Development of Exposure Scenarios for Manufactured Nanomaterials

Work Package 5

Report on exposure scenarios and release of nanomaterials to the environment
(Including Deliverable D5.1)

Fadri Gottschalk¹, Bernd Nowack¹, Bernd Gawlik²

December 2010

¹ Swiss Federal Laboratories for Materials Science and Technology (EMPA), St. Gallen, Switzerland
² European Commission – Joint Research Centre Institute for Environment and Sustainability, Ispra (Va), Italy
Project website: www.nanex-project.eu

Funded under the seventh framework programme: NMP-2009-1.3-2: Exposure scenarios to nanoparticles

Grant agreement no.: 247794
Funding scheme: Coordination and Support Actions (supporting action)
Executive summary

There is scientific agreement that manufactured nanomaterial (MNM) production, use and disposal leads to release of MNM to the environment. However, very little is known about such environmental emissions.

In WP5 the literature on such releases is reviewed. The availability and applicability of existing i) models, ii) experimental settings and iii) analytics for assessing MNM environmental release are discussed. Hence, the objective of this report is to answer the questions: a) what is the relevant knowledge regarding MNM release to the environment, b) what is known, has been modelled or measured, which methods are available, c) what can these models and measurements deliver, what not, d) in what way is the REACH approach suited for MNM, is it applicable or why not?

In addition to looking at exposures triggered by local emissions/point sources, as is done for occupational and consumer exposure assessments (WP3 and WP4), the evaluation of environmental release (WP5) and exposure to MNM must also consider emissions from diffuse sources that cover the whole life cycle of MNM and MNM containing products. As with many pollutants, most of the MNM release stems from non-point sources such as wearing or washing textiles containing MNM, or using MNM-containing cosmetics, sunscreen etc. Such sources are probably the most important and the most difficult to control. In this respect MNM are not different to other chemicals in consumer products. However, for pollutants emitted as nano-sized particles, a quantitative (and qualitative) detection is difficult. Currently there are almost no measurement techniques and data available to quantify MNM emissions and concentrations in the environment. Especially, distinguishing engineered nano-scaled particles from background particles at the same size is difficult. Such a distinction becomes particularly difficult when measurements of ubiquitous background aerosol concentrations show higher values than process-specific concentrations (Maynard 2006). Quantifying the portion of released airborne nanoparticles attaching to background aerosols is also difficult (Savolainen et al. 2010). Mass spectrometry (MS) promises reliable results for quantifying MNM environmental concentrations. In particular, field-flow fractionation-inductively coupled plasma mass spectrometry (FFF–ICP–MS) methods are increasingly used. In the future such methods should aim at allowing simultaneously sizing
and analyzing particles in their original environment using size separation of the sample with quantitative and elemental evaluation of the size fractions.

One of the first analytical studies on environmental release of MNMs (Kaegi et al. 2008) reports the detection of manufactured nano-TiO$_2$ in water leaching from exterior facades. Further experimental works show evidence for release of nano-sized Ag from commercial textiles during washing (Benn and Westerhoff 2008; Geranio et al. 2009). Other studies have been published that quantified concentrations of filterable Ti (smaller 700 nm) in sewage treatment plant effluents (Kiser et al. 2009). However, the method is not specific for engineered TiO$_2$ and includes all particulate Ti smaller than 700 nm. Based on mass spectrometry C$_{60}$ and, C$_{70}$ fullerenes and N-methylfulleropyrrolidine C$_{60}$ in wastewater effluents were recently detected as well (Farré et al. 2010).

However, for quantifying MNM release to the environment, measurements have to analyze the total amount of MNM reaching a particular environmental compartment and not simply to quantify the MNM concentrations in that compartment. Hence, measurements that provide only concentrations in indoor air or sewage water etc. are not useful without indications of the corresponding total air volume and air exchange rates or the time dependent stream flow. Also studies conducted to investigate air pollution in occupational settings that only provide MNM concentrations in indoor air do not assist in quantifying environmental release.

In addition to single measurements, a handful of modelling studies have investigated MNM release to the environment. Some of them evaluated release to the environment from single MNM-containing products during the consumption phase (Blaser et al. 2008; Boxall et al. 2008). Life cycle based release modelling was carried out as well (Mueller and Nowack 2008). Recently, stochastic/probabilistic mass partitioning models (Gottschalk et al. 2009; Gottschalk et al. 2010; Gottschalk et al. 2010) were developed and implemented to estimate environmental release throughout the whole life cycle of MNM and MNM-containing products (MNM production and manufacturing of products, use, recycling and disposal), and to quantify as far as possible the distinct model input uncertainties. Sewage sludge, wastewater, and waste incineration of products containing MNM were shown to be the major flows through which MNMs end up in the environment. Release results for the MNMs TiO$_2$, ZnO, Ag, and CNT were provided. Relevant release e.g. to water,
sediments and soils was observed for the metallic materials, whereas for the carbon based MNM only marginal amounts reach the environment.

Distinct uncertainties limit conceptualization and parameterization of all these models. More reliable data on MNM production and application amounts and empirical information on release coefficients for all mentioned life cycle stages of MNM-containing products and environmental compartments are needed. To improve and validate such release assessments, we need urgently need more empirical information on MNM production amounts. Quantitative indications on the allocation of the produced volume to the relevant product categories (e.g. cosmetics, plastics etc.) that contain the MNM are needed. Empirical (experimental / analytical) release information for the main release sources during the MNM life stages is needed as well (MNM production and nanoproducts’ manufacture processes, MNM products consumption and disposal). This report showed also that only very few data concerning the released form (single nanoparticles or larger pieces, e.g. in agglomerated form) is available. Information on bioaccumulation, a potential endpoint for many materials, is almost completely missing as well.
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1. Introduction

The impressive application prospects of nanosized materials, in a variety of consumer products (e.g. pharmaceutical, biomedical, cosmetic, electronic, energy, environmental, catalytic materials), could lead to a significant increase in the production, manufacture and use of MNMs in products and, consequently, to the release of such nanomaterials to the environment (Nowack and Bucheli, 2007; Andreev et al., 2009).

There are distinct knowledge gaps regarding the potential environmental release of and exposure to MNM (Borm et al., 2006; Helland et al., 2006; Hund-Rinke and Simon, 2006; Wiesner et al., 2006; Nowack and Bucheli, 2007; Ober dorster et al., 2007; Chaudhry et al., 2008; Handy et al., 2008; Klaine et al., 2008; Scheringer, 2008; Alvarez et al., 2009; Andreev et al., 2009; Nowack, 2009). Nevertheless, the possible negative environmental impacts of MNMs are under discussion worldwide (Roco, 2005; Helland et al., 2006; Siegrist et al., 2007a; Siegrist et al., 2007b; Hudson and Orviska, 2009). There are no nano-specific regulations to cover such impacts, either in the EU (Führ et al., 2007) or worldwide (Hodge et al., 2007). Existing environmental policies and regulations are almost exclusively focused on conventional chemical substances (i.e. bulk material) and do not consider the particular physicochemical properties of nanoscaled materials (Boverhof and David, 2010). REACH (2010) addresses chemicals in general, without focusing specifically on nanosized substances and their properties.

One of the first studies of MNM release to the environment identified that carbon nanotubes (CNTs) could be released into the environment when used in lithium ion batteries (Koehler et al., 2008). The US Environmental Protection Agency (US-EPA) discussed the example of the potential release caused by the application of nanoscale titanium dioxide (nano-TiO$_2$) (2009). The cosmetics industry uses high amounts of nano-TiO$_2$ as an active ingredient e.g. in sunscreens$^1$. Initial studies mainly addressed MNM release during product consumption. MNM-containing products were seen as safe as long as no unintended release of MNM occurred.

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$^1$ NANEWP4 has reviewed existing information on exposure scenarios and exposure estimation for nano-silver in textiles, carbon nanotubes (CNTs) in consumer products and nano-TiO$_2$ in sunscreen (see D.4.1).
However, MNMs can also be released during their primary production, as well as during the manufacture of MNM-containing products.

The US-EPA aims to regulate the growing class of nanotech products. The agency has jurisdiction in that antimicrobials based on nano-Ag are considered to be pesticides and therefore fall under the Federal Insecticide, Fungicide & Rodenticide Act (FIFRA). The problem facing the agency is to determine what data are needed to assess the potential environmental and health risks and the best way to collect such data (C&EN, 2010).

WP3 and WP4 of the NANEX project considered occupational and consumer exposure scenarios, reviewing available data together with the tools needed to estimate exposure during these scenarios. They attempted to build exposure scenarios based on publicly available data and data collected during a number of large surveys. WP5 reviewed the available information on MNM release to the environment from these occupational and consumer scenarios. In contrast to occupational and consumer exposure assessments (see WP3 and WP4), the evaluation of environmental release (WP5) and exposure to MNM has to consider an immense diffusive emission source setting that has to cover the whole life-cycle of MNMs and MNM-containing products. Hence, the definition of relevant MNM release-assessment settings for parameters such as MNM production, together with the distribution of their use (temporal and geographical), is crucial for framing MNM emission models as well as for experimental and analytic studies.

This WP5 report will first describe the current relevant knowledge regarding MNM release to the environment and review the available methods and models for the estimation of such release. Results from the literature will then be summarized and reviewed with regard to their adequacy for use under the REACH regulations. Finally, descriptions are provided of the environmental release-contributing scenarios within the occupational and consumer exposure scenarios developed in WP3 and WP4, respectively.
2. MNM release to the environment

2.1 Amounts of MNM release

MNM release to the environment may occur during the whole life-cycle of MNMs, i.e. MNM production, manufacture of (intermediate) products containing MNMs, use of these products by workers or consumers, and recycling or disposal of such products.

The most obvious case for defining the volume (and form) of MNMs that can get into the environment is from situations where they are directly and intentionally released. Such releases occur, for example, in the application of nano zero-valent Iron (nZVI) for groundwater remediation, where large amounts of nZVI (up to several tons per contaminated site) are pumped into the subsurface (Nowack, 2008). Also, MNM-containing agrochemicals end up directly and completely in the environment when applied outdoors.

However, most MNMs are not intentionally released into the environment, although some unintentional release may still occur. For example, there is experimental evidence that nano-Ag can be released from textiles during washing and that nano-TiO$_2$ can be released from paints into rainwater running off a facade. In other cases, the release of MNM is inevitable due to the nature of its application, such as when applying sprays, sunscreen, and other cosmetics. Such MNM release from consumer products is the most difficult to control. In this category, their form, quantity, and release kinetics, or their temporal variations, are not known.

Hence, to estimate the release it is essential to know the quantity of MNMs in the product, their form in the product (solid, liquid, aerosol), and where in the product the MNMs are included (e.g. embedded within a solid material matrix). Releases from the use of MNM-containing liquids, pastes, creams, powders and aerosol spray applications are expected to be especially significant (Dekkers et al., 2007). However, MNMs not bound strongly into the matrix of larger materials, e.g. as surface coatings or in textiles, might also be emitted during the use of products. Mechanical abrasion and physicochemical material aging due to thermal and photooxidative processes may have a considerable impact on any release (Koehler et al., 2008). It is also extremely difficult to monitor and quantify the long-term release
of MNMs during the waste disposal of MNM-containing products (Oberdorster et al., 2005).

Life-cycle concepts are needed covering the current knowledge on MNM release from MNM production, from manufacturing of MNM-containing products and from the use, recycling and disposal of such products. Such concepts provide information to decision-makers in industry and public authorities at an early stage of the development of the technology; allowing the development of safe nanotechnology-based products (Davis, 2007; Wardak et al., 2008).

The term “life-cycle” (Figure 1) normally covers the material/chemical life-span, including the production, use and disposal of a material/chemical or a product, in this case of MNMs and MNM-containing products. “Nanoproducts” (Som et al., 2010) are defined as commercially available products that either contain MNMs, or that derive specific functions from nanostructured materials that do or do not contain MNMs. MNMs (e.g. TiO$_2$) can form part of other nanomaterials such as polymer-MNM composites which, in turn, form part of products (e.g. a T-shirt, sun lotions, food packaging, etc.). Other examples of nanoproducts include batteries containing CNTs, nano-silver textiles, or windows coated with a nanosized layer of TiO$_2$ (Som et al., 2010).

**Figure 1.** Manufactured nanomaterial (MNM) life-cycle stages: production; incorporation into products; and the use, disposal and recycling of products containing MNMs.
Consequently, the use and end-of-life stages of the life-cycles of MNMs are largely determined by the life-cycles of the specific products they are integrated into. Considering that the life-cycle of a MNM is, above all, characterized by its application within nanoproducts, the release exposure scenarios are clearly strongly dependent on the life-cycle of these products.

The whole spectrum of MNM release (Figure 2), includes their discharge into the environment via MNM production, the incorporation of MNMs into products, the use of these products and their disposal via sewage treatment plants (STP), waste incineration plants (WIP), landfill (LAN), recycling (REC) and other disposal processes. It is important to realize that the characteristics of MNM formulations can change during their life-cycle, for example due to physical/chemical interactions and changes, or as a result of the aging/degradation of the MNM or MNM-containing product.

![Figure 2. MNM release to the environment (E) via: manufactured nanomaterial (MNM) production; manufacturing of MNM-containing products; use of MNM-containing products; and via sewage treatment plants (STP), waste incineration plants (WIP), landfills (LAN) and recycling processes (REC).]
As with many pollutants, most of the release of MNMs stems from non-point sources such as wearing or washing textiles, or using products such as cosmetics, sunscreen etc., all of which can contain MNMs. Such sources are probably the most important but are also the most difficult to control (Nowack and Bucheli, 2007). In this respect MNMs are not different to other chemicals used in consumer products. However, the quantitative (and qualitative) detection of pollutants emitted as nanosized particles is currently almost impossible, due to a lack of adequate measurement approaches.

Point sources, such as nanomaterial production and manufacturing facilities, their transport processes, landfills, wastewater treatments, waste incineration plants, or any storm-water runoff from manufacturing facilities or from city roads and highways (Nowack and Bucheli, 2007; Lowry and Casman, 2009) are basically easier to monitor, especially examples of intentional release, such as the use of nZVI mentioned previously (Nowack and Bucheli, 2007). Table 1 lists a number of examples of products and applications resulting in the direct release of MNMs into the environment.

To comprehensively describe release-scenarios, information is required on the conditions leading to MNM release, the release concentrations, and their destination (ie technical compartment, such as wastewater treatment plant, waste incineration plant; or environmental compartment, such as air, surface water, soil). Any assessment of the release of MNMs has to consider a wide range of product applications. However, such applications are mostly very poorly researched. It is, for example, a challenge to consider how such release “events” can best be captured, and how to address epistemic uncertainty (lack of knowledge in mechanisms and models/measurements) as well as model/measurement parameter uncertainty and variability (lack of data).
Table 1: Products and applications involving the direct release of MNMs into the environment.

<table>
<thead>
<tr>
<th>Example</th>
<th>Compartment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Point sources (direct release or release from technical compartments)</strong></td>
<td></td>
</tr>
<tr>
<td>Groundwater remediation</td>
<td>Groundwater</td>
</tr>
<tr>
<td>Application of agrochemicals</td>
<td>Soil, air</td>
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<tr>
<td>Use for water treatment</td>
<td>Water</td>
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<tr>
<td>Release from waste incineration plants</td>
<td>Air, soil</td>
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<tr>
<td>Release from wastewater treatment plants</td>
<td>Water, soil</td>
</tr>
<tr>
<td>Leaching/draining from landfills</td>
<td>Groundwater, soil</td>
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<tr>
<td><strong>Diffuse sources (release from products)</strong></td>
<td></td>
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<tr>
<td>Wear during use, e.g. nano-Ag in textiles, nano-Si in tyres etc.</td>
<td>Air, soil, water</td>
</tr>
<tr>
<td>Nano-TiO$_2$ wash-off from sunscreen (in lakes etc.)</td>
<td>Water</td>
</tr>
<tr>
<td>Weathering of nano-TiO$_2$ from paints</td>
<td>Soil, water</td>
</tr>
<tr>
<td>Use of CeO$_2$ in fuels</td>
<td>Air, soil, water</td>
</tr>
<tr>
<td>Spreading of biosolids onto land</td>
<td>Soil</td>
</tr>
</tbody>
</table>
2.2 Form of MNM release

Besides knowing the amounts of MNMs released into the environment, it is equally important to investigate the forms in which MNMs can be released (Kohler and Som, 2008). MNMs may be emitted as (1) free MNMs, (2) aggregated and agglomerated MNM particles, or (3) MNMs embedded in a matrix (Nowack and Bucheli, 2007). Hence, the spectrum of potential MNM emissions includes nanoscaled pollutants as well as bulk material containing nanosized particles/structures. Individual nanosized pollutants may arise, for example, from silica nanoparticles used as solid lubricants, metal oxide particles injected in groundwater for remediation, or from nano-TiO$_2$ added to cosmetics. MNMs in composites or mixtures could probably be released as both nanosized particles as well as embedded in larger forms as a result of attrition from products containing MNMs e.g., CNT composites used in tyres, brake pads, tennis rackets etc. (Gottschalk, 2008; Koehler et al., 2008)).

