CRITICAL REVIEW

The release of engineered nanomaterials to the environment†

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There is scientific agreement that engineered nanomaterial (ENM) production, use and disposal lead to environmental release of ENM. However, very little is known on emissions of ENM to the environment. Currently, techniques are lacking to quantitatively monitor ENM emissions to and concentrations in the environment, and hence data on emissions and environmental concentrations are scarce. One of the few available studies reports the detection of nano-TiO_2 in water leaching from exterior facades. Some experimental evidence is available on the release of nanosized materials from commercial textiles during washing. A handful of modeling studies have investigated ENM release to the environment. These studies modeled either the release of ENMs to the environment from ENM containing products during the consumer usage, or the release throughout the whole life cycle of ENM and ENM-containing products. Sewage sludge, wastewater, and waste incineration of products containing ENM were shown to be the major flows through which ENMs end up in the environment. However, reliable data are particularly lacking on release during ENM production and on the application amounts and empirical information on release coefficients for all life cycle stages and environmental compartments. Quantitative data linking occupational exposure measurements and ENM emission flows into the environment are almost completely missing. Besides knowing the amounts of ENM released into the environment, it is equally important to investigate in what form ENMs are released. First results show that much of the ENM released from products is present in matrix-bound form, but that also some fraction is released as single, dispersed nanoparticles.

Introduction

Impressive application prospects of nanosized materials in a wide variety of technical applications and consumer products (*e.g.* pharmaceutical, biomedical, cosmetic, electronic, energy, environmental) have led to a significant increase in engineered nanomaterial (ENM) production, manufacture and use of ENM-containing products.[1] Currently there is a lot of attention being paid to potential impacts of such material on humans and the environment.[2–6] Some ENM definitely have the potential to become hazardous pollutants that may affect human health or the environment. However, there is very limited data available on the actual release of ENM to the environment. The risk of a substance is determined by both effect and exposure and for ENM the knowledge of its environmental exposure is quite small. The study of the behavior and effects of ENM in the environment has up to now been a field where most research was performed based on a precautionary approach: what would happen if nanoparticles reached the environment? How would

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Environmental impact

Products containing engineered nanomaterials (ENM) are already on the market and are used by consumers and industry. A lot of research is carried out to evaluate the potential fate and effects of ENM in the environment. However, before ENM can reach the environment, they need to be released and the amount and form of the released particles determines their environmental fate and effects. This article reviews the available information on release of nanoparticles during production, manufacturing, use and disposal. It also emphasizes that the type, composition and form of the released particles may be very different from the particles that have been embedded into a product and that information on the released particles needs to be considered when assessing the risks of ENM.

they behave there and how would they affect organisms? The presence of ENM in the environment has been supposed because "given the increasing production of nanomaterials of all types, the potential for their release in the environment and subsequent effects on ecosystem health is becoming an increasing concern".[7] This assumption is based on the experience obtained with other pollutants[8] and has governed the field of environmental effects of nanoparticles so far.

This article reviews available information on ENM release to the environment and discusses the applicability of existing (i) models, (ii) experimental settings and (iii) analytics for assessing ENM environmental release. We conclude by identifying critical research needs and data gaps to map out how to fill such gaps in the next years.

Life cycle considerations

In contrast to occupational and consumer exposure assessments, any evaluation of the environmental release of and exposure to ENM has to consider an immense diffusive emission source setting that has to cover the whole life cycle of ENM and ENM containing products. Such a life cycle perspective thus has to distinguish among release from ENM production, ENM incorporation processes into products and release during the use, recycling or disposal of such products. Hence, defining relevant ENM release assessment settings for parameters such as *e.g.* ENM production and application, temporal and geographical ENM use distribution will be crucial for framing ENM emission models as well as experimental and analytic studies.

It is supposed that most ENM are released during their use (unintentional release). Experimental evidence is available that proves the emission of silver-ENM from textiles during washing[9] or the release of nano-TiO_2 from paints[10] into rainwater that runs off a facade. In other cases the release of ENM is inevitable when ENM are used in sprays, sunscreen, cosmetics, *etc.*

Hence, in order to assess release amounts, it is essential to know if the ENM are, *e.g.*, strongly embedded within a solid material matrix, present in liquid form in emulsions or suspensions or even used as aerosols that are emitted directly to the air. Especially the release of ENM contained in liquids, pastes, creams, and powders, and aerosol spray application is expected to be significant.[11] However, ENM not incorporated strongly into the matrix of larger-particle materials, *e.g.* ENM as surface coatings or in textiles, may also be emitted during the use of the solids. Mechanical abrasion and physicochemical material aging due to thermal and photooxidative processes may impact considerably such release.[12] It is extremely difficult to quantify and monitor the long-term release of ENM during the final disposal of ENM containing products.[13]

The whole release spectrum (Fig. 1) includes discharge into the environment *via* ENM production, incorporation of ENM into products, the use of ENM containing products as well as *via*
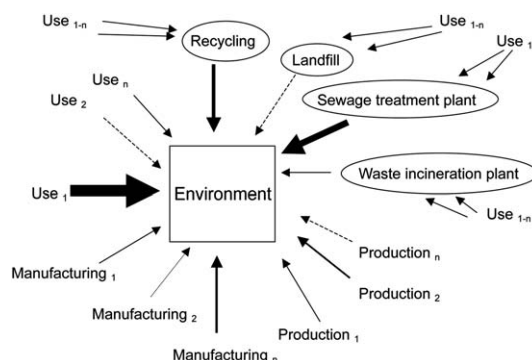

Fig. 1 The environment is integrating all possible ENM releases: from ENM production and manufacturing of ENM containing products, *via* direct use of ENM (*e.g.* nZVI for groundwater remediation), *via* use of ENM containing products and *via* sewage treatment, waste incineration, landfill and recycling processes.

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sewage treatment plants (STP), waste incineration plants (WIP), landfills (LAN) and recycling (REC) and disposal processes. The environment is integrating all these flows and without detailed knowledge about the relative importance of these different flows it is necessary to consider all of them in order not to overlook significant exposure pathways. It is also important to realize that the characteristics of ENM formulations can change during their life cycle (e.g. due to physical/chemical interactions and changes) and the aging/degradation of the ENM or ENM containing product.

As with many pollutants, most of the ENM release stems from non-point sources such as e.g. wearing or washing textiles containing ENM, or using nanomaterial containing cosmetics, sunscreen, etc. Such sources are probably the most important and the most difficult to control.[14] In this respect ENM are not different from other chemicals in consumer products. However, for pollutants emitted as nanosized particles a quantitative (and qualitative) detection is currently almost impossible due to the lack of adequate measurement approaches for such particle size ranges. Point sources such as nanomaterial production and manufacturing facilities or transport processes, landfill wastewater treatment or waste incineration plants or, e.g., storm-water runoff from manufacturing facilities or city roads and highways[14,15] are basically easier to monitor.

