Final Report

Environmental Exposure to Nanomaterials - Data Scoping Study

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Within the context of the study reported in this document, a workshop on “Environmental Exposure to Nanomaterials” was held in Brussels. The workshop was attended by key experts in the field, including Dr Karen Tiede, Dr Fadri Gottschalk and Dr Rickard Arvidsson, who provided details of their ongoing research on environmental exposure to nanomaterials and its relevance to regulation. The authors are very grateful to these experts for their valuable contribution to the study.

The views expressed herein are those of the consultants alone and do not necessarily represent the official views of the European Commission.

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Executive Summary

The scale of application of engineered nanomaterials (ENM) is very broad, with ENM used in a wide range of industrial sectors, including healthcare, agriculture, transport, energy, materials and information and communication technologies. Projections for both the volumes manufactured and the range of applications of ENM show significant expansion. The concentrations of substances manufactured by man in the environment have been found to increase in direct proportion to their use in society and we can therefore expect increasing environmental exposure to ENM in surface waters, air, groundwater and soils. Any attempt to assess the risk to human health or organisms in the ecosystem from nanomaterials (NM), including both ENM and unintentionally produced nanomaterials, requires two elements, an understanding of hazard and a quantification of exposure. Intentionally produced ENM are novel materials and are subject to data scarcity, introducing high uncertainty in to the characterisation of risk.

This study reviews the status quo in conducting exposure assessment for NM. In doing so, we review the available environmental exposure data for NM that has been generated through scientific research and published predominantly in peer-reviewed scientific journals. We discuss the practical methods that allow for the quantification of NM exposure, considering what the data requirements of each method are and how uncertainties are managed. Methods to estimate NM exposure are at the early stages of development, and we identify key areas of uncertainty and areas for future research.

We then make the link between the ongoing scientific research and the requirements of regulators seeking to manage environmental exposure to NM, by asking what demands risk assessment tools under the EU environmental acquis set for exposure data and setting available data against these demands. We go on to consider which of the methods for generating NM exposure data might serve under specific legislative acts and for particular media.

Specific Properties of Nanomaterials and Implications for Generating Exposure Data

Classification and Occurrence of Nanomaterials

There are a number of characteristics specific to NM that have implications for generating environmental exposure data. Three types of materials at the nanoscale of between approximately 1 nm and 100 nm can be identified, including: naturally occurring particles; incidental nanoparticles; and engineered ENM. In characterising NM, a particularly challenging issue relates to the fact that
multiple nanoforms of the same ENM are manufactured, even of the same basic chemistry, and that
different forms exhibit distinct properties. This variation throws up challenges in regulating
different nanoforms of the same material, particularly when a single product may contain several
different nanoforms.

**Fate and Behaviour**

The behaviour of NM in the environment is dependant both of the physicochemical properties of the
NM (and nanoforms thereof), and those of the environment into which they are released. NM possess
properties that affect fate and behaviour in different ways to dissolved chemicals and this limits the
applicability of existing exposure models. In particular, the high surface area to volume ration results
in highly reactive and physic-chemically dynamic materials in the environmental media. Important
aspects of how nanomaterials behave in the environment that will affect exposure include their
mobility, stability and transformation. In understanding environmental exposure, it is often more
important to understand the specific properties of NM released from diffuse and point sources that
have undergone transformation reactions, than it is to understand the specific properties of pristine
ENM.

Regarding the fate and behaviour of NM in water, researchers are agreed that ENM dispersed in water
will behave according to the mechanism of colloid science. NM may undergo a number of processes
in water, including partitioning to sediment and suspended particulate matter and transformation
through abiotic and/or biological degradation, with eventual concentrations depending on the stability
and the degradation rates of NM and their intermediates. The stability of NM in the aquatic
environment depends on their chemical structure, other particle properties (e.g. size and surface
coating), as well as environmental conditions. The surface properties of NM, including
hydrophobicity, are identified as critical in determining their transformation and aggregation
behaviour, and thus for their mobility in aquatic environment and their ultimate interaction with and
general bioavailability to organisms. Surface modifications, both intentional functionalization and
modifications resulting from natural processes, will complicate interactions and ultimate fate and
behaviour. In particular, polymeric surface coating are identified as stabilizers in autoaggregation. The
collector surface composition has also been found to affects the deposition of silver nanoparticles.
Researchers consistently report interactions between NM and natural organic matter in aqueous
compartments. The importance of colloidal mechanisms implies that NM are unlikely to display
equilibrium partitioning behaviour as reflected under current modelling approaches for soluble
chemicals. Authors therefore recommend that kinetic approaches that incorporate colloid chemistry
(DLVO theory) should be employed in environmental exposure models for NM.
While evidence suggests that NM are most likely to end up in association with sediments and soils, very little is known about how nanomaterials behave in soils and sediments. Environmental factors such as pH and ionic strength, together with the physicochemical properties of the NM and interactions with dissolved particles will determine whether they are bound within or transported out of soils. The lack of data is so pronounced, particularly for metal oxides and carbon nanotubes, that no general conclusions can be drawn.

Aerosol science is a developed and well documented scientific field that provides preliminary information regarding the fate and behaviour of engineered NM, as well as ultrafine particles (UFP) in air that include unintentionally-produced nanoparticles. However, some major issues still require validation, including methods for accurate sampling or tracking of nanomaterials within the air compartment, elucidation of the effect of differing particle morphologies, and overcoming the issue of differentiating airborne NM from background nanoparticle levels in the atmosphere. There is a need for systematic studies on different types of airborne nanomaterials using a range of physicochemical parameters to generate data and to support development of reliable models.

Implications of Nanomaterial Properties for Environmental Exposure Data

Given the particular properties of NM, researchers suggest that the current environmental fate and transport models used for chemicals are probably not generally applicable to NM. It has been suggested that given that inter-medium transport for NM is governed by diffusive processes in the absence of significant gravitational and inertial impaction processes, realistic models will likely require an emphasis on kinetic approaches. NM differ from most conventional dissolved chemicals, in that the spatial distribution of mass concentration might not be the most relevant parameter with which to describe the state of the environment, throwing into question the relevance of traditional mass-based metrics. The literature suggests a number of data characteristics relevant to environmental exposure data for NM, including:

- Mass concentrations in the range of µg L⁻¹–pg L⁻¹ and changes in concentrations over time;
- Particle size and shape and range of particle distribution: i.e. identifying and measuring the size fractions of different nanoforms;
- Available surface area;
- Distinguishing between NM and naturally occurring nanomaterials; and
- Data on the degree of aggregation and dissolution: i.e. ongoing fate and behaviour.

The characteristics of the resulting datasets on environmental exposure would therefore differ to those generated for bulk chemical substances and result in multi-metric reporting, influencing the methods
through which data can be fed into risk assessments and potentially demanding a revision of risk assessment tools.

**Comparison with other Chemicals**

Although neither data scarcity nor uncertainty are specific to NM, but rather common to chemical risk assessment, they are particularly acute due to the complexity of behaviour of NM in natural systems and the existence of multiple nanoforms. Tools such as read across or reliance on Qualitative or Quantitative structure-activity relationship ((Q)SAR) at present state of development are unlikely to be useful. In addition, the environmental matrix may influence NM structure, form and behaviour in site specific ways, making the calculation of predicted environmental concentrations (PEC) extremely challenging. As a consequence, uncertainties in PEC and predicted no-effect concentrations (PNEC) will be propagated during characterisation of environmental risk, amplifying overall uncertainties.

**Emission Pathways for Nanomaterials**

**Emission Pathways**

Completing a full exposure assessment requires extensive knowledge about the potential exposure scenarios for a specific substance. Given the rapid increases in production volumes of nanomaterials and their incorporation into multiple applications, it can be reasonably assumed that releases of nanomaterials into the environment have increased accordingly from multiple pathways. These include point source emissions, such as those from industrial installations or from urban waste water treatment plants, and diffuse source emissions, i.e. emissions from products along their life cycle. Point sources of emissions of NM are likely to include industrial emissions to air, water and soil, effluents released into surface waters from urban waste water treatment plants, emissions to air from construction sites, landfill leachates into soil and groundwater and direct releases of NM into soils and groundwater for remediation purposes. Available data on these pathways is presented and remains very limited. Possible examples of diffuse sources include NM leaching into groundwater and then into surface waters from landfills, run-off from agricultural land of pesticides that contain ENM and from sewage sludge, and spilt lubricants that are washed off roads into storm water discharges. Atmospheric deposition of NM is also likely to be relevant. A reliable estimate of diffuse source emissions from products would require data on: volumes of ENM on the market; volume fractions incorporation into products; market penetration and use patterns; and emissions of ENM from products along the life cycle.
Production Volumes and Nanomaterials in Products

Despite the availability of estimates of market value, very little concrete data on production volumes for ENM is available in the public domain, and that which is available is not broken down by nanoform. A report published by Global Industry Analysts in 2010 forecasts that the global market for nanomaterials will reach €4.26 billion by 2015. A number of nano product registers list products that voluntarily declare a nano content and provide estimates of current market size and market forecasts, including the Woodrow Wilson inventory and the 2010 BEUC inventory. In addition, Member State reports provide a snapshot of products on the market in their territories. A 2010 RIVM report identified 858 consumer products that claimed to contain NM as having been present on the EU market, with 805 on the market in 2010. The report built on equivalent data for 2007 and found a six-fold increase in the number of products with a nano-claim on the EU market over the interim three years. In terms of market estimates for nano-products, Lux Research estimate that nanotechnology was incorporated into $254 billion worth of products globally in 2009 and forecasted that this will increase to $2.5 trillion worth of products globally by 2015.

Nano Product Registers

A number of EU Member States, namely France, Denmark and Belgium, have taken recent action to establish product inventories that should led to the generation of valuable data on the volumes of ENM on the EU market and their application in consumer products. The French nano registry is to become mandatory as of 1 January 2013, with 1 May as the first annual reporting deadline. Those who manufacture, import or distribute substances in the nanoparticle state above 100g per year must submit a declaration, to include all available information related to the hazard of these substances and the exposure pathways, as well as information related to the identity, quantity and uses of these substances, and the identity of the downstream users. A penalty is foreseen for failure to declare. The proposed Belgian nano-products register requires those producing, placing on the market, and importing nanomaterials that comply with the EU definition of nanomaterials to submit an annual declaration by email. The declaration is to include information on the physicochemical properties, as well as uses, volumes and downstream users. In Denmark, plans include an order requiring producers and importers to report products containing or releasing nanomaterials.