An example of nanoparticle release embedded in larger particles is shown in Figure 3 (Vorbau et al., 2009). This study investigated nano-ZnO release into air by abrasion from coatings. Based on SEM, TEM and EDX analysis evidence, it was clear that nanoparticles were present within larger particles and that these nanoparticles showed the characteristic morphology of the ZnO particles.

![Figure 3: TEM image and EDX graph of wear from a steel panel with embedded ZnO nanoparticles. Reprinted from (Vorbau et al., 2009).](image)

Experiments into the leaching of Ag-MNMs from sock fabrics into distilled water (Benn and Westerhoff, 2008) showed that both ionic and particulate silver was released. Based on TEM and EDX analysis of the colloids in the wash water, the presence of silver material with diameters from one to a few hundred nm (Figure 4)
was shown. Thus, at least some of the nano-Ag was emitted into the wash water as nanoparticles and not only as dissolved ionic silver. Depending on the material, the proportion present as particulate Ag could represent either 70-90 or 5-70% of the emitted Ag.

Geranio et al. (2009) showed that the majority (at least 50% but mostly >75%) of the Ag released during the washing process in a washing machine was in the size fraction >450 nm. Such size fractions (Figure 5) indicate the dominant influence 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, the main release is of coarse Ag-containing particles.
Figure 5: Size fractionation of the silver released from various textiles during washing. Only a small fraction of the released silver is in the nano-range. Reprinted from (Geranio et al., 2009).

Kaegi et al. (2008) revealed that TiO$_2$ particles may be released from new and aged facade paints into facade runoff and discharged into natural waters through the effects of natural weather conditions. Electron microscopy of the released particles showed that MNM TiO$_2$ was partially still embedded in the organic binder but that many single particles were also released from aged facades. The top left picture in Figure 6 shows a particle still covered with the organic binder of the paint, while the bottom picture shows a single particle detected in urban runoff. The particles found in the runoff from a new facade showed a size range from a few tens to several hundreds of nm. This investigation is the first ever to show the presence of single MNM particles in the environment.
Figure 6: nano-TiO$_2$ in façade run-off of (top) and in an urban stream (bottom). Reprinted from (Kaegi et al., 2008).
3. Methods to assess MNM release into the environment

During the initial phase of the environmental release and risk assessment of MNMs (ca. 2000-2006), MNM emissions, behaviour and effects in the environment were only researched and discussed from a qualitative precautionary perspective (Nowack, 2009). The research questions that were addressed included:

What would happen if relevant MNM amounts ended up in the environment?

and

What would be their environmental fate and behaviour and how would they interact with organisms?

Quantitative evidence of the release of these substances was not available. The occurrence of MNMs in the environment had to be assumed theoretically “given the increasing production of MNMs of all types, the potential for their release in the environment and subsequent effects on ecosystem health had become an increasing concern” (Klaine et al., 2008).
3.1 Analytical Methods

Currently there are almost no measurement techniques available to quantify and characterize the release of MNMs into the environment or their environmental concentrations; at least no simple real-time operation equipment for ‘field work’. A range of microscopic methods, chromatography, filtration and centrifugation, and spectroscopic techniques might provide, under laboratory conditions, resolution down to the sub-nanometre range. The microscopic and spectrometric methods most used which can be applied to describe MNMs in different media are atomic force microscopy (AFM), scanning tunnelling microscopy (STM), electron microscopic techniques (transmission electron microscopy (TEM), scanning electron microscopy (SEM)), inductive coupled plasma optical emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) (Tiede et al., 2008). AFM, SEM and TEM allow the visualization the size, structure and shape of nanosized particles of MNMs as well as characterizing their dispersion, aggregation, and sorption (Mavrocordatos et al., 2004).

Tiede et al. (2008) comprehensively reviewed the advantages and limitations of such analytical methods for the detection and chemical/physical characterization of MNMs in environmental media. The authors point out the main challenges for such methodologies as:

1) Sufficient sensitivity/resolution to detect extremely low concentrations (small particles usually represent a very small part of the total mass);
2) Minimize sample disturbance to ensure laboratory results that reflect unperturbed environmental conditions;
3) Conduct real-time measurements under environmentally-relevant states (e.g. conventional TEM and SEM operate only under vacuum conditions);
4) Distinguish engineered nanoscaled particles from background particles of the same size;
5) Electron microscopy-based methods are destructive approaches, analyzing the same sample twice, or by an additional method, for validation is not possible;
6) Avoid significant impacts on imaging of the sensitivity of the detector to light and fluorescence; and
7) Deal with unintended charging effects caused by the accumulation of static electric fields on the specimen that might mask information in TEM and SEM analysis by using, for example, sampler coatings made of a conducting material.

One of the main problems is that TEM and SEM normally work only under vacuum although some recent approaches to work in liquids or with wet samples have been made (Tiede et al., 2008). In the case of AFM the main problem is that the tip is often larger than the individual particles of MNM that have to be analyzed. Also for AFM, samples have to be applied to a specimen holder, which can cause alterations. Tiede et al. (2008) mention possible scan errors in the onset and offset of particle topography. Finally, analyzing the produced images is at least as difficult as imaging itself. Evaluating the statistical significance of the results (e.g. size distribution depends on the number of particles measured) is in most of the cases not possible since only a few number of outputs are available. Such limitations remain often undiscussed by ignoring the need of statistical evaluation.

Mass spectrometry could become an important tool, promising reliable results for quantifying environmental release of MNM. In particular, field flow fractionation inductively-coupled plasma mass spectrometry (FFF–ICP–MS) is increasingly being used (Tiede et al., 2008). Such a method allows the simultaneous sizing and analyzing of particles in their original environment. It incorporates size separation of the sample with the quantitative and elemental evaluation of the size fractions (von der Kammer et al., 2004; Bolea et al., 2006).

However, for quantifying the MNM release into a particular environmental compartment, further critical aspects that determine the analytical setting have to be considered. Measurements need to analyze the amount of MNM reaching the environment and not only quantify the MNM concentrations in a particular occupational or consumption environment. Hence, measurements of indoor air levels are of little use without indications of the corresponding total air volume, air exchange rates and the effect of any filtration. Most studies conducted to measure the airborne
concentration of or exposure to MNMs in occupational settings can not therefore be used directly to quantify environmental release. Similarly, MNM concentrations in wastewater are not informative without knowledge of the mass flow of pollutant per unit time. Another complication is that the methods available to detect the presence of nanoparticles in air do not necessarily discriminate between engineered or naturally nanosized particles (SCENIHR (Scientific Committee on Emerging and Newly-Identified Health Risks), 2009).

Kaegi et al. (2008) studied synthetic nano-TiO$_2$ emissions from exterior facades into the aquatic environment and provided some of the first analytical results that identified an engineered nanosized material released to the environment. Analytical electron microscopy, optical emission spectrometry and mass spectrometry (TEM, ICP-OES and ICP-MS analysis) were used to show that nano-TiO$_2$ can be detached from new and aged paints on house facades under natural weather conditions and discharged into natural stream flows. The authors showed for the first time that TiO$_2$ particles are released in significant amounts into natural waters. Reliable results for synthesized particles (TiO$_2$) with a size of up to a few 100 nm (TiO$_2$ particles with a diameter between roughly 20 and 300 nm) were presented. Due to a double-centrifugation technique, only nanosized particles were deposited on TEM grids (Fig. 7).

![Fig. 7. Schematic layout of the sampling protocol for TEM, ICP-OES and ICP-MS analysis. Reproduced from Kaegi et al. (2008).](image)

The strength of this study is that the authors analyzed water samples under natural conditions and solid coatings of facades under semi-natural conditions (model
house). Hence, such results differ from other available experimental measurements (see next section) that were carried out only within artificial laboratory experimental settings.

Kiser et al. (2009) provided the first evidence for the release of nano- and larger sized Titanium into water from STP effluents and sewage treatment sludge. TiO$_2$ is expected to occur only in solid phases in the environment (not in ionic forms). For the analyses using ICP-OES, the solid phase TiO$_2$ was transformed into ionic form by acid digestion based on a HNO$_3$/H$_2$SO$_4$ digestion method (Fang and Jia, 1998).

Farré et al. (2010) described a first analytical method with a very low detection limit (ng l$^{-1}$) for C$_{60}$ and C$_{70}$ fullerenes and N-methylfulleropyrrolidine C$_{60}$ in ultra-pure water, surface water and wastewater. The approach includes ultrasonication extraction from suspended solids in wastewater and liquid chromatography (LC) coupled to a hybrid triple-quadrupole linear ion-trap mass spectrometer.
3.2 Experimental studies (simulation of physicochemical processes)

Although processes such as the release of MNMs from products are generally considered to be relevant, there is a distinct lack of information regarding the nanomaterial emission process itself (Bello et al., 2008; Benn and Westerhoff, 2008; Koehler et al., 2008; Kohler and Som, 2008; Geranio et al., 2009). Only two experimental studies have investigated the MNM-release process.

Benn et al. (2008) investigated MNM-release from textiles (nano-Ag in socks) into distilled water. The presence of nanosized silver in the sock material and in the water samples was observed by means of SEM and TEM. 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 MNM was not observed since the different textile manufacturing processes influence the release of silver, leading to variable leaching rates for different textile types.

The removal of both nanoparticulate and ionic silver from the wash water by wastewater treatment system biomass (activated sludge) was also investigated. The observed adsorption of leached silver onto STP biomass suggested that typical wastewater treatment facilities will remove most of the influent silver. However, as the authors state, the nano-Ag released from the socks adsorbs to biomass in a similar manner to ionic silver meaning that improved analytical techniques are needed to differentiate nanoparticles from ionic species.

The main problem in this first investigation (Benn and Westerhoff, 2008) was that the textiles were immersed in pure or tap water and did not generally reflect realistic washing processes and conditions. Conditions in distilled water clearly differ from those during normal washing processes, where high concentrations of surfactants are present, bleaching agents are used and the pH lies between 10 and 11. Also the probable mechanical stress on the textiles during the washing process has to be considered. More realistic experimental settings would require i) information on washing rates, ii) the use of real wash water and textile contact time (the authors used 1- or 24-h contact time), and iii) the use of relevant amounts of textiles per time unit. This study also made no distinction between nanoparticles and dissolved ionic species.
Geranio et al., (2009) addressed some of these shortcomings in an experimental study investigating nano-Ag release from silver-containing fabrics by simulating real washing procedures. ICP-OES was used to detect/quantify silver. Free Ag+ ion concentrations were measured by means of an Ag-ISE (Ion-Selective Electrode). The washing procedures were carried out based on ISO-methods for washing tests (ISO, 1997). Mechanical stress was produced by 10 steel balls. After washing, the authors dried the fabrics before the next washing cycle. The amount and the form of silver (particles or ionic) released 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 nanoparticle dissolution and release from textiles was also assessed. However, the authors state that even these more realistic settings for experimentation do not represent the whole spectrum of relevant washing conditions. MNM release from repeated washing (long time process) was not considered; the release of silver is likely to be reduced following repeated washing cycles of the textiles. Also, the use of commercially available washing machines would improve the representativeness of the results. Furthermore, the presence of chloride anions in tap water or the detergent formulation may result in precipitation of Ag+ as AgCl, thereby lowering the amount of dissolved Ag.

The generic limitations of such product-based experiments are as follows:

1) They are not representative of the whole spectrum of potential release situations that might arise throughout the whole life-cycle of a particular MNM-containing product;
2) Between-product variability in the release properties are often not addressed;
3) The experiments are usually not repeated often enough to get sufficient output data for statistical evaluation; and
4) The results reflect artificial laboratory conditions and may therefore not be representative of MNM release under realistic conditions.
3.3 Modelling/Estimation

Due to the lack of analytical measurements for MNM in the environment, modelling the MNM release to the environment is currently crucial for estimating MNM release and for carrying out risk assessments. There are some modelling studies for MNM available in the scientific literature. Most of these are aimed at linking the risks from these materials to organisms in the environment and to the MNM exposure concentration. A general risk-assessment framework for such a risk evaluation is described in the 'Guidance on information requirements and chemical safety assessment' (ECHA, 2008). This approach is also considered appropriate for assessing the potential risks posed by MNMs (Som et al., 2010). Based on this approach, the amount of MNM released to a particular environmental compartment is compared to a standard size of these compartments by considering simple dilution calculations. The result is the estimation of the predicted environmental concentration (PEC), an average expected concentration in a standard environment of a particular pollutant.

Usually, the release into and the distribution in the environment of chemicals is calculated by means of the octanol-water partition coefficient ($K_{ow}$). However, it cannot be assumed that the $K_{ow}$ of a particular bulk material is predictive for nanoparticles derived from the same material (SCENIHR (Scientific Committee on Emerging and Newly-Identified Health Risks), 2009). Jafvert et al. (2008) presented some of the first experimental results on the aqueous solubility of MNM. The log $K_{ow}$ of $C_{60}$ was measured to be high (6.67), resulting in a high affinity of such fullerenes for soil organic carbon or for biological lipids. This study showed that $C_{60}$ clearly has the potential to bioconcentrate in organisms. However, due to its very low concentration in water and possible degradation reactions within organisms, leading to concentrations below the thermodynamic threshold, such measurements are not adaptable to calculate the mass migration behaviour of $C_{60}$. Since the $K_{ow}$ is not applicable to non-soluble/volatile materials, a $K_{ow}$ cannot be derived for most MNMs, and mass transfer cannot be modelled by means of such material characteristics. Nevertheless, information on the extent to which MNMs dissolve and the rate at which this occurs is essential for assessing the time that MNMs remain in the environment.
New approaches are needed to model the uncertainty and variability of the environmental release and distribution of MNMs. Some model approaches have been developed and used to estimate such release (Blaser et al., 2008; Boxall et al., 2008; Mueller and Nowack, 2008; Park et al., 2008; Gottschalk et al., 2009; Gottschalk et al., 2010b; O’Brien and Cummins, 2010). The methodologies used by these studies vary considerably, including the model conceptualization (mathematical approaches), and parameterization (model geometry) as well as modelling input data collection and preparation. The mathematical concepts for dealing with the high MNM-specific uncertainties (and natural variability) in the estimation of model input and output, range from simple algorithms or single scenario analyses to more sophisticated stochastic simulations based on Monte Carlo (MC) approaches.

The latter approach provides a probabilistic/stochastic material flow analysis (PMFA) (Gottschalk et al., 2010a) that seems adequate to predict MNM release to the environment when little data are available. Based on a material-flow computer model, any kind of probability distribution function for all the input variables is programmable through the whole modelling procedure by incorporating a large number of processes such as emission, transmission flows, MNM deposition and elimination rates. The main advantage of this software is that it allows the quantification of the uncertainties concerning the estimation of the model parameters (e.g. transfer and partitioning coefficients, emission factors) as well as the uncertainties about the exposure, and the causal mechanisms (e.g. level of compound production and application) themselves. It utilizes and combines the following methods: sensitivity analysis, Monte Carlo algorithms, Bayesian and Markov Chain modelling. The model is programmed and carried out with the computational tool R (R Development Core Team, 2008).

Besides the different mathematical procedures used to run MNM-release simulations, the models also vary through different conceptualizations/framings of MNM-release modelling. The models can be subdivided into top-down and bottom-up approaches. From a top-down perspective some approaches consider only the MNM release from a small (relevant) set of MNM-containing products (Blaser et al., 2008; Boxall et al., 2008; Park et al., 2008; O’Brien and Cummins, 2010). In contrast and within a bottom-up approach, others include in their calculations the whole spectrum of
products and possible applications of MNMs (Mueller and Nowack, 2008; Gottschalk et al., 2009; Gottschalk et al., 2010b). Thus, in this latter approach, an inventory was made of all known MNM-containing products. Next, all products were categorized in product categories according to their potential MNM release behaviour. The release of MNM from primary production and from MNM product manufacturing and recycling processes was also considered (Gottschalk et al., 2009; Gottschalk et al., 2010b).

Table 2 shows the objectives and the differences between the various modelling studies.