A simple case of direct release is, e.g., nZVI injected into groundwater contaminated with chlorinated solvents.[14] For such groundwater remediation large amounts of nZVI (up to several tons per contaminated site) are directly pumped into the subsurface.[16] Also ENM-containing agrochemicals[17] end up directly and completely in the environment when applied, e.g., onto soils.

For all release scenarios we have to know the conditions leading to ENM release, the release concentrations, and destination (into what technical compartments, e.g. wastewater treatment plant, waste incineration processes, or into what environmental compartments). Such scenarios need to be considered for all life stages of a particular type of ENM and ENM product. The characteristics of ENM formulations can change during their life cycle (e.g. due to physical/chemical interactions and changes) and the aging/degradation of the ENM or ENM containing product.[5]

Release scenarios

Release during the production of ENM

During ENM production and product manufacturing, direct release of free ENM can be expected.[18] Direct release is possible, e.g., through open windows to the air when powdery material is used incautiously or from transport accidents and from all kinds of spills. Indirect release from production sites into a river is, e.g., imaginable via untreated or treated wastewater. Most of the environmental release assessments[19–22] ignore emissions of ENM to the environment arising from the ENM production. However, recently[23,24] direct ENM release to the environment from such production processes has also been studied. Uniform probability distributions ranging from 0 to 2% of the ENM produced were assumed to reach the environment from the production procedure. Generic worst case scenario release coefficients (ERCs)[25]

for chemicals and the manufacturing process of such chemicals consider 5% release to the air, 6% to surface waters before reaching an STP and 0.01% to soils. However, depending on the procedures used for production and maintenance of the equipment, only negligible release to the environment is also possible, especially when closed systems and solvent-free procedures are used and all waste from cleaning and maintenance is disposed of as special waste.

Release from manufacturing processes

Measurements carried out at factories producing different ENM products show that worker exposure already occurs, e.g., during the production and handling of dry powders.[26–30] However, it is currently unknown in what way and to what extent such worker exposure leads to ENM release to the environment. There is no doubt that once the ENMs are released, e.g., to indoor air such material is likely to enter sooner or later the environment. However, to estimate ENM emissions to the environment worker exposure measurements per se are not relevant. Such work exposure measurements are not utilizable as long as no information about the ENM volume or flow into at least one environmental compartment is considered. This means that ENM environmental release assessments also need the mass flow per unit time of the pollutant reaching air, e.g., from an exhaust in addition to, e.g., the indoor air concentrations of a pollutant. Or as a further example, knowing only the particle concentration in wastewater is not sufficient; instead, the mass flow of such an influent and its pollutant's concentration are needed as well.

Recent studies[23,24] considered for the first time besides the release of ENM from the production of ENM also environmental emissions from manufacturing processes of ENM containing products. Probability distributions between 0 and 2% of ENM release were assumed. Default parameters described as ERCs[25] assume for formulation of mixtures (not embedded into a matrix) the following release coefficients: 2.5 % into air, 2 % into water before ending up in STPs and 0.01% to soils. The equivalent values for formulations in materials (included into/onto a matrix) are 30%, 0.2% and 0.1%.

Release from products

The main possibility for ENM to be uncontrollably released into the environment is during the use, recycling and disposal of ENM containing products. The release of ENM during such life stages of the ENM can be caused by intended release from product applications such as putting ENM-containing sunscreen onto the skin or from unintended release from products caused, e.g., by abrasion of nano-textiles.

Whereas the source and magnitude of ENM release is known for intentional emissions, this is not the case for undesired emissions caused by product's degradation, alteration, recycling, etc. that occurs throughout the whole life cycle of products.[12] The level and pattern of ENM release from a product depends mainly on how the ENM are embedded in a product. ENM in fluids are quickly and in most cases completely released during the use phase, whereas ENM embedded in solid matrices are gradually and only partially released over a product's lifetime.[12] ENM in sprays are emitted immediately when applied. ENM in

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suspensions such as sunscreens, cosmetics are released within hours, while ENM in paints and textiles are supposed to remain within the matrix for years.

Many products can be identified that release ENM into the wastewater stream (collected and treated) or that emit the bulk of the ENM only during end-of-life-treatment. In such cases, ENM are potentially removed in the technical compartment (e.g. waste incineration or wastewater treatment process). However, we should consider that only carbonaceous materials can definitely be destroyed in such removal procedures. Metals and metal oxides may be retained, but will persist.

Release from technical compartments

Much of the unintentional release will be into wastewater or solid waste. Hence, wastewater treatment plants and waste incineration plants will be important sources for ENM release. Almost nothing has been reported to date regarding the fate and behavior of ENM in waste incineration processes, and leaching from landfills has also not been studied yet. The removal of ENM from wastewater is also only poorly investigated.[31] We should expect that at least part of the ENM in wastewater end up in freshwater. In order to minimize such indirect release of ENM, measures must be taken near the product itself and at the technical facilities that can be seen as clearly localized point sources.

However, technical compartments do not represent only single step emission scenarios for ENM. We should also consider that ENM may pass through several technical compartments, e.g. when the sludge from waste incineration plants is deposited in landfills and/or if biosolids from wastewater treatment plants are burned. A selection of products and applications with direct and indirect entry into the environment via technical processes are compiled in Table 1.

Modeling release of ENM

Different models have been used to assess ENM release to the environment.[19–21,23,24,32,33] The methodologies used vary considerably between these studies. This applies to the model conceptualization (mathematical approaches), the parametrization (model geometry) as well as to model input data collection, consideration and preparation. The mathematical approaches used to deal with the high ENM specific uncertainties (and natural variability) in the estimation of model input and output range from simple deterministic algorithms for single event scenarios[19–21,32,33] to more sophisticated stochastic/probabilistic computer simulations.[23,24]

In addition to the different mathematical procedures, the available models vary in particular due to their different conceptualizations/framings of the ENM release. We subdivide the modeling studies reviewed into top-down and bottom-up approaches based on the release assessment frameworks used. The top-down approach starts with information on the use of certain products and assumes a market fraction of ENM-containing products and information on the use of the product. In the bottom-up approach, information on the production of ENM is used together with distribution of the ENM to product groups. From the top-down perspective some models consider only the ENM release from a small (relevant) set of ENM containing products.[20,21,32,33] In contrast, within the bottom-up approach, others include in their calculations the whole spectrum of products and possible applications of ENM.[19,23,24] In this approach, an inventory was made of all known commercially relevant ENM containing products. Next, all products were categorized in product categories according to their potential ENM release behavior. The release of ENM from production and ENM product manufacturing and recycling processes was

Table 1 Products and applications as point or diffuse sources for direct and indirect release of ENM into the environment

