The Flows of Engineered Nanomaterials from Production, Use, and Disposal to the Environment

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Abstract The aim of this chapter is to evaluate what information is needed in order to quantify the flows of ENM to the environment by reviewing the current state of knowledge. The life cycle thinking forms the basis of the evaluation. The first step in release assessment is the knowledge about the production and use of ENM. Data on production are crucial for the assessment, because they determine the maximal amount that could potentially be released. The different life cycles of products containing the ENM are determining the release potential. The knowledge about the product distribution is therefore key to release estimation. The three important life cycle steps that need to be considered are production/manufacturing, the use phase, and the end of life (EoL) treatment. Release during production and manufacturing to the environment may occur because large amounts of pure material are handled. During the use and EoL phase, experimental data from real-world release studies are preferred; however, in most cases release has been estimated or guessed based on standard knowledge about product use and behavior. The mass flows discussed in this chapter provide the input data to derive environmental concentrations needed for environmental risk assessment of ENM. The mass flows to the environment will also be needed for environmental fate models that are based on mechanistic

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description of the reactions and the behavior of the released ENM in environmental compartments such as water or soils.

Contents

1   Introduction

The assessment of the environmental exposure to engineered nanomaterials (ENM) is still an area with limited information available. An ENM in the context of this chapter means any intentionally manufactured material, containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm [1]. The direct measurements of ENM at environmentally relevant concentrations are currently not possible with the existing analytical techniques [2, 3], and thus modeling is the only way to estimate environmental exposure concentrations. Nevertheless, we have sufficient information to conclude that environmental exposure to ENM is a reality and that numerous materials are actually present in the environment [2, 4]. However, quantitative information on the flows from products to the environment is still very scarce. This is due to the limited knowledge on the actual use of nanomaterials in products and processes and the dearth of investigations on release under real-world conditions. Within this chapter we combined the information available in the literature about production amounts, distribution to products, and release from products and to present the currently available mass flow models that quantitatively describe the flows of ENM from production to the environment. These mass flow data are needed as inputs to environmental fate models that are able to provide environmental concentrations of ENM, e.g., predicted environmental concentrations (PEC) values, needed for risk assessment.

The approach is based on the life cycle of production, manufacturing, use, and release (see Fig. 1). The knowledge about the production and use of ENM stands at
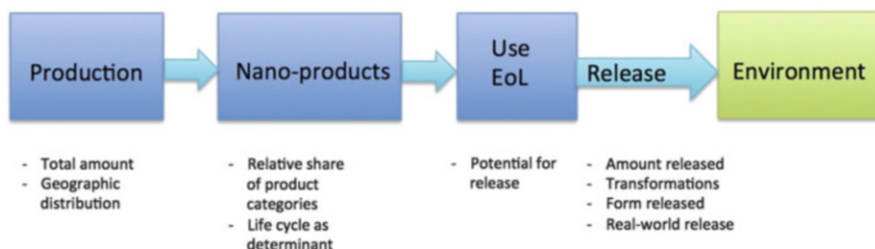
Fig. 1 Life cycle steps where information needs to be obtained in order to assess the flows of nanomaterials to the environment: production, distribution to product categories, and release. These steps are discussed in detail in this report. The *arrows* indicate information and not material flow. *EoL* end of life

the beginning of the exposure assessment. Data on production are crucial for exposure assessment, as they determine the maximal amount that could potentially be released. The life cycle of products is determining the potential for release, and thus knowledge on the actual product distribution is paramount to any exposure estimation [5]. The two important life cycle steps that need to be considered are the use phase and the end of life (EoL) treatment. The next steps are then investigations on actual release from products, preferably under real-world conditions so that finally the mass flows to the environment can be quantified. In addition release during production and manufacturing may occur, which is mainly of relevance for occupational exposure but also constitutes a possible release pathway to the environment. These aspects will be discussed in detail in this chapter, and the current knowledge that is available to enable quantifying the flows of ENM to the environment will be presented. Finally a toolbox is presented that allows in a systematic way to assess the flows of ENM to the environment.

The mass flows discussed in this chapter provide the input data to derive environmental concentrations. The mass flows to the environment will also be needed for environmental fate models that are based on mechanistic description of the reactions and the behavior of the released ENM in environmental compartments such as water or soils.

2 Production Amounts

When industry is approached for production volumes of ENM, the general reluctance of industry to reveal business-sensitive information is further aggravated by two nano-specific uncertainties: First, the legal framework in Europe and elsewhere currently undergoes a dynamic development. The future regulatory requirements for ENM are highly uncertain, but might incur costs that can easily nil the profit margin of specialty grades (low production volume nano-forms).

Second, the internal databases of companies specify chemical identity and performance criteria, but "novel," "engineered," "intentional," or number metrics

are not part of the specifications. The coexistence of differently sized forms of same chemical composition and the technical irrelevance of size for intermediates (here: particulate chemicals that perform after dissolution or melting) make it challenging to decide which is to be considered as ENM. The fact that national inventories (France 2014, Belgium 2015, Denmark 2015) each carve out different materials from the overarching EC definition and from applicable legal frameworks (Cosmetics directive 2012, Food directive 2014, REACH Annexes expected in 2015) does not contribute much to transparency within and between companies.