**Table 2: Modelling studies of environmental MNM release, concentrations of MNM or metal concentrations resulting from the use of MNMs.**

<table>
<thead>
<tr>
<th>Study</th>
<th>MNM</th>
<th>Compartments</th>
<th>System</th>
<th>Release</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Boxall et al., 2008)</td>
<td>TiO$_2$, ZnO, CeO$_2$, AlO$_3$, SiO$<em>2$, Au, Ag, C$</em>{60}$</td>
<td>Water, sludge, soil, air</td>
<td>UK</td>
<td>Simplicistic release modelling 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 MNM products. Release to water is modelled from: i) bioremediation (direct entry of MNMs), ii) spray drift following use of agrochemicals, iii) runoff from contaminated soils, iv) aerial deposition; and v) sewage treatment plants. Release to soils through i) the use of remediation technologies and plant protection products, ii) the excretion of nanomedicines used in veterinary products, iii) aerial deposition and iv) sewage sludge used as a fertilizer.</td>
</tr>
<tr>
<td>(Mueller and Nowack, 2008)</td>
<td>TiO$_2$, Ag, CNT</td>
<td>Water, air, soil</td>
<td>CH</td>
<td>Worst case and realistic scenario analysis. Release of all considered MNMs to environmental compartments and several technical compartments (sewage treatment plants, waste incineration plants, and landfills) from the use of products containing MNMs (categorized into different product categories):</td>
</tr>
<tr>
<td>(Blaser et al., 2008)</td>
<td>Ag</td>
<td>Water</td>
<td>EU</td>
<td>For Nano-Ag that only served as Ag$^+$ source, no particulate Ag release was modelled (deterministic approach without uncertainty analysis).</td>
</tr>
<tr>
<td>(Park et al., 2008)</td>
<td>CeO$_2$</td>
<td>Air, soil</td>
<td>generic</td>
<td>Release from fuel additives (deterministic approach without uncertainty analysis).</td>
</tr>
<tr>
<td>(Gottschalk et al., 2009)</td>
<td>TiO$<em>2$, ZnO, Ag, CNT, C$</em>{60}$</td>
<td>Water, sludge, soil, sediments, soils, groundwater</td>
<td>CH, EU, USA</td>
<td>Stochastic simulations of the release of all considered MNMs to all environmental compartments and several technical compartments (sewage treatment plants, waste incineration plants, recycling, landfill) from i) MNM production, ii) manufacturing of MNM products, iii) use of products (categorized in different product categories): nano-TiO$_2$: cosmetics, filter aggregates, coatings &amp; cleaning agents, plastics, consumer electronics, paint, glass &amp; ceramics, light bulbs, metals, batteries &amp; capacitors, textiles, ink, dietary supplement; nano-ZnO: plastics, cosmetics, coatings &amp; cleaning agent, textiles, dietary supplement; nano-Ag: cosmetics, filter aggregates, coatings &amp; cleaning agents, plastics, consumer electronics, paint, glass &amp; ceramics, metals, textiles, dietary supplement; CNT: composites, consumer electronics, research &amp; development; fullerenes: composites, cosmetics, research &amp; development.</td>
</tr>
<tr>
<td>(O’Brien and Cummins, 2010)</td>
<td>TiO$_2$, Ag, CeO$_2$</td>
<td>Air, surface waters</td>
<td>Ireland</td>
<td>Release from exterior paints (TiO$_2$), food packaging (Ag) and fuel additives CeO$_2$ (deterministic approach without uncertainty analysis).</td>
</tr>
</tbody>
</table>
In the top-down approaches, Blaser et al. (2008) modelled silver release from the nano-Ag incorporated into textiles and plastics, based on a silver mass-flow analysis. This model reflects only one single estimated silver use without any indications of the model input-uncertainty and is based on three deterministic release scenarios (minimal, realistic and worst-case release). Plastics and textiles containing biocidal nanomaterials were predicted to account for up to 15% of the total silver release into surface waters, although no indications of the variability or uncertainty of this estimation were provided. In this study no specific nanoscaled silver release was calculated, but the total amount of silver emitted from the nanoparticles incorporated into textiles and plastics was estimated, irrespective of whether the release was in the form of nano-Ag particles or as silver ions. It was assumed that most of the silver released into wastewater ends 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, together with the fraction of wastewater treated in and removed by the treatment plants.

Boxall et al. (2008) provided a series of simple algorithms, developed to calculate the release of MNMs into air, soil, and water. MNM release from different products and routes to water was estimated for the following scenarios:

1) The direct input of MNM to surface waters from bioremediation;
2) Inflows from use of agrochemicals;
3) Runoff from contaminated soils;
4) Aerial deposition; and
5) Release from wastewater treatment plants.

The main routes of release were modelled, based on simple equations for:

1) The application of remediation technologies;
2) The application of plant protection products;
3) The excretion of nanomedicines used in veterinary products;
4) Aerial deposition; and
5) The application of sewage sludge as a fertilizer.

However, this study was only focused on a non-comprehensive selection of MNM applications and MNM release was mainly considered to arise from direct MNM applications to natural compartments. Thus, the main parameter of such release
modelling is expressed in these algorithms by assumptions, for example on direct MNM application rates for remediation processes or cosmetic and hygiene product use, MNM-containing sludge application rates, and the fraction of MNMs removed during sewage treatment. Direct MNM release from products is modelled for example as mass flow from product application to wastewater treatment. Hence, such approaches are only applicable for single hypothetical MNM-usage scenarios, restricted to single product types and are applied to a very limited range of products and life-cycle stages of MNMs. By means of assumed market penetrations of nanoproducts (10%) and known product usage, MNM concentrations in air, water and soil were predicted. A discussion/consideration of the hypothetical input parameters was not provided.

Park et al. (2008) presented estimations of nano-CeO$_2$ release into air and soil from its use as a fuel additive. MNM emissions were calculated based on established models for PM emission calculations: COPERT (Ntziahchristos and Samaras, 2000), (a programme for modelling air pollution from road transport), and TRENDS (Giannouli et al., 2006) (a computer code for assessing emissions from road traffic, transport and environmental database systems). CeO$_2$ releases were calculated for a highway and a street canyon, assuming worst-case conditions (all cars using CeO$_2$-containing fuels) and varying driving conditions. However, this study only used single specific model input parameters without any indications of the uncertainty/variability of these parameters. For the highway scenario the authors assumed the following conditions: 14,000 vehicles per hour traffic density, all vehicles were using diesel fuel (as a worst case assumption), a crossroad wind with a speed of 1 ms$^{-1}$ and stable atmospheric conditions. The soil contamination along a typical highway was modelled, based on the rough assumption that all of the cerium oxide emissions would accumulate over a 40 year period.

O’Brien and Cummins (2010) investigated the release of nano-TiO$_2$ from exterior paints, Ag from food packaging and CeO$_2$ from use as a fuel additive to the air and surface waters. The release factors in this study were obtained from an unpublished work. Hence, no insights into the parameterization are available. The method includes a semi-quantitative three-level risk model (O’Brien and Cummins, 2009) based on inter-relationships between the different material properties and
environmental behaviours and their relationship to MNM release and exposure scenarios. In particularly the release of MNMs from industrial manufacturing and consumer products, as well as from intentional environmental application, was seen to be relevant. However, how the equations linking each risk level were derived from the literature and expert opinion remains unclear.

Amongst the bottom up approaches, Mueller and Nowack (2008) presented the first model to consider MNM-release from a whole life-cycle perspective. MNM emissions in Switzerland were calculated for nano-Ag, nano-TiO$_2$ and CNT by means of a substance-flow analysis which considered emissions from products to the air, soil and water. The model input included:

1) The estimation of the worldwide MNM production amounts,
2) The allocation of the production amounts to product categories,
3) MNM release from products, and
4) Flow coefficients for all MNM transmission flows between the environmental compartments.

To cope with the almost complete lack of data for these input parameters, two scenarios were modelled: a realistic scenario (RE: realistic emission) and a worst-case scenario (HE: high emission). The subsequent risk estimation was carried out by comparing the PEC-values derived with current toxicological data from the literature. The main limitation of this model stems from the lack of data leading to high uncertainties in the calculations of the two scenarios for MNM production; the allocation of produced MNMs to product categories with particular release characteristics; and the release coefficients.

Recent studies (Gottschalk et al., 2009; Gottschalk et al., 2010b) extended this type of MNM-release modelling (Mueller and Nowack, 2008) by replacing the deterministic scenario analysis by probabilistic/stochastic MNM release simulations (Gottschalk et al., 2010a). For the first time, MNM releases to the sediment and groundwater compartments were included in the release simulations. In addition, MNM releases to the environment from MNM production, and the manufacturing and recycling processes of MNM-containing products were also addressed. All of the parameters were calculated throughout the modelling process by means of probability (or frequency) distributions. The uncertainty and variability of the MNM-release coefficients, as well as the release causal mechanisms such as level of MNM
production and application, were considered by means of Monte Carlo (MC) algorithms. In contrast to a single scenario analysis, such models provide insights into the likelihood of each produced output as well as a higher amount of simulation results (100,000 MC iterations). This approach also includes a sensitivity analysis relating the impact of a model input parameter to the model output and its estimation uncertainty (Gottschalk et al., 2010a; Gottschalk et al., 2010b).

In subsequent work (Gottschalk et al., 2010b) such stochastic results were compared with the corresponding results from the initial and comparative scenario analysis (Mueller and Nowack, 2008). In general, the stochastic approach confirmed the nanomaterial release calculations presented in Mueller and Nowack (2008). However, comparisons between the stochastically-modelled MNM release and the scenario results were difficult given an enlargement of the system to more compartments (e.g. soils, sediments) and MNM release-flows connected to these compartments. Additionally, new model input data and new and updated product categorization and MNM mass allocation to the product categories cause further difficulties. A first comprehensive sensitivity analysis allowed the identification of the key parameters that impact on MNM environmental release and exposure. A detailed discussion on the uncertainties of the single model input parameters and their impact on the model output has been included in this sensitivity analysis. This evaluation showed that the major limitations of these stochastic/probabilistic calculations are that reliable data on MNM production and MNM-release behaviour from all the emission processes considered are still missing. A closer look is needed also at the release of MNMs from the products to the STP, the STP removal efficiency and overflow; together with the sludge from this compartment ending up in the WIP, where it is incinerated, exported, or deposited in landfills. Changes in the STP inflow, STP overflow, and STP removal-efficiency explained almost all of the variations in the nano-TiO$_2$ and nano-Ag concentrations in water. The dominant influence of this parameter shows that most nano-TiO$_2$ is used in cosmetics and coatings, and nano-Ag in coatings, cosmetics, paints, and textiles. Releases from such applications result mostly in emissions of MNM to STP inflows. This sensitivity analysis showed that, to improve the prediction of the main MNM release paths to the environment,
the most critical information refers to the usage of MNMs in products and their release during use.

However, further limitations of these studies have to be mentioned. For all of the simulations, a complete lack of quantitative data was apparent, relating to MNM release during the manufacturing of MNM-containing products and during the production of MNMs. MNM production information varies sometimes by a factor of 100 (Gottschalk et al., 2009). Reliable information on MNM production is not available because producers do not have to advertise nanoscaled ingredients. The only quantitative overview of MNM volumes incorporated in MNM products is presented in Schmid and Riediker (2008). Even less or almost no empirical data are available on MNM release from products into the environment. Information on the release of MNMs from a wide range of products is not currently available other than some data on MNM release from textiles (Benn and Westerhoff, 2008; Geranio et al., 2009) and paints (Kaegi et al., 2008). In addition, first measurements from companies producing MNM have shown that indoor air exposure to these materials also occurs (Maynard, 2004; Mazzuckelli et al., 2007; Yeganeh et al., 2008).

A major shortcoming of these studies is that, due to missing data, all of the different specific forms of the same type of MNM (e.g. different surface-coatings of a particular material) had to be combined in the model calculations. Nowack and Bucheli (2007) mention as an example untreated CNTs that are not dispersible in water (Chen et al., 2004). However, for solubilising such pristine material, the tubes may be modified by cutting the tubes in strong acid under sonication. These shortened CNTs are then hydroxylated at the ends and at defects and can easily be suspended in water before they immediately aggregate due to the presence of cations (Sano et al., 2001). Such MNM behaviour in the liquid phase may be essential for studying the transfer of MNMs from surface waters to sediments or the fate of MNM from STPs.

A further critical point in such models is the assumed steady-state approach for MNM release and transmission-flow calculations. For example, time-dependent storage of MNMs in products or the re-suspension of settled material in rivers, which could considerably impact on the amount of MNM released to the different environmental compartments per unit time, were not considered. Temporal dynamics of MNM
production amounts and the consumption and storage volumes of nanoproducts were not considered.
3.4 Exploratory chemometric approaches

As mentioned above, sewage sludges from municipal wastewater treatment plants are a depository for nano-silver (Blaser et al., 2008; Gottschalk et al., 2009). Environmental contamination of silver can thus arise from the reuse of sludge, for example in agricultural soil (affecting soil microbiology and/or groundwater quality) (Blaser et al., 2008). Assuming that under different scenarios for release to the sewer system the respective fraction of nano-silver should be more or less correlated to the other tracers of the release process (e.g. domestic washing of fabrics containing nano-silver) it should be possible to develop a chemometric approach in combination with traditional analytical chemistry to determine the fraction of nano-silver in this sewage sludge.

Environmental monitoring data are increasingly handled in terms of mathematical models that allow managing different kind of data sets with multiple observations. Multivariate models are nowadays used successfully in different branches of scientific research to uncover information on data sets containing a number of features (chemical or physical properties) related to the measured samples. In particular they are used to estimate the number and composition of pollutant sources, starting from the information carried by the samples and to identify any trends and/or correlations among observations (Kaplunovsky, 2004; Viana et al., 2008).

The application of such techniques (i.e. Cluster Analysis, Principal Component Analysis and Positive Matrix Factorization) to data sets containing chemical/physical parameters from sewage sludge samples is currently used by the European Commission’s Joint Research Centre (JRC) to extract information on the nano-Ag fraction and to provide an easy visualization of the relationship existing between the nano-material and the other parameters (e.g. ingredients of domestic washing powders), as well as to quantify its content. Another important aspect in this exploratory application of a multivariate procedure is the possibility of detecting an element/compound that could be a marker for the nano-Ag fraction. In this way, the detection of the marker could be used to predict the nano-Ag level in sewage sludge samples and thus to monitor its release into the environment.
The approach is currently being tested in an EU-wide screening exercise on sewage sludge samples from some 100 wastewater treatment plants receiving influents from different sources. If successful, it will be tested on other MNMs such as cerium dioxide.
3.5 Methodology for estimating environmental release under REACH

The Guidance on Information Requirements and Chemical Safety Assessment of the EU (ECHA, 2010) provides a methodology for quantifying the environmental release of chemicals (R.16. ESTIMATION OF ENVIRONMENTAL EXPOSURE). Release to air, wastewater, surface water and soil is discussed on a local scale for point sources and on a national or continental scale for a larger area covering all point sources and wide dispersive sources in a defined area.

Three scenarios have been introduced:

1) Industrial setting scenario on a local scale;
2) Wide dispersive scenario on a local scale;
3) Releases in a standard region for all identified uses.

The “Industrial setting” describes emissions from industrial point sources; the “Wide dispersive use” scenario includes emissions from consumption processes, professional, and service life uses. In the third part, regional releases for industrial and wide disperse use are cumulated to calculate the total regional release.

Release is described based on release rates. Such release rates are determined in a similar way as for operational conditions in exposure scenarios under REACH (e.g. daily and annual use at an industrial site and daily wide dispersive use). Release rates for all of these scenarios are calculated by means of release factors and the tonnage assigned to a particular use/source. Default assumptions are defined for the definition of a tonnage for each single use at local and regional scale.

Although REACH does not so far consider any nano-specific issues, the general approach to estimating environmental release is also applicable to MNM-containing products or activities and is presented in the following section.

i) Releases from industrial settings

Emission flows to water are, by default, treated in an industrial wastewater treatment plant (WWTP) or municipal sewage treatment plant (STP), before being discharged into surface water. Release to air via the STP, as a result of water treatment, and release to soil via the application of STP sludge to agricultural soil and via the atmospheric deposition of substances released to air are considered as well.
Default daily release rates are reported for manufacture, formulation and industrial end uses:

1) Manufacture is defined as the stage where the substance is produced, i.e. formed by chemical reaction(s), isolated, purified, drummed or bagged, etc.
2) Formulation means, for example, blending and mixing materials to obtain a mixture in a formulation such as paints or as mixtures on carrier materials e.g. photographic films.
3) Industrial use: Use of the substance as such or of the mixture containing the substance with the goal of embedding such a substance into a product, or using it as a processing aid.

The release rates to a particular environmental compartment are estimated as follows:

\[ E_{local, IU, j} = Q_{daily, IU} \times RF_{IU, j} \times 1000 \]  
(see Equation R. 16-1)

\( E_{local, IU, j} \): Release rate (kg/day) to the compartment “j” at the local scale for an identified use (IU).
\( Q_{daily, IU} \): Daily use (tonnes/day) at a site for an identified use (daily use and/or annual use divided by 365 days). \( RF_{IU, j} \): Release factor (% or kg/kg) to compartment “j” for identified use. The default value is set by ERCs.

Release factors determine the fraction (either kg kg\(^{-1}\) or %) released to a particular environmental compartment. To derive such release factors, environmental release categories (ERCs) have been developed. These ERCs are listed in Section R.12.3.4, Appendices R.12.4.1 and R.12.4.2. Appendix R.16-1 contains the default ERCs expressed in % and derived, based on considerations of:

1) Life cycle stage;
2) Level of containment;
3) Type of use and technical fate of a substance;
4) Dispersion of release sources;
5) Indoor or outdoor use;
6) Release potential during service life and waste stage.
**ii) Releases from wide dispersive uses**

Wide dispersive use is seen as use of the substances as such, or of the substances in mixtures, by many consumers in the public domain, including also small non-industrial companies. The following scenarios are described:

1) Professional use to deliver services to business or private customers.
2) Consumer use, where it assumed that the user is not trained. Examples are given of lubricants for vehicles or hydraulic systems (closed system) or lubricants for bicycles (open systems).

All of these releases are assumed to constitute constant continuous fluxes that can be summed and averaged over the year. By default, the release to water is calculated via STP for a standard 10000-inhabitants town, which collects the emissions to water from a particular use. Direct release to air and soil is not considered for wide dispersive use.