Source and release characteristics		Examples	Technical facility (where measures for ENM-capturing could be taken)	Environmental compartment
Indirect release	Point sources (direct release or release from technical compartments)	Nano-paints (where the run-off from facades is collected in the sewer system)	Wastewater treatment plant	Water, sediment Soil (if biosolids with ENM removed during water treatment are applied on land)
		Application of sunscreen containing TiO_2		
		ENM as food additive		
		Medical use		
		CeO_2 in fuels	Filter	Air, Soil
		Dismantling of batteries	Recycling facility	Air, Soil
		Recycling of plastic/glass/metal with nano-coating		
		End-of-life treatment (incineration) of nanotextiles, nanocomposites	Waste incineration plant	Air
Direct release		Groundwater remediation	–	Groundwater
		Application of agrochemicals	–	Soil, air
		Use for water treatment	–	Water
		Leaching/draining from landfills	–	Groundwater, soil
	Diffuse sources (release from products)	Wear during use, e.g. from tires, textiles, etc.	–	Air, soil, water
		nano-TiO_2 wash off from sunscreen (in lakes, etc.)	–	Water
		Weathering, e.g. of outside paints	–	Soil, water
		Use of CeO_2 in fuels	–	Air, soil
		Spreading of biosolids onto land	–	Soil

Table 2 Modeling studies to environmental ENM release, concentrations of ENM or metal concentrations resulting from the use of ENM

Study	ENM	Compartments	System	Release
21	TiO_2, ZnO, CeO_2, Al_2O_3, SiO_2, Au, Ag, C_{60}	Water, sludge, soil, air	UK	Simplistic release modeling framework based on simple algorithms for hypothetical usage scenarios and market penetrations applied to a limited range of products and life cycle stages of the ENM products
19	TiO_2, Ag, CNT	Water, air, soil	CH	Worst case and realistic scenario analysis. Release of all considered ENM to environmental compartments and several technical compartments from the use of products containing ENM
20	Ag	Water	EU	Nano-Ag only served as Ag^+ source, no particulate Ag release was modeled
32	CeO_2	Air, soil	Generic	Release from fuel additives
23	TiO_2, ZnO, Ag, CNT, C_{60}	Water, sludge, air, sediments, soils, groundwater	CH, EU, USA	Stochastic simulations of the release of all considered ENM to environmental and technical compartments during all life-cycle stages
33	TiO_2, Ag, CeO_2	Air, surface waters	Ireland	Release from exterior paints (TiO_2), food packaging (Ag) and fuel additives CeO_2

also considered.[23,24] Table 2 shows the objectives and the differences among the modeling studies.

Top-down approaches

Blaser et al.[20] have modeled silver (Ag) release from nano-Ag incorporated in nano-functionalized biocidal textiles and plastics based on a silver mass flow analysis. The use of such products was seen to cause the release of silver ions into wastewater, which may either be treated or directly discharged untreated into a river like the Rhine. The authors found that the most of the silver emitted into wastewater ends up in sewage sludge and may be spread on agricultural fields. Only a marginal fraction of silver that is not removed with sewage sludge reaches natural waters via STP effluents. The sewage sludge is either applied to soils, disposed in landfills or incinerated in WIPs. During incineration, the released silver reaches slag, bottom and fly ash. The release to air is marginal: 1% of the volume that is leaving such incineration plants. Pollution of soil and groundwater via leachate from landfills was not calculated.

Seen from ENM-release perspective, some limitations have to be mentioned. Real nanosized and particulate release flows were not modeled because nano-Ag only served as Ag^+ source. Hence, no specific nanoparticulate silver transfer was calculated, but silver amounts emitted from the nanoparticles incorporated into textiles and plastics (release rate of silver ions from these products) were considered. In addition, this model only reflects one single estimated silver use event based on three deterministic release scenarios (minimal, realistic and worst case release). No further indications to the model input uncertainty (variability) are given. Biocidal nanomaterial containing plastics and textiles was predicted to account for up to 15% of the total silver release into surface waters, although no indications of variability or the estimation uncertainty of such a parameter were provided. It was assumed that most of the silver released into wastewater will end up in sewage sludge. Hence, the model (the volume of silver reaching surface waters) depends strongly on the fraction of wastewater that is effectively treated in a particular region.

Connection rates to sewage treatment plants have to be known in order to be able to apply this model, since the final silver input into receiving waters is characterized by the amount of silver predicted in wastewater, the fraction of wastewater treated in and removed in the treatment plants.

Boxall et al.[21] presented a framework of simple algorithms to calculate release of ENMs to air (from personal hygiene and skin care products, traffic and industrial stack sources), soil (from application of sewage sludge to land, through the application of remediation technologies and of plant protection products), and water (via the sewage system, direct entry e.g. via bioremediation). This work focuses on generic approaches to calculate the release of ENM via single products (such as pharmaceuticals, cosmetics and personal care products, paints and coatings). The scenarios (routes of entry) presented, e.g., for estimating the ENM release from different products to water were (1) the direct input of ENM to surface waters, e.g., from bioremediation; (2) inflows from use of agrochemicals (e.g. plant protection products); (3) runoff from contaminated soils (e.g. excretion of nanomedicines used in veterinary products); (4) aerial deposition (e.g. from the use of aerosol sprays); and (5) release from wastewater treatment plants (sewage sludge used, e.g., as a fertilizer).

However, such scenarios are not really relevant for environmental purposes as long as they only indicate the likelihood of the exposure caused by using, e.g., individual personal hygiene products or, e.g., nanomedicines. Hence, such an approach is focused only on a very limited selection of ENM applications and release events. Such models are only applicable to individual hypothetical ENM usage scenarios, since they are restricted to individual product types and applied to a non-comprehensive range of products and life cycle stages of ENMs. In addition, these calculations were also based on single uncertain hypothetical market penetration factors (e.g. 10, 50 and 100%) of the nanoproducts.

Park et al.[32] provided estimations of nano-CeO_2 release into air and soil from their use as a fuel additive. ENM emissions were calculated based on established models for particle emission

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calculations. The CeO_2 release was, *e.g.*, calculated for a highway and a street canyon, assuming worst-case conditions (all cars using CeO_2-containing fuels) and varying driving conditions. Emissions of CeO_2 to the air were calculated up to the year 2020 for the EU Member States. A 5 ppm concentration of CeO_2 in the diesel fuel was assumed. A best-case approach assumed CeO_2-based additives only for the trap-equipped vehicles. In such cases CeO_2 emissions were retained by the traps. For the worst-case scenario, all diesel fuel was doped with CeO_2, and cerium totally emitted to the air (*e.g.*, due to total trap failure).