As a consequence, little is known about production amounts of ENM on a quantitative level, e.g., tons/year produced in different regions. We need to consider differentiating between amount of "production," "manufacturing," and "consumption." The produced amount of ENM in one region, the ENM manufactured in products, and the amount of products consumed in one region are all different. So far this aspect has not really received a lot of attention, and production and consumption are used interchangeably, mainly due to the absence of basic data. Very few scientific papers are actually providing data about production/consumption volumes. One of the earliest reports is from Schmid and Riediker [6] who provided quantitative production data based on a survey of the Swiss industry. Hendren et al. [7] provided an in-depth evaluation of production of five ENM in the USA. By using a variety of sources, companies producing ENM in the USA were identified and production volumes determined. Piccinno et al. [8] reported the results from a survey of companies producing and using ENM about the estimate of the worldwide/Europe-wide production amounts. In this work quite a spread of answers was obtained, most probably indicative of problems related to the definition of ENM. This work was conducted before the EC definition of "nanomaterial" was released [1]. For some materials such as nano-SiO_2, there is a huge spread in reported amounts, reflecting conflicting replies from different experts, part of whom considered a certain form of chemicals as ENM, whereas the other part considered this form as conventional chemical. This discrepancy is also visible in some higher estimated European compared to worldwide production amounts. Keller et al. [9] have used for their modeling of ENM flows a commercially available report as basis for the ENM production data [10]. The production values were taken as reported by FutureMarkets and no uncertainty range is provided. Worldwide production amounts for ten different ENM are presented in this work.

Another source reporting production amounts is the recent evaluation of nanomaterial registrations from France [11]. The highest production/use amounts (carbon black and silica) are those of conventional materials that fall under the French Decret definition of a nanomaterial (which is the same than the EU-definition [1]). The compiled list provided in the ANSES report only contains materials with more than 100 tons/year production/import. Silver was only reported for scientific research with a mass of 0.1–1 kg in the detailed lists provided in the report. With more than 3,000 registrations, the registry is clearly the most exhaustive compilation on production and use of nanomaterials, so it is very reasonable to assume that indeed almost no nano-Ag is imported or produced in France. Import in final products (e.g., textiles) was not covered by the register.

Table 1 Comparison of production amounts from six different sources scaled to the EU (according to the GDP) (in tons/year)

ENM	Schmid and Riediker [6]	Hendren et al. [7]	Piccinno et al. [8]	Keller et al. [9]	ANSES [11]	Sun et al. [12]
TiO_2	11,500	8,600–42,000	550	20,000	92,000	10,000
Ag	82	3–20	6	100	0.006	30
ZnO	1,900	–	55	7,900	1,900	1,600
CNT	26	60–1,200	550	740	–	380
C_{60}	–	2–90	0.6	–	<100	20
CeO_2	–	40–770	55	2,300	700	–
Al-ox	0.1	–	550	8,100	15,000	–
Fe-ox	9,700	–	550	9,700	6,100	–
SiO_2	2,000	–	5,500	22,000	990,000	–
Nanoclays	–	–	–	2,400	<100	–
Cu	–	–	–	46	<100	–
Quantum dots	–	–	0.6	–	–	–

In Table 1 the production amounts from the six sources mentioned above are compared on the basis of a scaling of the original estimates to the EU based on the gross domestic product (GDP). This scaling procedure has been used by several authors to scale production data from one region to another [12, 13]. Using this approach data obtained for different regions can be directly compared.

For nano-TiO_2 and Ag, all six sources provide production data, and for nano-ZnO and CNT, five sources provide data. A comparison of the data in Table 1 shows significant differences between the values from some sources with factors for most materials in the range from two to five and up to 45 for nano-SiO_2. For most nanomaterials, there is a general agreement on the order of magnitude of production, so $TiO_2 > ZnO > CNT > Ag > C60$. The largest variability is observed for materials that are also produced in conventional form, e.g., all the metal oxides such as SiO_2, Fe-oxides, and Al-oxides. For these materials a major problem associated with production amounts is clearly to define when a certain material is considered an ENM and when a conventional material. The very high production of nano-SiO_2 reported in the French ANSES registry clearly includes what in many other sources might be considered non-nano silica. Also for TiO_2 the value obtained from the French source is much higher than all the other values, and a similar issue might also play a role here. Worldwide production of pigment TiO_2 is more than four million tons [14]. However, we also have to consider that the values in Table 1 have been extrapolated in many cases to the EU based on the GDP.

Sun et al. [12] have combined the available information on production of ENM and have obtained probability distributions for five ENM (see Fig. 2). Two of the sources mentioned above, the ANSES report and Keller et al. [9], were published later and were not included in the evaluation. Sun et al. [12] classified the available data according to source of the data and considered some data to be of higher quality than others (e.g., peer-reviewed studies scored higher than reports without
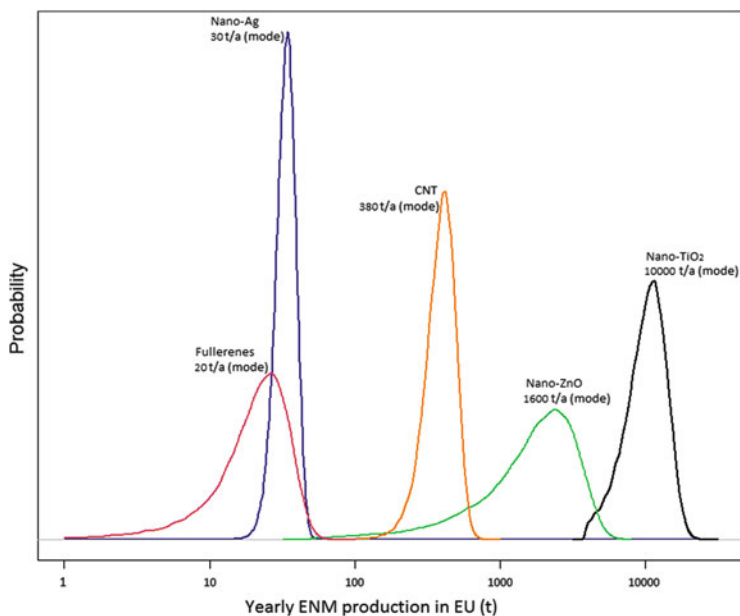
Fig. 2 Yearly production/use of five ENM in the EU. Shown are the probability distributions for fullerenes, nano-Ag, CNT, nano-ZnO, and nano-TiO$_2$ by considering data from a variety of sources. Figure taken from Sun et al. [12]