The local tonnage used is calculated from the manufactured tonnage. Such tonnage is a fraction of the total registrant’s tonnage at EU level, used in the standard town of 10000 inhabitants. The default daily use is estimated, starting from the registrant’s total tonnage at EU level for an identified use, dividing it by 10 (fraction of the registrant’s total tonnage at EU level used in the region (regional tonnage)), by 2000 (fraction of the regional tonnage used in the standard town (20,000,000 inhabitants in the region / 10000 inhabitants in the standard town)) and by 365 (days per year). A factor of four is considered to account for geographical or temporal peaks in the use and release of a substance.

The daily wide dispersive use is then calculated as follows:

$$Q_{\text{daily, } R} \text{ (tonnes / day)} = \frac{\text{total registrant's tonnage at EU level (tonnes / year)}}{\text{number of days}} \cdot \frac{1}{4}$$

Subsequently, the above mentioned equation R.16-1 is also used for this scenario to determine the release rates of single environmental compartments for a particular dispersive use.

**iii) Regional release estimation**

In this scenario, both industrial and wide dispersive sources are cumulated to estimate the total regional release (kg day\(^{-1}\)) to surface water, wastewater, air and soil. Such
release is assumed to occur continuously over the year and over the total service life of products containing a defined substance. Releases to water assume 80% (representing the EU average) of the wastewater being treated in STPs and the remaining 20% directly emitted into surface waters. The regional releases associated with specific-use scenarios are based on the tonnage at regional level for each use and the same release factors used at local scale. The tonnage at the regional level for the industrial settings (i.e. manufacture, formulation and industrial uses) equals by default 100% of the tonnage at EU level. For wide dispersive uses such tonnage is seen as being 10% of the registrant’s supply volume at EU level.

Hence, default regional release is estimated based on the following equation:

\[ E_{\text{regional, IU, j}} = Q_{\text{regional, daily, IU}} \times RF_{\text{IU, j}} \times 1000 \]

\( J = \) environmental compartment (air, soil, wastewater); \( E_{\text{regional, IU, j}} \) (kg/day): release rate to the compartment “j” at the regional scale for an identified use (IU); \( Q_{\text{regional, daily, IU}} \) (tonnes/day): average daily use at the regional scale for an identified use (IU) = regional tonnage for each use/365 days; regional tonnage for each use (tonnes/year) = 100% * total registrant’s tonnage at EU level (for industrial setting); regional tonnage for each use (tonnes/year) = 10% * total registrant’s tonnage at EU level (for wide dispersive uses); \( RF_{\text{IU, j}} \): Release factor (% or kg/kg) to compartment “j” for identified use. This default value is set using ERCs.

Finally, it must be emphasised that all of the release estimations in R.16. must be regarded as preliminary conservative assessments for initial and tentative release/exposure scenarios. If new data e.g. for market developments, application amounts of a substance or release characteristics of the substance become available, a higher-tier assessment will be possible and necessary. For such scenarios that have been updated by means of empirical information the default values can be overwritten.
4. Quantification of MNM release

This chapter summarises the available results from the literature and discusses the adequacy of the REACH-release estimations for modelling MNM-release to the environment.

As seen above, the release of MNMs to the environment is likely to occur from:

1) MNM production and transport;
2) The manufacturing of products containing this material; and
3) The use, recycling or disposal of such products.

The amount of MNM released during the different life stages of MNMs and MNM-containing products depends on: the amounts of MNM produced and used in products; the MNM concentration in products; the lifetime of such products; the way MNMs are embedded in the products; the type of use/usage of a particular product; and the external physical/chemical impacts on the product during its whole life-cycle (Koehler et al., 2008).

Section R16 of the REACH (REACH, 2006; ECHA, 2010) (Guidance on Information Requirements & Chemical Safety Assessment (IR&CSA guidance)) presents the Environmental Release Categories (ERC) proposed for an initial generic assessment of the environmental release of substances. Although critiques from industry suggest that the proposed ERCs might lead to unrealistically conservative release estimates (Cefic SPERC Core Team, 2010), such coefficients are applied to form conservative release estimations for chemicals with a sparsely filled database concerning the release behaviour of such chemicals from products and different processes. How far such generic release coefficients may be applied to MNMs is discussed in each of the following subsections.
4.1 Release from production

Production (and manufacturing processes) can result in the direct or indirect release of MTMs. Direct release can occur for example to the air through open windows when powdery material is used incautiously, or from transport accidents and from all kinds of spills. Indirect release from production sites, for example into a river, can occur via untreated or treated wastewater. Most of the modelling studies (Park, 2007; Blaser et al., 2008; Boxall et al., 2008; Mueller and Nowack, 2008) ignore the release of MNMs to the environment arising from MNM production. However, worst-case generic environmental release coefficients (ERCs) for chemicals propose the following factors for the release of such chemicals from the manufacture process (ECHA, 2010): 5% to the air, 6% to surface waters before reaching an STP, 0.01% to soils. Other studies (Gottschalk et al., 2009; Gottschalk et al., 2010b) considered direct MNM release to the environment from MNM production to be of similar orders of magnitude. Uniform probability distributions ranging from 0 to 2% of the MNMs produced were calculated to reach the environment from the production procedure.
4.2 Release from manufacturing processes

During manufacturing processes, direct human exposure to free MNMs is expected (Maynard, 2004). Measurements carried out at factories producing different MNM products have indicated that worker exposure occurs during the production and handling of dry powders (Mazzuckelli et al., 2007; Bello et al., 2008; Fujitani et al., 2008; Han et al., 2008; Yeganeh et al., 2008). The manner in which such worker exposure might lead to MNM release to the environment is currently unknown. However, there is no doubt that, once the MNMs are released to indoor air, such material is likely to enter the environment sooner or later. However, worker exposure measurements are not directly relevant for estimating the release to the environment, if no information is available about the volume or flow of MNMs into at least one environmental compartment. Besides the indoor air concentrations of a pollutant, MNM environmental release-assessment requires the mass flow per unit time of the pollutant reaching outdoor air, e.g. from an exhaust. In the case of release via wastewater, not only the particle concentration in the wastewater, but also the mass flow of the MNM is required.

Recent studies by (Gottschalk et al., 2009; Gottschalk et al., 2010b) provided the first consideration of the release from manufacturing processes of MNM-containing products, as well as the release of MNM from MNM production and the use of MNM-containing products. Probability distributions between 0 and 2% of MNM release were assumed.

Default parameters described as ERCs (ECHA, 2010) assume the following release coefficients for formulations of mixtures (not embedded into a matrix): 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%.
4.3 Release from products

Besides releases during manufacturing, the main possibility for the release of MNMs into the environment during their life-cycle is during the use, recycling and disposal of MNM-containing products. In this context it is necessary to distinguish between intentional and unintentional release. Release of MNMs during their life-cycle can result from intended release (e.g. applications such as putting MNM-containing sunscreen onto the skin) or from unintended release from products, for example that caused by the abrasion of nano-textiles.

Whereas the source and magnitude of MNM release is known for intentional emissions, this is not the case for any undesired release caused by a product’s degradation, altering, recycling etc. (Koehler et al., 2008). The level and pattern of MNM release from a product depends mainly on how the MNM is embedded within that product. MNMs in fluids are quickly and in most cases completely released during the use phase, whereas MNMs embedded in solid matrices are gradually and only partially released over the product’s lifetime (Koehler et al., 2008). MNMs in sprays are released immediately when applied. MNMs in suspensions such as sunscreens, cosmetics are released within hours, while MNMs in paints and textiles are supposed to remain within the matrix for years.

Many products can be identified that either release MNMs into the wastewater stream (collected and treated) or that release the bulk of their MNMs only during end-of-life-treatment. In such cases, the MNMs are potentially removed in the technical compartment (waste incineration plant, wastewater treatment). However, it should be acknowledged that only carbonaceous materials can definitely be destroyed in such removal processes. Metals and metal oxides will persist, although their chemical form might have been altered.

4.3.1 Experimental/analytic results

Experimental information on the release of MNMs during the use or disposal of products is very scarce. One first study investigates MNM release into air by abrasion (Vorbau et al., 2009). This analysis is based on the combination of a defined abrasion process with sensitive methods to quantify the airborne particle
concentrations generated. A sophisticated interconnection between the aerosol-generating and the measuring units provided enough sensitivity and prevented artefacts by measuring abrasion of ZnO-containing coatings (Vorbau et al., 2009). During the abrasion tests no significant releases were detected in the aerosol of particles <100nm.

Emissions of nano-TiO$_2$ from coatings on polymer, wood and tile have also been investigated (Hsu and Chein, 2007). The influence of sunlight, wind, and human contact on the release was studied. The tiles coated with TiO$_2$ nano-powder were found to have the highest particle emission. The UV light treatment was shown to increase the release of particles below 200 nm in size from TiO$_2$ nano-powder coated materials. The number/concentration of particles 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.

Besides the release of particles into air, the release path from products into water was also investigated. Textiles are a relevant product category from which release into water can be expected. Due to antimicrobial, antifungal and partially antiviral properties nano-Ag is one of the most promising MNMs for applications e.g. in textiles (Morones et al., 2005). However, during use, the nano-Ag slowly dissolves as Ag$^+$, which is one of the most toxic metals for microorganisms (Ratte, 1999). Information is only available for the release of ionic Ag$^+$ from polymers containing nano-Ag, not for the release of particulate Ag (Kumar et al., 2005; Kumar and Munstedt, 2005). However, it is known that particulate release might also be relevant, a textile that is disposed of at the end of its use phase has lost up to 10% of its weight through abrasion during washing and usage (Koehler et al., 2008).

Two studies investigated MNM release from socks when immersed in a liquid phase. One study referred to leaching of nano-Ag from socks into distilled water (Benn and Westerhoff, 2008). The socks contained up to a maximum of 1360 µg Ag (per g sock material) and leached as much as 650 µg of silver in 500 ml of distilled water (see Figure 8). Figure 8 shows the cumulative mass of silver emitted during four sequential washes. The silver content in the 500 ml wash waters ranged from 1.5 to 650 µg of silver.
FIGURE 8. Cumulative mass of silver released from three sock types (four socks total) into four consecutive 24-h washings in distilled water (Benn and Westerhoff, 2008).

The results from a second study (Geranio et al., 2009), conducted under conditions relevant for washing (high pH, presence of detergents and bleaching agents), showed little dissolution of nano-Ag under conditions relevant to washing (pH 10) with dissolved concentrations 10 times lower than those at pH 7. However, bleaching agents (e.g. hydrogen peroxide or peracetic acid formed by the perborate/TAED system) can greatly accelerate the dissolution of Ag. The amount and form of Ag released from the fabrics was shown to depend on the manner in which Ag was incorporated into the textile. The percentage of the total silver emitted during one washing of the textiles varied considerably among the products used, from less than 1% to 45%.

The release of nanoparticles by weathering is possible if a product containing such particles is exposed to sun and rain. An application where this has definitely been shown to occur is the use of nano-TiO$_2$ in façade paints (Kaegi et al., 2008). Synthetic nano-TiO$_2$ particles were successfully detected and identified in façades and urban runoffs. Based on this information, the authors gave a rough estimate of the number of nano-TiO$_2$ in runoff samples. Based on ICP-MS measurements, Ti concentrations collected, for example, from the runoff from new façade, were as high as 600 mg l$^{-1}$ (Figure 9). Ti concentrations in the raw samples (collected directly from the façade) were about 10 to 15% higher, compared to centrifuged samples, showing
that 85–90% of the collected material occurred in the range of 20–300 nm. In the urban area runoff the concentrations between raw and centrifuged samples showed a difference of about 50% (mass based). This means that half of the collected particles were >300 nm diameter and were released from other emitters, e.g. road paints.

Figure 9. Mass concentrations (ICP-MS measurements) of Ti in the surface runoff measured directly and after the first centrifugation step. Left axis: runoff from the model façade. Right axis: runoff from the real façade and from the urban runoff (Kaegi et al., 2008).

4.3.2 Modelling results

Several modelling studies have researched the release of MNMs into the environment. Some of them quantified release to the environment from some specific MNM-containing products during the consumption phase. In other studies, the release was modelled throughout the whole life-cycle of MNMs and MNM-containing products (MNM production and manufacturing of products, use, recycling and disposal).

Boxall et al. (2008) provide only simple equations for estimating the release of MNMs into the air in single specific situations. However, the results are not relevant for environmental purposes since they only indicate the likely exposure of an individual while using personal hygiene products (e.g. aerosol sprays).

Blaser et al. (2008) presented results for silver emitted from nano-functionalized biocidal products (textiles and plastics). However, only emission flows into sewage
treatment plants were considered, the release flows of nanosized Ag were not really modelled, and only nano-Ag served as the Ag$^+$ source.

Mueller and Nowack (2008) modelled the direct release of nano-Ag, nano-TiO$_2$ and CNT from products into the air, water and soil, WIP and STP. Processes such as abrasion during use and the washing of products (for example textiles), as well as product treatment in STPs and recycling processes etc. were considered. Table 3 contains the estimated release coefficients into technical and environmental compartments for MNMs (Ag, TiO$_2$ and CNT) from products.

Figure 10 shows the nano-TiO$_2$ release flow from products to the environmental compartments, STP, WIP, and landfill for the High Exposure-scenario. These flows were derived by distributing the total MNM production to the relevant MNM-containing product category and by estimating the release factors for each category.

Table 3. Substance Flow Analysis for the Release of nano-Ag, nano-TiO$_2$ and CNT from Products (Mueller and Nowack, 2008)

<table>
<thead>
<tr>
<th>NP</th>
<th>product category</th>
<th>% of total amount</th>
<th>release</th>
<th>% release</th>
<th></th>
</tr>
</thead>
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<tr>
<td>nano-Ag</td>
<td>textiles</td>
<td>10</td>
<td>abrasion during use</td>
<td>5</td>
<td>air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>abrasion during washing</td>
<td>5</td>
<td>STP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal (WIP)</td>
<td>2.5</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>recycling</td>
<td>0.5</td>
<td>leaving system</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>discharge</td>
<td>85</td>
<td>leaving system</td>
</tr>
<tr>
<td></td>
<td>cosmetics</td>
<td>25</td>
<td>application</td>
<td>95</td>
<td>STP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal</td>
<td>5</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td>sprays, cleaning agents</td>
<td>15</td>
<td>application</td>
<td>95</td>
<td>air (10%), STP (85%), soil (5%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal</td>
<td>5</td>
<td>STP</td>
</tr>
<tr>
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<td>metal products</td>
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<td>abrasion</td>
<td>5</td>
<td>WIP</td>
</tr>
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<td>47.5</td>
<td>leaving system</td>
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<td>dissolution</td>
<td>2.5</td>
<td>leaving system</td>
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<tr>
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<td>abrasion</td>
<td>5</td>
<td>STP</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>disposal</td>
<td>50</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td>paint</td>
<td>35</td>
<td>run off</td>
<td>5</td>
<td>soil (50%), STP (50%)</td>
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<td></td>
<td></td>
<td>dissolution</td>
<td>45</td>
<td>leaving system</td>
</tr>
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<td>nano-TiO$_2$</td>
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<td>abrasion</td>
<td>5</td>
<td>air (50%), STP (50%)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>disposal</td>
<td>95</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td>cosmetics</td>
<td>60</td>
<td>application</td>
<td>95</td>
<td>STP (95%), water (5%)</td>
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<td></td>
<td></td>
<td>disposal</td>
<td>5</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td>coatings</td>
<td>2</td>
<td>application</td>
<td>95</td>
<td>STP (95%), air (5%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal</td>
<td>5</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td>metals</td>
<td>1</td>
<td>abrasion</td>
<td>5</td>
<td>STP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>recycling</td>
<td>90</td>
<td>leaving system</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal</td>
<td>5</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td>energy storage/ production</td>
<td>10</td>
<td>disposal</td>
<td>25</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>recycling</td>
<td>75</td>
<td>leaving system</td>
</tr>
<tr>
<td></td>
<td>paint</td>
<td>25</td>
<td>run off</td>
<td>50</td>
<td>STP (50%), soil (50%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal</td>
<td>50</td>
<td>disposal site</td>
</tr>
<tr>
<td>CNT</td>
<td>plastics, sporting equipment</td>
<td>50</td>
<td>abrasion</td>
<td>5</td>
<td>air</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal</td>
<td>95</td>
<td>WIP</td>
</tr>
<tr>
<td></td>
<td>electronics, batteries</td>
<td>50</td>
<td>abrasion</td>
<td>40</td>
<td>leaving system</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>disposal</td>
<td>10</td>
<td>WIP (50%), disposal site (50%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>export</td>
<td>50</td>
<td>leaving system</td>
</tr>
</tbody>
</table>
Gottschalk et al. (2009) provide a comprehensive description of the emissions of MNMs into all environmental compartments from a whole life-cycle perspective of MNMs and MNM-containing products. Release is calculated for nano-TiO$_2$, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes for the three regions: USA, Europe and Switzerland. Table 4 gives an overview of the release coefficients used to model the MNM emission flows from product categories to all environmental compartments. These values refer to the fraction of the total amount of MNM released, transferred or dissolved from product categories; during MNM production; and during the manufacture of MNM products. Depending on the MNM-containing product, MNM release pathways to all the environmental compartments (air, soil, surface water, sediments, groundwater) and to several technical compartments (sewage treatment plants, waste incineration plants, recycling processes, landfills) were assumed during the whole life-cycle of products and the MNM they contain.