Cerium oxide release to the air was also modeled for two high-traffic scenarios:[32] a highway and a street canyon. For the highway scenario the authors assumed the following conditions: 14 000 vehicles h^{-1} traffic density, all vehicles using diesel fuel (as a worst case assumption), and stable atmospheric conditions. The soil contamination along a typical highway was modeled based on a rough assumption that all the cerium oxide emissions would accumulate over a 40 year period. Rural areas were modeled to be loaded with about 6.6 g CeO_2 km^{-2} per year. Such depositions were compared to suspended particulate matter (PM) (annually 5 kg km^{-2}). The release along the EU highways was modeled to amount annually to 0.3 kg km^{-1}, this release amount was again compared to PM (220 kg km^{-1} annually).

O'Brien and Cummins[33] investigated the release of nano-TiO_2 from exterior paints, Ag from antimicrobial food packaging and CeO_2 from use as a particulate-reducing fuel additive to the air and surface waters. The method used included a semi-quantitative three-level risk model[34,35] based on inter-relationships between the different material properties and environmental behaviors and their relationship to ENM release and exposure scenarios. The release of nano-TiO_2, nano-Ag and nano-CeO_2 to surface waters was predicted to increase significantly the baseline concentrations. Such nanomaterial increase was attributed to the fact that such materials are available in a more "freely available" form (*i.e.* liquid suspension) than the equivalent bulk material.

Bottom-up approaches

Mueller and Nowack[19] presented the first model that considered ENM release from a whole life-cycle perspective. ENM emissions were calculated by means of a substance flow analysis considering emissions from products to air, soil and water in Switzerland. For nano-Ag, nano-TiO_2 and CNT direct release from the products to air water and soil, WIP, STP and landfills were modeled as mass flows in tons/year. Processes such as abrasion during use and washing of products (*e.g.* textiles), after product treatment in STPs and recycling processes, *etc.*, were considered. The model input covered the estimation of the worldwide ENM production amounts, the allocation of the production amounts to product categories, the assessment of release coefficients from products and the calculation of flow coefficients for all ENM transmission flows between environmental and technical compartments. To cope with the almost complete lack of data for these input parameters, two scenarios were modeled: a realistic scenario and a worst-case scenario. The main limitation of this model stems from the lack of data that leads to high uncertainties in the calculations of the ENM production, the distribution of produced ENM volumes to product categories with particular release characteristics and the release coefficients.

Recent studies[23,24] extended this type[19] of ENM release modeling by replacing the scenario analysis by a probabilistic/stochastic approach.[36] The uncertainty and variability of the ENM release coefficients, as well as release causal mechanisms such as level of ENM production and application, were considered by means of Monte Carlo algorithms. In contrast to individual scenarios, such models provide insights into the likelihood of each produced output. This material flow computer model[36] allows (developed for cases of distinct scarcity of empirical model input data) programming any kind of probability distributions for all the input variables thorough out the whole modeling procedure by incorporating a large number of processes such as emission and transmission flows, ENM deposition and elimination rates. One of the main advantages of this software is that it allows one (whenever new empirical data become available) to improve prior information to posterior results by formulating and incorporating also Bayesian algorithms. This approach also includes a sensitivity analysis[36] that relates the impact of a model input parameter to the model output and its estimation uncertainty.

Release was calculated for nano-TiO_2, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes for the three regions—USA, Europe and Switzerland. For the ENM production, ENM-containing product manufacturing and ENM-containing products life-cycle, different release pathways of ENMs to the environment were modeled. Complete disposal was assumed for composites and plastics. Also ENM from glass and ceramics and light bulbs, ended up in the environment mostly *via* waste incineration processes. For wastewater treatment of nano-Ag, nano-TiO_2, nano-ZnO, a removal of 90.6 and 99.5% (uniform distribution) was modeled considering other results.[31] In the case of CNT, 96.3 to 99.7% (uniform distribution) was assumed in accordance to values regarding settling in water containing 100 mg L^{-1} NOM.[37,38] Due to the availability of multiple types (functionalizations) of fullerenes, it was not possible to determine a typical treatment efficiency for this material. Textiles, metals, batteries, filters, consumer electronics, *etc.* were recycled or discharged to waste incineration plants or to landfills. For textiles, abrasion and release from the washing procedure were modeled as well. ENM from cosmetics, cleaning agents, and coatings and dietary supplements ended up in the environment mostly *via* STPs. Released ENMs, *e.g.*, from paints were assumed to reach STPs, landfills, soils, and surface waters. Additionally, ENM release *via* untreated wastewater that is discharged into surface water during and after heavy rainfall was considered as well.

In this work an initial sensitivity analysis allowed us to identify the key parameters that impact ENM environmental release. Changes in the STP inflow, STP overflow, and STP removal efficiency explained, *e.g.*, for nano-TiO_2 and nano-Ag almost the whole variation of the ENM in water. The reason for the dominance of that factor is that most nano-TiO_2 are, *e.g.*, used in the product categories cosmetics and coatings, nano-Ag in coatings, cosmetics, paints, and textiles. Releases from such applications result mostly in emissions of ENM to STP inflows. This sensitivity analysis showed that in order to improve the prediction of the main ENM release paths to the environment, the most critical information refers to the ENM production volume, the usage of ENMs in products and their release during such use. A detailed discussion on the uncertainties of the

individual model input parameters and their impact on the model output was included in this sensitivity analysis as well. This evaluation showed that the major uncertainties stem from the calculations of the ENM production. A closer look is also needed at the release of ENMs from the products to the STP, the STP removal efficiency and overflow and the sludge from this compartment ending up in the WIP, where it is incinerated, exported, or deposited in landfills.

However, one of the main limitations for all these bottom-up studies is that for all the simulations a complete lack of quantitative data was observed on the ENM release during the manufacturing of ENM-containing products and during the production of ENMs. ENM production information varies sometimes by a factor of 100.[23] The only quantitative overview of ENM volumes incorporated in ENM products is presented in Schmid and Riediker.[39]

Experimental investigation of ENM release

ENM release under natural conditions or from technical compartments

Currently almost no analytical measurements of ENM in the environment have been done.[40] Only a few studies have been published that quantified nanomaterials in natural samples or conducted release experiments under laboratory or field conditions.

The release of nanoparticles by weathering is possible, e.g., if a product containing nanoparticles is exposed to the sun and rain. An application where this occurs is the use of nano-TiO_2 in facade paints.[10] Synthetic TiO_2 particles have been detected and identified in facades and urban runoffs. Analytical electron microscopy, optical emission spectrometry and mass spectrometry (TEM, ICP-OES and ICP-MS analysis) were used to show that nano-TiO_2 may be detached from new and aged paints from house facades under natural weather conditions and discharged into natural stream flows. Ti concentrations collected from the new facade runoff were as high as 600 mg L^{-1}. These Ti concentrations in the raw samples (collected directly from the façade) were about 10 to 15% higher compared to centrifuged samples. This shows that 85–90% of the collected material occurred in the range of 20–300 nm. The strength of this study is that the authors analyzed for the first time water samples under natural conditions and solid coatings of facades under semi-natural conditions (model house).