information on the methods that were used). Figure 2 shows that of the covered ENMs (TiO$_2$, ZnO, Ag, CNT, C$_{60}$), the largest production is that for nano-TiO$_2$ with a production in the EU of about 10,000 tons/year, followed by nano-ZnO with about 1,600 tons/year and CNTs with 380 tons/year. Nano-Ag with 30 tons/year and fullerenes with 20 tons/year have only low production amounts. These values are the mode values (most likely value) from the probabilistic assessment; the shape of the curve represents the current level of uncertainty.

3 Product Distribution

Whereas on production amounts at least some information has been published as was shown in the previous section, almost no quantitative information is available on the distribution of the produced ENM amount to different product categories. A lot of the knowledge we have about products stems from inventories such as the Woodrow Wilson Inventory [15], but such inventories have substantive deficiencies [16]. The main deficiency is that they just list articles claiming to contain ENM without proof that they actually contain an ENM; also information on concentrations of ENM in the products is seldom given. Many papers and reports list possible application areas of ENM [17–19], but this is only qualitative information that tells
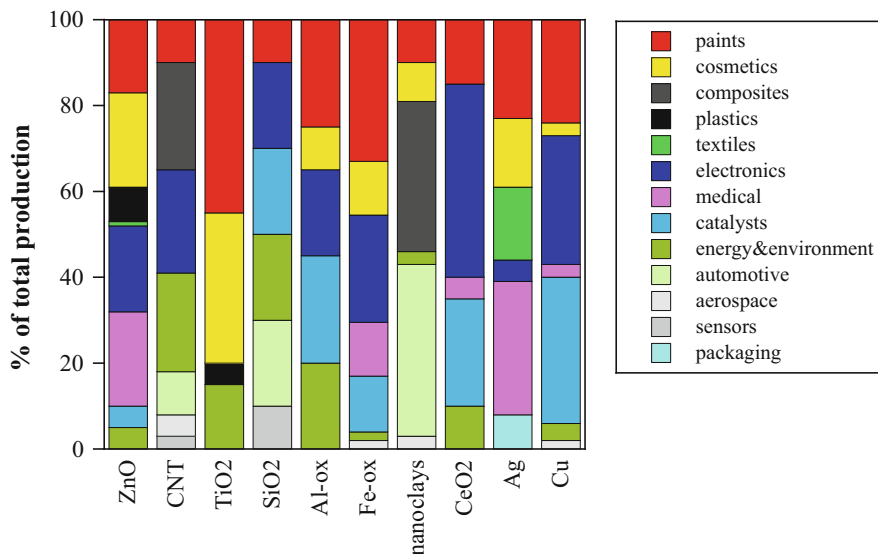
Fig. 3 Product distribution adapted from Keller et al. [9] in % of the total production of the ENM

us in which products an ENM might be used but not how important this product category is in terms of the share of the total ENM production that is used. What we need are data on the distribution of the produced ENM amount to different product categories.

Piccinno et al. [8] performed a survey among industries producing or using ENM and obtained some quantitative information on the distribution of the production amount to different product categories. The replies refer to the percentage of the total production that is used in certain product categories.

Keller et al. [9] used the FutureMarkets report not only as source of production amounts but also to get data on the product distribution. As with the production data, Keller et al. [9] did not further evaluate the data from the FutureMarkets report but used them as they were reported. Figures 3 and 4 present the distribution of the production for the different ENM to various product categories that we extracted from the mass flow data presented in the paper. In Fig. 3 the data are shown in relative amounts for each of the ten investigated ENM; in Fig. 4 the absolute amounts are given.

Sun et al. [12] combined the available information to derive best estimates of product distribution. Figures 5 and 6 show the relative and absolute product distribution for five ENM and pigment TiO$_2$.