Regarding action at EU level, the recent Commission Communication of 3 October 2012 on the “Second Regulatory Review on Nanomaterials” indicates that the Commission will create a web platform with references to all relevant information sources on NM. In addition, in 2013 work will start on a proposal for an EU Nano Registry.
Environmental Exposure Data for Nanomaterials

While there is scientific agreement that NM production, use and disposal leads to releases of NM to the environment, the total environmental load from current uses of nanomaterials is unclear. There is currently very limited information available to build well-informed and evidence based exposure scenarios covering the life cycle of NMs for known uses. In the body of the report, we systematically provide a short review of each of the studies identified as generating relevant environmental exposure data for NM, divided into the following categories on the basis of the method used to generate data: analytical in situ methods; laboratory measurements and extrapolations; material mass flow analysis and simple models; probabilistic mass flow analysis; and kinetic modelling.

A number of analytical measuring techniques are currently available to provide data on the concentrations of NM in the environment. Techniques for measuring ultrafine particles (UFP) and nano-scale particles (aerosols) in air are most developed, although they have not yet been applied in a regulatory context. Researchers have started investigating NM in water samples more recently and, as a consequence, the application of these techniques remains at the laboratory scale. Still fewer studies have looked at NM in sludge and soils. Experimental studies have simulated various exposure scenarios in the laboratory in order to then apply analytical methods to measuring releases. Modelling methods have been used to make various estimates both for individual products, nanomaterials and applications as well as product types. Many of these have been able to apply fairly simple mathematical equations to estimate the current and future exposure. Probabilistic mass flow analysis treats all parameters in the model as distributions. Monte Carlo and Markov Chain Monte Carlo computer simulations are used to generate estimates of sediment and groundwater concentration as well as emissions from production, manufacturing and recycling processes. Kinetic models specifically try to reflect the dynamic behaviour and fate of ENM in environmental media.

Set of Methodologies for Assessing Nanomaterial Exposure

Available methods for assessing NM releases into the environment are reviewed.

Analytical in Situ Measurements

In terms of techniques for undertaking analytical measurements, there is a range of measuring techniques that can be applied under laboratory conditions to air and water samples and can provide resolution down to the sub-nanometre range, including microscopic methods, chromatography,
filtration and centrifugation and spectroscopic techniques. However, techniques are not yet cost-effective and cannot be applied to widespread routine monitoring.

Regarding the detection and analysis of NM in aquatic systems, key challenges include: achieving comparability and reproducibility; distinguishing NM from natural and incidental nanoparticles; problems with the insensitivity of current detection methods; sample preparation; and difficulties in isolating the nanomaterials fraction in water. While there is a range of available methods, each has advantages and disadvantages and researchers suggest that combination of techniques is therefore needed. Light scattering methods (e.g. dynamic light scattering (DLS), turbidimetry and laser diffraction) have been found to be useful and can be used to determine size related properties and also concentrations. Microscopic methods for the analysis of NM, including atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), enable the investigation of properties at the level of individual particles as well as aggregates. Hydrodynamic chromatography allows for sizing and, combined with inductively coupled plasma mass spectrometry (ICP-MS), can be used to detect multiple elements and isotopes. Other available methods include fractionation techniques and, finally, spectroscopic techniques that can be used to probe chemical entities on whole samples and on the nanoparticle ensembles in fractionated samples. Only very few university laboratories currently possess the relevant equipment for the analyses described above.

A research team at Arizona State University is working to develop methods to quantify nanomaterials in matrices including drinking water, commercial products, blood and other biological matrices. Thus far, the team has generated a number of publications and reported successes with specific methods for detecting “classes” of NM in solutions, namely: metal/metallic nanoparticles, C60 and C70, and carbon nanotubes. This supports suggestions by other researchers that testing methods will not be generic to all NM, but rather for “classes” of NM.

Regarding the detection of airborne ENM, incidental nanoparticles and UFP in air, available techniques include the analysis of electrical mobility of aerosol particles, and the determination of the number concentration and size distribution using mobility particle sizers. Key challenges include: interference from naturally occurring airborne nanoparticles; the need for sensitive and specific techniques to measure the required metrics; and the need to measure several properties in parallel.

Methods for measuring NM in soils and sediments include analytical scanning transmission electron microscopy (STEM), TEM combined with energy-dispersive X-ray spectrometry, and scanning electron microscopy/electron dispersive X-ray microanalysis (SEM/EDX).
Some of the major challenges presented by undertaking analytical measurements of ENM in environmental media include the high diversity of different ENM and nanoforms therefore, and the impact on fate and behaviour. There is a need for techniques that allow for simultaneous sizing and analysis of NM in situ. In measuring NM using currently available techniques, a number of methodological questions have been found to significantly affect study results, including the choice of sample materials; pre-concentration/fractionation methods, and analytical methods to characterize and quantify collected particles. Several research teams are taking steps towards the development of test methods and protocols for certain classes of NM.

**Laboratory Measurements and Extrapolations**

A limited number of experimental or simulation studies have used analytical measurement methods to estimate an overall NM environmental exposure from specific applications under conditions are that created and measured within the artificial setting of the laboratory. Resulting data provide a valuable insight into releases of NM from products containing NM during the product life cycle, an area that is considered important in terms of overall emissions but where there is a severe lack of data. At the same time, data from simulation studies provide only a snapshot of environmental exposure under a specific set of conditions.

**Material Mass Flow Analysis and Simple Modelling**

Material mass flow analysis and simple modelling methods use calculations based on a quantitative substance flow analysis of how nanoparticles are released from point and diffuse sources to estimate PEC. High levels of uncertainty concerning results stem from the lack of empirical quantitative data relating to releases along the product life cycle, ENM production volumes; volumes incorporated into specific product categories and types. In addition, material mass flow analysis assumes a steady-state approach for NM release and transmission-flow calculations and does not consider particle behaviour. One of the main limitations of PEC calculations at regional scale is the assumption of homogeneous material distribution within aggregated environmental compartments. One study has addressed this deficiency by incorporating spatial and temporal variability into the model. Such models can provide representative data that can serve to inform decision making as to whether action is required.

**Probabalistic Mass Flow Analaysis**

In the light of data scarcity, probabilistic mass flow analysis treats all parameters in a mass flow analysis or model as probability distributions. Using Monte Carlo and Markov Chain Monte Carlo computer simulations as well as a sensitivity and uncertainty analysis, nanomaterial concentrations
have been derived for surface water, sewage treatment plant effluent and sewage treatment plant sludge for the region of Switzerland. Besides uncertainties relating to the lack of data, one of the main limitations of PEC calculations at regional scale probabilistic mass flow analysis is the assumption of homogeneous material distribution within aggregated environmental compartments. Probabilistic mass flow analysis furthermore fails to acknowledge the particulate nature of the material. Nevertheless, once more data become available to populate the probabilistic sub-models, probabilistic mass flow analysis may prove very valuable.

**Kinetic Modelling**

Kinetic models try to include the fact that nanomaterials in environmental media undergo dynamic, non-equilibrium processes. Available models have sought to accommodate the influence of sedimentation, agglomeration and dissolution in modelling exposure. The challenge of kinetic modelling is assigning values to the various rate constants, which need to be measured for each individual NM.

**Exploratory Chemometric Approaches**

The possibility of developing so-called exploratory chemometric approaches has so far only been sketched as an idea. It involves the application of multivariate mathematical models (cluster analysis, principle component analysis and positive matrix factorization) to data sets containing chemical/physical parameters in order to estimate the number and composition of pollutant sources and identify trends and correlations.

**Overall Assessment of Available Methods**

Each of the different methodologies for generating data and the resulting data sets have particular strengths and limitations. In addition, overall data is limited, although certain ENM have received more attention than others, in particular nano-Ag, nano-TiO₂, nano-CeO and C60. The assessment suggests that data generated using different methods can be combined to provide a more comprehensive picture of overall exposure.

With regards to NM in aqueous samples, researchers have begun to identify methods, or combinations of methods for both quantification and qualitative analysis, that best suit particular “classes” of ENM (i.e. metal-based, fullerenes, CNT) and are developing suitable test protocols that can be applied across laboratories. The quantitative data generated using these methods are in the form of mass
concentrations (µg/L), with mass concentrations for specific size fractions reported. Data suffers for limitation in comparability, reliability and interference from naturally occurring nanoparticles.

Regarding measurements of nanoparticles and UFP in air, although combinations of analytical techniques are available for qualitative and quantitative analysis, techniques allowing for the rapid assessment of a range of parameters of air-borne nanoparticles as would be required for the regulatory context are not yet available. Studies suffer from a lack of coherence in terms of sampling strategies, metrics and other parameters, as well as details on the ENM and nanoforms, inhibiting effective comparison of results.

Nevertheless, it can be expected that the application of analytical techniques to a range of ENM and emission scenarios will begin to generate more comprehensive and comparable datasets. It would seem useful to continue to draw on predictions from both models and simulation studies when selecting emissions scenarios and specific ENM for analysis, given the limited availability of analytical techniques.

Experimental/simulation studies generate data bodies that reflect artificial laboratory conditions and may not be representative of releases under actual conditions. Despite these limitations, data from simulation studies can be extremely useful in validating exposure pathways for specific ENM predicted using models of exposure, and for providing indicative data of how ENM might behave in processes such as waste water treatment or incineration. These initial data can then be tested against data from in situ studies to corroborate results.

Modelling methods have effectively begun to address the gaps in empirical data regarding environmental exposure to nanomaterials. Researchers have been able to estimate PEC of certain NM for water, sediment and air, for scales ranging from river stretches to individual countries and regions, including the EU, and as such data are useful in providing a preliminary indication to regulators of which ENM might be a source of risk in the environment. Assumption regarding ENM production volume, fraction going to specific products and types and emissions assumptions introduce considerable uncertainty into resulting data. Researchers have addressed these by generating a range of scenarios, including optimistic and conservative (worst case) scenarios. It would be productive to reduce uncertainties concerning emissions by generating data through simulation studies and analytical measurements of relevant waste flows, and by establishing product registries to generate data on production volumes and uses.

A key challenge relates to understanding the influence of fate and behaviour processes on NM, in particular ENM. Researchers argue that the properties of nanomaterials released from point and
diffuse sources, and hence subject to transformation reactions during use and processing, are more relevant for risk assessment that those of pristine ENM. The incorporation of colloidal mechanisms into the later kinetic models begins to reflect growing knowledge regarding the fate and behaviour of ENM in water, and as such these models hold significant promise. Model-based approaches should be tested against empirical data as they becomes available, in order to test their accuracy in predicting both emissions of ENM and the fate and behaviour of ENM in particular environmental media over time.