Kiser et al.[41] provided initial evidence for the release of nano-sized and larger Ti particles into water from STP effluents and into sewage treatment sludge. The authors measured concentrations of filterable Ti (smaller 700 nm) in STP effluents that ranged from <5 to 15 µg L^{-1}. Whenever Ti was removed, it accumulated in settled solids. The concentrations ranged from 1 to 6 mg Ti g^{-1}. Solids containing Ti were imaged in sewage, STP effluents and biosolids, as well as in commercially available products that contain engineered TiO_2. Particles (from 50 nm to a few hundred nm) composed of sub-50 nm spheres of Ti and oxygen only (presumably TiO_2) were observed in all samples. However, the method was not specific to engineered TiO_2 and included all particulate Ti smaller than 700 nm, thus only indicating that the true nano-TiO_2 concentrations have to be below the measured value.

Farré et al.[42] studied C_{60}, C_{70} and N-methylfulleropyrrolidine C_{60} in surface water and wastewater. Effluents of 22 wastewater treatment plants in Catalonia (NE of Spain) were analyzed and 50% of the samples were found to contain fullerenes. The values for C_{60} ranged from 0.5 ng L^{-1} to 19 µg L^{-1}. The equivalent results for C_{70} fullerenes were 181 ng L^{-1} and 1.7 µg L^{-1}, for N-methylfulleropyrrolidine C_{60} 60 ng L^{-1} and 66 µg L^{-1}.

Release experiments

Although the release of ENMs from products is generally considered to be relevant, there is a distinct lack of analytical information regarding the nanomaterial emission process itself. Textiles, e.g., have been seen as a relevant product category where release into water can be expected. Due to antimicrobial, antifungal and partially antiviral properties Ag-ENMs are, e.g., one of the most promising ENM for applications in textiles.[43] Information is available for the release of ionic Ag^+ from polymers containing Ag rather than for the release of particulate Ag.[44,45] However, we know that particulate release may also be relevant, as the textiles disposed at the end of their use phase lost up to 10% of the weight through abrasion during washing and usage.[12]

Two studies investigated ENM release from socks when immersed in a liquid phase. One work referred to the leaching of Ag-ENM from nano-socks into distilled water.[46] Electron microscopy made it possible to investigate the presence of nanosized silver in the sock material and in the water samples, respectively. The results showed that both nanosized particles and ionic silver leach from socks immersed in water. A general (single) release coefficient for a particular type of textile and ENM was not observed, since the different textile manufacturing process determines the release of silver leading to variable leaching rates for different textile types. The socks contained up to 1360 µg Ag per g sock and leached as much as 650 µg of silver in 500 mL distilled water.

In addition, the removal of colloidal as well as ionic silver from the washwater by wastewater treatment system biomass (activated sludge) was also investigated. The observed adsorption of the leached silver to STP biomass suggested that typical wastewater treatment facilities will adsorb most of the influent silver. However, the authors state that the nano-Ag released from the socks adsorbs to biomass in a way similar to that of ionic silver. Hence, improved analytical techniques are needed to differentiate nanoparticles from ionic species, since almost no detection methods are available that would be applicable to environmental matrices (low pollutant concentrations).

A subsequent study[9] updated the experimental setting by investigating the nano-Ag release from silver-containing fabrics under real washing procedures. Free Ag^+ ion concentrations were measured by means of an Ag ion-selective electrode. The washing was carried out based on ISO methods for washing tests.[47] The amount and the form of Ag released (colloidal or ionic) into the washing solution was investigated by using a solution of pH 10 and by washing for 30 min at 40 °C. The influence of surfactants, pH, and oxidizing agents on silver nanoparticles dissolution and release from textiles was assessed as well. The results—conducted under conditions relevant for washing (mechanical stress, high pH, presence of detergents and

bleaching agents)—showed little dissolution of Ag-ENMs at pH 10 with dissolved concentrations ten times lower than at pH 7. However, the authors stated that bleaching agents (*e.g.* hydrogen peroxide or peracetic acid formed by the perborate/TAED system) can greatly accelerate the dissolution of Ag. The amount of Ag released from the fabrics was shown to depend on the type of Ag incorporation in the textile. The percentage of the total silver released during one single washing varied considerably among the different products (from <1% to 45%). Most of the Ag (at least 50%, but mostly >75%) was emitted in the size fraction >450 nm. The authors explain this coarse Ag release as caused by the dominant role of mechanical stress. The amount of Ag leached from the socks ranged from 0.3 to 377 μg g^{-1} and was higher than the range (1–68 μg g^{-1}) observed by Benn and Westerhoff[46] that only used distilled water and gentle agitation.

However, the authors[9] also state that even such more realistic settings for experimentation do not represent the whole spectrum of relevant washing conditions. ENM release from repeated washing (long time process) was not considered; the release of Ag is likely to be reduced following repeated washing cycles of the textiles. Also the use of commercially available washing machines would lead to more realistic results. Furthermore, the presence of chloride anions in tap water or the detergent formulation which may result in precipitation of Ag$^+$ as AgCl and thereby lowering the amount of dissolved Ag was not considered.[48]

Benn *et al.*[49] used a washing protocol designed to investigate nano-Ag emissions into tap water as opposed to "real-world"[9] experimental settings. The potential release of nano-Ag into complex aquatic systems (wastewater, surface water, saliva, landfill leachate, *etc.*) with differences in water conditions (temperature, pH, redox potential, particulate matter, *etc.*) was investigated. The content of nano-Ag in different consumer products was measured (athletic shirt, unfinished cloth fabric, medical mask, medical cloth, toothpaste, shampoo, detergent, towel, teddy bear and two humidifiers). In addition, the release of nano-Ag from these products into water was quantified by means of electron microscopy and filtration.[46] Different product samples were washed with municipal tap water and mixed for 1 h at room temperature. Releases of up to 46 μg Ag g^{-1} per product were seen. However, the products released highly different quantities of silver. The medical mask that contained approximately 27% silver by weight released <0.01% of its silver into the washwater, the shirt containing 44 μg g^{-1} 2% (34 μg) of its silver.

Release during the use and disposal of products

Experimental information on the release of ENM during use or disposal of products is very scarce. One initial study investigated the ENM release by abrasion into air from surface coatings.[50] This analysis was based on the combination of a defined abrasion process with sensitive methods to quantify the airborne particle (<100 nm) release and concentration. A sophisticated interconnection between the aerosol generating and the measuring units was developed to provide enough sensitivity and prevent artifacts by measuring release from abrasion of ZnO-containing coatings. However, during the abrasion tests no significant released particle concentration <100 nm was detected in the aerosol.