One difficulty in comparing the results from these three data sources is that the used product categories are different. Sun et al. [12] used product categories mainly based on similar life cycles, whereas some other sources used also categories based on technical sectors. In the automotive sector, many ENM are used either in polymer composites or in electronic parts. For a quantitative estimation or even
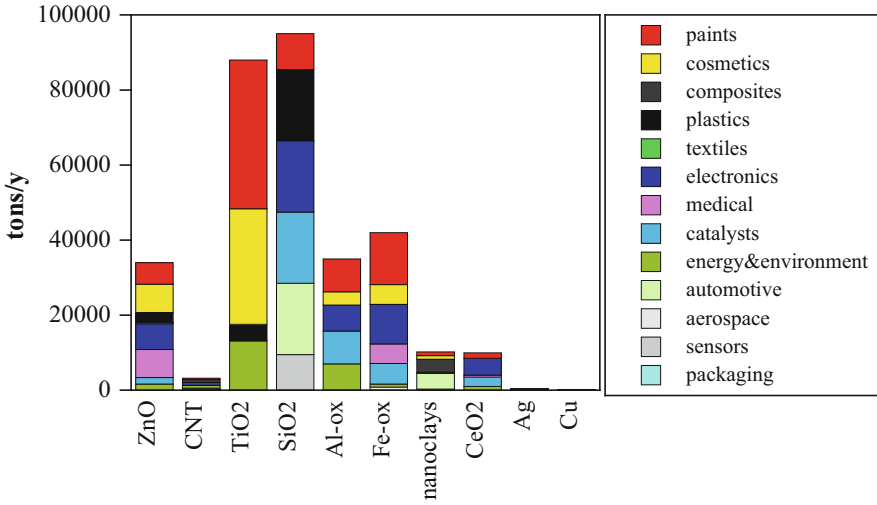
Fig. 4 Product distribution adapted from Keller et al. [9] in absolute amounts (tons/year) for the different ENM
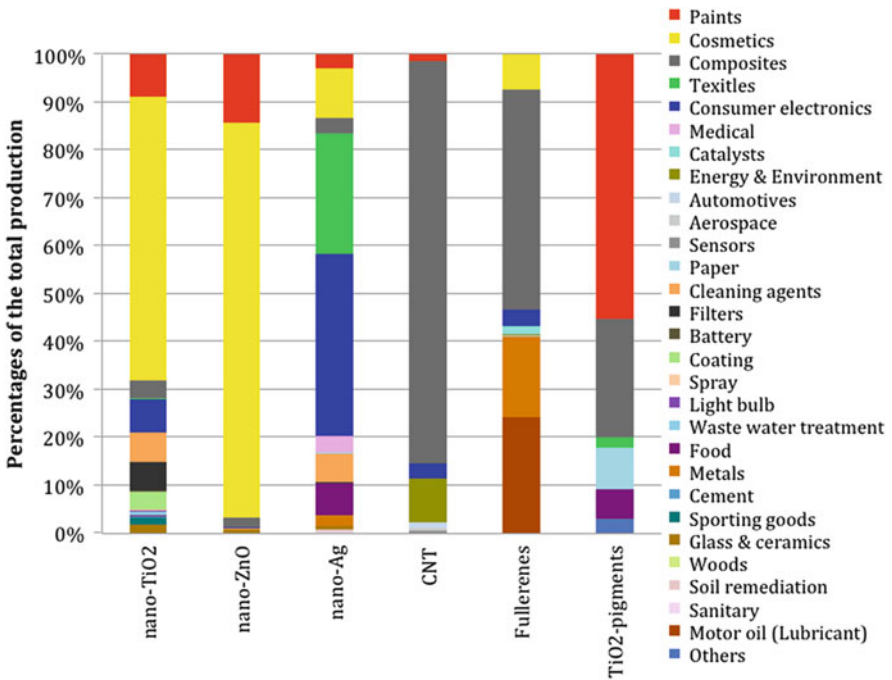

Fig. 5 Product distribution for 5 ENM and pigment TiO$_2$ adapted from Sun et al. [12]. The values are derived by combining various sources to obtain a "best estimate"
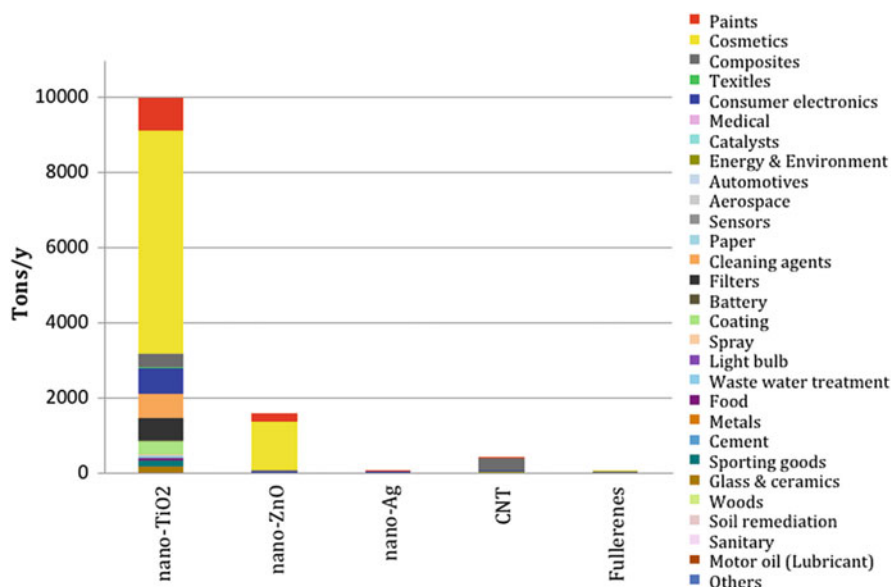
Fig. 6 Product distribution used absolute amounts for the different ENM adapted from Sun et al. [12]

modeling of ENM flows, these data, together with the production amount, form the basis for any flow estimation or model. The knowledge about the product categories can directly be used to estimate the potential for release, as shown in the next section.

