Review

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

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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.

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1. Introduction

Nanotechnology research and the production of engineered nanomaterials (ENMs) have grown steadily worldwide, but particularly in developed countries (EC, 2013). Nanoproducts 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; Stark et al., 2015). 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 nanoproducts 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 nanoproducts, use, and disposal of the nanomaterial and the nanoproduct. 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., 2009; Sun et al., 2016). 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. (2013) 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 nanoproducts, 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. 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., 2013).

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 (Fig. 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.

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 nanoproducts 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., 2013). An example of indirect transfer would be when nano-TiO$_2$ 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 nanoproduct 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., 2013). 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 nanoproduct, 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 nanoproduct 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 nanoproducts 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.
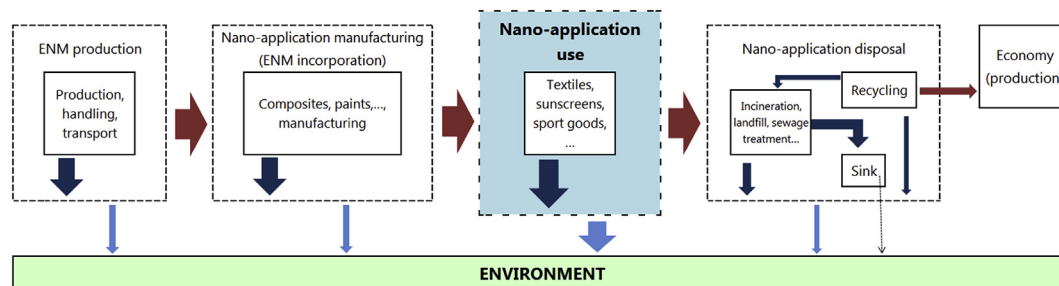
Fig. 1. ENM release during its life cycle, from ENM production to the nanoproduct disposal. The diagram highlights the fact that release may occur in two steps: the first step (dark blue arrows) occurs during the ENM or nanoproduct handling. The second step (light blue arrows) constitutes the final transfer 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). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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 ΔQ_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.

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.

3.1. 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.

3.2. 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.

Table 1
ENM release coefficients as a proportion of the initial mass content throughout the life cycle of a nanoproduct. This Table illustrates the case of a nanoproduct 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.

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

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. (2009)	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	Scenarios for ENM concentration in application and water treatment plant removal efficiency
Arvidsson et al. (2014)	Mechanistic	None	None	None	Scenarios for concentration of silver in clothes
Keller et al. (2014)	Product category assessment	None	None	None	Probabilistic assessment
Sun et al. (2014)	Product category and release scenario assessment	Ag and ZnO sulfidation	None	None	Probabilistic assessment of all model parameters
Sun et al. (2015)	Product category and release scenario assessment	Ag and ZnO sulfidation	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 ZnO sulfidation, and CeO_2 agglomeration	None	None	Probabilistic assessment of all model parameters
Bornhoeft et al. (2016)	Product category and release dynamics	CNT burning	None	ENM production and release coefficients	Probabilistic assessment

3.3. 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 larger amount of release assessment studies exists.

3.4. 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., 2014). 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 (Fig. 2). 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_2 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) (Fig. 2).

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).

3.5. 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 nano-silver concentration, multiplied by the fraction of silver released.

3.6. 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. (2009). 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. (2015) implemented
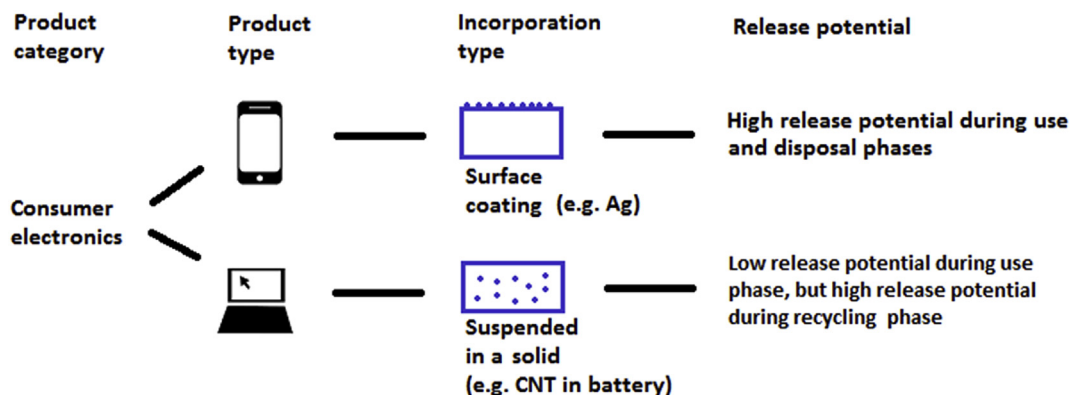