Assessment of Available Environmental Exposure Data for Nanomaterials Against the Demand for Data under EU Legislation

The assessment of the usefulness and comprehensiveness of the available NM exposure data starts with the identification of the of EU environmental legislation that uses exposure data. However, it should be noted from the outset that none of these legislative acts currently demand exposure data specifically on NM. As such, this discussion of the possible value of exposure data for NM to EU environmental legislation is largely speculative. Possible exceptions include the Water Framework Directive and the Air Quality Directive.

Water Framework Directive 2000/60/EC

Under, the Water Framework Directive 2000/60/EC, exposure data plays a key role in the identification of priority substances. Although there are no nanomaterials specifically included as priority substances at this stage, it is relevant to consider whether the implementation tools used to select substances as priority substances and to then monitor environmental concentrations could be applied to NM. The overall approach to identifying priority substances was recently revised in generating the proposal for a Directive amending the WFD and the EQSD as regards priority substances in the field of water policy (COM(2011)876). The approach used a combination of different approaches to generate separate but complementary lists of substances, the highest priority substances on each list were then amalgamated and subject to a short listing procedure involving expert review. Short listed substances were subject to a detailed expert review in order to identify those substances that were then included in the final proposal.

The main method considered to have the potential to lead to the identification of nanomaterials in the water compartment under the current legislative framework is the use of a simplified risk-based assessment procedure. Regarding the exposure assessment, the simplified risk-based assessment procedure can accommodate exposure data generated either through monitoring or through modelling using two distinct approaches to assessing exposure data. The use of monitoring data overlooks
substances that may pose a risk to or via the aquatic environment but that are not monitored, including NM. The modelling approach is expected to fill in the gap for non-monitored substances, and as such would apply to NM. However, application of the modelling approach to NM would be challenging due to the demand for reliable production volume data and data product use fractions in estimating exposure. In addition, the existing correlations and property predictors in the models are designed for organic chemicals and resulting predictions may not be valid for metals and organometallic compounds. This calls into question the applicability of the model to NM, the fate and behaviour of which is influenced by different physical forces to classical bulk chemicals due to their specific properties. In addition, researchers suggest that it will be nanoforms of metal NM that pose the greatest risk to the aquatic environment. However, were specific aspects of fate and behaviour to be clearly understood, it is possible that with substantial efforts the model could be re-calibrated to serve specific nanoforms.

The Water Framework Directive also set monitoring requirements, and regarding chemical status, Member States must carry out surveillance monitoring and operational monitoring programmes and where relevant, investigative monitoring. In terms of the quality elements to monitor, Member States must monitor all priority substances and other pollutants discharged in significant quantities. The potential future application of these requirements to NM raises a number of challenges related to: the availability of analytical measurement techniques; an understanding of what environmental exposure for NM might be considered “significant”; relevant metrics; and interference from naturally occurring nanoparticles.

Were NM to be monitored by Member States in the future, decisions would need to be taken regarding the parameters to be measured. Parameters proposed by Vonk et al (2009) as being relevant for the aquatic environment include: concentration (g/l), reactive surface area (m²/l) and number of particles (#/l), with data accompanied by information on methods and the test protocols. In the interest of generating comparable sets of monitoring data for NM across the EU, parameters to measure should be decided at EU level and consistently applied.

At this point in time (November, 2012) Member States are not currently engaged in monitoring NM within the context of monitoring programme under the WFD. As such, no monitoring data is available to feed into an exposure assessment for NM in surface waters. While a number of techniques have been applied to water samples, including drinking water and effluent from WWTP, no measurements have been made of NM in surface waters that are reported in the scientific literature. Initial data on PEC for NM in surface waters is available from a number of published studies using modelling, with only one study providing EU wide data. Key limitations in these studies stem from their use of highly
uncertain available production volume data for the main NM and volume allocations to specific products.

Regarding its use under the Water Framework Directive, mass concentrations based PEC could theoretically be fed into a revised risk ranking system under the modelling-based exposure assessment step of the simplified risk-based assessment procedure used to identify priority substances. Models using material mass flow analysis are similar to the multimedia model and tiered approach already used in that they draw on production volume data and use allocation data. However, the use of available data is seriously hampered by the scale. Only one study provides EU-wide data, with the remaining data relevant to individual countries or limited stretches of rivers. Further studies could usefully expand the geographical scope to EU wide and include a wider range of NM.

**The Groundwater Directive 2006/118/EC**

The Groundwater Directive uses exposure data in three possible scenarios: assessing chemical status; identifying upward trends in specific pollutants; and establishing starting points for trend reversal. Chemical status is assessed against groundwater quality standards and threshold values set by Member States. Should specific nanomaterials be identified as significant pollutants of groundwater in a Member State in the future, then threshold values would need to be established for those NM. Key challenges with threshold values include questions regarding dose-response and toxicity, metrics and interference from naturally occurring nanoparticles when measuring concentrations. In addition, background levels from nanoparticles in groundwater are as yet unknown. Regarding trends, since there are currently no Member States testing for NM in groundwater, there is no body of historical data against which to assess trends and establish starting points.

In terms of available exposure data for NM in groundwater, no raw data on the concentrations of NM in groundwater could be found. While the analytical methods that have been used to measure NM mass concentrations in water under other studies may be relevant, particular challenges may arise due to the effects of sampling techniques and the very low concentrations of NM in groundwater.

Regarding data from modelling, while the probabilistic mass flow analysis model includes groundwater in its “geometry” (meaning in the multi-box map of materials flows) and showed groundwater receiving emissions of NM, the researchers have not yet gone so far as to calculate PECs for groundwater. One study looked at the potential environmental risks associated with using nZVI in groundwater remediation. While they do not go so far as to estimate PECs in sites following nZVI application, they consider factors likely to influence PECs and highlight nZVI migration behaviour, transformation, degradation and the potential for bioaccumulation.
**Drinking Water Directive 98/83/EC**

Directive 98/83/EC on the quality of water intended for human consumption sets out parametric values for chemicals in drinking water and uses exposure data generated through monitoring to ensure compliance. Monitoring requirements do not specifically mention NM, although some NM could be captured under certain parameters (cadmium, nickel, copper, iron). Also, additional monitoring should be carried out for substances for which no parametric value has been set if there is reason to suspect that they are present in volumes that constitute a potential danger to human health. This affords a theoretical possibility for Member States to include NM.

Were monitoring of NM in Drinking Water to be considered, requirements would need to be revised in order to account for the state of development of analytical methods to measure NM in drinking water. Secondly, given uncertainties regarding dose-response, the use of mass-based thresholds against which to measure quality may not be appropriate or feasible, and as such other parameters (e.g. size-specific particle numbers and surface area metrics) with which to measure the presence of NM in drinking water may be required.

In terms of available exposure data, one study has generated data on NM (C60) in drinking water using analytical measurements. Drinking water presents particular challenges since mass concentrations are expected to be very low, often below current detection limits for analytical techniques. Regarding data from modelling, one study predicted mass concentrations and particle number concentrations for a range of NM in raw water and treated drinking water in the UK. Uncertainties arise for the use of estimates of production volumes and use patterns in the modelling approach.

**Urban Waste Water Directive**

Directive 91/271/EEC concerning urban waste water generates exposure data through monitoring of discharges, sludges disposed of to surface water, and waters receiving discharges in cases where the receiving environment is expected to be significantly affected. Monitoring covers biochemical oxygen demand without nitrification, chemical oxygen demand, total suspended solids, total phosphorus and total nitrogen. As such, the Directive does not require the monitoring of the concentration levels of any NM in treated urban waste water. This review of available exposure data against the exposure data demands of the Urban Waste Water Directive is therefore speculative.

Emissions of NM from treated waste water have been identified as a key exposure pathway and several studies have therefore sought to either measure or estimate concentrations of NM in effluents
from waste water treatment plants (WWPTs). Five studies have used analytical methods to generate mass concentrations of specific NM in urban waste waters, with a focus on the removal efficiency of the WWTP for NM. Regarding data from modelling, studies have used material mass flow analysis to generate estimates of mass concentrations in the influent and effluent of WWTPs, notably highlighting the importance of flows from production, manufacturing and consumption to WWTPs and from WWTPs to water in effluents and to soil in sludges for specific NM. In particular, fullerenes were identified as being channelled to surface waters in the effluent of WWTPs.

Given the limited requirements of the Urban Waste Water Directive on concentrations of pollutants in effluents, it would seem that the value of the exposure data generated under these studies lies in demonstrating the importance of treated urban wastewaters as an exposure pathway for specific NM, suggesting a possible need for upstream controls. The data is particularly informative regarding the deposition of NM in sewage sludge.

**Sewage Sludge Directive 86/278/EEC**

The Sewage Sludge Directive demands exposure data is required to ensure compliance with limit values for sludge and receiving soils, and sets requirements regarding analysis and sampling. Chemical parameters for analyses include: cadmium, copper, nickel, lead, zinc, mercury, chromium, using atomic absorption spectrometry following strong acid digestion.

In terms of available exposure data, several studies using analytical measurements have estimated deposition rates into sludge in WWTPs, as well as characterising NM in sewage sludge and demonstrating transfers to soil. A number of studies have also modelled emissions of NM into soil through sludge. Collectively, these studies have effectively demonstrated the transfer of NM from wastewaters into sludges and from there into soils. These initial findings suggest that the spreading of sludges on soils may represent a significant environmental exposure route for specific NM and that further investigation is warranted.
Landfill Directive 1999/31/EC

Directive 1999/31/EC on the landfill of waste foresees the generation of exposure data through two specific channels. Firstly, waste testing may be required in order to characterise waste and determine whether it can be accepted in relevant landfill types. Secondly, the Directive requires the monitoring of surrounding downstream and upstream surface waters and groundwater, as well as emissions from landfills in the form of leachate and gas, with the aim of identifying emissions of specific parameters.

Waste testing involves assessment against waste acceptance criteria, which include both determining the composition of the waste and assessing the waste against leachate limits for chemical parameters set out for specific classes of landfill. Current leachate test methods are not designed to capture NM, and as such testing is not required.

The requirements for generating emission data on water, leachate and gas control through monitoring include sampling and measuring the volume and composition of leachate at each discharge point. Parameters to be measured in leachate vary according to the composition of the waste deposited and should industrial waste consisting of NM be sent to landfill, this composition could make monitoring of NM in leachate relevant.