4   Potential for Release

The knowledge about the products that contain ENMs can be used in a life cycle perspective to evaluate the potential for release [5]. Such an evaluation has been performed by Nowack et al. [20] to assess the exposure potential from ten technology sectors for workers, consumers, and the environment. The exposure was rated with four levels from "unlikely" over "low" and "medium" to "high." The main pathways of potential environmental release across the life cycle that were identified in this work were:

- Release of free ENM used during manufacturing into waste streams and air
- Intentional or unintentional release during product use
- Release during disposal or recycling of the product, mainly if this involves shredding or combustion processes

Such a qualitative evaluation can be used as starting point for further exposure evaluations and to guide research to areas where release and exposure can be

Table 2 Release potential for CNTs used in polymers

Release scenario	Professional user	Consumer	Environment	Recycling
Injection molding	Unlikely	–	Unlikely	–
Manufacturing	Very likely	–	Unlikely	–
Sports equipment	–	Unlikely	Very unlikely	Likely
Electronics	–	Unlikely	Unlikely	Likely
Windmill blades/ fuel system parts	–	Very unlikely	Unlikely	Likely
Tires	–	Very likely (through environment)	Very likely	Likely
Textiles		Very likely	Very likely (through wastewater)	Likely
Incineration	–	–	Unlikely	–
Landfill	–	–	Unlikely	–

Modified from Nowack et al. [21]
–: not applicable (life cycle stage not considered in scenario)

Table 3 Possible release mechanisms of ENM for different product categories

Product category	Release mechanism	Environmental compartment	Release potential
Cosmetics	Application of product	Water, wastewater	100%
Medical uses	Application of product	Wastewater	100%
Food	Application of product	Wastewater	100%
Water treatment, remediation	Direct release	Water, soil	100%
Sprays	Direct release	Air	100%
Textiles	Washing	Wastewater	High
Paints, coatings	Application of product Weathering, photodegradation	Air, water, soil	Moderate
Food packaging	Leaching	Food, wastewater	Low
Composites, plastics	Abrasion, weathering, photodegradation	Air, soil	Low
Tires	Abrasion	Air, soil	High
Electronics, batteries	Recycling, disposal	Air, wastewater	Low
Automotive/ aerospace	Recycling, disposal	Air, wastewater	Low

expected to occur. In this assessment the starting point was the technology sector and not product category.

A similar assessment was also performed for CNTs contained in polymers, see Table 2. Again the life cycle perspective approach was chosen in order to identify product types with significant release potential. The use in tires and textiles was

Table 4 Published release studies with ENM and actual products: model and real-world studies, excluding studies with lab test without relevance to real products (e.g., by "washing" or leaching with distilled water)

Product type	ENM	Model study	Real world	Reference
Textiles	Ag	Washing test		[22]
	Ag	Washing test		[23]
	TiO$_2$	Washing test		[24]
	Ag		Home washing	[25]
	Ag		Release from washing machine	[26]
	Ag		Direct release to environment	[27]
Paints	Ag		Model house	[28]
	TiO$_2$	Climate chamber		[29]
	SiO$_2$	Climate chamber		[30]
Wood coating	Ag		Outdoor weathering	[31]
Food containers	Ag	Leaching tests		[32]
	Ag	Leaching tests		[33]
	Ag	Leaching test		[34]
	Ag	Leaching tests		[35]
Polymer composites	CNT	Weathering tests		[36, 37]
	SiO$_2$	Weathering tests		[38]
Sprays	Ag	Spray chamber		[39]
	ZnO/ Ag	Spray chamber		[40]
Sunscreens	TiO$_2$	Model water		[41]
	TiO$_2$		Bathing lake	[42]
	TiO$_2$		Swimming pool	[43]

identified to result in likely release, and also recycling operations were found to be highly likely sources of released particles to the environment.

The release potential evaluations are possible to be carried out because in a certain product type only a limited number of release mechanisms will play a role. The mechanisms of release from products are not nano-specific but are determined by the environment the product is used in, the forces that act upon it, and the way it is used. For pure ENM, e.g., powders, the fact that they are nano influences the release, but this is more relevant for occupational exposure than for release to the environment during product use. In Table 3 the most relevant release mechanisms for the different product categories covered in this report are listed.

It is clear from looking at Table 4 that different product categories have completely different release potential. It is also important to note that in most cases material release will be into a technical compartment (wastewater treatment plants, waste incinerations plants, landfills) where most of the ENM will be removed and are not released to the environment. There are many product

categories where no or only a very small release is expected during use but where release might occur during disposal or recycling. This stage is therefore of utmost importance for evaluating ENM flows. However, the modeling of ENM flows during waste handling has shown that only minor releases are expected to the environment, major flows are going into different types of landfills [44]. The fate of ENM during recycling operations is still unknown, but first results are expected to come out from the SUN project soon.

5 Release Experiments of ENM During Use

In the previous section, the potential for release was covered. In this section studies that actually measured release of ENM from products are discussed. Recently a few reviews on this topic have been published. Froggett et al. [45] have reviewed the data on release of materials from solid nanocomposites. They state that very little attention has been focused so far on understanding the conditions for release of ENM from nanocomposites. They identified studies that investigated the release of ENM and reviewed them according to various release scenarios: machining, weathering, washing, contact, and incineration. The materials released from nanocomposites contain a mixture of four types of (1) particles of matrix alone and, slightly less often, the (2) matrix particles with the nanomaterial partially or fully embedded; far less frequently is the added nanomaterial entirely dissociated from the matrix identified, and most rare are (4) dissolved ionic forms of the added nanomaterial. However, depending on the nanomaterial, dissolution can be a major process during aging/release. Some textile release studies have found significant release of dissolved silver [46, 47].