Complete disposal was modelled for composites and plastics. MNMs from glass and ceramics and light bulbs ended up in the environment, mostly via waste incineration processes. MNMs from cosmetics, cleaning agents, and coatings and dietary supplements ended up in the environment mostly via sewage treatment plants. Released MNMs, for example from paints, were assumed to reach sewage treatment
plants, landfills, soils, and surface waters. 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 also modelled.

Table 4: Release of manufactured nanomaterials (MNM) from products, manufacturing of MNM-containing products and MNM production. The values (averages enlarged and reduced by 50% (EU, USA) and 20% Switzerland (CH) to build uniform model input distributions) refer to the fraction of the total amount of MNM released, transferred or dissolved from a particular source.

<table>
<thead>
<tr>
<th>Product Category</th>
<th>STP</th>
<th>WP</th>
<th>Atmosphere</th>
<th>Landfill</th>
<th>Soil</th>
<th>Water</th>
<th>REC</th>
<th>Dissolution</th>
<th>Export</th>
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</thead>
<tbody>
<tr>
<td>nano-TiO₂ Plastics</td>
<td>0.32 0.19 1.00</td>
<td>0.68 0.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Cosmetics</td>
<td>0.90 0.90 0.50 0.02 0.01 0.05</td>
<td>0.03 0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coatings &amp; Cleaning Agent</td>
<td>0.90 0.90 0.90 0.02 0.01 0.05 0.05 0.05 0.05 0.05 0.05 0.05</td>
<td>0.03 0.04</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Batteries &amp; Capacitors</td>
<td>0.04 0.15 0.26</td>
<td>0.09 0.63</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Metals</td>
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<td>0.03 0.04</td>
<td>0.90 0.90</td>
<td></td>
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<td>Paint</td>
<td>0.20 0.20 0.20</td>
<td>0.50 0.50 0.25 0.25 0.25 0.25 0.05 0.05 0.05</td>
<td>0.09 0.63</td>
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<tr>
<td>Light Bulbs</td>
<td>0.32 0.19 0.10</td>
<td>0.68 0.81</td>
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<tr>
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<td>0.68 0.81</td>
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<td>Filter Aggregates</td>
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<td>0.09 0.63</td>
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<td></td>
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<tr>
<td>Consumer Electronics</td>
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<td>0.09 0.63</td>
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<td>Textiles</td>
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<tr>
<td>Dietary Supplement</td>
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<td>0.07 0.08</td>
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</tr>
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<td>Production</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cosmetics</td>
<td>0.90 0.90 0.90 0.02 0.01 0.05</td>
<td>0.03 0.04</td>
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<tr>
<td>Coatings &amp; Cleaning Agent</td>
<td>0.90 0.90 0.90 0.02 0.01 0.05 0.05 0.05 0.05 0.05 0.05 0.05</td>
<td>0.03 0.04</td>
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<tr>
<td>Dietary Supplement</td>
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<td>0.07 0.08</td>
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<tr>
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<td>Production</td>
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<tr>
<td>Metals</td>
<td>0.05 0.05 0.05 0.02 0.01 0.05</td>
<td>0.03 0.04</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Cosmetics</td>
<td>0.73 0.73 0.73 0.01 0.01 0.04</td>
<td>0.03 0.03</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Coatings &amp; Cleaning Agent</td>
<td>0.73 0.73 0.73 0.01 0.01 0.04 0.04 0.04 0.04 0.04 0.04 0.04</td>
<td>0.03 0.03</td>
<td></td>
<td></td>
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<tr>
<td>Textiles</td>
<td>0.13 0.13 0.20 0.05 0.03 0.14 0.02 0.02 0.02 0.05 0.11 0.13</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Dietary Supplements</td>
<td>0.01 0.01</td>
<td>0.07 0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ink</td>
<td>0.04 0.14 0.26</td>
<td>0.08 0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manufacturing</td>
<td>0.33 0.33 0.33 0.11 0.06 0.33 0.33 0.33 0.33 0.33 0.23 0.27</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>0.75 0.75 0.75</td>
<td>0.25 0.25 0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT Composites</td>
<td>0.32 0.19 1.00</td>
<td>0.68 0.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Consumer Electronics</td>
<td>0.04 0.15 0.28</td>
<td>0.09 0.63</td>
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<td></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>R&amp;D</td>
<td>0.05 0.05 0.05 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01</td>
<td>0.04 0.04 0.04</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Manufacturing</td>
<td>0.33 0.33 0.33 0.11 0.06 0.33 0.33 0.33 0.33 0.33 0.23 0.27</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>0.75 0.75 0.75</td>
<td>0.25 0.25 0.25</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Fullerene Composites</td>
<td>0.32 0.19 1.00</td>
<td>0.68 0.81</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cosmetics</td>
<td>0.90 0.90 0.90 0.02 0.01 0.05</td>
<td>0.03 0.04</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R&amp;D</td>
<td>0.50 0.50 0.50 0.16 0.10 0.50</td>
<td>0.34 0.41</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manufacturing</td>
<td>0.33 0.33 0.33 0.11 0.06 0.33 0.33 0.33 0.33 0.33 0.23 0.27</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>0.75 0.75 0.75</td>
<td>0.25 0.25 0.25</td>
<td></td>
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</tbody>
</table>

*Averages enlarged and reduced by 50% (EU, USA) and 20% Switzerland (CH) to build uniform model input distributions.*
4.4 Release from technical compartments

Much unintentional release of MNMs will be into wastewater or waste stream or landfills. Hence, wastewater treatment plants and waste incineration plants will be important sources for MNM release. Almost nothing is reported to date regarding the fate and behaviour of MNMs in waste incineration processes or in landfill (for example, leaching from landfill is not researched). Similarly, there have been few studies of the removal of MNMs from wastewater (Limbach et al., 2008). However, it should be expected that at least part of the MNMs in wastewater will end up in freshwaters. To minimize such indirect release of MNMs, measures must be taken with the product itself and at the technical facilities (STPs) that can be seen as clearly localized point sources.

However, technical compartments do not represent single step emission scenarios for MNMs. It should also be recognised that MNMs might 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 indirect entry of MNMs into the environment via technical processes, are presented in Table 5.
Table 5: Products and applications with indirect release of MNM into the environment.

<table>
<thead>
<tr>
<th>Technical facility (where measures for MNM-capture could be taken)</th>
<th>Environmental compartment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-paints (where the run-off from facades is collected in the sewer system)</td>
<td>Wastewater treatment plant</td>
</tr>
<tr>
<td>Use for water treatment</td>
<td></td>
</tr>
<tr>
<td>Application of sunscreen containing TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Filter on the car</td>
</tr>
<tr>
<td>MNMs as food additives</td>
<td>Recycling facility</td>
</tr>
<tr>
<td>Medical use</td>
<td></td>
</tr>
<tr>
<td>CeO&lt;sub&gt;2&lt;/sub&gt; in fuels</td>
<td></td>
</tr>
<tr>
<td>Dismantling of batteries</td>
<td></td>
</tr>
<tr>
<td>Recycling of plastic/glass/metal with nano-coatings</td>
<td></td>
</tr>
<tr>
<td>End-of-life treatment (incineration) of nanotextiles, nanocomposites</td>
<td>Waste incineration plant</td>
</tr>
</tbody>
</table>

4.4.1 Analytical results

Only two studies have been published that have quantified nanomaterials in natural samples to some extent. Using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Kiser et al. (2009) measured concentrations of filterable Ti (<700 nm) in STP effluents. The author reported values ranging from <5 to 15 µg l<sup>-1</sup>. However, the method is not specific for manufactured TiO<sub>2</sub> and includes all particulate Ti smaller than 700 nm, thus only indicating that the true nano-TiO<sub>2</sub> concentration has to be below these measured values.

Using mass spectrometry, Farré et al (2010) measured C<sub>60</sub>, C<sub>70</sub> fullerenes, and N-methylfulleropyrrolidine C<sub>60</sub> in wastewater effluents. The values for C<sub>60</sub> ranged from 0.5 ng l<sup>-1</sup> to 19 µg l<sup>-1</sup>. The equivalent results for C<sub>70</sub> fullerenes were 17 µg l<sup>-1</sup> to 181 µg l<sup>-1</sup> while, for N-methylfulleropyrrolidine C<sub>60</sub>, they were 60 µg l<sup>-1</sup> to 66 µg l<sup>-1</sup>.

4.4.2 Modelled results

Blaser et al. (2008) described how the use of biocidal products leads to the release of silver ions into wastewater which, in turn, could either be treated or discharged
directly into the Rhine river. The authors found that most of the silver emitted into wastewater was ending up in sewage sludge and might therefore be spread on agricultural fields. Only a marginal fraction of silver, not removed with sewage sludge, reaches natural waters via sewage treatment plant effluents. The sewage sludge is applied to soils, disposed of in landfills, or incinerated in waste incineration plants. During incineration, the released silver reaches slag, bottom, and fly ashes. 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.

Mueller and Nowack (2008) (supporting information) estimated flow coefficients in percent of the total mass flow, to model the transmissions between air water and soil, WIP, STP and landfill for two assumed scenarios: a realistic scenario, and a high-release scenario. Within the first scenario, the amount of nano-Ag and nano-TiO$_2$ (incombustible material) becoming airborne was assumed to be 50%. In the case of carbon nanotubes (CNT), it was assumed that 50% were incinerated, 25% ended up in the slag, and 25% became airborne. The suspended material was filtered to 99.9%. In the high-release scenario it was assumed that 100% of the incombustible MNMs became airborne during the incineration process and that 1% of the volatile material was released to the atmosphere. For CNT it was assumed that 25% was burned, 25% remained in the slag, and 1% became airborne with 50% then being emitted to the air. For sewage treatment plants, the average removal efficiency of suspended MNMs was assumed to be 97% for the realistic scenario and 90% for the high-emission scenario.

Boxall et al. (2008) presented a generic approach to calculate the indirect release of MNMs from single products (such as pharmaceuticals, cosmetics and personal care products, paints and coatings) which were considered to reach surface water via the runoff from contaminated soils and from wastewater treatment plants.

$$\text{PEC}_{\text{sw}} = \frac{C_{\text{ENP}} \cdot U_{\text{prod}} \cdot (1 - R_{\text{stp}}) \cdot F_{\text{pen}}}{\text{WW}_{\text{inhab}} \cdot D}$$

PEC$_{\text{sw}}$ = predicted concentration in surface water (mg l$^{-1}$), $C_{\text{MNPs}}$ = concentration of manufactured nanoparticle in product (mg g$^{-1}$), $U_{\text{prod}}$ = daily usage of product (g capita$^{-1}$ d$^{-1}$), $R_{\text{stp}}$ = fraction of MNM removed during sewage treatment, $F_{\text{pen}}$ = market penetration of nano product, WW$_{\text{inhab}}$ = amount of wastewater produced (l capita$^{-1}$ d$^{-1}$), D is the dilution factor in the receiving water.
For some parameters, generic values were proposed: $WW_{inhab} = 200$ (CHMP, 2006), $F_{pen} = 0.1, 0.5, 1$, $D = 10$ (CHMP, 2006). Usage scenarios for generic MNM emissions to wastewater treatment are presented as well. However, results for specific MNMs are not provided.

In a further study (Gottschalk et al., 2009) (Figure 11, purple arrows), a form of differentiated modelling for MNMs entering the environment through the air, via flue-gas cleaning of waste incineration plants was first conducted. The MNMs not removed were distributed randomly, either to the slag or to the flue-gas cleaning. Incombustible material (i.e. nano-Ag, nano-TiO$_2$, and nano-ZnO) ended up randomly (without elimination) either into the slag or into the flue-gas cleaning. During wastewater treatment for nano-Ag, nano-TiO$_2$, nano-ZnO, removal efficiencies between 90.6 and 99.5% (uniform distribution) were modelled, based on other results (Limbach et al., 2008). In the case of CNT, removal efficiencies from 96.3% to 99.7% (uniform distribution) were assumed, in accordance to values regarding settlement in water containing 100 mg l$^{-1}$ Natural Organic Matter (NOM) (Hyung et al., 2007; Kennedy et al., 2008). Because of the several available types (functionalisations) of fullerenes involved, a typical treatment efficiency for this material could not be determined. This lack of knowledge was considered by using a distribution from 0 to 100%. Additionally, MNM release via untreated wastewater, discharged into surface water during and after heavy rainfall, was considered. For the U.S. and EU, 20% stormwater overflow was assumed (ECB, 2003) and, for Switzerland, uniform distributions between 3 and 16% (Gottschalk et al., 2010b) were used.

REACH (ECHA, 2010) lists generic release coefficients for different industrial and wide-dispersed uses ranging from 0% to 100%. Low and high-release scenarios (2.5% and 20%) are indicated e.g. for industrial processing of products with abrasive techniques. However, such parameters are not adequate for direct/deterministic use for MNMs.
Figure 11. Simulation results (mode values >0.0005 t/a) of nano-TiO$_2$ and CNT flows for the United States in t/year taken from (Gottschalk et al., 2009). Red arrows show direct MNM release to the environment, brown, direct release to technical compartments and violet arrows, indirect release via technical processes. The thickness of the arrows indicates the proportions of the MNM flows, the thickness of the horizontal line within the compartments the proportional magnitude of the removal or accumulation.
5. Environmental release in NANEX exposure scenarios (nano-Ag in textiles, nano-TiO$_2$ in sunscreens, CNT in composites)

5.1 Occupational Exposure Scenarios (WP3)

In WP3, the worker exposures from MNM production, formulation and ‘use’ scenarios (identified in WP2) have been analyzed and listed (but not commented upon) on a database. Occupational scenarios need to consider: operational conditions and processes; standardized activities; estimates of involved populations; and risk management measures. Environmental aspects are mostly neglected in such assessments. MNM release to the environment is discussed only in a few cases (and predominantly in a very brief and imprecise manner) within the database.

French experts (afsset, 2010) refer to the estimation of dermal exposure to TiO$_2$ from the use of sunscreen. All of the product (230 tonnes year$^{-1}$ from the French market) (daily, 3 weeks per year) was assumed to be released into water. Also, cement containing nano-TiO$_2$ was seen as a potential source of human respiratory exposure and consequently also for environmental exposure to MNMs. Release during wall drilling was indicated (300 µg l$^{-1}$ of TiO$_2$).

Others (Pronk et al., 2009) presented a nano-Ag case study. A worst-case approach was studied, in which 100% of the substance ended up in surface water as silver ions. The report assumed that 100 tonnes year$^{-1}$ of bathroom cleaner containing 1% of silver are produced within the EU. In addition, this cleaner was assumed to be used only for private use, leading to its environmental release (to aquatic compartments) via sewer systems and municipal wastewater treatment plants. For regional calculations it was furthermore assumed that 10% of the 100 tons was released over a whole year. By using the defaults in EUSES (version 2.1) (i.e. local emission is 2 ‰ of the total emission) a release of silver to a STP was calculated, of 0.0548 kg d$^{-1}$.

A further study in the WP3-database (Yeganeh et al., 2008), characterized airborne particle concentrations during the production of carbonaceous nanomaterials (fullerenes and CNTs) in a commercial nanotechnology facility. The authors measured fine-particle mass concentrations (PM2.5), sub-micrometre size
distributions, and photoionization potentials at three locations inside the facility (i.e. inside the fume hood where nanomaterials were produced; just outside the fume hood; and in the background). However, the measurements were not selective for MNMs since both manufactured nanomaterials and naturally occurring particles were considered.

Measurements of the physical properties of aerosols in a fullerene factory (Fujitani et al., 2008) allowed assessment of the inhalation exposure. During the removal of fullerenes from a storage tank, the particle number concentration (for particle diameters (Dp) < 50 nm) was no greater than that in the non-work period. When a vacuum cleaner was in use, the particle number concentration (Dp < 50 nm) was higher than that during the non-work phase. However, the origin of these particles could not be determined. The only plausible source of nanosized particles from an operating vacuum cleaner seemed to be the carbon brushes of the motor.

Although these studies are listed in the WP3 database and provide some links to environmental aspects, the utility of such results for studying MNM release to the environment is very limited. The main limitations are that (i) knowing release flows from single occupational processes is not very relevant within a total environmental release framework that contains an immense range of MNM sources; and (ii) in most of such occupational MNM exposure scenarios, indoor air concentrations rather than MNM release amounts are given. It would be much more important to know how much MNM (mass flow per unit time) passes an air filter, or a waste water treatment process, or the amount (per unit time) of MNMs that are transferred from occupational areas into the environment without any technical treatment.
5.2 Consumer Exposure Scenarios (WP4)

NANEX WP4 focused on a small number of consumer exposure scenarios: nano-Ag in textiles, nano-TiO$_2$ in sunscreen and CNT in textiles. Assessing MNM release to the environment (WP5) based on single consumer exposure scenarios is difficult. In contrast to usual consumer exposure assessments, environmental exposure has to consider a distinct diffusive release of MNM. Thus, obtaining emission flows for a few single consumer products and exposure situations normally represents only a very small number of release paths out of a whole spectrum of potential environmental-release situations.

In the WP4 scenarios, MNMs emitted from textiles or sunscreen resulted in dermal exposure to such material. By taking a shower or a bath, or through continuous renewal of the skin, such MNMs will undoubtedly largely end up in wastewater or, to some extent, directly in surface waters. After sewage treatment these MNMs will, to some extent, reach landfills, soils, and surface waters.