Data on potential emissions of NM from landfill is limited. A number of studies modelling PEC have included leachate from landfills as an exposure pathway, with suggestions of prominent flows of CNT and fullerenes to landfill. One analytical study measured releases of nano-Ag through leaching in a simulated landfill scenario. Further research on the fate and behaviour of NM in landfills is required. This is particularly relevant for landfills that may be receiving industrial waste containing a high proportion of NM, such as can be found in the disposal of production residues from the manufacturing of fullerenes.


No specific demand for exposure data was identified under the Waste Framework Directive. With regards to the impact of NM in waste on application of the waste hierarchy, further understanding of the behaviour of NM within the various processes involved is required in order to deduce which options deliver the best environmental outcome. Key questions concern the effect of NM on the integrity of waste management processes and their release into the environment.

Data on NM in waste and data on emissions of NM from waste treatment processes are limited. In terms of available analytical data on emissions on NM from waste management processes, one study
provides data on emissions of CeO from a waste incinerator, while another estimated exposure to CNT during general waste treatment of CNT containing products. In terms of modelling studies, quantitative substance flow analysis has been used to model emissions of CNT from incinerators, while probabilistic material flow analysis model was used to estimate emissions from waste incinerators.

**Air Quality Directive 2008/50/EC**

Directive 2008/50/EC defines and establishes objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment. Of relevant to NM, it establishes risk management for specific pollutants, including particulate matter (PM$_{10}$ and PM$_{2.5}$). Both airborne NM and UFP may constitute part of the PM$_{10}$/PM$_{2.5}$ size fraction. The role of exposure data in implementing Directive 2008/50/EC is to monitor compliance with limit and target values for pollutants in ambient air, including the particulate matter PM$_{2.5}$ and PM$_{10}$.

For the purpose of air emissions, nanomaterials and ultrafine particles in air emissions are likely to have been generated incidentally in some kind of combustion process, as opposed to ENM. Significant sources of nanomaterials and UFP include: road and other transport; residential/commercial combustion; industrial combustion and industrial process emissions; power generation; and agriculture.

Regarding possible limit values for airborne NM or UFP, there is probably insufficient reliable information at present to define comparable specific limit values for the protection of human health. In addition, other metrics such as particle number and surface area are likely to be more appropriate in reflecting potential risk. Furthermore, factors such as chemical composition become increasingly important at the nano-scale, meaning that qualitative characteristics may need to be considered.

The Air Quality Directive sets reference methods for monitoring PM$_{10}$ and PM$_{2.5}$. These methods are unlikely to be sufficient for nanomaterials and ultrafine particles, which will be captured in the fractions but not specifically identified and measured.

It is also important to mention Directive 2004/107/EU which sets target values for arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air with the aim of avoiding preventing or reducing harmful effects on the environmental and human health. The target values for arsenic, cadmium, nickel and benzo(a)pyrene apply to the total content of these elements and compounds in the PM$_{10}$ fraction averaged over a calendar year.
As a result of the requirements in the Air Quality Directive, concentrations of particulate matter in ambient air within the PM\(_{10}\) and PM\(_{2.5}\) size ranges are measured across the EU and these data are available on the website of the European Environment Agency. Airborne nanoparticles and UFP will be captured under these size fractions and hence included in these data. However there are no specific EU wide data available with a specific focus on nanoparticles (i.e. PM\(_{0.1}\)) and UFP in air.

A fairly large number of research studies have employed analytical techniques to identify, quantify and qualitatively describe nanoparticles and UFP in ambient air, the majority focusing on traffic emissions in urban areas. These studies have demonstrated the importance of traffic emissions as a source of UFP in ambient air, with evidence from Europe, the USA and China. Studies have found daily variation in UFP total particle number concentrations linked to daily variation in traffic density, characterised UFP by particle size and quantified the contribution of each particle size to total particle concentrations. One study modelled mean EU-27 population exposure levels to UFP (as PM\(_{0.1}\)) in urban areas and estimated exposure to UFPs by source. While this data is modelled and subject to considerable uncertainties, it is the only available data that is EU-wide and has value in providing an overview.

Studies with a specific focus on NM are less common, although one study modelled NM in ambient air near to a fullerene production installation.

**Industrial Emissions Directive**

The IED sets a demand for analytical exposure data on emissions to air and water, in order to determine compliance with emission limit values (ELVs) set out for certain types of installations. Where ELVs are not included in the Directive, the exposure data is to be compared against the emission levels associated with Best Available Techniques (BAT) for each specific sector, as set out in the BAT Reference Documents (BREFs). In addition, the IED specifies that local environmental quality standards (EQS) shall not be transgressed, and in cases where air and water standards are above EQS, stricter emissions limit values are to be set in the permits of installations emitting relevant pollutants.
Currently, particles at nano-scale may be covered by ELV and BAT-AELs set for emissions to air of dust (or particulate matter) for a number of specific sectors. The ELVs and BAT-AELs are almost all based on units of mass concentration, with a limited number based on mass emissions per unit of production. ELVs for air emissions generally expressed in terms of mass concentration g/m\(^3\) - mg/Nm\(^3\). The mass metric may not be the most relevant for NM, rather metrics such as particle number and surface area concentration may be more important.

In terms of available analytical data to feed into an assessment of the overall emissions from an installation, there are limited data available, with the majority of data focused on emissions to air of particulates and UFP in flue gases from combustion processes.

On emissions to air, one study modelled the fullerene exposure levels within 500 m of a factory manufacturing fullerenes, although they did not actually measure concentrations in flue gases from the installation. A recent study suggests that emissions of NM (i.e. not resulting from combustion processes) from industrial sources are likely to represent a very small fraction (<1-2% per volume) of emissions from industrial sources, given that NM are manufactured in modern installations and are valuable materials. The paucity of data on emissions of nanoparticles and UFPs in the PM\(_{0.1}\) range is partly due to difficulties in measuring air quality in conditions found in most industrial installations, including high temperatures, semi volatile flue gas components and dynamic physicochemical processes. Another explanation is the lack of regulatory requirements.

Regarding emissions of NM to water from IED industrial installations, no analytical data is currently available. In terms of modelling data, the probabilistic material based mass flow analysis model has been used to estimates emissions of NM from production, manufacturing and consumption facilities to air water and soil, as one of the boxes in the multi-box geometry of the model, although raw data is not available.

No data are currently available on emissions of NM from industrial installations to soil or in industrial wastes.

**Overall Analysis of Available Data and Methods Against the Demand for Exposure Data in EU Environmental Legislation**

Table 0.1 below provides an overview of available exposure data broken down into analytical, simulation and modelling data, against potential legislative demand under EU environmental
legislation. A cross indicates the availability of data specific to that medium or emission pathway for at least one NM, generated under one study or more.

Table 0.1: Indication of the availability of exposure data for NM that could feed into risk assessment under EU environmental legislation

<table>
<thead>
<tr>
<th>Legislation</th>
<th>Analytical data</th>
<th>Simulation studies</th>
<th>Modelling data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Framework Directive</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Groundwater Directive</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Drinking Water Directive</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban Waste Water Directive</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewage Sludge Directive</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfill Directive</td>
<td></td>
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</tr>
<tr>
<td>Waste Framework Directive</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Air Quality Directive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial Emissions Directive</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Currently available data suffer from limitation due to uncertainties, limited geographical scale, and a focus on specific ENM. Most data are presented in the form of mass concentrations, with limited data in particle number concentrations. Nevertheless, available data does begin to point towards certain ENM and specific emission pathways as being worthy of further attention.

**Application of Existing Chemical Risk Assessment Tools to NM**

**REACH**

The EU regulatory framework for chemical risk assessment for manufacturers and importers of chemical substances is set under Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). Experts have identifies a number of limitations with the Technical Guidance on environmental exposure assessment. Attempts to apply the REACH Chemical Safety Assessment to NM have met with significant challenges due to data limitations.

**Biocides**

Regulation (EU) No 528/2012 on Biocidal Products is the first piece of legislation to incorporate the EU definition on NM. The Regulation requires that, where nanomaterials are used in a product, the risk to human health, animal health and the environment be assessed under a separate risk assessment
specific to the nanoform. This legislative change will therefore generate impetus for the development and validation of new test methods specific for NM.

**Food and Feed Chain**

Regarding nanomaterials in the food and feed chain, current EU guidance notes that the existing risk assessment paradigm is appropriate for these applications. However, uncertainties are flagged relating to the identification, characterisation and detection of NM related to the lack of suitably validated test methods. In 2011, the European Food Safety Authority (EFSA) published a scientific opinion entitled “Guidance on the risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain”, which provides practical guidance for the risk assessment of applications involving NM in the food and feed chain.

**Cosmetics**

In 2011, the European Commission Scientific Committee on Consumer Safety (SCCS) published “Guidance on the safety assessment of nanomaterials in cosmetics”. The document is intended to provide guidance on how to consider the specific properties, interactions with biological systems, and/or effects of ENM that are different from conventional or bulk ingredients when testing and reporting data for ENM.

**European Union System for the Evaluation of Substances (EUSES)**

EUSES is a decision-support instrument used to carry out rapid and efficient assessments of the general risks posed by chemical substances to man and the environment. EUSES is intended mainly for initial and refined risk assessments rather than for comprehensive assessments. Researchers assessing the application of EUSES to NM deemed it insufficient for nanoparticles given that a number of key mechanisms are unknown and not reflected in the model, including: the extent/rate of dissolution; the extent / rate of aggregation / settling; and the extent of association with sediment.

**Risk Forecasting for NM**

A group of researchers have stepped back from existing risk assessment model to speculate on possible approaches that could begin to cope with the current uncertainties resulting for data scarcity on NM and in particular ENM. They call for an evolving process to allow for the risks associated with emerging nanomaterials-related industries. In a subsequent publication, researchers have described the use of Bayesian networks in NM risk forecasting and develop a baseline probabilistic model using
expert elicitation techniques called Forecasting the Impacts of Nanomaterials in the Environment (FINE). The model incorporates nanoparticle specific characteristics (particle behaviour) and environmental parameters, along with elements of exposure potential, hazard, and risk related to NM. The Bayesian nature of FINE allows for updating as new data become available, a critical feature for forecasting NM risk, and allow for the incorporation of expert judgment when other knowledge bases are lacking. This may provide a practical option for conducting risk assessments for ENM in the absence of comprehensive data on exposure and hazards.