Nowack [48] discussed the different types of release studies (see Fig. 7). This figure compares the different types of release studies and lists the possibilities and advantages of them. All studies have their merits and ideally data from all three levels are available, allowing us to understand the mechanisms as well as having data that can be used for exposure scenarios.

Release studies can be performed at different levels of complexity. At the basic level, experiments with simplified and standardized test materials allow controlling the physical and chemical conditions of the release. These tests are therefore suitable to investigate the mechanisms of release and to develop new experimental and analytical methods. The results from these studies may have only a limited value in estimating the amounts of nanomaterials released in the real world.

At the next level of complexity, studies are performed that mimic the real world but are still carried out under controlled conditions. Examples include tests with laboratory washing machines to study release from textiles or the use of weathering chambers to investigate release from paints. In these tests more parameters are fixed but still a sufficient control over the chemical and physical conditions is possible. However, because the tests are performed on a larger scale, the number of replicates or treatments is more limited. Very often these tests are based on established

Type of release study	Main purpose	Advantages/ Disadvantages
Mechanistic – Batch tests – Simplified systems	– Method development – Understanding mechanisms	– Conditions can be controlled – Fast and simple experiments
Model – Climate chamber – Test washing	– Method development – Understanding mechanisms – Release scenarios	– Conditions are to some extent controlled
Real-world – Washing machine – Outdoor weathering	– Release scenarios – Exposure scenarios – Risk assessment	– Specific trace analytical methods needed – Very little control of conditions

Fig. 7 Classification of release studies. Figure modified after Nowack [48]

standards or norms, and thus certain parameters are fixed according to the standard. An example is the use of ISO washing tests for color fastness that were adapted to investigate release of nano-Ag from textiles [22]. In order to be able to collect the released materials and to guarantee sufficiently low levels of silver background, several adaptations were made. Although these release studies are not directly transferable to the real world, they provide information that allows estimation of the order of magnitude of a certain release as well as the characterization of the released materials.

The highest level of relevance for understanding release under real-world conditions are studies performed under normal use of products. This could be to follow weathering and release of materials from facades painted with nano-paints or washing of clothes in normal washing machines. However, the exposure conditions are much less controlled. When a single nano-T-shirt is washed together with several kg of other textiles in a normal washing machine, the quantification and characterization of the released materials in several liters of washing and rinsing liquid is very difficult, if not impossible. The released ENMs are diluted to a large extent and occur together with a large variety of other materials released from the various textiles. In the lab washing machine, the solid/water ratio and the amount of textiles can be optimized to allow detection of released materials under the chosen analytical methods. However, if performed well, real-world studies provide data that can be directly used for environmental release and exposure scenarios.

6   Environmental Release from Occupational Settings

Nanomaterials that enter an occupational setting leave the workplace in normal circumstances either as pure ENM, inside a product, by general or special waste collection, by wastewater, or by natural or artificial air ventilation. Some ventilation systems will be equipped with filters, in which case the material will end of in solid or special waste. Cleaning and maintenance activities (including those involving nanomaterials) will in most cases lead to nanomaterials reaching both wastewater and general or special waste. Some nanomaterials may also accumulate within the facilities and will be removed only during major renovation activities. These may end up, in principle, also on landfills. In the case of accidents or fires, nanomaterials may be released in larger amounts into the air and into natural waters in cases where there are no detention basins in place to collect excessive amounts of fire-extinguishing water.

Little information is available on environmental release from occupational settings. These settings are:

- Production of nanomaterials
- Manufacture of intermediates/products containing nanomaterials
- Professional use of products containing nanomaterials

The focus of occupational studies is usually production processes involving nanomaterials and their relation to workers exposure. Most studies aim to answer either how much nanomaterial gets released into the work space or what concentrations workers experience during their work shift or during specific tasks and activities. Release of ENM from occupational settings to the environment could be addressed following a life cycle approach. The evaluation of each activity across the life cycle together with the risk management measures and cleaning practices used for such activities would provide an insight on the likelihood of release. However, technical protection measures such as encapsulations and ventilation systems strongly affect release into indoor environments and workers' exposure, and thus ventilation data is frequently collected. By combining ventilation flow data with concentration measurements in the exhaust flow, one can estimate the release into the outdoor environment. For nanomaterials that are used for cleaning purposes, one can obtain an initial estimate by assuming that most of the material used will eventually end up in the wastewater and be transported to a wastewater treatment plant (at least in most developed countries). For accidental or fire scenarios, one can assess the quantities stored on site to obtain worst-case release numbers.

Release by waste disposal has also to be accounted, not only for ENM intentionally used for cleaning but also for the ENM collected from cleaning instruments, laboratory material, spills, etc., usually end up in the general waste bin.

In the scientific literature, information about treatment methods for material wastes such as ventilated air or water that leaves a washing process is usually not described. Thus, most of the materials will be released into the environment or will

be captured by an exhaust filter, depending on the safety measures at each workplace. In many chemical fume hoods, there is no retention system and related rules differentiate by countries. For example, industrial processes usually include exhaust gas treatment processes such as filtration or burning off (in the case of high VOC content). In most of the cases, airborne particles are found to be emitted during the manufacturing and handling processes. Ventilation systems are used to control potential exposures, such as laboratory fume hood, local exhaust ventilation (LEV), natural ventilation (door, window), rooftop fan, and central ventilation.