The basic estimation of subsequent MNM release to liquid phases (e.g. after dermal deposition) is possible by using estimates of MNMs reaching the human skin. However, such calculations have first to include a quantification of the percentage of a particular consumer exposure/release scenario for such types of MNM use, within the whole environmentally-relevant release spectrum. Secondly, such products (e.g. products applied in textiles or used for skin treatment) do not necessarily represent the whole spectrum of products containing a particular MNM. Products for other uses could also lead to environmental releases and cannot be ignored. Hence, extrapolations of release amounts from a small and generic consumer exposure scenario to a wide environmental release framework will certainly be affected by error propagation. Error propagation is determined in such estimations by the necessity to take into account the whole relevant range of products (that are heterogeneous in respect of MNM concentrations, MNM incorporation and release characteristics) and by the difficulty in allocating the whole MNM use volume (and potential release amounts) to all of the products consumed.

Consumer scenarios that include MNMs used in cosmetics are relevant for environmental release since such MNMs deposited on the skin will inevitably reach
wastewater (and to some extent also directly surface waters) either by taking a shower/bath or due to continuous renewal of the epidermis. After emission into sewage treatment in wastewater, such material can end up in surface waters, and in landfills and soils. Especially for nano-Ag there are some uncertainties over which form (ionic form, particulate metal, etc.) of silver the environment will be exposed to. MNMs that remain in a particular product during their whole use phase will mostly end up in waste incineration processes or in landfill. Subsequently, deposition of incineration slag in landfills or release to air probably occurs. In addition, it should also be considered that the scenarios for consumer products considered in WP4 may also cover MNMs bound into solid matrices (textiles, wound dressings) in order to improve material and/or surface properties. MNMs bound into such matrices mainly result in consumer exposure due to wear and tear, but at very low levels.

Table 6 shows the consumer exposure model output parameters derived in WP4 for nano-Ag in textiles, TiO$_2$ in sunscreens, and CNT in composites. In addition, the potential subsequent use of such values for environmental exposure/release assessment is discussed.

In general, very limited information is available about CNTs in textiles, resulting in very conservative exposure scenarios and estimates. More is known about the presence in and release from textiles of nano-Ag. However, uncertainties regarding its potential migration/release from textiles, both in terms of the quantities and of the form of silver released (ions, nanoparticles or silver embedded in worn off textile fibres) make it difficult to develop realistic release estimates. A little more is known about the application of nano-TiO$_2$ sunscreen and, based on reasonable worst-case assumptions about duration and frequency of use, reasonable worst-case exposure scenarios and estimates can be developed for dermal exposure. However, one of the most important parameters for environmental studies, i.e. the total amount of these materials (nano-TiO$_2$, nano-Ag, CNTs) used in products (e.g. TiO$_2$ in sunscreens, Ag in textiles and CNT in batteries), is still very uncertain (Gottschalk et al., 2010b). Hence, it is essential to discuss or consider the model input uncertainties in relation to consumer exposure estimations. However, such a discussion is partially missing in WP4.
The developed consumer scenarios in WP4, which cover consumer exposure to MNMs used in cosmetics and textiles, also provide in principle a basis for estimating MNM release to the environment. As mentioned above, the MNMs in sunscreen will inevitably reach wastewater or surface waters. It is possible to estimate the total release of nano-TiO$_2$ from sunscreen in Europe, combining the consumer exposure scenario parameters (nanomaterial content in sunscreen and dermal load per day) with assumptions on: the total number of people that annually use such sunscreens; the fraction of the sunscreen that is washed off directly into surface water; and the fraction that ends up in wastewater treatment (following showers or swimming pools). However, without any reliable indications of the market penetration of the relevant nanoparticles, such combined calculations are of very limited value. Currently, for potential nanosized contaminants and products containing such material, such kind of market data is not available. Hence, quantifying release on the basis of single uncertain deterministic consumer-scenario parameters and including crude and extremely uncertain assumptions on the market penetration of the products involved, makes such environmental release modelling totally hypothetical, at least for nanomaterials.
Table 6: Consumer exposure-model output parameters derived in WP4 for nano-Ag in textiles, TiO$_2$ in sunscreens, and CNT in composites, together with remarks on the potential subsequent use of such values for environmental exposure/release assessment.

<table>
<thead>
<tr>
<th>Manufactured nanomaterial, scenario and product (emitter)</th>
<th>Characterization in WP4 of the MNM in the product</th>
<th>MNM concentrations in the product</th>
<th>Release scenario / destination</th>
<th>Release amount (range of the results)</th>
<th>References and models used</th>
<th>Remarks regarding potential subsequent environmental release modelling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nano-Ag</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in socks</td>
<td>Not available</td>
<td>20-40 mg kg$^{-1}$</td>
<td>dermal load</td>
<td>0.109-0.153 mg cm$^{-2}$ and 0.188-3.98 mg kg$^{-1}$ day$^{-1}$</td>
<td>(Geranio et al., 2009), (Ecetoc TRA model) default parameters, (ConsExpo model version 4.1) default parameters.</td>
<td>MNMs released to the skin will reach waste water by the person taking a shower/bath or through continuous renewal of the epidermis. After sewage treatment MNMs will, to some extent, end up in landfills, soils, and surface waters. However, there are many uncertainties about the chemical form of the nano-Ag entering the environment (ionic, particulate metal, etc.). The release measured by Geranio et al. 2009 was under conditions relevant for washing and not for skin exposure, probably greatly overestimating the release to skin, due to much harsher conditions. Nano-Ag that remains in the socks after final use will end up in waste treatment processes. Subsequent deposition on landfills or release to air is possible. Results from modelling in Gottschalk et al (2009) indicate 13-20% of the nano-Ag in textiles reach sewage treatment processes, up to 14% reach waste incineration plants, and around 60% rapidly dissolves in liquid phases.</td>
</tr>
<tr>
<td>in T-shirt</td>
<td>Not available</td>
<td>5-10 mg kg$^{-1}$</td>
<td>dermal load</td>
<td>3.2 E-04-4.8E-04 mg cm$^{-2}$ and 1.0E-02-6.9E-02 mg kg$^{-1}$ day$^{-1}$</td>
<td>(Vlachou et al., 2009), (Ecetoc TRA model) and (ConsExpo model version 4.1) both default parameters.</td>
<td>See scenario for nano-Ag in socks.</td>
</tr>
<tr>
<td>in wound dressing</td>
<td>Size: 1-30 nm</td>
<td>Ionic Ag concentration in released water, 70-100 mg kg$^{-1}$ of product</td>
<td>dermal load</td>
<td>1 E-02-1E-03 mg cm$^{-2}$ and 2.5 E-02-2.48 E-02 mg kg$^{-1}$ day$^{-1}$</td>
<td>(Geranio et al., 2009), (Ecetoc TRA model) and (ConsExpo model version 4.1) both default parameters.</td>
<td>MNMs released to the skin will reach waste water (see nano-Ag in socks). Non-released nano-Ag ends up in waste and hazardous waste.</td>
</tr>
<tr>
<td>Manufactured nanomaterial, scenario and product (emitter)</td>
<td>Characterization in WP4 of the MNM present in the product</td>
<td>MNM concentrations in the product</td>
<td>Release scenario / destination</td>
<td>Release amount (range of the results)</td>
<td>References and models used</td>
<td>Remarks regarding potential subsequent environmental release modeling</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
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</tr>
<tr>
<td>Carbon nanotubes (CNTs)</td>
<td>bound into the matrix</td>
<td>20 wt%; dermal load</td>
<td>worst case dermal external dose of $4.77 \times 10^2 \text{ mg kg}^{-1} \text{ day}^{-1}$</td>
<td>(Koehler et al., 2008), Chaudhry et al. (2009), (Ecetoc TRA model) and (ConsExpo model version 4.1) both default parameters.</td>
<td>Currently, textiles containing CNT are not on the market in relevant amounts. Relevant amounts are presently incorporated in composites and consumer electronics (Gottschalk et al., 2009). Results from modelling suggest that such MNMs either end up in waste incineration processes or in landfills.</td>
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<td></td>
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<td></td>
<td>worst case dermal load of 6.98 mg cm$^{-2}$</td>
<td>(ECHA, 2010)</td>
<td>See remarks regarding worst case dermal external dose.</td>
<td></td>
</tr>
<tr>
<td>Nano-$\text{TiO}_2$</td>
<td>Not available</td>
<td>10% dermal load</td>
<td>34-284 mg kg$^{-1}$ day$^{-1}$</td>
<td>(ConsExpo model version 4.1), (Hansen et al., 2009)</td>
<td>Nano-$\text{TiO}_2$ on the skin will reach waste water (see comments above on dermal exposure for other MNMs). Gottschalk et al. (2009) modelled 90% of the released MNMs reaching sewage treatment, 5% ending up directly into surface water. However, if such material stems from deposition on skin, or from other consumer exposure, scenarios are not relevant for environmental exposure assessment.</td>
<td></td>
</tr>
<tr>
<td>in sunscreen creams and lotions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in sunscreen sprays</td>
<td>Not available</td>
<td>5% inhalation, oral, dermal exposure</td>
<td>dermal: 41-483 mg kg$^{-1}$ day$^{-1}$, inhalation; 35-46 mg kg$^{-1}$ day$^{-1}$, oral: 0.3 mg kg$^{-1}$ day$^{-1}$</td>
<td>(ConsExpo model version 4.1), (Boxall et al., 2007), pg. 45</td>
<td>Subsequent MNM release from inhalation and oral immissions will be marginal, however such material will end up in waste water (the fraction applied on skin) or on soil/sand (for the fraction of the spray that missed the body and is deposited on the ground).</td>
<td></td>
</tr>
<tr>
<td>in sunscreen products on lips</td>
<td>Not available</td>
<td>oral exposure</td>
<td>0.04-0.48 mg kg$^{-1}$ day$^{-1}$</td>
<td>(ConsExpo model version 4.1)</td>
<td>See remarks to nano-$\text{TiO}_2$ in sunscreen sprays.</td>
<td></td>
</tr>
</tbody>
</table>
6. Conclusions

There is undoubtedly a lot of attention currently paid to the potential life-cycle impacts (and toxicity) on the environment of manufactured nanomaterials (Borm et al., 2006; Helland et al., 2006; Hund-Rinke and Simon, 2006; Wiesner et al., 2006; Nowack, 2007; Nowack and Bucheli, 2007; Oberdorster et al., 2007; Chaudhry et al., 2008; Handy et al., 2008; Klaine et al., 2008; Nowack, 2008; Alvarez et al., 2009; Andreev et al., 2009; Nowack, 2009; Wiesner et al., 2009; Som et al., 2010). However, there is very limited scientific data available on the environmental release, fate and effects of MNMs and almost no MNM-and-environment-specific regulations available. Very little is also known about industrial release assessments, although they are considered vital to questions on the effects of MNMs on the environment (Helland et al., 2007).

In the past, a human poisoning or an ecotoxicological effect, e.g. Minamata Bay mercury pollution, DDT disaster etc. has often been followed by the development of analytical methods for the detection in the environment of the toxic compounds involved. In other instances, discussions about the potential effects of compounds have been prompted by the improved ability of analytical chemists to detect lower and lower concentrations of pollutants in natural samples (e.g. pharmaceuticals). However, the absence of analytical methods for MNM detection in the environment means that the evaluation of the impact of MNMs on that environment differs to some extent. In the case of MNMs, the release, risk and exposure discussion clearly anticipates the possibility of the quantitative detection of such material. In addition, no effects of MNMs on the environment have been observed to date. Hence, the modelling of the MNM release into the environment, based on mathematical modelling, is currently the most important avenue for environmental risk assessments for such materials.

In this modelling, life-cycle concepts should be used to ensure a comprehensive identification of priorities for the analysis of MNM release (Som et al., 2010). Empirical data, or emission measurements of the main sources of MNM release, as well as modelling MNM release, are crucial for improving environmental exposure assessment. Only if it is possible to model (forecast) correctly monitored concentrations, can we fully understand a pollutant’s environmental behaviour and
risks. Such modelling has to cover release during all life-stages of the contaminants i.e. emissions from MNM products, from MNM production, and from the processes involved in the manufacture of nanoproducts. Although there are high levels of uncertainty regarding the conceptualization and parameterization of such MNM release assessment, modelling the release is currently the only way to identify the environmental compartments that might be affected by emitted MNMs.

There was insufficient data for the reviewed modelling studies to distinguish between different specific forms of MNMs, or modifications/functionalisations (e.g. surface-coatings of the MNMs). For example, no distinction was made between single and multiwalled CNTs and the various forms of fullerenes (e.g. C60, C70). To fit the purpose of the end-products, MNMs may be technically altered such as being rendered water-soluble or insoluble. In addition to such intended modifications (i.e. functionalization or coatings), changes in the properties of MNMs will be induced by the chemical and physical processes attributable to product degradation, or as a result of reactions with natural compounds.

In analyzing the results from these first models of MNM release it is essential to consider the extent to which different particle sizes and functionalisations of MNMs were considered and whether such factors could have influenced the release of MNMs, both from products and during any production and preparation processes. It should be noted that some of the modelling studies reviewed did not include release from production and manufacturing sites. Hence, some MNM release, for example around such sites, could be much higher than suggested.

In conclusion, early analytical studies have provided evidence for the presence of MNMs in the environment. Emissions of nano-TiO$_2$ have been shown to occur from exterior facades into water (Kaegi et al., 2008) and Nano-Ag emissions have been measured from laundering nano-enhanced textiles (Benn and Westerhoff, 2008; Geranio et al., 2009). Mass partitioning models (Blaser et al., 2008; Boxall et al., 2008; Mueller and Nowack, 2008; Gottschalk et al., 2009; Gottschalk et al., 2010b) have quantitatively modelled the environmental release of different MNMs.

Blaser et al. (2008) calculated Ag release from biocidal products that contained nano-Ag. However, no particulate emission flows were included in the modelling,
and nano-Ag was seen exclusively as the source of Ag. Boxall et al. (2008) presented equations to predict emissions of MNMs into air, soil, and water, based on hypothetical usage scenarios of single product types and life-cycle stages of MNMs. Mueller and Nowack (2008) have reported the first published modelling of MNM release into the environment (air, soil, water) from a complete life-cycle perspective of MNM-containing products.

Recent studies (Gottschalk et al., 2009; Gottschalk et al., 2010b), based on a stochastic/probabilistic mass balance multi-compartment model (Gottschalk et al., 2010a), have shown that the most dominant metallic MNMs (nano-Ag, nano-TiO₂, nano-ZnO) transfer from products to STP and WIP, from STP to WIP, and from there to landfills. For CNTs, the majority of the emitted material ends up in the WIP. A first comprehensive sensitivity analysis (Gottschalk et al., 2010b) has allowed the identification of the key parameters that impact MNM environmental release and exposure. Attention has to be paid to the release of MNMs 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, or deposited in landfills. A further crucial parameter, although associated with high uncertainties, is the assignment of the mass of MNMs that could be released from the products which are seen as the main MNM emitters in such modelling. There is an urgent need for quantitative data on MNM emissions during the manufacturing of MNM-containing products and during the production of MNMs. Experimental results from companies producing MNMs have shown that exposure of workers to these materials occurs (Mazzuckelli et al., 2007; Bello et al., 2008; Fujitani et al., 2008; Han et al., 2008; Yeganeh et al., 2008). However, in order to use such worker exposure results in environmental release studies, the release of MNMs to work areas has to be quantified.

Finally, no methods sensitive enough for the quantitative analysis of MNMs in the environment (and the validation of the results from this modelling) are currently available. However, it can be expected that, within the next few years, such methods will become available, at least for some MNMs in some matrices. Although without definitive validation based on reliable measurements, the release model results presented provide the first PECs for MNMs in different
environmental compartments and will help analytical chemists to develop trace methods for MNM analysis by indicating the release amounts and concentration levels that can be expected.
7. Literature


ConsExpo model version 4.1, w.C.n.


Ecatoc TRA model, h.w.e.o.t.


8. Appendix: Review of available studies of environmental exposure to manufactured nanomaterials

Content

8. Appendix: Review of available studies of environmental exposure to manufactured nanomaterials ................................................................. 71
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Section A: Experimental (analytical) studies that quantify manufactured nanomaterial release to and/or concentrations in the environment


Focus:
This paper evaluates nanoparticle release from TiO2 nanopowder coating materials by means of a simulation of a specific utilization. UV light/fluorescent lamps, a fan, and use of a rubber knife in a scraping motion were the sunlight, wind, and human contact with the materials. The simulation was carried out in a closed box system using the selected substrates of wood, polymer and tile. Tile coated with TiO2 nanopowder was found to have the highest particle release. Exposure to UV light was shown to increase this release.

Content:
In this study, the emission of nanoparticles from a TiO2 nanopowder coating on different substrates (wood, polymer, and tile), was evaluated in a simulation box. Emissions were measured for the first time with a Scanning Mobility Particle Sizer (SMPS). The coating process for the substrate followed the instructions given by the supply company. In the simulation box, UV light, a fan, and a rubber knife were used to simulate the effects of sunlight, wind, and human contact. Among the three selected substrates, tile coated with TiO2 nanopowder was found to have the highest particle emission due to nanopowder separation during the simulation process. Exposure to UV light was shown to increase the release of particles less than 200 nm in size from materials coated with TiO2 nanopowder. The results showed that, under the conditions described, particle number concentration or average emission rate decreased significantly after 60 and 90 min for TiO2/polymer and TiO2/wood, respectively. However, the emission rate continued to increase after 2 h of testing for TiO2/wood. It is suggested that nanoparticle emission evaluation is necessary for products with nanopowder coating.

