <sub>2</sub>	Release of ENM on weather chamber	Yes
4	Artiaga et al. (2015)	Plastic food container	Ag	Migration of ENM in food containers into food simulants	Yes
5	Bello et al. (2008)	CNT forests	CNT	Exposure to CNT during its production in university labs	No
6	Bello et al. (2009)	CNT hybrid advanced composites	CNT	Airborne exposure to nanoparticles and fibers generated during dry and wet abrasive machining	No
7	Bello et al. (2010)	CNT hybrid advanced composites	CNT	Airborne exposure to nanoparticles and fibers generated during solid core drilling	No
8	Benn and Westerhoff (2008)	Socks	Ag	Release of ENM during washing of socks	Yes
9	Benn et al. (2010)	Shirt, medical mask, medical cloth, toothpaste, shampoo, detergent, towel, teddy bear	Ag	Release of ENM during washing of consumer products	Yes
10	Bernard et al. (2011)	Graphene/polyurethane composite	C60	Release of ENM during UV exposure	No
11	Bielefeldt et al. (2013)	Ceramic pot filter	Ag	Release of ENM from coated surfaces representative of ceramic pot filter	Yes
12	Blazquez et al. (2014)	-	-	SURVEY on the experimental approaches to assess ENM release from nanocomposites	No
13	Bott et al. (2011)	Low density polyethylene (LDPE) films	Ag	Migration of ENM from low density polyethylene (LDPE) to aqueous food simulant	Yes
14	Botta et al. (2011)	Sunscreen	TiO <sub>2</sub>	Characteristics and behavior of ENM in sunscreens when released into water	Yes
15	Bouillard et al. (2013)	"Acrylonitrile butadiene styrene matrix"	CNT	Release of ENM during combustion of composites at EoL stage	No
16	Bourbigot et al. (2010)	PS, PS/P16, PS/OH16, PS/VB16	CNT	Effect of incorporation of ENM to polymers on flammability retardance	No
17	Busquets-Fité et al. (2013)	PA6, PP, EVA	TiO <sub>2</sub>	Release and recovery from model nanocomposites	No
18	Cena et al. (2011)	Epoxy	CNT	Release of ENM from epoxy samples during manual sanding	No
19	Cleveland et al. (2012)	Sock, wound dressing, teddy bear	Ag	Release of ENM in textiles deposited in a mesocosm	No
20	Cushen et al. (2013)	PVC nanocomposites	Ag	Migration of ENM from PVC nanocomposite to chicken meat	Yes
21	Cushen et al. (2014)	PE nanocomposites	Ag	Migration of ENM from PE nanocomposite to chicken meat	Yes
22	Cushen et al. (2014)	PE nanocomposites	Ag	Migration of ENM from PE nanocomposite to food simulant	Yes
23	Duncan (2015)	Polymer composites	-	REVIEW what is known about the release of ENMs from polymer nanocomposites by matrix degradation	No
24	Duncan and Pillai (2015)	Polymer composites	-	REVIEW what is known about the release of ENMs from polymer nanocomposites by diffusion, dissolution, desorption	No
25	Echegoyen and Nerin (2013)	Plastic bags and boxes	Ag	Migration of ENM from food storage bags and boxes to food simulant	Yes
26	Farkas et al. (2011)	Washing machine	Ag	Release of ENM during the operation of a washing machine with silver filter	Yes
27	Fiorentino et al. (2015)	Paints	SiO <sub>2</sub>	Factors influencing release of ENM in paints	Yes
28	Geranio et al. (2009)	Socks and textile fabrics	Ag	Release of ENM from textile fabrics during washing	Yes
29	Goehler et al. (2010)	Paint	ZnO	Release of ENM from painted surfaces during sanding	No
30	Goehler et al. (2013)	Paint	TiO <sub>2</sub>	Release of ENM from painted surfaces	No

#	Study	Application	ENM	Description	Sel
				during sanding, dynamic friction and wind erosion	
31	Golanski et al. (2010)	Polymethyl methacrylate	CNT	Release of ENM from polymethyl methacrylate during abrasion	No
32	Golanski et al. (2011)	Paint	TiO <sub>2</sub>	Release of ENM from PVC and glass substrates during wet and dry abrasion tests	No