**Chemical risk assessment and the precautionary principle**

In the absence of concrete evidence regarding current concentrations of ENM in environmental compartments, trends in concentrations and any related negative environmental impacts in situ, traditional chemical risk assessment cannot be conducted. The precautionary principle provides the legal basis in EU legislation for decision-making in the absence of comprehensive data to feed into a traditional risk assessment, or where “potentially dangerous effects deriving from a phenomenon, product or process have been identified” and where “scientific evaluation does not allow the risk to be determined with sufficient certainty”. The procedures surrounding application of the precautionary principle set a framework for assessing available exposure data, as well as possible gap-filling techniques.

**Possible Future Approaches to Regulating Nanomaterials**

The review of exposure data throws up a number of key questions regarding possible future approaches to regulating nanomaterials. A key question concerns whether certain ENM should be prioritised for regulatory action on the basis of higher levels of environmental exposure. Based on the review of available exposure data, there is general agreement that the metal-based ENM and CNTs are a main focus of concern.

Secondly, it should be considered how to address the variation in nanoforms of an ENM. In terms of identifying particular nanoforms, it is not possible to distinguish particular nanoforms of concern using the currently available exposure dataset.

The literature suggests a number of data characteristics that will need to be investigated and recorded when monitoring and/or modelling the concentrations of NM in environmental media in order to provide a complete picture. Parameters include mass concentrations in the range of µg L⁻¹–pg L⁻¹ and
changes over time; particle size and shape; range of particle distribution; and available surface area. In addition, measurements must distinguish between NM and naturally occurring nanomaterials and describe ongoing fate and behaviour.

The relevance of mass-based thresholds to nanomaterials has been questioned in a context where risk characterisation is not considered to be dependent on mass concentration for NM. Were thresholds to be development for NM, multiple metrics would be required. The large variety of nanoforms (NM of different sizes and shapes) and the large and highly variable multi-metric dataset that would result from monitoring generates practical challenges in developing and applying thresholds. Therefore, thresholds would not include a single value, but rather it might be possible to envisage ranges of values for particular metrics to capture groups of nanoforms.

Finally, a clearer understanding of the fate and behaviour of specific ENM, and nanoforms thereof, in products, emission pathways and in the relevant environmental media is required to inform possible regulatory action. For the water compartment, aspects identified as being of particularly deterministic in fate and behaviour include: interaction with suspended particulate matter; Trojan functions, whereby NM can carry other pollutants; and the impact of NM surface chemistry.

Conclusions and Recommendations

Key Data Gaps

Key gaps in environmental exposure data for NM include:

- complete lack of analytical data on NM in surface waters and groundwater
- very limited data for drinking water (one study) focussing on one NM
- data on emissions of ENM from landfills is very limited (one study), very initial data on possible flows to landfill for specific ENM from mass flow analysis;
- comprehensive EU-wide data on concentrations of airborne ENM and incidental nanoparticles (UFP) is lacking, although analytical data is available for a large number of site-specific studies;
- data on emissions to air from industrial installation is very limited;
- virtually no data on emissions of ENM to water, soil and in wastes from industrial installations.
In terms of that availability of data to feed into methods for generating exposure data, there are also major gaps. In order to provide reliable, consistent data sets on ENM exposure, the following knowledge gaps require immediate attention:

- worldwide production volumes of ENM;
- type of use on the life cycle stage, in particular during manufacturing;
- what ENM are being used in which products, which qualities and nanoforms are being used;
- allocation of production volumes amongst these products;
- current and future market penetration of these products;
- release from products throughout the life-cycle of the products by mass or other relevant metric(s);
- waste management of products containing ENM, including whether they are incinerated, landfilled, channelled to sewage treatment plants, or end up directly in the environment;
- releases from waste incinerators and removal efficacy in the sewage treatment plants; and
- distribution in time and space of the emissions; and
- empirical data on releases through specific emission pathways.

In addition, a more complete understanding of the fate and behaviour of ENM along the product life cycle, including in any waste management processes, and in environmental media is required.

Data input to enable environmental exposure models for NM are presented in table 0.2 below.

**Table 0.2: Data input needs to enable environmental exposure models for NM**

<table>
<thead>
<tr>
<th>Substances identifications:</th>
<th>Synthesis methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary size distribution</td>
<td></td>
</tr>
<tr>
<td>Coating</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physicochemical substance properties:</th>
<th>Size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolution rates (coating/core)</td>
<td>Agglomeration state</td>
</tr>
<tr>
<td>Affinity for adsorption of NOM</td>
<td>Shape</td>
</tr>
<tr>
<td>Zeta potential with NOM</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Degradation and transformation rates:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolution rate (coating/core)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Emissions:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tonnages reported in particle number</td>
<td>Ratio between nanoparticles and nanoparticles</td>
</tr>
<tr>
<td>Number of individual nanoparticles</td>
<td>embedded into other materials</td>
</tr>
</tbody>
</table>
Information Requirements under REACH

In comparing the data needs for conducting an exposure assessment for NM against the standard information on the physicochemical properties of a substances that registrants are obliged to report in registration dossiers, key omission are identified, including:

- Data on particle size, size range and number size distribution, for both primary particles and secondary (i.e. agglomerates);
- Physical form and morphology, including surface area;
- Surface chemistry; and
- Surface charge.

Guidance on information requirements could suggest that these additional data be included for registrations concerns with the nanoform of substances.

Regarding exposure data generated under REACH, studies conducted under the CSA are likely to represent a main future source of data. While it can be assumed that the CSA will not be performed for all ENM on the EU market as production volumes will be below the 10 tonne threshold, the requirements of the CSA as set out in Annex I of REACH could be adapted to specify that uses of the nanoform be identified and that a separate exposure assessment be conducted where data indicate different exposure scenarios as compared with the other forms addressed under the dossier.

EU-Wide Nano Product Registry

The recent Commission Communication of 3 October 2012 on the “Second Regulatory Review on Nanomaterials” indicates that the Commission will create a web platform with references to all relevant information sources on NM. At the same time, the Commission will be launching an impact assessment on an EU Nano Registry with the aim of gathering the data required for regulatory purposes, and capturing those nanomaterials that currently fall outside existing notification, registration or authorisation schemes. Work on the EU Nano Registry is due to commence in the second half of 2013, due for completion in late 2014 or early 2015.

The development of an equivalent EU-wide product register would serve to significantly increase the availability and importantly the quality of data to be fed into models used to estimate environmental exposure to NM, reducing uncertainties and making results more robust. Researchers would then be in a position to more confidently make EU-wide PEC estimates of specific nanoforms for environmental
Remaining uncertainties would relate to the fate and behaviour of NM over the product life cycle, including in waste treatment processes. On-going analytical research can serve to address these uncertainties in parallel. The increased availability of data on physicochemical properties would serve the needs of analytical researchers, and contribute towards studies on fate and behaviour.

### Monitoring Requirements for NM

Another option for galvanising the production of environmental exposure data for NM would be for regulators to establish monitoring requirements for NM in environmental media, in particular surface waters and air. However, with regards to monitoring NM in surface waters, analytical methods and test protocols are not yet validated. It may therefore be more constructive to work in parallel with Member States in sharing ongoing research and developments and in doing so to support ongoing efforts. With regards to air, monitoring is already undertaken in the framework of the Air Quality Directive, although this is not specific to the nano-scale fraction. The introduction of monitoring requirements for the PM$_{0.1}$ fraction in urban areas could be considered, although this would need to be supported by a process of standardisation of available methods and test protocols.
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<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BAT</td>
<td>Best available technique</td>
</tr>
<tr>
<td>BAT-AELs</td>
<td>Best available technique associated emission levels</td>
</tr>
<tr>
<td>BREF</td>
<td>Best available technique reference document</td>
</tr>
<tr>
<td>BS</td>
<td>Black smoke</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation particle counter</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential mobility analyzer</td>
</tr>
<tr>
<td>DMPS</td>
<td>Differential mobility particle sizer</td>
</tr>
<tr>
<td>DWCNT</td>
<td>Double-walled carbon nanotube</td>
</tr>
<tr>
<td>EDX</td>
<td>Electron dispersive X-ray microanalysis</td>
</tr>
<tr>
<td>ELV</td>
<td>Emission limit value</td>
</tr>
<tr>
<td>ENM</td>
<td>Engineered nanomaterial</td>
</tr>
<tr>
<td>EQS</td>
<td>Environmental quality standard</td>
</tr>
<tr>
<td>FDCU</td>
<td>Fan dry coil unit</td>
</tr>
<tr>
<td>FDH AS</td>
<td>Freeze dried, heat treated activated sludge</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
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<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectroscopy</td>
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<tr>
<td>IED</td>
<td>Industrial emissions Directive 2010/75/EU</td>
</tr>
<tr>
<td>ISE</td>
<td>Ion selective electrode</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid chromatography</td>
</tr>
<tr>
<td>LPS</td>
<td>Laser Particle Spectrometer</td>
</tr>
<tr>
<td>LS/MS</td>
<td>Liquid chromatography coupled with mass spectrometry</td>
</tr>
<tr>
<td>MOUDI</td>
<td>Micro-orifice uniform deposition impactor</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>nanoDMA</td>
<td>Nano differential mobility analyzer</td>
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<tr>
<td>NM</td>
<td>Nanomaterial</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>OECD</td>
<td>Organisation for Cooperation and Development</td>
</tr>
<tr>
<td>OPC</td>
<td>Optical particle counter</td>
</tr>
<tr>
<td>PEC</td>
<td>Predicted environmental concentrations</td>
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<td>PM</td>
<td>Particulate matter</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>PMC</td>
<td>Particle mass concentrations</td>
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<td>Particle number concentrations</td>
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<td>Particle number distributions</td>
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<tr>
<td>PNEC</td>
<td>Predicted no-effect concentrations</td>
</tr>
<tr>
<td>REACH</td>
<td>Regulation (EC) No. 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals</td>
</tr>
<tr>
<td>RTSP-MS</td>
<td>Real time single particle ICP mass spectrometry</td>
</tr>
<tr>
<td>SCENIHR</td>
<td>Scientific Committee on Emerging and Newly Identified Health Risks</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SEM/EDX</td>
<td>Scanning electron microscopy/electron dispersive X-ray microanalysis</td>
</tr>
<tr>
<td>SF-ICP-MS</td>
<td>Sector field inductively coupled plasma-mass spectroscopy</td>
</tr>
<tr>
<td>SMPS</td>
<td>Scanning mobility particle sizer</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid-phase extraction</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>TCLP</td>
<td>Toxicity characteristic leaching procedure</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>UFP</td>
<td>Ultrafine particle</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>UWWTP</td>
<td>Urban waste water treatment plants</td>
</tr>
<tr>
<td>WetSEM</td>
<td>Wet Scanning Electron Microscopy</td>
</tr>
<tr>
<td>WFD</td>
<td>Water Framework Directive</td>
</tr>
<tr>
<td>WPSTM</td>
<td>Wide-range particle spectrometer</td>
</tr>
<tr>
<td>WQX</td>
<td>Water quality eXtension</td>
</tr>
<tr>
<td>WWTP</td>
<td>Waste water treatment plant</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
</tbody>
</table>
1. Introduction

Any attempt to assess the risk to human health or organisms in the ecosystem from nanomaterials (NM), including both engineered nanomaterials (ENM) and unintentionally produced nanomaterials, requires two elements, an understanding of hazard and a quantification of exposure.¹ Exposure is a precondition for potential ecotoxicological effects within ecosystems. If there is no exposure, there is no risk. This study focuses on the exposure assessment required under environmental risk assessment.