Hsu and Chein[51] analyzed emissions of nano-TiO$_2$ from coatings on polymer, wood and tile in a simulation box using SMPS (scanning mobility particle sizer). Among the three studied substrates (wood, polymer and tile), tile coated with TiO$_2$ nano-powder showed the highest particle emission. The influence of sunlight, wind and human contact on the release was studied as well. The UV light treatment increased the release of particles below 200 nm from TiO$_2$ nano-powder coated materials. The number concentration decreased significantly after 60 and 90 min for TiO$_2$/polymer and TiO$_2$/wood, respectively. For the TiO$_2$/tile sample the emission rate continued to increase after 2 h of testing. The experiments showed also that a rubber knife scraping motion can reduce significantly the binding force between the TiO$_2$ nano-powder and the substrate.

Generic limitations of all these product-based experiments are as follows: (i) they only represent a small part of the whole spectrum of all the potential environmental release situations that might arise throughout the whole life cycle of a particular ENM-containing product; (ii) between-product variability in the release properties are often not addressed; (iii) the experiments are often not repeated often enough to get sufficient output data for real statistical evaluation; and (iv) the results reflect only artificial laboratory conditions leading to findings that could vary significantly from the results obtained under more realistic ENM release conditions.

The form of ENM release

Besides knowing the amounts of ENM released into the environment, it is equally important to investigate in what forms ENMs are released.[8] ENM may be emitted as (1) free ENM, (2) ENM aggregated and ENM agglomerated particles, or (3) embedded in a matrix.[14] Hence, the spectrum of potential ENM emissions includes nanoscaled pollutants as well as released bulk material containing nanosized particles/structures. Individual nanosized pollutants may arise, for example, from the silica nanoparticles used as solid lubricants, or from metal oxide particles injected in groundwater for remediation; or from nano-TiO$_2$ added to cosmetics. ENM in composites or mixtures are probably released as nanosized particles as well as embedded in larger forms (attrition from products containing ENM, *e.g.*, CNT composites used in tires, brake pads, tennis rackets, *etc.*).[12]

An example where nanoparticles were released embedded in larger particles is shown in Fig. 2.[50] ZnO release into air by abrasion from coatings was studied. Based on electron microscopy and EDX (energy dispersive X-ray) analysis evidence was given that nanoparticles were present within larger particles and that these nanoparticles showed the characteristic morphology of the ZnO particles.

Kaegi *et al.*[10] revealed that TiO$_2$ may be released in nanoparticulate form into facade runoff (and discharged into natural waters) from new and aged facade paints by natural weather conditions. Electron microscopy of the released particles showed that some ENM TiO$_2$ was still embedded in the organic binder (see Fig. 2), but that also many single particles were released from aged facades. Particles were observed that were still covered with the organic binder of the paint. The particles found, *e.g.*, in the runoff of the new facade showed a size range from a few tens to several hundreds of nanometres. This investigation is the first
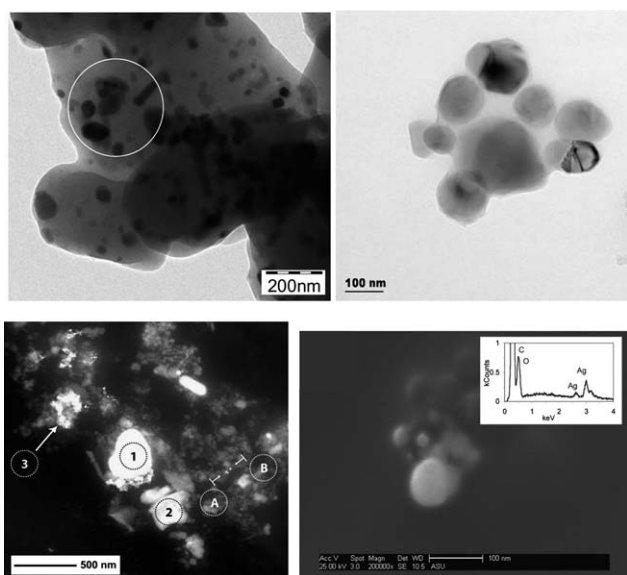
Fig. 2 Nanoparticles released from products. Top left: wear from a steel panel with embedded ZnO nanoparticles[50]; top right: TiO$_2$ particles embedded in organic binder released from paint[10]; bottom left: Ag particles released from paint containing nano-Ag[52]; bottom right: agglomerated Ag particles with sizes <100 nm released from a medical mask into tap water.[49] Figures from references 10, 50 and 52 reprinted with permission from Elsevier, from reference 49 with permission from the American Society of Agronomy.

ever to show that single ENM particles are actually released to the environment. The same authors also showed that Ag is released from nano-Ag containing paints.[52] Fig. 2 shows that both small, single Ag-NP as well as larger Ag-containing particles are released.

Experiments investigating the leaching Ag-ENM from nano-socks into distilled water[46] showed that both ionic and particulate Ag was emitted. Based on TEM and EDX analysis of the colloids in the washwater, the presence of silver material with diameters ranging from one to a few hundred nanometres was shown. Thus, at least some of the nano-Ag was released into the washwater as nanoparticles and not only as dissolved ionic silver. Depending on the material either 14–28 or 30–95% of the emitted Ag was present as particulate Ag.

Geranio et al.[9] showed the majority of the released Ag (at least 50% but mostly >75%) during the washing process in a washing machine in the size fraction >450 nm. Such size fractions (Fig. 3) indicate the dominant impact of mechanical stress. Compared to many of the nano-Ag containing textiles, conventional silver socks did not show any significant difference in the size distribution of the released silver. These results show that under washing conditions primarily coarse Ag-containing particles are released.

Ben et al.[49] investigated with electron microscopy and filtration methods form, shape, and size of silver released from various products. Released particles or agglomerates at size fractions larger and smaller than 100 nm were observed. Silver emitted from a shirt, mask, and medical cloth mostly passed a 20 nm filter. In contrast, a 100 nm pore size filter removed, e.g., most of the silver emitted by a toothpaste, shampoo, and detergent. The latter case shows that the silver was either released in form of
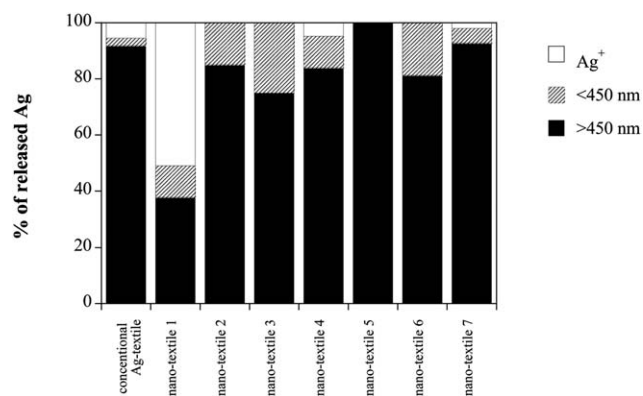

Fig. 3 Size fractionation of the silver released from various textiles during washing. Only a small fraction of the released Ag is in the nano-range (part of fraction <450 nm). Adapted from ref. 9.

nanoparticles or associated with particles larger than 100 nm. The SEM analysis revealed that the particles in the washwater of the toothpaste were much larger in size (100–500 nm) than those from the medical cloth and mask. Fig. 2 (bottom right) shows agglomerations of particles with sizes <100 nm released from the medical mask into the tap water. However, particle size ranges shown in TEM/SEM images (Fig. 2) should be interpreted cautiously because the sample preparation (deposition onto and evaporation of liquid from TEM grids for example) may introduce major artifacts in agglomeration/aggregation of primary particle sizes.