33	Golanski et al. (2012)	PC epoxy and PA11 polymers	CNT	Release of ENM by simulation of mechanical stresses (abrasion, scratching, mechanical shocks)	No
34	Gomez et al. (2014)	Epoxy-based polymers and paints	CNT	Release of ENM from nanoproducts during sawing and sanding	No
35	Gondikas et al. (2014)	Sunscreen	TiO <sub>2</sub>	Survey on the amount and characteristics of ENM released into the Old Danube river	No
36	Gorham et al. (2012)	Epoxy composites	Si	Release of ENM from epoxy resins during exposition to UV light	No
37	Guiot et al. (2009)	PET+PVC composite	Clay	Release of ENM from composite during abrasion	No
38	Hauri and Niece (2011)	Food container boxes	Ag	Migration of micro-sized silver to water and acetic acid	Yes
39	Hirth et al. (2013)	TPU, POM and cementitious composites	CNT	Release of ENM from composites during UV exposure and mechanical stress	No
40	Holbrook et al. (2013)	Sunscreen	TiO <sub>2</sub>	Survey on the amount of ENM released into a swimming pool	Yes
41	Holbrook et al. (2014)	Wound dressing	Ag	Dynamic assessment of release during wetting of wound dressing	Yes
42	Hsu and Chein (2007)	Coating	TiO <sub>2</sub>	Release of ENM coating in wood/polymer/tile by weathering (UV, fan) and rubber knife stress	Yes
43	Huang et al. (2011)	Polyethylene plastic bags	Ag	Migration of ENM from plastic bags to food simulant	Yes
44	Huang et al. (2012)	Epoxy-based nanocomposite material and 2 commercial products not identified	CNT	Release of ENM in epoxy resin by sanding and 2 commercial products not identified	No
45	Impelliteri et al. (2009)	Socks	Ag	Speciation of released ENM from socks exposed to hypochlorite/detergent solution	Yes
46	Jiang et al. (2014)	PS composite	CNT	Release during thermal treatment and abrasion	No
47	Jokar and Abdul-Rahman (2014)	PE nanocomposites	Ag	Migration of ENM from plastic bags to food simulant	Yes
48	Joyce-Wöhrmann and Münstedt (1999)	Polyurethanes	Ag	Description of ions release from catheters.	No
49	Joyce-Wöhrmann et al. (2000)	Catheters	Ag	Testing of the mechanical characteristics of catheters coated with silver and compare to non-coated ones.	No
50	Kaegi et al. (2008)	Outdoor paint	TiO <sub>2</sub>	Release of ENM into the runoff water from outdoor painted surfaces	Yes
51	Kaegi et al. (2010)	Outdoor paint	Ag	Release of ENM into the runoff water from outdoor painted surfaces	Yes
52	Kingston et al. (2014)	Polymer composites	CNT	REVIEW of the studies on ENM release from epoxy, polyamide, polyurethane, polyethylene and polycarbonate	No
53	Koponen et al. (2009)	Paint	TiO <sub>2</sub>	Release during sanding	No
54	Koponen et al. (2011)	Wall and wood coatings	TiO <sub>2</sub>	Release during sanding of ENP doped paints, lacquers and fillers	No
55	Kulthong et al. (2010)	Laboratory produced and commercial fabrics	Ag	Release of ENM from lab-produced fabrics and commercial shirts immersed into artificial sweat	Yes
56	Künninger et al. (2014)	Silane and Alkine coatings	Ag	Release of ENM into runoff water from outdoor wood surfaces	Yes
57	Le Bihan et al. (2013)	Iron alloy shaft cap	C60	Release of ENM from an iron alloy coated, during 9 different scenarios (8 realistic and one extreme)	Yes
58	Lin et al. (2014)	Food packaging films	TiO <sub>2</sub>	Migration of ENM from food packaging films into food simulants	Yes
59	Lombi et al. (2014)	Socks, shirts, trousers	Ag	Release of ENM from clothes during	Yes

#	Study	Application	ENM	Description	Sel
60	Lorenz et al. (2011)	Anti-perspirant, shoes and plant food sprays	Ag	washing Release of ENM from spray products during their application	Yes
61	Lorenz et al. (2012)	Socks, shirts, trousers	Ag	Release of ENM from clothes during washing	Yes