Regarding intentionally produced ENM, these are novel materials, and as such a scarcity of data introduces potentially high uncertainty into the characterisation of risk². The scale of application of ENM is very broad with ENM used in a wide range of industrial sectors, including healthcare, agriculture, transport, energy, materials and information and communication technologies. In particular, applications of ENM that have a wide distribution, such as cosmetics, composite materials, civil engineering materials and leisure materials, pose a potential environmental risk.³ The projections for both the volumes manufactured and the range of applications of ENM show significant expansion, with estimated product sale of USD 250 billion in 2009⁴. In terms of the market penetration of ENM, Lux Research calculate that nanotechnology will be incorporated into $254 billion worth of products globally in 2009 and is forecasted to be incorporated into $2.5 trillion worth of products globally by 2015⁵. The concentrations of substances manufactured by man in the environment have been found to increase in direct proportion to their use in society⁶. Therefore, if these predictions prove correct, we can expect increasing environmental exposure to ENM in surface waters, air, groundwater and soils⁷.

¹ DEFRA (2005) “A scoping study to identify hazard data needs for addressing the risks presented by nanoparticles” SID 5 (2/05), Research Project Final Report, DEFRA, UK
Since early discussions of the risks associated with NM, Chemical Risk Assessment (CRA) has been put forward as the most relevant approach to understanding, evaluating and qualifying these risks. CRA is a four-step process consisting of 1) hazard identification; 2) hazard characterisation; 3) exposure assessment; and risk characterisation. The main outcome of a CRA is a statement of the probability and degree of harm to human and/or the environment following exposure to a chemical agent.

In 2003, the JRC published “Technical Guidance on Risk Assessment” to support legislation on the assessment of the risks of chemical substances to human health and the environment, specifically to support assessments under Directive 93/67/EEC on risk assessment for new modified substances and Regulation (EC) No.1488/94 on risk assessment for existing substances. According to the Technical Guidance, exposure assessment involves “an estimation of the concentrations/doses to which human populations (i.e. workers, consumers and man exposed indirectly via the environment) or environmental compartments (aquatic environment, terrestrial environment and air) are or may be exposed.”

The guidance does not specifically address nanomaterials in its discussion of exposure assessment, or any other stage of risk assessment. European Commission’s Scientific Committee for Emerging and Newly Identified Health Risks (SCENIHR) have pointed out that amendments have to be made to the 2003 Technical Guidance for risk assessment of chemicals “due to the physico-chemical properties of nanoparticles, their behaviour and their potential adverse effects are not solely dependent on exposure in terms of the mass concentration.” In response and in order to draw in work from scientific research, in 2009 the Commission launched a REACH Implementation Project on Nano (RIPoN). This resulted in the generation of targeted guidance on Information Requirements and Chemical Safety Requirements.

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11 Scientific Committee for Emerging and Newly-Identified Health Risks, The appropriateness of the risk assessment methodology in accordance with the Technical Guidance Documents for new and existing substances for assessing the risks of nanomaterials, European Commission, Brussels, Belgium, 2007
Assessment\(^\text{13}\) for ENM under REACH. In April 2012, ECHA drew on these outputs to update the 2008 guidance with appendices on NMs, specifically updating Chapters R.7a, R.7b and R.7c of the Guidance on Information Requirements and Chemical Safety Assessment.\(^\text{14}\) The recommendations cover endpoint specific guidance, dose-response for human health and the environment and occupational exposure estimation. At this point (November 2012), there is no NM-specific guidance for environmental exposure estimation.

Also of importance in setting the policy background to this project, is the recent Commission Communication of 3 October 2012 on the “Second Regulatory Review on Nanomaterials”\(^\text{15}\). The Communication highlights the considerable lack of data on exposure to nanomaterials via the environment, noting that as a result of this data shortage, no specific provisions for nanomaterials have yet been established in EU environmental legislation, triggering measures to control such pollutants through monitoring, separate treatment or environmental quality standards. The Communication identifies the development of validated methods to assess exposure as an important challenge in risk assessment. The accompanying Commission Staff Working Paper on the “Types and uses of nanomaterials, including safety aspects”\(^\text{16}\) also recognises the paucity of data on environmental exposure to NM, and calls for additional work to develop exposure data and detection methods for NM in the environment. Regarding NM risk assessment, the Paper notes that “mainly as a result of the lack of exposure data, risk characterisation and combining hazard and exposure data necessarily remains at a very preliminary and qualitative level.”

This study reviews the status quo in conducting exposure assessment for NM. In doing so, we review the available environmental exposure data for NM that has been generated through scientific research and published predominantly in peer-reviewed scientific journals. We discuss the practical methods that allow for the quantification of NM exposure, considering what the data requirements of each method are and how uncertainties are managed. Methods to estimate NM exposure are at the early stages of development, and hence we identify key areas of uncertainty and include a discussion of future research directions.

We then make the link between the ongoing scientific research and the requirements of regulators seeking to manage environmental exposure to NM, by asking what demands risk assessment tools under the EU environmental acquis set for exposure data and setting available data against these demands. We focus specifically upon EU legislative acts that serve to control emissions to the environment, or that set environmental quality standards. Here, it should be noted that none of the legislative acts explicitly identify NM as pollutants for control. As such, there is a speculative nature to our assessment. We go on to consider which of the methods for generating NM exposure data might serve under specific legislative acts and for particular media. Our final aim is to make some early suggestions as to what a toolbox of methods for generating environmental exposure data on NM might contain.

The report closes with some recommendations regarding options for generating data to feed into methods for generating exposure data, with the goal of reducing uncertainties in available datasets in the future.

1.1 Project Objectives

The Invitation to Tender sets forth three main objectives, including to:

- Identify relevant information on the products containing nanomaterials available on the EU market, the emissions of NM from the manufacture, use and end-of-life (including recycling), and concentrations of NM in the environment, that can be used to estimate human and environmental exposure in the EU as support to implementation of EU environmental legislation;
- Identify methodologies that link information on NM products and emissions with exposure, with particular focus on the information relevant for the implementation of the EU environmental legislation (i.e. health and ecosystem risk assessment aspects related to environmental rather than workplace exposure); and
- Identify principal data gaps and relevant gap-filling techniques and the potential to fill these gaps with the adaptation of the existing reporting tools at EU level, or development of a new one.

The expected outcome is a thorough assessment providing a picture of the status quo regarding NM exposure data, as well as identifying future developments, and providing recommendations on future steps.
An overall goal of the project is to take the first steps towards developing a toolbox of methods for generating environmental exposure data on nanomaterials and to signal for which pieces of legislation specific methods may best serve. In addition, the project aims to identify specifically which data on NM is required to feed into methods for estimating exposure, being it data on production volumes, or data on the specific properties of the nanoform.
2. **Specific Properties of Nanomaterials and Implications for Generating Environmental Exposure Data**

2.1 **Introduction**

There are a number of characteristics specific to NM that have implications for generating environmental exposure data. This section discusses these characteristics and reflects on how they might affect the generation of exposure data and the degree of uncertainty associated with the data.

2.2 **Classification and Occurrence of Nanomaterials**

Three types of materials at the nanoscale of between approximately 1 nm and 100 nm can be identified, including:

- naturally occurring particles;
- incidental nanoparticles; and
- engineered nanomaterials (ENM).

Naturally occurring nanomaterials, otherwise known as ultrafine particles (UFP), are produced during natural processes such as volcanoes and forest fires, as well as during combustion processes. Incidental nanoparticles are produced unintentionally as a by-product of human activity, for instance, welding fume and diesel emission particulates would be considered incidental nanomaterials.\(^{17}\) ENM are deliberately engineered in order to make use of optical, electrical, magnetic, chemical and mechanical properties that differ from those of the bulk form. These properties manifest because the large surface area to volume ratio results in increased adsorption of surrounding atoms and the small size means that quantum effects start to predominate.\(^{18}\)

While this report focuses predominantly on ENM, we also touch upon naturally occurring NM or nanoparticles and incidental nanoparticles. In air, the latter includes ultrafine particles (UFP) generated during combustion processes, such as in large combustion plants and waste incinerators, as well as through secondary particle formation. In water, sediments and soil, naturally-occurring nanoparticles

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\(^{17}\) The project on emerging nanomaterials, see website available at:  
[http://www.nanotechproject.org/inventories/ehs/learn/classes_nanomaterials/](http://www.nanotechproject.org/inventories/ehs/learn/classes_nanomaterials/)

\(^{18}\) Hristozov D and Malsch I, 2009 “Hazards and risk of engineered nanoparticles of the environment and human health” Sustainability 1: 1161-1194
in the range of 1-200 nm are present in stable suspension the form of natural colloids (dissolved organic carbon and mineral colloids) and dissolved ions. We consider the interference of naturally occurring nanoparticles when seeking to use analytical methods to measure nanomaterials in samples, and when estimating predicted environmental concentrations (PEC). Categories of nanomaterials are presented in box 1 below.

Box 1: Categories of nanomaterials

**Engineered nanomaterials (ENM):** ENM are nanoscale particles which are products of processes involving combustion and vaporization which are designed with very specific physical and chemical properties that make them very attractive for commercial development (Medina *et al.*, 2007). Some of the most common types of ENP are fullerenes, metal ENPs, oxides, complex compounds, quantum dots and organic polymers (Joner *et al.*, 2007).

**Nano-agglomerate:** An agglomerate is a group of coarse accumulations of material particles held together by weak forces such as van der Waals forces, electrostatic forces and surface tension (ISO, 2006).