When LEV is not used and the only air exchange is with outdoor air, the concentration of nanomaterials released to the environment could be estimated from the indoor concentration and the ventilation flow rate. However, published papers do not often include quantitative data on ventilation flow rates. In a study conducted in a laboratory with only general mechanical ventilation, the rate of 1 room exchange per hour was reported [49]. No direct air exchange through windows or doors was possible (there were no windows and the main door was kept closed during the experiments). The source and personal breathing zone (PBZ) particle concentrations were measured. In this case, one way to estimate the environmental release flow can be first to calculate the room average particle concentration from the source and PBZ data by using transport or diffusion kinetics (e.g., near-field/far-field two zone model) and then combine it with the room volume and air change rate (ACH) to estimate the final mass flow rate to the environment. This is, however, only possible if the air exchange is with outdoor air and there are no local controls such as LEV. Another study reported an ACH of 2–10 per hour in research laboratories of particle synthesis [50]. In one of their previous studies, an ACH of 0.706/h was also given in an industrial pilot plant [51]. In this study, a one-box model based on particle number conservation was employed to estimate particle emission rate from the average number concentration profile. This data can then be directly used for the calculation of environmental flow rates. In the cases where natural ventilation are employed [52–54] such as doors and windows, the room ACH can be calculated if wind speed and total area of open surfaces are available. There are also references on typical ACHs if these data are not directly given, such as handbooks (Exposure Factors Handbook, EPA; 2011) and scientific publications [55–57].

When exhaust ventilation is used (without filters), then the exhaust flow rate and concentration at the exhaust can be used to estimate the release of nanomaterials.

7 Release Data and Mass Flows

The main aim of this chapter is to derive mass flows from products to the environment. So the final goal is to have flows in mass/time unit for the use phase of the product, either for one unit of the product or for all products used within a certain region. Preferably population-normalized values, e.g., mass/time/capita, should be available, allowing a simple adaptation of the total release in different regions based

on population. Unfortunately, often release data have units of mass/volume of leachate or mass/surface area exposed. The mass/volume data are useful to prove that release takes place and understand the mechanisms, but are less useful for deriving mass flows. Critical issues when using such data for deriving mass flows are:

- How to extrapolate a short-term experiment to years of use (release kinetics, aging)
- How to convert mass/volume to mass/product

An additional issue is that release data are often not nano-specific, so they do not provide sufficient characterization of the released materials in real-world studies. For example, textile studies reporting only release of Ag are not really useful to estimate the flows of nanomaterials because only a fraction of the silver release from textiles is still in the original nano-form [58]. Significant dissolution and transformation was observed, with only a small fraction still present in original nanoparticulate form. There were also significant nanoparticulate fractions observed in the washing liquid of conventional silver textiles, further complicating the assessment of release of nanomaterials. Such total release measurements can be used to derive the total flows originating from nanoproducts but not to quantify the nanomaterial flows. However, so far only very few studies have actually characterized quantitatively the released materials so that mass flows of nanoparticulate releases can be distinguished from other releases.

8 Review on Mass Flows of ENM to the Environment

Several studies are available that modeled mass flows from products to the environment. These studies collated the available information and derived mass flows, using different approaches. These models have already been reviewed with respect to the type of model and the advantages and disadvantages of the different approaches [4, 59]. In this chapter only the mass flow result from these studies is discussed and compared.

The most recent and most complete study has been published by Sun et al. [12]. This work is based on the predecessor models of Mueller and Nowack [60] and Gottschalk et al. [61]. Figure 8 shows an example of the material flow diagrams that were published in that work. It shows the yearly flows of nano-TiO$_2$ in the EU originating from production, manufacturing, and use to the technical systems (e.g., wastewater treatment, waste incineration) and finally to the environment. Such flows were calculated for nano-TiO$_2$, nano-ZnO, nano-Ag, CNT, and fullerenes. The flows correspond to total nano-flows, irrespective of the form the particles have (e.g., single, agglomerates, attached to larger particles). Transformation, e.g., dissolution or sulfidation, was included for some materials, resulting in flow into an elimination compartment.
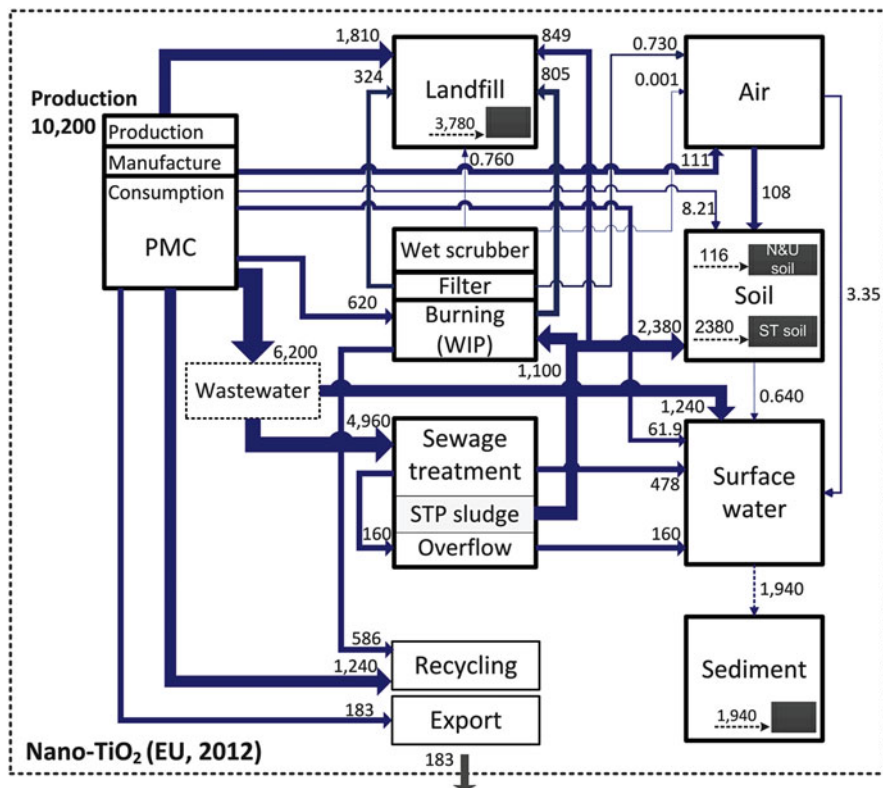
Fig. 8 Material flow model for nano-TiO$_2$ from production/manufacturing/use to the environment in EU in 2012. Figure taken from Sun et al. [12]