Conclusions

Initial analytical and experimental studies have provided evidence for the release of ENM into the environment from products (textiles, paints, etc.) containing ENM. These results show that ENM are actually released but also highlight the main difficulty in quantifying what has been released: the materials that are released may have very little in common with the material that was inside the product. Its composition may have been altered, but more importantly it is likely that the ENM is still embedded in the matrix and not released as an individual particle.

Studies investigating, e.g., the release from textiles are limited since they generally do not reflect realistic washing processes and conditions. Conditions for textiles immersed in pure, tap or in distilled water differ clearly from those during washing processes where high concentrations of surfactants are present, bleaching agents are used and the pH lies between 10 and 11. Also, mechanical stress on the textiles during the washing process as well as information on washing rates, washwater and textile contact time and total amounts of textiles washed have to be considered.

To overcome such experimental limitations future research needs to enhance the representativeness of the single examined release processes. Experiments must cover a relevant release event out of all the potential release situations during the whole life cycle of a particular product. Such relevancy may be improved by keeping experimental settings close to reality and by estimating variability in the release between single exemplars of

the same product and different products as well as by producing in each case sufficient experimental data for statistical output evaluation.

Experimental results at companies producing ENM have shown that worker exposure to these materials occurs.[26–30] However, for quantifying the ENM release to a particular environmental compartment some critical aspects that determine the analytical and experimental setting have to be considered. Measurements need to analyze the amount of ENM reaching the environment and not only to quantify the ENM concentrations in a particular occupational or consumer environment. Hence, measurements of indoor air are not useful without indications of the corresponding total air volume, air exchange rates and effect of any filtration. Thus, most studies conducted to measure airborne concentration or exposure in occupational settings cannot be used directly to quantify environmental release. Similarly, ENM concentrations in wastewater are not informative without knowledge of the mass flow of pollutant per time unit. Another complication is that available methods that detect the presence of nanoparticles in air do not necessarily discriminate between engineered or naturally nanosized particles.

Hence, mathematical modeling of ENM release into the environment is currently the most important tool to conduct environmental risk assessment for such materials. Doing this, life cycle concepts should be used to ensure a comprehensive identification of priorities of the analysis of ENM release.[5] However, ENM release assessment suffers from low quality and/or scarcity of input data. Therefore, to improve such models we urgently need more empirical information:

• Industrial data on ENM production amounts, including quantitative indications on the allocation of the produced volume to relevant product categories (*e.g.* cosmetics, plastics, *etc.*) that contain the ENM.

• Experimental and analytical data about the main release sources during all ENM life stages: ENM production, manufacturing of nanoproducts, consumption and disposal of nanoproducts.

• Experimental and analytical data regarding the form the ENM are released, such as whether the ENM are agglomerated or present as single particles or if they are embedded within a matrix.

A major shortcoming of the current release models is that due to scarcity of data all the different specific forms of the same type of ENM (*e.g.* different surface-coatings of a particular material) had to be lumped together in the model calculations. A critical point in such models is also the assumed steady state approach for ENM release and transmission flow calculations. Future research needs to include time-dependent storage of ENM in products or re-suspension of settled material in rivers, which could considerably impact the amount of ENM released to the different environmental compartments per unit time. Also time dependent dynamics of ENM production amounts and nanoproducts consumption volumes need to be considered.