62	Mazzuckeli et al. (2007)	Polymer composites	CNF	Release during laboratory operations	No
63	Methner et al. (2012)	Epoxy-based composite	CNF	Release during dry material handling, wet cutting, grinding and sanding	No
64	Mitrano et al. (2014)	Socks	Ag	Release and speciation of ENM during textiles household washing	Yes
65	Mittelman et al. (2015)	Ceramic water filter	Ag	Release of ENM in ceramic water filter and the influence of water chemistry on release	Yes
66	Moreau et al. (2012)	Dental restoration composites	Ca	Effect of wear, thermal-cycling and water aging in the mechanical durability of dental nanocomposites	No
67	Mosurkal et al. (2008)	PS organoclay composite	TiO <sub>2</sub>	Flame retardant properties of nanoclay based polymers	No
68	Motzkus et al. (2011)	PMMA and PA-6 composites	Al <sub>2</sub> O <sub>3</sub>	Characterization of the aerosols emitted during the combustion of composites	No
69	Nguyen et al. (2011)	Amine-cured composites	CNT	Release during UV exposition	No
70	Nguyen et al. (2012)	Epoxy polymer filled with nanosilica	Si	Release of ENM from nanocomposite degraded by UV light	No
71	Njuguna and Sachse (2014)		-	REVIEW of analytical techniques for measuring airborne ENM	No
72	Noonan et al. (2014)	No specific product	-	REVIEW of release from food container composites	No
73	Nyden and Gilman (1997)	NSP	C	Dynamic simulations of thermal degradation of a model of polypropylene/graphite nanocomposite	No
74	Ogura et al. (2013)	Polystyrene composite	CNT	Release during grinding	No
75	Olabarrieta et al. (2012)	Glass coated	TiO <sub>2</sub>	Release of ENM from a coated glass subject to weathering and a constant flow of water	No
76	Pasricha et al. (2012)	Fabrics	Ag	Release of ENM during washing of textiles fabrics	Yes
77	Quadros and Marr (2011)	Hunter, disinfecting and throat sprays	Ag	Release of ENM from spray products during their application	Yes
78	Quadros et al. (2013)	Toy, blanket (+8)	Ag	Leaching of ENM from consumer products for babies over different release scenarios	Yes
79	Rabb et al. (2010)	Epoxy films	Si	Release of ENM from artificially weathered epoxy film	No
80	Raynor et al. (2012)	Polypropylene resins	Clay	Release during shredding, a characteristic procedure in recycling	No
81	Ren and Smith (2013)	Ceramic water filter	Ag	Release of ENM from ceramic filter evaluating the effect of NP size, capping agent, application method and others.	Yes
82	Rigo et al. (2012)	Burn wounds dressing	Ag	Release of ENM from burn-wound dressings in different liquid media	Yes
83	Saber et al. (2012)	Paint and lacquer	TiO <sub>2</sub> , SiO <sub>2</sub> , +3	Release of ENM during sanding	No
84	Sachse et al. (2012a)	PA6 composites	Clay	Release of ENM during drilling of PA6 composites	No
85	Sachse et al. (2012b)	PA6 composites	Clay	Release of ENM during drilling of PA6 composites	No
86	Sachse et al. (2013)	Crash cones	Si	Release of ENM from crash cone simulating low velocity impacts	No
87	Schlagenhauf et al. (2012)	Epoxy-based composite	CNT	Release during abrasion of epoxy composites	No
88	Schlagenhauf et al. (2014)	Polymer composites	CNT	REVIEW paper of CNT release due to mechanical impact, weathering and fire	No
89	Shandilya et al. (2015)	Photocatalytic coating applied on a masonry brick	TiO <sub>2</sub>	Release of ENM from a masonry brick during weathering and abrasion	Yes
90	Song et al. (2011)	Polyethylene plastic bags	Ag	Migration of ENM from plastic bags to food simulant	Yes
91	Stefaniak et al.	Polyester fabrics	Ag	Release of ENM from polyester textiles	Yes

#	Study	Application	ENM	Description	Sel
	(2014)			which are immersed in artificial biological human liquids	
92	Sung et al. (2014)	Epoxy coating	Si	Release of ENM from an epoxy coating subject to UV irradiation	No