Specific information on nanomaterial release to the environment:
- TiO2 release from a spray-coated wooden plate, PET polymer film substrates, and a tile plate using a commercial TiO2 photo-catalyst paint (Allstar Painting Inc., Taiwan) into a simulation box.

**Focus:**
This paper deals with the behaviour of different nano-silver fabrics under conditions relevant for washing. Release from "real" washing conditions was studied which took mechanical stress on the textiles into account. The amount and the form of silver released (particulate or ionic) into the washing solution was evaluated. The fabrics were immersed in a solution with a pH 10 and washed for 30 min at 40 °C. The impacts of pH, surfactants, and oxidizing agents on the dissolution and release of Ag-nanoparticles were studied.

**Content:**
The widespread use of silver nanoparticles (Ag-NPs) in commercial products, especially textiles, is likely to result in an unknown spread of Ag into the environment. The quantification and characterization of the Ag released from nano-Ag-products is an important parameter needed to predict the effect of Ag-NPs on the environment. The aim of this study was to determine the amount and form of Ag released during washing from nine fabrics with different ways of silver incorporation into or onto the fibres. The effect of pH, surfactants, and oxidizing agents was evaluated. The results showed that little dissolution of Ag-NPs occurred under conditions relevant to washing (pH 10) with dissolved concentrations 10 times lower than at pH 7. However, bleaching agents such as hydrogen peroxide or peracetic acid (formed by the perborate/TAED system) can greatly accelerate the dissolution of Ag. The amount and form of Ag released from the fabrics as ionic and particulate Ag depended on the type of Ag-incorporation into the textile. The percentage of the total silver emitted from the textiles during one wash cycle varied considerably between products (from less than 1% to 45%). In the washing machine the majority of the Ag (at least 50% but usually >75%) was released in the size fraction >450 nm, indicating the dominant role of mechanical stress.

Compared to many of the textiles containing nano-Ag, a conventional silver textile did not show any significant difference in the size distribution of the silver released. These results have important implications for the risk assessment of Ag-textiles and also for studies of the environmental fate of nano-Ag, because they show that, under conditions relevant to washing, it is primarily coarse Ag-containing particles that are released.

**Specific information on nanomaterial release to the environment:**
- Ag release (particulate or ionic) into washing solutions

Focus:
This paper deals with the release of nano-Ag from socks into water, together with the form taken by this silver and its fate in sewage treatment plants. The nano-Ag volume in the sock and the concentration and form (nanoparticle or ionic) of the released silver are examined during repeated washings of the socks with distilled water. Batch adsorption isotherm studies were carried out with wastewater biomass and two sources of silver: (1) silver released from the socks into the wash water (nanoparticle or ionic), and (2) reagent ionic silver. These isotherms were then used to determine the silver content in the sewage treatment effluent and biosolids.

Content:
Manufacturers of clothing articles employ nanosilver (nano-Ag) as an antimicrobial agent, but the environmental impacts of nano-Ag release from commercial products are unknown. The quantity and form of the nanomaterials released from consumer products should be determined to assess the environmental risks of nanotechnology. This paper investigates silver released from commercial clothing (socks) into water, and its fate in wastewater treatment plants (WWTPs). Six types of socks contained up to a maximum of 1360 µg-Ag/g-sock and leached as much as 650 µg of silver in 500 ml of distilled water. Microscopy conducted on sock material and wash water revealed the presence of silver particles from 10 to 500 nm in diameter. Physical separation and ion-selective electrode (ISE) analyses suggest that both colloidal and ionic silver leach from the socks. Variable leaching rates among sock types suggests that the sock manufacturing process may control the release of silver. The adsorption of the leached silver to WWTP biomass was used to develop a model which predicts that a typical wastewater treatment facility could treat a high concentration of influent silver. However, the high silver concentration may restrict the disposal of the biosolids as agricultural fertilizer.

Specific information on nanomaterial release to the environment:
- Ag release (particulate or ionic) into washing solutions, sewage treatment effluent and biosolids
Focus:
This paper investigates whether the TiO$_2$ particles used in exterior paints and
plasters for facades can end up in surface water via urban transport pathways.
Solid coatings of facades and water samples were analyzed with a combination of
electron microscopy (transmission electron microscopy (TEM), scanning electron
microscopy (SEM)), inductive-coupled plasma optical emission spectrometry (ICP-
OES) and mass spectrometry (ICP-MS).

Content:
Direct evidence of the release of synthetic nanoparticles from urban applications
into the aquatic environment is presented. The authors investigated TiO$_2$ particles
as these particles are used in large quantities in exterior paints as whitening
pigments and are, to some extent, also present in the nano-size range. TiO$_2$
particles were traced from exterior facade paints to the discharge into surface
waters. A centrifugation-based sample preparation which recovers TiO$_2$ particles
between roughly 20 and 300 nm was used. Analytical electron microscopy
revealed that TiO$_2$ particles are detached from new and aged facade paints by
natural weather conditions and are then transported by facade runoff and
discharged into natural receiving waters. Microscopic investigations were
confirmed by bulk chemical analysis. By combining results from microscopic
investigations with bulk chemical analysis, the number densities of synthetic TiO$_2$
particles in the runoff was calculated.

Specific information on nanomaterial release to the environment:
- TiO$_2$ release into surface water via urban transport pathways.
Section B: Modelling studies that quantify manufactured nanomaterial release to and/or concentrations in the environment


**Focus:**
This paper quantifies the first carbon-based nanoparticles (MCNPs) levels in sediments for assumed realistic MCNP release scenarios and compares such levels with concentrations for black carbon nanoparticles (BCNPs). In addition, in these scenarios the effect of MCNPs on hydrophobic contaminant binding in sediments is evaluated.

**Content:**
In this paper, the authors show that the concentrations of manufactured carbon-based nanoparticles (MCNPs) in aquatic sediments will be negligible compared to levels of black carbon nanoparticles (BCNPs). This is concluded from model calculations accounting for MCNP sedimentation fluxes, removal rates due to aggregation or degradation, and MCNP burial in deeper sediment layers. The resultant steady state MCNP levels are compared with BCNP levels calculated from soot levels in sediments and weight fractions of nanosized fractions of these soot particles. MCNP/BCNP ratios range from $10^{-7}$ to $10^{-4}$ (w:w). This suggests that the often acclaimed effect of MCNPs on organic pollutant binding and bioavailability will probably be below the level of detection if natural BCNPs are present, even if binding to MCNP is one to two orders of magnitude stronger than to BCNPs. Furthermore, exposure to and toxic effects of MCNPs in sediments and soils will be negligible compared to that of BCNPs.

**Specific information on nanomaterial release to the environment:**
- None.

**Focus:**
This paper estimates the amount of silver released to the environment from biocidal plastics and textiles. The emissions were modelled as the release of silver from manufactured nanomaterials. Nano-Ag was considered exclusively as the source of Ag\(^{+}\). Thus, no particulate emission flows were considered.

**Content:**
Products with an antimicrobial effect based on silver nanoparticles are increasingly used in Asia, North America and Europe. This study presents an analysis of the risk to freshwater ecosystems from silver released from these nanoparticles, incorporated into textiles and plastics. The analysis is presented in four stages; (i) silver mass flow analysis and estimation of emissions, (ii) assessment of the fate of silver in a river system and estimation of predicted environmental concentrations (PECs), (iii) critical evaluation of available toxicity data for environmentally relevant forms of silver and estimation of predicted no-effect concentrations (PNECs), and (iv) risk characterization. The assessment is based on estimated silver use in the year 2010, focusing on the Rhine river as a case study. In 2010, biocidal plastics and textiles are predicted to account for up to 15% of the total silver released into water in the European Union. The majority of silver released into wastewater is incorporated into sewage sludge and may be spread on agricultural fields. The amount of silver reaching natural waters depends on the fraction of wastewater that is effectively treated. Modelled PECs in the Rhine river are in satisfactory agreement with monitoring data from other river systems. Because a complete characterization of the toxicity of environmentally relevant silver species is lacking, only a limited risk assessment is possible at this time. However, our study indicates that PEC/PNEC ratios greater than 1 cannot be ruled out for freshwater ecosystems, in particular sediments. No risk is predicted for the microbial communities in sewage treatment plants.

**Specific information on nanomaterial release to the environment:**
- Ag release from nanoparticles incorporated into textiles and plastics into the Rhine river.
Focus:
This work provides a framework of simplistic models and algorithms for estimating concentrations in water, soil and air. However, this framework has been developed and applied to a range of manufactured nanoparticles (MNPs) to estimate the likely concentrations of MNPs in water and soil for only a limited range of usage scenarios.

Content:
It is inevitable that, during their manufacture and use, manufactured nanoparticles (MNPs) will be released into the environment. This study was therefore performed to: 1) identify the potential releases of MNPs into the environment; 2) review the fate of MNPs in environmental systems; and 3) to assess the potential current and future environmental exposures.

Whilst MNPs may be emitted during the manufacturing process, the route of input to the environment will primarily depend on the end use of the MNP-containing product. In many of the applications considered, nanoparticles are in a fixed or bound form, and hence pose minimal risk to the environment. Applications that contain free manufactured nanoparticles, and/or those that are likely to give rise to a greater likelihood and extent of release into the environment (e.g. airborne nanoparticles, or those in products likely to be disposed of in wastewaters) include cosmetics, paints & coatings, catalysts & lubricants, water treatment and bioremediation products, food & food packaging, human and veterinary medicines and plant protection products. A number of products that are currently on the UK market that contain MNPs have been identified. However, due to a lack of published data, it is not currently possible to estimate the UK market penetration for these products. Moreover, whilst some data are available on the concentrations of MNPs in selected products, for some products this is totally lacking.

Available data indicate that, following release to water and air, nanoparticles will aggregate to some degree and that the behaviour of the resulting aggregates will be very different from the free nanoparticles. The degree of aggregation, and the size range of the aggregates, is dependent on: the characteristics of the particle; the concentration of the particles; and the characteristics of the environmental system. MNPs will exhibit differing mobilities in soils and bodies of water, and in water treatment processes, compared to their corresponding parent form. The behaviour of nanoparticles in environmental systems is therefore highly complex and appears to be dependent not only on the particle type but also on the particle size and the nature of the receiving environments.

Due to the lack of data on usage and environmental fate, a framework of simplistic models and algorithms for estimating concentrations in water, soil and air has been developed and applied to a range of MNPs. This modelling framework was applied to estimate the likely concentrations of MNPs in water and soil for a range of usage scenarios. For the 10% market penetration scenario, which probably overestimates current exposure levels, concentrations of silver, aluminium and fullerene C60 concentrations were predicted to be in the ng l⁻¹ range, whereas,
titanium dioxide, zinc oxide, nanolatex and hydroxyapatite are predicted to be in the mg l\(^{-1}\) range (Table E.1). Predicted concentrations in soil ranged from <0.01 (cerium dioxide) to around 4.3 mg kg\(^{-1}\) (nanolatex). Predictions were also obtained for concentrations of selected MNPs in the air compartment. If, in the future, all of the product types investigated contained manufactured nanoparticles, then concentrations in water could range from < 1 ng l\(^{-1}\) (cerium dioxide) to 1 mg l\(^{-1}\) (nanolatex).

The exposure data developed in this study provide a benchmark to a) inform the development of new analytical methodologies for environmental systems; b) inform the design of environmental fate studies; and c) interpret the significance of existing ecotoxicology data on MNPs. A comparison of the results of the exposure estimations with the available ecotoxicological data (Table E.1) is reassuring and indicates that even the conservative exposure concentrations generated in this study are many orders of magnitude lower than concentrations likely to cause acute effects in invertebrates, fish algae or sublethal effects on fish, invertebrates or bacteria.

Whilst this study has identified the potential environmental exposure arising from a range of key MNP types, the assessment has been limited by the availability of data and knowledge. Work in the future should therefore focus on 1) establishing a detailed knowledge of the content and use in the UK of products containing MNPs; 2) developing an understanding of the factors and processes affecting the fate and transport of MNPs in the environment; 3) the development and evaluation of more complex exposure assessment models; and 4) the development of a better understanding of the ecotoxicity of MNPs under environmentally-relevant exposure situations.

**Specific information on nanomaterial release to the environment:**
- Release to water, soil and air for Ag, Al, fullerene, TiO\(_2\) ZnO, nano-latex and hydroxyapatite (HA).

Focus:
This paper provides, for the first time, expected concentrations of manufactured nanoparticles (nano-Ag, nano-TiO₂, and CNT) in the environment. The risk assessment was carried out for the three environmental compartments water, air, and soil for Switzerland, based on the comparison of the PEC to the PNEC.

Content:
The aim of this study was to use a life-cycle perspective to model the quantities of manufactured nanoparticles released into the environment. Three types of nanoparticles were studied: nano silver (nano-Ag), nano TiO₂ (nano-TiO₂), and carbon nanotubes (CNT). The quantification was based on a substance flow analysis from products to air, soil, and water in Switzerland.

The following parameters were used as model inputs: estimated worldwide production volume; allocation of the production volume to product categories; particle release from products; and flow coefficients within the environmental compartments. The predicted environmental concentrations (PEC) were then compared to the predicted no-effect concentrations (PNEC) derived from the literature, to estimate a possible risk. The expected concentrations of the three nanoparticles in the different environmental compartments vary widely, due to the different life-cycles of the nanoparticle-containing products. The PEC values for nano-TiO₂ in water are 0.7-16 µg l⁻¹ and close to or higher than the PNEC value for nano-TiO₂ (<1 µg l⁻¹). The risk quotients (PEC/PNEC) for CNT and nano-Ag were much smaller than one, therefore presenting no reason to expect adverse effects from those particles. The results of this study make it possible for the first time to carry out a quantitative risk assessment of nanoparticles in the environment and suggest further detailed studies of nano-TiO₂.

Specific information to nanomaterial release to the environment:
- Release of nano-Ag, nano-TiO₂, and CNT to water, soil and air.
Focus:
This non-peer reviewed manuscript aims to predict the environmental quantities of nanomaterials that result from products and environmentally relevant processes which potentially lead to human exposure.

Content:
Risk assessments that explicitly consider the human and environmental exposure potential of nano-functionalised products and processes are required for regulatory frameworks. There is a large range of products commercially available, with many more products and processes in development, awaiting regulatory clarification. A scoping model, Nano- EXP, is presented, which describes potential environmental nano-quantities and behaviours arising from the environmental use of products and processes. The potential quantities of nanomaterials in surface water originating from various products are determined. This results in a scale of contribution from highest to lowest as follows: 1. Groundwater remediation, 2. Exterior paints, 3. Fuel additives, 4. Food packaging.

Specific information on nanomaterial release to the environment:
- Qualitative discussion to release of TiO$_2$, Ag, Fe$_2$O$_3$, CeO$_2$ into water.

**Focus:**
This paper provides a probabilistic/stochastic material flow analysis (PMFA) framework to derive probability distributions of PEC values for any compound or material and for a whole life-cycle perspective of potential contaminants in complex systems, covering all environmental compartments and life stages of these contaminants. As a first case study the simulation of PECs of manufactured nano-TiO$_2$ particles in Switzerland has been chosen.

**Content:**
An elementary step towards a quantitative assessment of the risks to the environment of new compounds or pollutants (chemicals, materials) is to estimate their environmental concentrations. Thus, the calculation of predicted environmental concentrations (PECs) builds the basis of a first exposure assessment. This paper presents a probabilistic method for computing distributions of PECs by means of stochastic stationary substance/material flow modelling. The evolved model is basically applicable to any substance with a distinct lack of data concerning its environmental fate, exposure, emission and transmission characteristics. The model input parameters and variables consider production, application quantities and fate of the compounds in natural and technical environments. To cope with the uncertainties concerning the estimation of the model parameters (e.g. transfer and partitioning coefficients, emission factors), as well as uncertainties about the exposure causal mechanisms themselves (e.g. level of compound production and application), sensitivity and uncertainty analyses, Monte Carlo simulation and Markov Chain Monte Carlo modelling were utilized and combined. The combination of these methods is appropriate for calculating realistic PECs when facing a lack of data. The proposed model is programmed and carried out with the computational tool R and, by way of an example, implemented and validated with data for a case study of the flows in Switzerland of the manufactured nanoparticle nano-TiO$_2$.

**Specific information on nanomaterial release to the environment:**
- Release of TiO$_2$, into water, soil, sediments, air, groundwater.

**Focus:**
This paper models the environmental concentrations of nano-TiO$_2$, nano-ZnO, nano-Ag, CNT, and fullerenes for the U.S., Europe, and Switzerland, for all environmental compartments. To assess the potential risks posed by these MNMs, the calculated PEC was compared to the predicted no-effect concentration (PNEC) based on toxicity data for the corresponding environmental compartment. Different release pathways to the environment of manufactured nanomaterials (MNMs) were assumed during nanomaterial production, manufacturing of nanomaterial containing products and during the product’s life-cycle.