Acknowledgements

References

1 Royal Commission Report, *Novel Materials in the Environment: The Case of Nanotechnology*, Royal Commission on Environmental Pollution, TSO, 2008.
2 G. B. Andreev, V. M. Minashkin, I. A. Nevskii and A. V. Putilov, *Russ. J. Gen. Chem.*, 2009, **79**, 1974–1981.
3 P. J. J. Alvarez, V. Colvin, J. Lead and V. Stone, *ACS Nano*, 2009, **3**, 1616–1619.
4 B. Nowack, *Environ. Pollut.*, 2009, **157**, 1063–1064.
5 C. Som, M. Berges, Q. Chaudhry, M. Dusinska, T. F. Fernandes, S. I. Olsen and B. Nowack, *Toxicology*, 2010, **269**, 160–169.
6 M. R. Wiesner, G. V. Lowry, K. L. Jones, M. F. Hochella, R. T. Di Giulio, E. Casman and E. S. Bernhardt, *Environ. Sci. Technol.*, 2009, **43**, 6458–6462.
7 S. J. Klaine, P. J. J. Alvarez, G. E. Batley, T. F. Fernandes, R. D. Handy, D. Y. Lyon, S. Mahendra, M. J. McLaughlin and J. R. Lead, *Environ. Toxicol. Chem.*, 2008, **27**, 1825–1851.
8 A. R. Kohler and C. Som, *Hum. Ecol. Risk Assess.*, 2008, **14**, 512–531.
9 L. Geranio, M. Heuberger and B. Nowack, *Environ. Sci. Technol.*, 2009, **43**, 8113–8118.
10 R. Kaegi, A. Ulrich, B. Sinnet, R. Vonbank, A. Wichser, S. Zuleeg, H. Simmler, S. Brunner, H. Vonmont, M. Burkhardt and M. Boller, *Environ. Pollut.*, 2008, **156**, 233–239.
11 S. Dekkers, L. C. H. Prud'homme De Lodder, R. de Winter, A. J. A. M. Sips and W. H. de Jong, *RIVM/SIR Advisory Report 11124*, RIVM, Bilthoven, 2007.
12 A. Koehler, C. Som, A. Helland and F. Gottschalk, *J. Clean. Prod.*, 2008, **16**, 927–937.
13 G. Oberdorster, E. Oberdorster and J. Oberdorster, *Environ. Health Perspect.*, 2005, **113**, 823–839.
14 B. Nowack and T. D. Bucheli, *Environ. Pollut.*, 2007, **150**, 5–22.
15 G. V. Lowry and E. A. Casman, in *Nanomaterials: Risks and Benefits*, ed. I. Linkov and J. Steevens, NATO Science for Peace and Security Series C: Environmental Security, 2009, vol. 2, pp. 125–137.
16 B. Nowack, in *Nanotechnology, Volume 4 "Environmental Aspects"*, ed. H. F. Krug, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008, pp. 1–15.
17 R. J. Aitken, M. Q. Chaudhry, A. B. A. Boxall and M. S. Hull, *Occup. Med.*, 2006, **56**, 300–306.
18 A. D. Maynard, *Nano Today*, 2004, **1**, 22–33.
19 N. C. Mueller and B. Nowack, *Environ. Sci. Technol.*, 2008, **42**, 4447–4453.
20 S. A. Blaser, M. Scheringer, M. MacLeod and K. Hungerbuehler, *Sci. Total Environ.*, 2008, **390**, 396–409.
21 A. B. A. Boxall, Q. Chaudhry, A. Jones, B. Jefferson and C. D. Watts, *Current and Future Predicted Environmental Exposure to Engineered Nanoparticles*, Central Science Laboratory, Sand Hutton, UK, 2008.
22 B. Park, *Environ. Sci. Technol.*, 2007, **24**, 1–18.
23 F. Gottschalk, T. Sonderer, R. W. Scholz and B. Nowack, *Environ. Sci. Technol.*, 2009, **43**, 9216–9222.
24 F. Gottschalk, T. Sonderer, R. W. Scholz and B. Nowack, *Environ. Toxicol. Chem.*, 2010, **29**, 1036–1048.
25 ECHA, *Guidance on information requirements and chemical safety assessment, Chapter R.16: Environmental Exposure Estimation*, European Chemicals Agency, 2010.
26 D. Bello, A. J. Hart, K. Ahn, M. Hallock, N. Yamamoto, E. J. Garcia, M. J. Ellenbecker and B. L. Wardle, *Carbon*, 2008, **46**, 974–977.
27 L. F. Mazzuckelli, M. M. Methner, M. E. Birch, D. E. Evans, B. K. Ku, K. Crouch and M. D. Hoover, *J. Occup. Environ. Hyg.*, 2007, **4**, D125–D130.
28 B. Yeganeh, C. M. Kull, M. S. Hull and L. C. Marr, *Environ. Sci. Technol.*, 2008, **42**, 4600–4606.
29 J. H. Han, E. J. Lee, J. H. Lee, K. P. So, Y. H. Lee, G. N. Bae, S. B. Lee, J. H. Ji, M. H. Cho and I. J. Yu, *Inhalation Toxicol.*, 2008, **20**, 741–749.
30 Y. Fujitani, T. Kobayashi, K. Arashidani, N. Kunugita and K. Suemura, *J. Occup. Environ. Hyg.*, 2008, **5**, 380–389.
31 L. K. Limbach, R. Bereiter, E. Müller, R. Krebs, R. Gälli and W. J. Stark, *Environ. Sci. Technol.*, 2008, **42**, 5828–5833.
32 B. Park, K. Donaldson, R. Duffin, L. Tran, F. Kelly, I. Mudway, J. P. Morin, R. Guest, P. Jenkinson, Z. Samaras, M. Giannouli, H. Kouridis and P. Martin, *Inhalation Toxicol.*, 2008, **20**, 547–566.

33 N. O'Brien and E. Cummins, *J. Environ. Sci. Health, Part A*, 2010, **45**, 992–1007.

34 N. O'Brien and E. Cummins, in *Nanomaterials: Risks and Benefits*, ed. I. Linkov and J. Steevens, Springer Netherlands, 2009, pp. 161–178.

35 N. J. O'Brien and E. J. Cummins, *Risk Anal.*, 2010, DOI: 10.1111/j.1539-6924.2010.01540.x.

36 F. Gottschalk, R. W. Scholz and B. Nowack, *Environ. Modell. Software*, 2010, **25**, 320–332.

37 A. J. Kennedy, M. S. Hull, J. A. Steevens, K. M. Dontsova, M. A. Chappell, J. C. Gunter and C. A. Weiss, *Environ. Toxicol. Chem.*, 2008, **27**, 1932–1941.

38 H. Hyung, J. D. Fortner, J. B. Hughes and J. H. Kim, *Environ. Sci. Technol.*, 2007, **41**, 179–184.

39 K. Schmid and M. Riediker, *Environ. Sci. Technol.*, 2008, **42**, 2253–2260.

40 K. Tiede, A. B. A. Boxall, S. P. Tear, J. Lewis, H. David and M. Hassellov, *Food Addit. Contam.*, 2008, **25**, 795–821.

41 M. A. Kiser, P. Westerhof, T. Benn, Y. Wang, J. Pérez-Rivera and K. Hristovski, *Environ. Sci. Technol.*, 2009, **43**, 6757–6763.

42 M. Farré, S. Pèrez, K. Gajda-Schrantz, V. Osorio, L. Kantiani, A. Ginebreda and D. Barcelü, *J. Hydrol.*, 2010, **383**, 44–51.

43 J. B. Morones, J. L. Elechiguerra, A. Camacho, K. Holt, J. B. Kouri, J. T. Ramirez and M. J. Yacaman, *Nanotechnology*, 2005, **16**, 2346–2353.

44 R. Kumar, S. Howdle and H. Munstedt, *J. Biomed. Mater. Res., Part B*, 2005, **75B**, 311–319.

45 R. Kumar and H. Munstedt, *Biomaterials*, 2005, **26**, 2081–2088.

46 T. M. Benn and P. Westerhoff, *Environ. Sci. Technol.*, 2008, **42**, 4133–4139.

47 ISO, *Textilesstests for Colour Fastnessspart C06: Colour Fastness to Domestic and Commercial Laundering*, International Organization for Standardization, Geneva, 1997.

48 C. A. Impellitteri, T. M. Tolaymat and K. G. Scheckel, *J. Environ. Qual.*, 2009, **38**, 1528–1530.

49 T. Benn, B. Cavanagh, K. Hristovski, J. D. Posner and P. Westerhoff, *J. Environ. Qual.*, 2010, **39**, 1875–1882.

50 M. Vorbau, L. Hillemann and M. Stintz, *J. Aerosol Sci.*, 2009, **40**, 209–217.

51 L. Y. Hsu and H. M. Chein, *J. Nanopart. Res.*, 2007, **9**, 157–163.

52 R. Kaegi, B. Sinnet, S. Zuleeg, H. Hagendorfer, E. Mueller, R. Vonbank, M. Boller and M. Burkhardt, *Environ. Pollut.*, 2010, **158**, 2900–2905.

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J. Environ. Monit., 2011, **13**, 1145–1155 | 1155