Fig. 2. Release potential of a nano-application is not dependent on the product category it belongs to, as some environmental exposure models assume. Rather, it depends on the initial allocation of the ENM and how it is incorporated into the application (surface bound, suspended in liquids, bound in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

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.

3.7. 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.

3.8. 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. (2010), numerous authors have implemented this method to describe the uncertainty using a probabilistic approach.

3.9. 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.

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 are 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 (Fig. 3). The used articles are mainly about nano-Ag release from textiles and other applications; only two nano-TiO_2 release articles have been used to derive a transfer coefficient.

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,
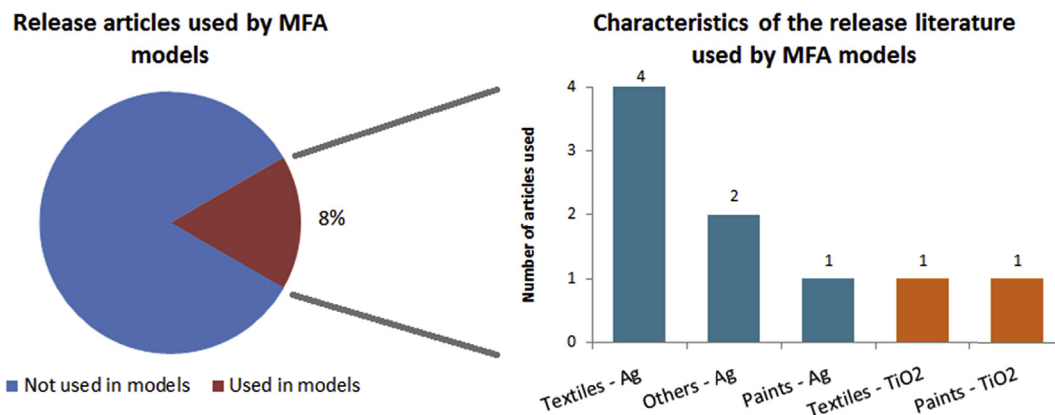
Release articles used by MFA models

Characteristics of the release literature used by MFA models

Fig. 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$_2$ in paints and textiles (right panel).

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 released 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$_2$ 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$_2$ 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.

4.1. 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 Fig. 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. (2014) 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 same assessment for all the 106 articles is available in the Supplementary Material as Fig. 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.

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) and the report produced by the French Ministry of Ecology (ANSES, 2014) 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.