93	Tang and Lewin (2014)	Polymer composite	Clay	Release of ENM from polypropylene composites during and after annealing	No
94	Uddin et al. (2011)	PE foam	CNF	Release during firing of polyurethane (PE) foam	No
95	Vilar et al. (2013)	PA6 composite	SiO <sub>2</sub>	Release of ENM from PA6 composite subject to accelerated climatic aging	No
96	von Goetz et al. (2013)	Polypropylene containers	Ag	Migration of ENM from plastic bags to food simulant	Yes
97	von Goetz et al. (2013)	Socks, shirts, trousers, pants	TiO <sub>2</sub>	Release of ENM from diverse fabrics (cotton, polyester, etc.) into artificial sweating	Yes
98	Vorbau et al. (2009)	PE coating, UV curable clearcoat, white pigment coating applied on fiberboard plate, steel panel and fiber cement plate	ZnO	Method development for the characterization of particles released during abrasion of surfaces coatings	No
99	Windler et al. (2012)	Shirts + reference materials	TiO <sub>2</sub>	Release of ENM during washing	Yes
100	Wohlleben et al. (2011)	CEM, PA, POM composites	CNT	Release of ENM from thermoplastics and cementitious composites due to abrasion, sanding and UV exposure	No
101	Wohlleben et al. (2013)	Thermoplastic PU	CNT	Release of ENM from PU thermoplastic during sanding, abrasion and UV exposure	No
102	Wohlleben et al. (2014)	PA composite	SiO <sub>2</sub>	Release of ENM from PA composite during weathering	No
103	Yan et al. (2012)	Textiles	Ag	Release of ENM from textile fabrics immersed into artificial sweat	Yes
104	Zanna et al. (2010)	Anti-fouling coating	Ag	Release of ENM from stainless steel coated with antifouling material and immersed in salted water	Yes
105	Zuin et al. (2014a)	Paint	TiO <sub>2</sub>	Release of ENM from painted fiber-cement panels during UV exposure and water immersion	Yes
106	Zuin et al. (2014b)	Paint	SiO <sub>2</sub>	Release of ENM from paint debris	Yes





**Figure S1.** How the literature on ENM release (all studies) covers the different types of ENM used currently in applications (top), the product categories of the whole spectrum of applications (middle), and different possible release scenarios (bottom). The top and middle charts on the left use as reference the number of ENMs according to DaNa 2.0 (2015) and the product categories defined by Sun et al. (2014).

Flow No	StDev (%)	Begin experiment																Information on the type of modeled function and on the value derivation for time periods with no measurements (NM)		
		00:30	01:00	01:30	02:00	02:30	03:00	03:30	04:00	04:30	05:00	05:30	06:00	06:30	07:00	07:30	08:00		08:30	
1	0	8139.5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	f(t): for t <= 1: m <sub>11</sub> ·t; for t > 1: m=0 (cumulative modeling of detected material up to a particular time)	
2		Values calculated with the model																		
3	20	0.0311	0.0311	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	f(t) = m <sub>11</sub> ·exp(-λ·t), range of λ (degradation constant): 3.2-4.8	
4	2.5	4069.6	4069.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	f(t) = for t <= 1: m <sub>11</sub> ·t (approx. 20 s delay considered compared to FI1); for t > 1: m=0; with StDev in % as indicated (up front), (cumulative modeling of detected material up to a particular time)	
5		≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	default value smaller than 10 <sup>-9</sup> at any time	
6		Values calculated with the model																		
7	20	0.1553	0.1553	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	f(t) = m <sub>11</sub> ·m <sub>11</sub> ·exp(-λ·t); range of λ (degradation constant): 2-3	