Table 5 Mass flows to the environment (and landfills)

ENM	Wastewater	Water	Sludge-treated soil	Soil (diffuse)	Air	Landfill
TiO$_2$	6,200	1,940	2,380	116	112	3,780
Ag	8.85	2.1	0.42	0.84	0.52	5.2
ZnO	1,050	328	0.006	10.6	8.2	300
CNT	1.9	0.71	0.77	3.6	3.7	190

Data based on Sun et al. [12]. Values in tons/year in the EU

Table 5 provides the mass flows for four nanomaterials summed up for different environmental compartments. These mass flows can then be converted into environmental concentrations using established procedures [62]. Sun et al. [12] also provide ENM concentrations in technical systems, e.g., wastewater, municipal waste, and waste incineration slag and filter ash. These concentrations provide the currently most advanced estimates of environmental exposure to the five studied materials.

Table 6 Mass flows to the environment (and landfills) in the EU

ENM	Water	Soil	Air	Landfill
TiO_2	3,600	8,900	370	7,600
Ag	15	35	3	46
ZnO	860	2,000	140	4,900
CNT	8	120	10	630

Data based on Keller et al. [9], values extrapolated to Europe based on GDP, in tons/year

Keller et al. [9] provide similar material flow diagrams for ten different materials. However, whereas Sun et al. [12] use probabilistic modeling, incorporating the variability and uncertainty of the input values, Keller et al. [9] use only one single input (from one single source) without considering any uncertainty or variability and also use a very simplistic release model. However, they extend the flow modeling to additional materials not covered by Sun et al. [12]: SiO_2, Al-oxides, Fe and Fe-oxides, nanoclays, CeO_2, Cu, and CuO. To allow a comparison with the data from Sun et al. [12], the mass flows for the same four ENM are shown in Table 6, extrapolated to the EU.

9   Conclusions

This chapter has systematically evaluated what information is needed in order to quantify the flows of ENM to the environment and has reviewed the current state of knowledge. The life cycle thinking forms the basis of the evaluation. The first step in release assessment is the knowledge about the production and use of ENM. Data on production are crucial for the assessment, because they determine the maximal amount that could potentially be released. This starts with data on production amounts of ENM, where the main issue seems to be the definition what is actually an ENM and what is considered a conventional material. This is especially important for materials that have been on the market for decades, e.g., SiO_2, and are now, depending on the source [63], considered to be a nanomaterial or not. It can be expected that in the future data will be more comparable between different sources if the underlying definition that is used is the one proposed by the EU.

The different life cycles of products that are manufactured with the ENM are determining the release potential. The knowledge about the product distribution is therefore key to release estimation. This is needed in order to quantify the flows of ENM – the qualitative information that is available in many reviews, e.g., which potential applications exist, is only of limited relevance. Whereas product registers are helpful to some extent, it is much more important to get first-hand industry estimates about sectors and applications where the ENM are used. The current best way to go forward is to use probabilistic modeling as developed by [64] which is able to fully consider the uncertainty in model input values.

The two important life cycle steps that need to be considered are the use phase and the EoL treatment. During these steps experimental data from real-world release studies are the gold standard. However, in most cases release has been estimated or guessed based on standard knowledge about product use and behavior. In addition, release to the environment during production and manufacturing may occur. Information is lacking about real-world release studies that allow to quantify the transfer factors from product use to the receiving compartment. What is available are mostly lab-based studies that quantify the release of total chemical element under conditions mimicking more or less the release in real-world situations. A main issue is how the short-term data in laboratory experiments can be extrapolated to the whole life cycle of products. An example is that most washing experiments report percent silver released in one washing – how to extrapolate this to several years of washing at home? The transfer factors needed for material flow modeling integrate release over the whole lifetime of the product. The current models take the available short-term data and either apply a factor to derive full lifetime release or use the release data as is without any further adjustments. Release kinetics may be considerably different between the initial and later stages, and simple extrapolation may not be possible – both decreasing release overtime by rapid removal of weakly bound particles and an increase due to degradation of the matrix are possible.

The mass flows discussed in this report provide the input data to derive environmental concentrations [2]. In a simple approach, the ENM mass is mixed into environmental compartments of defined size in a regional assessment to derive PEC, and such values have been published [12, 60, 61]. The mass flows can also be adjusted to the local population to derive inputs into the environment in a local scenario. This approach has been used to calculate ENM concentrations in Swiss rivers with a high geographic resolution [65]. The mass flows to the environment will also be needed for environmental fate models that are based on mechanistic description of the reactions and the behavior of the released ENM in environmental compartments such as water or soils [66].

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