4.2. Aspects of release described by the ENM release literature

The summary of the results on this sub-section are described as Fig. 5. We start the description of the aspects that we consider
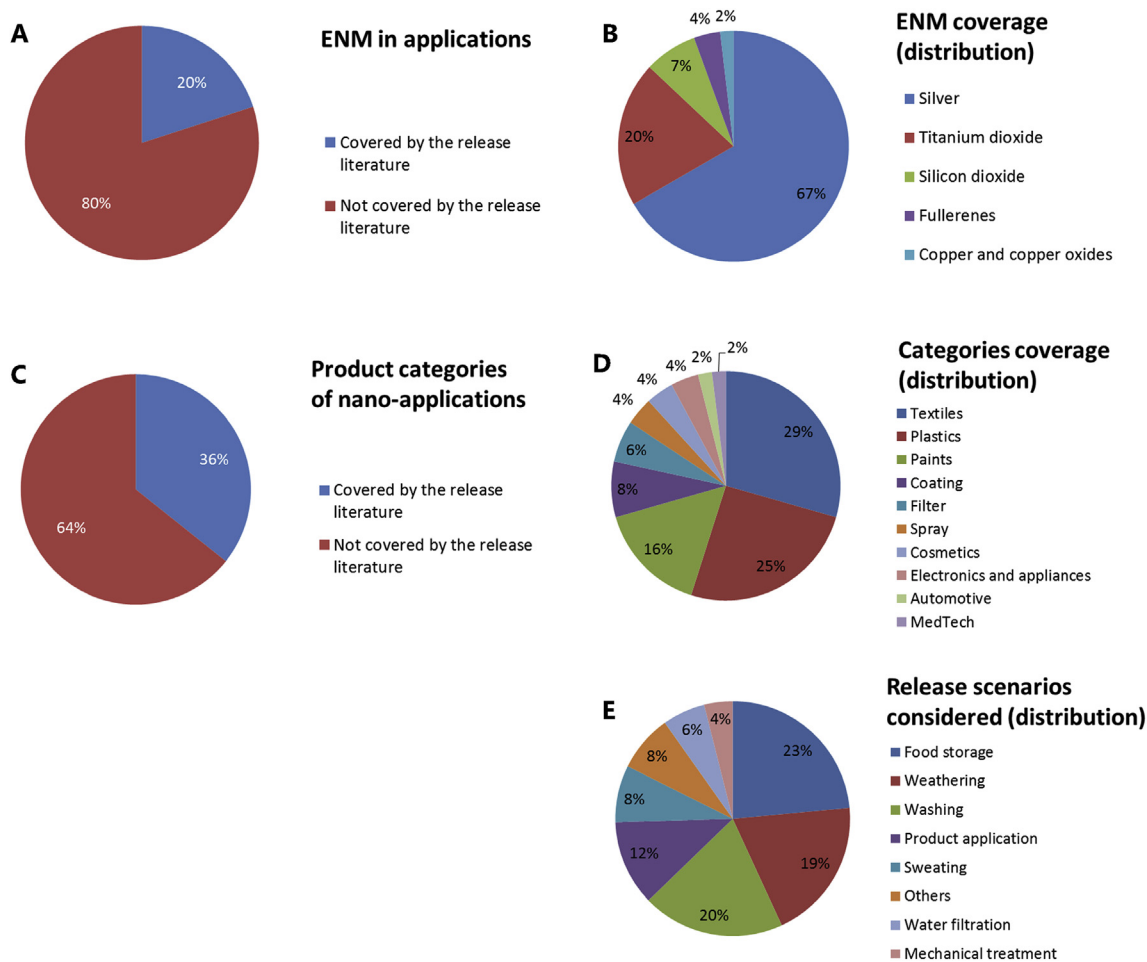

Fig. 4. How the literature on ENM release covers the different types of ENM used currently in applications (top), the product categories of the whole spectrum of applications (middle), and different possible release scenarios (bottom). The top and middle charts on the left use as reference the number of ENMs according to DaNa2.0 (2015) and the product categories defined by Sun et al. (2014). Note that these numbers apply only to the 49 articles selected. The same assessment for the all the 106 studies is available in Fig. S1 of the Supplementary Material.