**Nano-aggregate:** Nano aggregates are heterogeneous particles held together by relatively strong forces that cannot easily breakup (ISO, 2006). These aggregates can adhere to each other through Van der Waals forces to form agglomerates (Friedlander and Pui, 2003). Murr *et al.* (2004) showed that airborne particles are agglomerates of aggregates of aerodynamic diameters ranging from a few nanometres to several micrometres.

**Ultrafine particles (UFP):** Although ultrafine particles are neither purposefully manufactured nor of a constant composition or size, they are less than 100nm and hence nano-sized. The term ultrafine particles have been used to define aerosol and airborne particles less than 100 nm in diameter. There is no clear distinction between ultrafine particles and nanoparticles. The two terms are often used to make a distinction between engineered (nanoparticle) and incidental/naturally occurring (ultrafine) nanoscale particles (Jacobson and Seinfeld, 2004). However, this does not imply that significant differences exist among their properties in relation to measurement, risk assessment, and control of exposures.

**Nano-aerosol:** A nano-aerosol is composed of nanoparticles suspended in a gas, and may be present as discrete particles, or as clusters of nanoparticles (Heim *et al.*, 2005). These assemblies may have diameters larger than 10 nm.

On 18th October 2011, the European Commission published a definition of nanomaterials under Commission Recommendation 2011/696/EU\textsuperscript{19}. The EU definition of nanomaterials in provided in box 2 below.

**Box 2: EU Commission Definition of nanomaterial**

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm.

In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %. By derogation from the above, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.

For example, it will be relevant to consider whether specific categories of products containing NM (i.e. cosmetics) might be excluded from future data generating requirements due to the particles in their material consisting >50% of nanomaterials in the size range 1-100nm.

To date, this definition has been applied under one piece of legislation, namely the Biocidal Products Regulation\textsuperscript{20}. In addition, the Recommendation invites Member States, Member States, EU agencies and economic operators to use the definition in the adoption and implementation of legislation and policy and research programmes concerning products of nanotechnologies. The more recent 2012 Commission Communication on the “Second Regulatory Review on Nanomaterials” confirms that the definition is intended to be used by Member States, European Union agencies and companies and states that the Commission will use it in EU legislation and instruments of implementation, where appropriate. The 2012 Communication also notes that where other definitions are used in EU legislation, provisions will be adapted in order to ensure a consistent approach, although sector specific solutions may be necessary. The definition will be reviewed by the Commission in 2014.

In characterising NM, a particularly challenging issue relates to the fact that multiple nanoforms of the same ENM are manufactured, even of the same basic chemistry, and that the different forms exhibit distinct properties (e.g. due to differences in size, shape, ionic charge, coatings and functionalizations, etc.).

\textsuperscript{19} Commission Recommendation of 18 October 2011 on the definition of nanomaterial, OJ L275/38

nanotails).\textsuperscript{21} In providing an example of this diversity we consider the various nanoforms of carbon. There are multiple different carbon-based nanoforms, such as carbon black, multiple forms of fullerenes ($C_{60}$, $C_{70}$, $C_{74}$, $C_{76}$, $C_{78}$ etc.) including carbon nanotubes (CNT), and endofullerenes. Carbon nanotubes are fibrous fullerenes consisting of rolled-up graphene sheets that may or may not be capped at the ends by a half fullerene sphere. CNT may consist of a single layer of C (single walled carbon nanotubes), double layers (DWCNT) or multiple layers (MWCNT). The electric and thermal conductive properties of the CNT varies depending on the symmetry of the carbon to carbon bonds in the, making different CNT useful for different applications in electronics and other fields. The dimensions of the CNT also affect the manner in which they aggregate, be in it bundles of nanofibres, nanoropes or nanowires (Joner \textit{et al}, 2007).

In practice, a product may contain several nanoforms of the same NM. This variation throws up challenges in regulating different nanoforms of the same material.

### 2.3 Fate and Behaviour of Nanomaterials

Behaviour of NM in the environment is dependant both of the physicochemical properties of the NM (and nanoforms thereof) in question and those of the environment into which they are released.\textsuperscript{22} The specific physicochemical properties of NM will affect environmental exposure of these substances, approaches to measuring exposure and how resulting data can be fed into risk assessments. NM possess properties that affect what happens to them when released into the environment in different ways to dissolved chemicals and this limits the applicability of existing exposure models for assessing the risk associated with their environmental dispersal. In particular, the high surface area to volume ration results in highly reactive and physic-chemically dynamic materials in the environmental media.\textsuperscript{23}

Important aspects of how nanomaterials behave in the environment that will affect exposure include mobility (their ability to move from one place to another or from one recipient to another) and stability (how stable and long-lived specific nanoforms are) and transformation (whether they disintegrate or agglomerate, are soluble, interact with other particles, chemicals and/or surfaces and whether they are

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\textsuperscript{22} Chen Z, Westerhoff P, Herckes P (2008) Quantification of C60 fullerene concentrations in water, Environmental Toxicology and Chemistry 27: 1852-1859

\textsuperscript{23} Lowry GV, Gregory KB, Apte SC and Lead JR (2012) Transformations of nanomaterials in the environment, Environmental Science and Technology 46: 6893-6899
degraded) and how their properties may change during these processes and impact on mobility. Indeed, Nowack et al (2012) point out that it is more important to understand the specific properties of NM released from diffuse and point sources that have undergone transformation reactions than it is to understand the specific properties of pristine ENM, since the released nanoforms will determine risk to the environment.\textsuperscript{24}

To add to the complexity, the heterogeneous distributions of NM, and the multiple nanoforms thereof, in terms of size, shape, surface charge, composition leads to significant variation in fate and behaviour, even when the base material is the same. This implies that generalisations cannot be made on the basis of the parent material.

While investigation of these questions is ongoing, the variation in nanoforms and a lack of standard reference and test protocols to make results comprehensive and comparable imply that considerable work remains\textsuperscript{25}. In a recent study, Nowack et al (2012) note that “almost nothing” is known about the environmental behaviour and the effects of released and transformed NM, although despite their presence in the environment today\textsuperscript{26}. However, a number of studies have investigated the fate and behaviour of specific NM in water, soil or air. Conclusions from the literature are summarised in table 1 below and discussed in sections 2.3.1-3 below.


Table 1: NM environmental fate and behaviour

<table>
<thead>
<tr>
<th>Water</th>
<th>Soil</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slower settling</td>
<td>Poor understanding of NM</td>
<td>Key processes: diffusion, agglomeration, wet</td>
</tr>
<tr>
<td>Stability of colloidal suspensions in</td>
<td>solid/water partitioning</td>
<td>and dry deposition and gravitational settling</td>
</tr>
<tr>
<td>natural waters sensitive to ion concentration, suggest aquatic transport of NM most likely in rainwater and low ionic strength freshwaters</td>
<td>NM likely to display slow kinetics with regards to adsorption onto env. Solid phases</td>
<td>Rapid aggregation of NM emitted to air into a size range of 0.1µm to 1µm predicted, with an atmospheric residence time of 10-20 days</td>
</tr>
<tr>
<td>Dissolution may result in the release of the ionic form of the material – of particular relevance for metallic NM</td>
<td>NM may readily sorb to soil sediment particles and may become inert and immobile (influenced by size, chemical composition and surface characteristics)</td>
<td>ENPs with anti-agglomeration coatings are an exception</td>
</tr>
<tr>
<td>Possible biotic and abiotic degradation &amp; photoreactions</td>
<td>In contrast, some NM may show increased mobility</td>
<td>Deposited ENP not likely to be re-suspended</td>
</tr>
<tr>
<td>Insoluble NM (e.g. MWCNTs) may become stabilized in aquatic environments</td>
<td>Strong influence of electrical charge difference in soils and sediments</td>
<td>Possible photodegradation of photoactive NM?</td>
</tr>
<tr>
<td>NM readily sorb from water to soil sediment particles</td>
<td>Humic acid may attach ENP to their surface and transport them in sea surface microlayers</td>
<td></td>
</tr>
<tr>
<td>Humic acid may attach ENP to their surface and transport them in sea surface microlayers</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


2.3.1 Fate and Behaviour of Nanomaterials in Water

It is in water that many substances have their most significant environmental effects making it important to understand the fate and behaviour of NM in water. Researchers are agreed that NM dispersed in water will behave according to the mechanism of colloid science. Colloidal suspensions of NM are generally expected to be unstable; for example, upon collision, particles may approach each other close enough for weakly attractive Van der Waals forces to become dominant over repulsive electrostatic forces and steric hindrance. NM may agglomerate and then settle due to gravity.

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suggesting that suspensions of dispersed nanomaterials may only be stable under narrow ranges of well-defined environmental conditions\textsuperscript{29}.

Although many ENM are not water-soluble in the laboratory, they may nevertheless disperse in water. For example, although C\textsubscript{60} (fullerene) is a hydrophobic nanomaterial, they have been found to form negatively charged colloids that disperse in water, with aggregate size influenced by water pH\textsuperscript{30}. Within sea water, with high pH and ionic strength, electric double layers of colloid particles are much smaller than in freshwater, allowing for closer inter-particle approach, a process which usually leads to increased aggregation.

ENM may undergo a number of processes in water, including partitioning to sediment and suspended particulate matter and transformation through abiotic and/or biological degradation. Eventual environment concentrations will depend on the stability and the degradations rates of ENM and their intermediates (for example composites used in suncreams)\textsuperscript{31}. The stability of ENM in the aquatic environment depends on their chemical structure, as well as other particle properties (e.g. size and surface coating), as well as environmental conditions. Characterising and predicting transformations can be extremely challenging, with the type of transformation depending on solution conditions (pH, redox state, organic matter content, types of serum components present, temperature), with even slight variations leading to different behaviours. In addition, many dynamic transformations are not readily reversible, implying that the history of the NM will affect its properties and state in the environment. Predicting how an NM will behave in the aquatic environment therefore requires information on the environment properties and the history of the NM over relevant time scales\textsuperscript{32}.