8	14.4	nm	nm	nm	nm	147.5778	147.5778	45.2807	50.1807	50.1723	70.0223	16.5724	nm	nm	nm	nm	nm	nm	f(t) = measurements and for t <= 0.5: m <sub>12.5</sub> /2·t; for t > 0.5 and t <= 2 the same values as for t > 2 and t <= 3; for t > 5.5: halving every hour (7 times) the one hour mass of the previous period (cumulative modeling of detected material up to a particular time)	
9	14.4	nm	nm	nm	nm	nm	nm	158.303	155.709	697.209	1037.500	551.500	nm	nm	nm	nm	nm	nm	f(t) = measurements and for t <= 2: m = 10 <sup>-9</sup> ·t (almost zero value); for t > 2 the one hour mass of the following one hour period; for t > 8: halving every hour (7 times) the one hour mass of the previous period (cumulative modeling of detected material up to a particular time)	
10		≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	see comments on FI5	
11	7.5	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	see comments on FI5	
12	24.7	nm	nm	nm	nm	nm	nm	158.300	155.700	697.200	1037.500	551.500	nm	nm	nm	nm	nm	nm	f(t) scaled on f(t) of FI9 with approx. 120 seconds delay compared to FI9 and StDev in % as indicated up front	
13		Values calculated with the model																		
14	7.5	nm	nm	nm	nm	0.0034				0.0184				nm	nm	nm	nm	nm	f(t) = measurements and for t < 2: 10 <sup>-9</sup> ·t; for t > 6: halving every hour (5 times) the one hour mass of the previous period combined with a 1/10 mass loss per hour of pre-existing cumulative mass (semi cumulative modeling)	
15		Values calculated with the model																		
16		nm	nm	nm	nm	0.0315	0.0048	0.0107	0.0074	0.0035	nm	nm	nm	nm	nm	nm	nm	nm	f(t) scaled on f(t) of FI8 with StDev in % as indicated for f(t) of FI8	
17	25	nm	nm	nm	nm	103.2938	15.8375	35.1050	24.5000	11.5850	nm	nm	nm	nm	nm	nm	nm	nm	f(t) scaled on f(t) of FI8 with StDev in % as indicated up front	
18		nm	nm	nm	nm	95.9238	95.9238	29.4272	32.6122	32.6122	45.5147	10.7575	10.7575	nm	nm	nm	nm	nm	f(t) scaled on f(t) of FI8 with StDev in % as indicated for f(t) of FI8	
19		≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	see comments on FI5	
20		Values calculated with the model																		
21		nm	nm	nm	nm	0.0073	0.0011	0.0024	0.0017	0.0008	nm	nm	nm	nm	nm	nm	nm	nm	f(t) scaled on f(t) of FI16 with StDev in % as indicated for f(t) of FI16	
22	25	nm	nm	nm	nm	191.8313	29.4125	65.1950	45.5000	21.5150	nm	nm	nm	nm	nm	nm	nm	nm	f(t) scaled on f(t) of FI18 with StDev in % as indicated up front	
23	55.6	0.0096000		0.0325600				0.0586520				nm	nm	nm	nm	nm	nm	nm	f(t) measurements and for t > 5 the same periodical values as for the previous period; for t > 7: halving every hour (3 times) the one hour mass of the previous period (cumulative modeling of detected material up to a particular time)	
24		≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	see comments on FI5	
25		≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	see comments on FI5	
26	55.6	0	0	0.0166000				0.0185000				0.0224000				nm	nm	nm	nm	f(t) scaled on f(t) of FI23 with approx. 300 seconds delay compared to FI 23 and StDev in % as indicated up front
27		≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	Sampling filter below quantification limit of ICP-MS, see also comments on FI5	
28		Values calculated with the model																		
29	55.6	nm	nm	0.0099600	0.0060000	0.0228000	0.0060000	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	f(t) measurements and for t < 2: m <sub>12</sub> /2·t; for t > 3 and t <= 4: inconsistent 0.0288 replaced by 0.006; for t > 2.5: 1/40 mass loss per hour of pre-existing mass and transfer delay as for FI 26, for t > 5: halving every hour the one hour mass of the previous period with no new mass (t > 7.5) and mass halving (t > 15) in four-hourly intervals	