Table 3

Coverage of applications and the ENM types in the literature on ENM release. 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. (2014), 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-changing mats, knickers, overalls, pants, pillow protector, shirts, shorts, socks, sweaters, ties, towels, trousers, working uniforms, leg warmer and more.	Ag, Au, Bamboo charcoal, $CaCO_3$, Carbon Black, CNT, Silica, TiO_2, ZnO	Shirts, socks, teddy bears and plush toys (Ag and TiO_2).	Washing of clothes, leaching into saliva and sweat 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., 2012; Yan et al., 2012; Quadros et al., 2013; 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, $CaCO_3$, Fe_2O_3, Graphite, Iron hydroxide, Silica, TiO_2, ZnO, (in)organic pigments.	Food containers (Ag and TiO_2).	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., 2013; 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, $CaCO_3$, Kaolins, Carbon black, CeO_2, CNT, Cu, SiO_2, TiO_2, ZnO, (in)organic pigments	Outdoor paints (Ag, SiO_2, TiO_2).	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 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, $BaSO_4$, $CaCO_3$, Carbon black, CeO_2, CNT, Cu, Pd, SiO_2, TiO_2, ZnO, (in)organic pigments	Coatings for bricks, metals, plastics, tiles and wood (Ag and TiO_2).	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_2, 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_2O_3, Au, Bisoctrizole, Carbon Black, Fe_2O_3 Magnesium salt, Silane, SiO_2, TiO_2, ZnO	Sunscreen (TiO_2).	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_2, 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 polyshing liquid, vinyl revitalizer, wheel protector liquid.	Al_2O_3, $CaCO_3$, Carbon black, CeO_2, CNT, SiO_2, Ti, Fullerenes 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, $CaCO_3$, CeO_2, CNT, Cu, Mn, Pd SiO_2, TiO_2, ZnO	Washing machines (Ag)	Machine operation	(Farkas et al., 2011) TOTAL: 1
MedTech	Bathing chair, mouth guard, acupuncture set, water flosser (dental cleaner), burn wound dressings	Ag, Attapulgite, CaO, Si, Silane SiO_2, TiO_2,	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_2	Toothpaste and disinfecting spray (Ah)	Toothpaste and spray application	(Quadros et al., 2013) TOTAL: 1
Aerospace	Fuselage parts	CNT	None	—	—
Batteries	—	Carbon black, Graphene, CNT, SiO_2	None	—	—
Cements	Cement, mortar	CNT, SiO_2, TiO_2	None	—	—

Table 3 (*continued*)

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
Cleaning agents	Deodorant bag, all purpose cleaner, liquid cleaner for bikes, floors, garments, refrigerators, stones, walls and more	Ag, Carbon black, TiO_2, SiO_2, ZnO	None	–	–
Composites	Rackets, bicycles, bicycles components,	Al, Carbon black, CNT, Graphite, Iron hydroxide	None		–
Energy	Thermal insulators	CeO_2, CNT, SiO_2	None	–	–
Food	Nutrition supplements	Ag, Ca, $CaCO_3$, Mg, SiO_2, TiO_2, Zeolite	None	–	–
Glass and ceramics	Self-cleaning glass	Ag, TiO_2, ZnO	None	–	–
Ink	Toners	$CaCO_3$, Carbon black, TiO_2	None	–	
Light bulbs	–	TiO_2	None	–	–
Metals	*See coatings*	$Al2O_3$, Carbon black, Iron hydroxide, Silane, SiO_2	None	–	–
Paper	–	Ag, $CaCO_3$, SiO_2, TiO_2, ZnO, cellulose	None	–	–
Sensors	–	CNT	None	–	–
Soil remediation	–	Ag, Ba, Ca, Carbon black, Mesotrione, SiO_2, TiO_2	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_2	None	–	–
Water treatment	–	Ag, SiO_2, TiO_2, Z nano-VI	None	–	–

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).