**Content:**
Manufactured nanomaterials (MNM) are already used in many products and consequently released into environmental compartments. This study calculated predicted environmental concentrations (PEC) based on a probabilistic material flow analysis from a life-cycle perspective of MNM containing products. The authors modeled nano-TiO$_2$, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes for the U.S., Europe and Switzerland. The environmental concentrations were calculated as probabilistic density functions and were compared to data from ecotoxicological studies. The simulated modes (most frequent values) range from 0.003 ng L$^{-1}$ (fullerenes) to 21 ng L$^{-1}$ (nano-TiO$_2$) for surface waters and from 4 ng L$^{-1}$ (fullerenes) to 4µg L$^{-1}$ (nano-TiO$_2$) for sewage treatment effluents. For Europe and the U.S., the annual increase of MNM on sludge treated soil ranges from 1 ng kg$^{-1}$ for fullerenes to 89 µg kg$^{-1}$ for nano-TiO$_2$. The results of this study indicate that risks to aquatic organisms may currently emanate from nano-Ag, nano-TiO$_2$, and nano-ZnO in sewage treatment effluents for all considered regions and for nano-Ag in surface waters. For the other environmental compartments for which ecotoxicological data were available, no risks to organisms are presently expected.

**Specific information on nanomaterial release to the environment:**
- Release of: TiO$_2$, ZnO, Ag, CNT, fullerenes into: water, soils, sediments, air, groundwater.

**Focus:**  
This paper discusses the possibilities and limitations of the use of a developed probabilistic material flow analysis (PMFA) in MNM exposure modelling. Flows to and concentrations in the environment for nano-TiO$_2$, CNTs, and nano-Ag for Switzerland were calculated. The potential risks caused by these three MNMs were assessed by comparing the PEC values to available PNEC values. This study extends the exposure modelling of Mueller and Nowack (2008) by considering the sediment and groundwater environmental compartments as well as production, manufacturing and recycling processes.

**Content:**  
Information on environmental concentrations is needed to assess the risks that manufactured nanomaterials (MNMs) may pose to the environment. In this study, predicted environmental concentrations (PEC) were modelled for nano-TiO$_2$, carbon nanotubes (CNT) and nano-Ag for Switzerland. Based on a life-cycle perspective, the model considered as input parameters the production volumes of the MNMs, the manufacturing and consumption quantities of products containing those materials, and the fate and pathways of MNMs in natural and technical environments. Faced with a distinct scarcity of data, the authors used a probabilistic material flow analysis model, treating all parameters as probability distributions. The modelling included Monte Carlo and Markov Chain Monte Carlo simulations as well as a sensitivity and uncertainty analysis. The PEC values of the MNMs in the different environmental compartments vary widely due to different MNM production volumes and different life-cycles of the nanoproducts. The use of MNMs in products with high water relevance leads to higher water and sediment concentrations for nano-TiO$_2$ and nano-Ag, compared to CNTs, where smaller amounts of MNMs reach the aquatic compartments. This study also presents a sensitivity analysis and a comprehensive discussion of the uncertainties of the simulation results and the limitations of the used approach. To estimate potential risks, the PEC values were compared to the predicted no-effect concentrations (PNEC) derived from published data. The risk quotients (PEC/PNEC) for nano-TiO$_2$ and nano-Ag were larger than one for treated wastewater and much smaller for all other environmental compartments (e.g., water, sediments, soils). The authors conclude that probabilistic modelling is very useful for predicting environmental concentrations of MNMs given the current lack of substantiated data.

**Specific information on nanomaterial release to the environment:**  
- Release of: TiO$_2$, Ag, CNTs into: water, soils, sediments, air, groundwater.

Focus:
The release of nanoscale materials (TiO$_2$ from exterior paints, Ag from food packaging and CeO$_2$ from use as a fuel additive) to surface waters and the atmosphere was considered. A comparison to other European exposure scenarios is provided as well.

Content:
As nanomaterials find increased application in commercial and industrial products and processes, the potential for release of these novel materials into the environment also increases. The characteristics of these materials also may result in novel toxicological actions related to their nanoscale, which will have implications for their ecotoxicological and toxicological limits of exposure and eventual regulation. A framework for nanomaterial risk assessment on regulatory, ecotoxicological and toxicological bases, developed from recent exposure and toxicity studies, is presented. The release of nanoscale TiO$_2$, Ag and CeO$_2$ to the atmosphere and surface waters is assessed against provisional toxicological benchmark doses (BMDs) and critical effect doses (CEDs) developed from best available data. Predicted levels of nanomaterial release to surface waters and the atmosphere resulted in regulatory risk rankings of moderate concern based on worst-case provisional regulatory limits. Inhalation and ingestion risk rankings were of very low concern based on the provisional inhalation and ingestion toxicity BMDLs and CEDLs determined for the nanomaterials in question. More toxicological data is needed on nanoscale material inhalation to develop a true dose response as in vitro cytotoxicity studies yielded an inhalation risk ranking of lower concern. The moderate to high ecotoxicological risk rankings posed by the release of nanoscale TiO$_2$ and Ag to surface waters highlights the need for guidance and restriction on the use and disposal of commercial products containing nanomaterial. The risk rankings presented in this assessment give a first indication of the relative risks presented by the usage and release of these materials into the environment and indicate which materials require further investigation into their nano-specific toxicological actions. As more nano-relevant toxicity studies are published, end-points and risk levels related to nano-specific toxicity actions may be determined and the provisional BMDLs developed as part of this framework refined, resulting in more confident risk rankings.

Specific information on nanomaterial release to the environment:
- Release of TiO$_2$, Ag, CeO$_2$ into water and air.

**Focus:**
The report outlines those nanomaterials that potentially show environmental health and safety impacts. It identifies possible and significant EHS issues summing up current research to EHS impacts, and, in the technical sector report, provides specific considerations to be regarded in relation to particular use scenarios.

**Content:**
The ObservatoryNANO report on the technology sector Environment summarizes the technologies and applications used for the treatment of air, water and soil (MUELLER and NOWACK, 2009). This EHS analysis considers those nanomaterials outlined, within the context of their application, and provides a summary of what is known in relation to the potential hazards from and exposure to the material in question. Finally, the analysis outlines some key EHS considerations & basic guidance for those developing or using the technologies outlined within the report.

For all of those nanoparticles identified as having potential EHS impact, toxicological knowledge is still emerging, although based on what is known to date a reasonable approximation of potential hazard may be made. The key common knowledge gap across all nanoparticles however is the lack of exposure measurements for the scenarios and applications in question. As the ObservatoryNANO project progresses, it is expected that these knowledge gaps will be addressed (at least in part) and thus that later EHS reports will be able to reach firmer conclusions on the risks posed by the nanomaterials considered.

**Specific information on nanomaterial release to the environment:**
- Reflections to release into water for nZVI, into air and/or wastewater for magnetite, maghemite, CNT and metal oxides (e.g. Si-Al oxides, Mn-oxides).
Section C: Analytical (field) studies that quantify manufactured nanomaterial release to and/or concentrations in the environment


Focus:
This paper deals for the first time with the occurrence, characterization, and removal of nano- and larger sized Ti in wastewater treatment plants. Ti concentrations in sewage treatment effluents and solids were quantified.

Content:
Titanium (Ti) occurs naturally in soils and as highly purified titanium dioxide (TiO$_2$) in many commercial products that have been used for decades. The authors report for the first time the occurrence, characterization, and removal of nano- and larger sized Ti at wastewater treatment plants (WWTPs). At one WWTP studied in detail, raw sewage contained 100 to nearly 3000 µg Ti l$^{-1}$. Ti particles larger than 0.7 µm accounted for the majority of the Ti in raw sewage, and this fraction was well removed by WWTP processes. Ti concentrations in effluents from this and several other WWTPs ranged from <5 to 15 µg l$^{-1}$ and were nearly all present in the <0.7 µm size fraction. As Ti was removed, it accumulated in settled solids, at concentrations ranging from 1 to 6 µg Ti mg$^{-1}$. Ti-containing solids were identified in sewage, biosolids, and liquid effluent as well as in commercial products containing manufactured TiO$_2$. Single nanoparticles plus spherical aggregates (50 nm to a few hundred nanometres in size), composed of sub-50 nm spheres of Ti and oxygen only (presumably TiO$_2$), were observed in all samples. Significantly larger silicate particles, containing a mixture of Ti and other metal atoms, were also observed in the samples. To support the field work, laboratory adsorption batch and sequencing batch reactor experiments using TiO$_2$ and activated sludge bacteria verified that the adsorption of TiO$_2$ onto activated sludge biomass occurs. Monitoring for TiO$_2$ in the environment, where WWTP liquid effluent is discharged (rivers, lakes, oceans), or biomass disposed (landfills, agriculture and soil amendments, incinerator off-gas or residuals), will increase our knowledge of the fate and transport of other nanomaterials in the environment.

Specific information on nanomaterial release to the environment:
Release of nano- and larger-sized Ti into sewage treatment effluents.

**Focus:**
This paper describes a novel method for the analysis of C60 and C70 fullerenes and N-methylfulleropyrrolidine C60 in the environment (suspended organic material of effluents of sewage treatment plants) in a low ng l⁻¹ level. For the first time, the real concentration levels of these fullerenes, retained on suspended solids in 22 wastewater effluents in Catalonia (NE of Spain) were monitored.

**Content:**
The increasing use and production of carbon-based nanoparticles demands new analytical approaches able to achieve sensitivities in the low ng l⁻¹ range in order to assess their presence in environmental samples.

This paper describes the development, optimization and validation of a novel method for the analysis of C60 and C70 fullerenes and N-methylfulleropyrrolidine C60 in the environment. The method relies on ultrasonication extraction from suspended solids in wastewater, followed by liquid chromatography (LC) coupled to a hybrid triple quadrupole linear ion trap mass spectrometer (QqLIT-MS) for trace quantification. The recoveries obtained were generally higher than 60% for both surface water and wastewaters. The overall variability of the method was below 15%, for the three fullerenes and all tested matrices: ultra-pure water, surface water and wastewater. For the effluents of wastewater treatment plants the method quantification limits (MQL) ranged from 0.2 to 1 ng l⁻¹. The precision of the method, calculated as the relative standard deviation (RSD), ranged from 1% to 2% and from 5% to 9% for intra and inter-day analysis, respectively. The analytical method developed was applied to the analysis of fullerenes in the effluents of 22 wastewater treatment plants in Catalonia (NE of Spain). 50% of the analyzed samples contained fullerenes, nine of them in the lg l⁻¹ concentration range. This work constitutes the first report on the occurrence of fullerenes in suspended solids of wastewater effluents, highlighting the need for nanotechnologies residues assessment for evaluating the risks from nanoparticles in the environment.

**Specific information on nanomaterial release to the environment:**
None.
Section D: Studies that discuss (or review other studies) potential manufactured nanomaterial release to and/or concentrations in the environment


**Focus:**
Exposure to and toxicity of cerium oxide nanoparticles, as well as of combustion-derived nanoparticles (CDNP) emitted from engines using Envirox were studied.

**Content:**
Envirox is a scientifically and commercially-proven diesel fuel combustion catalyst based on nanoparticulate cerium oxide and has been demonstrated to reduce fuel consumption, greenhouse gas emissions (CO$_2$), and particulate emissions when added to diesel at levels of 5 mg l$^{-1}$. Studies have confirmed the adverse effects of particulates on respiratory and cardiac health and, while the use of Envirox contributes to a reduction in the particulate content in the air, it is necessary to demonstrate that the addition of Envirox does not alter the intrinsic toxicity of particles emitted in the exhaust. The purpose of this study was to evaluate the safety in use of Envirox by addressing the classical risk paradigm. Hazard assessment has been addressed by examining a range of in-vitro cell and cell-free endpoints to assess the toxicity of cerium oxide nanoparticles as well as particulates emitted from engines using Envirox. Exposure assessment has taken data from modelling studies and from airborne monitoring sites in London and Newcastle adjacent to routes where vehicles using Envirox pass. Data have demonstrated that, for the exposure levels measured, the estimated internal dose for a reference human in a chronic exposure situation is much lower than the no-observed-effect level (NOEL) in the in-vitro toxicity studies. Exposure to nano-size cerium oxide as a result of the addition of Envirox to diesel fuel at the current levels of exposure in ambient air is therefore unlikely to lead to pulmonary oxidative stress and inflammation, which are the precursors for respiratory and cardiac health problems.

**Specific information on nanomaterial release to the environment:**
None. Suspended particulate matter (PM) air concentrations were assessed by atmospheric monitoring and also based on modelling studies.

Focus:
Editorial to special issue on the behaviour and effects of nanoparticles in the environment. The papers in this special issue evolved to a large degree from selected presentations given at the nanoECO conference, held from March 2 to 8, 2008, in Ascona, Switzerland. They are complemented with a few papers on the same topic that have been submitted to the journal in recent months.

Content:
The 18 papers in this special issue constitute a representative cross-section of the research on nanoparticles and the environment, aiming at advance our understanding of nanoparticles' behaviour and effects.

Specific information on nanomaterial release to the environment: None.

Focus:
In this paper, types of nanoparticles (NP), their distribution and prevalence (environmental processes) in the environment are discussed. The effects of NP on organisms, and their ecotoxicity are also highlighted.

Content:
The increasing use of manufactured nanoparticles (NP) in industrial and household applications will very likely lead to the release of such materials into the environment. Assessing the risks of these NP in the environment requires an understanding of their mobility, reactivity, ecotoxicity and persistency. This review presents an overview of the classes of NP relevant to the environment and summarizes their formation, emission, occurrence and fate in the environment. The manufactured NP are compared to natural products such as soot and organic colloids. To date, only a few quantitative analytical techniques for measuring NP in natural systems are available, which results in a serious lack of information about their occurrence in the environment. Results from ecotoxicological studies show that certain NPs have effects on organisms under environmental conditions, though mostly at elevated concentrations. The next step towards an assessment of the risks of NP in the environment should therefore be to estimate exposures to the different NP. It is also important to note that most NP in technical applications are functionalized and therefore studies using pristine NP may not be relevant for assessing the behaviour of the NP actually used.

Specific information on nanomaterial release to the environment:
None.

Focus:
This report (opinion) deals with developments and needs in the human and environmental risk assessment of nanomaterials; presenting the views of independent scientists who are members of the committees. A large range of potential hazards, from the possibility of nanoparticles to induce protein fibrillation, to different (size) effects in the form of biodistribution have been discussed. The lack of knowledge on methodologies for both exposure quantification and hazard identification has been emphasized.

Content:
This Opinion deals with recent developments in the risk assessment of nanomaterials for both man and the environment. The in-depth characterisation of a manufactured nanomaterial on the basis of its physical-chemical characteristics is essential. Due to the size and material-specific temporal evolution of some nanomaterials, potentially hazardous nanomaterials need to be characterised both ‘as manufactured’ and in the various possible forms ‘as delivered’: in biological systems; or to a human in a specific application; or to a particular ecosystem of concern. The characterisation ‘as manufactured’ provides information for the material safety data sheet of the product itself. The characterisation ‘as used’ in biological systems is needed, as the properties of nanomaterials may change considerably, notably the size distribution, due to agglomeration/aggregation of the particles. An issue of specific importance is the properties of the nanomaterial as it is actually used in products and to which consumers may be exposed. For the risk assessment the latter characterisation is of highest relevance.

Some specific hazards, discussed in the context of risk for human health, have been identified. These include the possibility of some nanoparticles to induce protein fibrillation, the possible pathological effects caused by specific types of carbon nanotubes, the induction of genotoxicity, and size effects in terms of biodistribution. Knowledge is gradually becoming available on the behaviour of manufactured nanoparticles in the environment in terms of the development of possible fate scenarios.

For some nanomaterials, toxic effects on environmental organisms have been demonstrated, as well as the potential to transfer across environmental species, indicating a potential for bioaccumulation in species at the end of that part of the food chain. Although, for some manufactured nanomaterials, adverse effects were observed: they should not be extrapolated to other manufactured nanomaterials. These observations indicate potential hazards which should be taken into consideration in the safety evaluation of manufactured nanomaterials. As there is not yet a generally applicable paradigm for nanomaterial hazard identification, a case by case approach for the risk assessment of nanomaterials is warranted.

One of the main limitations in the risk assessment of nanomaterials is the general lack of high quality exposure data both for humans and the environment. A differentiation between background and incidental exposure is generally difficult in real life situations, as the methods employed mainly measure the presence of (nano)particles and do not generally discriminate between the different types of
particles (manufactured or naturally occurring) that may be present. Currently, the risk assessment procedure for the evaluation of potential risks of nanomaterials is still under development. It can be expected that this will remain so until there is sufficient scientific information available to characterise the possible harmful effects on humans and the environment. Therefore knowledge on the methodology for both exposure estimations and hazard identification needs to be further developed, validated and standardised.

Specific information on nanomaterial release to the environment:
None. Some reflections are e.g. available on the applicability of the octanol-water partition coefficient for buckminsterfullerenes (C$_{60}$) (log Kow) based on Jafvert et al. 2008$^2$. However, the Kow is not applicable for non-soluble materials.

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$^2$ Jafvert C, Kulkarni P. Buckminsterfullerenes (C$_{60}$) octanol-water partition coefficient (Kow) and aqueous solubility. Environ Sci Technol 2008; 42:5945-50.