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, which is critical for the definition of TCs in MFA models. 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^2, 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, 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
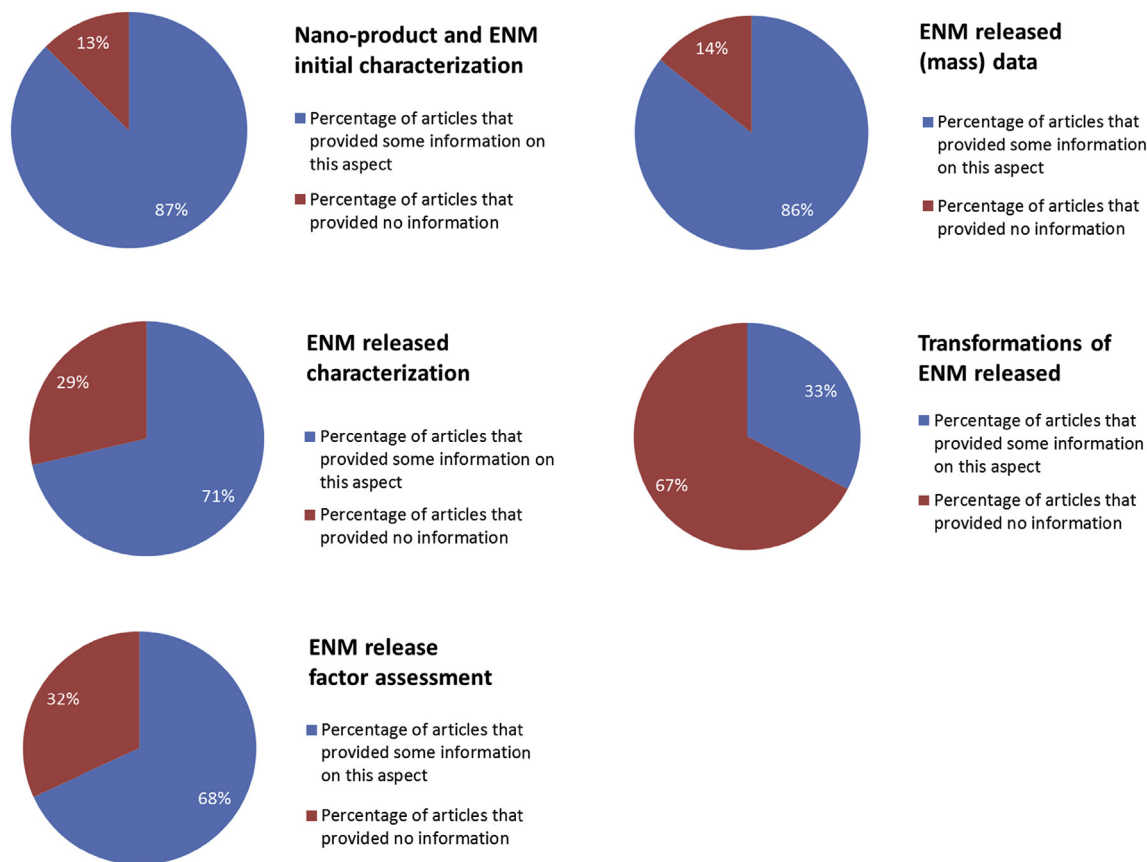
Nano-product and ENM initial characterization

13%
87%

- Percentage of articles that provided some information on this aspect
- Percentage of articles that provided no information

ENM released (mass) data

14%
86%

- Percentage of articles that provided some information on this aspect
- Percentage of articles that provided no information

ENM released characterization

29%
71%

- Percentage of articles that provided some information on this aspect
- Percentage of articles that provided no information

Transformations of ENM released

33%
67%

- Percentage of articles that provided some information on this aspect
- Percentage of articles that provided no information

ENM release factor assessment

32%
68%

- Percentage of articles that provided some information on this aspect
- Percentage of articles that provided no information

Fig. 5. Percentage of the selected studies 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.

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 we 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 ($\#/cm^3$), and the average emission rate ($\#/min$). Botta et al. (2011) assessed the characteristics and behavior of nano-TiO_2 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_2. 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_2 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_2 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$_2$. 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).

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 it 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 is 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 it 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 subspecies 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 (Wohlleben 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
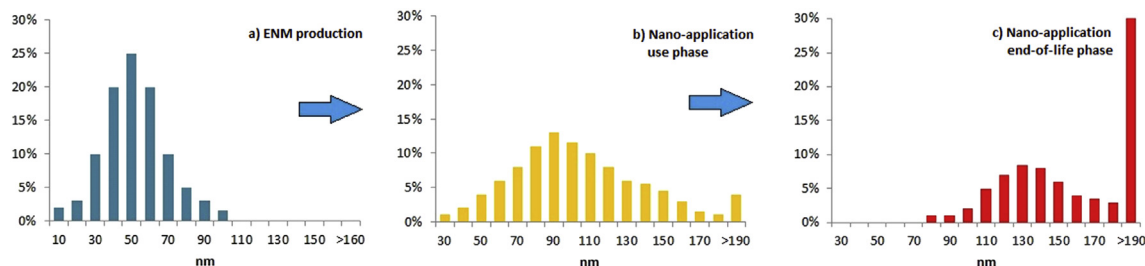

Fig. 6. Variation in the size distribution of engineered nanomaterials throughout their life cycle. (a) During production, the size distribution of the ENM powder will be largely within the nano-range. (b) During its incorporation into a nano-product, the ENM size can change due to agglomeration or functionalization 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.

environment (Fig. 6); (iii) be able to provide enhanced explanations of the ENM transformations; and (iv) be able to improve the dynamic modeling of release.

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 Fig. 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.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.02.028.

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