A number of articles provide evidence of the importance of the surface properties of NM in determining their transformation and aggregation behaviour, and thus for their mobility in aquatic and their ultimate interaction with and general bioavailability to organisms. The affinity between nanoparticles and environmentally relevant surfaces will be a determinant factor in the fate, transport, and exposure of nanomaterials\textsuperscript{33}. The affinity between nanoparticles and the surfaces they encounter

\textsuperscript{32} Lowry GV, Gergory KB, Apte SC and Lead JR (2012) Transformations of nanomaterials in the environment, Environmental Science and Technology 46: 6893-6899
will affect the transport of nanoparticles used in groundwater remediation, as well as the removal of nanoparticles in water and wastewater treatment processes. ENMs often have surface coatings that control surface chemistry and may dominate the effects of the nanoparticle core. Lin et al (2012) argue that the affinity of nanoparticles for various surfaces is relevant to understanding heteroaggregation in surface waters (i.e., the scavenging of nanoparticles by larger flowing collectors), autoaggregation between nanoparticles (i.e., aggregation between particles of the same species), and the affinity of nanoparticles for biotic surfaces, which may in turn affect bioavailability and uptake. They investigated the propensity of silver nanoparticles (AgNPs) having two different polymer coatings (poly(vinylpyrrolidone), PVP, or gum arabic, GA) to aggregate, or to deposit to a reference surface (silica), as a basis for differentiating the effect of surface coating on the stability of nanoparticles in aggregation and in deposition. Their results suggest that polymeric coatings that are stabilizers in the case of autoaggregation, might not necessarily stabilize nanoparticles against deposition unless the collector surfaces are also coated with polymer.

With regards to fullerenes, Pycke et al (2012) note that the study of occurrence, fate and transport is complicated by the variety of surface modifications that occur either intentionally or through natural processes. They conclude that reliable data on the parent compounds and their congeners is required in order to understand fate and behaviour, and in addition, identify the need for methods for quantitative and qualitative analysis of fullerene derivatives in environmental matrices.

Xiao and Wiesner (2012) identify hydrophobicity as one of the key elements of surface chemistry that affects fate, behaviour and bioavailability, and used three methods (surface adsorption, affinity coefficient and contact angle) to investigate the hydrophobicity of seven carbon and metal-based ENM with and without coatings. Aqueous-nC60 and tetrahydrofuran-nC60 were observed to be more hydrophobic than nano-Ag coated with polyvinylpyrrolidone or gum arabic, followed by nano-Ag or nano-Au with citrate-functionalized surfaces. Fullerol was shown to be the least hydrophobic of seven ENM tested.

Natural waters will contain other dissolved materials, both colloidal and solid (including natural nanoparticles) and NM introduced into water bodies are expected to adhere to such materials.\textsuperscript{38} Natural organic matter present in water, sediments and soils contain hydrophobic domains and hence are likely to interact with hydrophobic nanomaterials, such as fullerenes and carbon nanotubes. In their review of the literature, Ross and Aitken (2011) note that researchers consistently report interactions between NM and natural organic matter, and point out that this will influence the fate and behaviour of NM in water\textsuperscript{39}.

Lin et al (2012)\textsuperscript{40} investigated how variation in the collector surface composition affects the deposition of silver nanoparticles. They studied the transport of uncoated silver nanoparticles (nanoAg) in a porous medium composed of silica glass beads modified with a partial coverage of iron oxide (hematite) and compared it to that in a porous medium composed of unmodified glass beads, and found the affinity of nanoAg to be significantly higher for the hematite-coated glass bead surface than that for an uncoated surface.

In addition, Levard et al. (2012)\textsuperscript{41} investigated the transformation of nanoAg in various aqueous environments and found that NanoAg transforms easily to various forms of oxidized silver in the environment, with subsequent modification of properties and alterations to their transport, fate, and toxicity. They argue that a full understanding of these impacts requires data on the surface structures, compositions, and morphologies of Ag-ENM and their transformation products (nanoAg\textsubscript{2}S in particular), as well as a picture of the different states of aggregation and sulfidation. Work in this area is ongoing, for example Lowry et al (2012)\textsuperscript{42} investigated the long term behaviour of nano-Ag in freshwater mesocosms and distribution among water, solids, and biota (discussed in section 4.3.9).

In addition, NM may themselves age and hence transform. As an example of the effects of aging, metallic copper nanoparticles, which often have a thin surface oxide layer, can age in the ambient

\textsuperscript{38} SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks) (2009) Risk assessment of products of nanotechnologies, 19 January 2009
environment to become even more oxidized over time. These aged nanoparticles will then have different properties compared to the original nanoparticles\textsuperscript{43}.

Finally, another significant concern is the potential for the transfer and magnification of NM in foodwebs, through the exposure of low trophic level organisms and their consumption by higher level organisms. However evidence to date is limited, with one study demonstrating dietary transfer between aquatic organisms and suggesting that dietary intake may constitute a major exposure route for the higher trophic levels of aquatic organisms\textsuperscript{44}.

Regarding the application of current models to the environmental exposure for NM in water, the importance of colloidal mechanisms implies that NM are unlikely to display equilibrium partitioning behaviour within the time frames associated with environmental transport phenomena, as reflected under current modelling approaches for soluble chemicals.\textsuperscript{45} Loux et al (2011) suggest that in order to incorporate the mechanisms of colloid suspension stability into exposure models for NM, kinetic approaches that incorporate colloid chemistry (DLVO theory) should be employed.\textsuperscript{46}

2.3.2 Fate and Behaviour of Nanomaterials in Sediments and Soils

While evidence suggests that NM are most likely to end up in association with sediments and soils\textsuperscript{47}, very little is known about how nanomaterials behave in soils and sediments. The constituents of sediment and soil typically have large specific surface areas (300-500m\textsuperscript{2}/g) and a high electrochemical surface charge that is likely to make them interact with charged particles like many nanomaterials. As with water, environmental factors such as pH and ionic strength, together with the physicochemical properties of the NM will determine whether they are bound within or transported out of soils. Again,

\begin{quote}
\textsuperscript{43} Mudunkotuwa IA, Pettibone JM, and Grassian VH, 2012, Environmental Implications of Nanoparticle Aging in the Processing and Fate of Copper-Based Nanomaterials, Environmental Science & Technology 46 (13): 7001-7010
\end{quote}
interactions with dissolved particles, in particular dissolved organic matter, are likely to affect dispersion and transport.\(^{48}\)

In their review of available data on the fate and behaviour of NM in soils and sediments, Ross et al (2011)\(^{49}\) state that the lack of data is so pronounced, particularly for metal oxides and carbon nanotubes, that no general conclusions can be drawn. They note that much of that research conducted to date is not really comparable due to, for example, the use of nanoparticles with different functionalisation, different experimental approaches, different levels of attention to characterisation of the ENP used. The current lack of analytical tools for the detection and quantification of NPs in soil matrices is also a problem. They do note that studies addressing various aspects of the use of NM in soil remediation offer some information.

While Loux et al (2011) recognise that the transport of EMNs associated with natural soils/sediments is a potentially significant environmental transport and exposure mechanism, they state that developing procedures to understand the phenomena leading to the solid/water partitioning of NM is extremely challenging. For example, they note that the filtration of water column samples may well composite suspended particulate matter that is not necessarily associated in the natural state. In addition, NM are likely to display relatively slow kinetics with respect to adsorption onto environmental solid phases (when compared to truly dissolved species). Therefore only systems of prolonged duration may begin to exhibit the patterns of solid/water partitioning phenomena that are customarily attributed to thermodynamic equilibrium processes and hence played out using current soil/sediment exposure models\(^{50}\).

2.3.3 Fate and Behaviour of Airborne ENM, nanoparticles and UFP in Air

Aerosol science is a developed and well documented scientific field that provides preliminary information regarding the fate and behaviour of airborne ENM, as well as unintentionally-produced nanoparticles and UFP in air. However, Ross et al. (2011) identify some major issues that still require validation in current hypotheses regarding the behaviour, transport and fate of air-borne particles of nano-scale. These include methods for accurate sampling or tracking of nanomaterials within the air

\(^{50}\) Loux NT, Su YS and Hassan SM (2011) Issues in Assessing Environmental Exposures to Manufactured Nanomaterials, International Journal of Environmental Research and Public Health 8(9): 3562-3578
compartment, elucidation of the effect of differing particle morphologies (of both nanoparticles and their agglomerates), and overcoming the issue of differentiating airborne NM from background nanoparticle levels in the atmosphere.\textsuperscript{51}

In addition, the processes governing the transport of airborne nanoparticles vary with particle size from molecular transport mechanisms at very small sizes (circa 1 nm) to mechanisms similar to those reflected in the gas continuum model.\textsuperscript{52} Aitken et al (2004) note that in traditional aerosol science, the key process governing aerosol behaviour is particle size, with inertial, gravitational and diffusional forces also being important. As particle size decreases, diffusional forces become increasingly important and nanoscale particles are thus likely to behave in a manner more akin to a gas or vapour.\textsuperscript{53}

Ross et al (2011) identify a need for systematic studies on different types of airborne nanomaterials using a range of physicochemical parameters (e.g. size, shape, form, surface area) to generate data and to support development of reliable models. In addition, predictive modelling of emission scenarios and subsequent transport pathways (both for indoor and outdoor air) will play an important role in furthering understanding in this area. The development of more sophisticated predictive models is currently underway, driven chiefly by occupational health and safety concerns.

\section*{2.4 Implications of Nanomaterial Properties for Environmental Exposure Data}

Given the particular properties of NM, researchers suggest that the current environmental fate and transport models used for chemicals are probably not applicable to NM and nanoparticles\textsuperscript{54}. Researchers at the 2009 workshop on the “Environmental fate and behaviour of nanomaterials – beyond listing of limitations” developed a distribution model of the inputs, processes, distributions and degradation parameters affecting NM in environmental compartments, and this is provided in figure 1 below. Participants considered diffusion from waste and soil into air to be unlikely, although advection was considered possible.


\textsuperscript{52} Mädler L, Friedlander SK (2007) Transport of Nanoparticles in Gases: Overview and Recent Advances; Aerosol and Air Quality Research 7(3):304-342


Figure 1: Distribution model showing inputs, processes, distribution and degradation parameters for NM in environmental compartments.

Loux et al (2011) also argue that NM differ from both molecular species and bulk particulate matter in the sense that they are unlikely to exhibit significant settling under normal gravitational conditions and they are also likely to exhibit significantly diminished diffusivities (when compared to truly dissolved species) in environmental media. They suggest that since air/water, air/soil, and water/soil intermedium transport for NM, nanoparticles and UFP is governed by diffusive processes in the absence of significant gravitational and inertial impaction processes, realistic models of MN environmental intermedium transport behavior will likely require an emphasis on kinetic approaches.55

In particular, their specific behaviour in terms of aggregation and dispersion imply that NM differ from most conventional dissolved chemicals for which a concentration can be unequivocally determined.56 As such, the relevance of traditional mass-based metrics are questioned for many NM, there is a need to establish dose metrics that can serve to capture the potential impact of NM in ecosystems.57 A recent OECD report noted that when describing dose metrics across a range of particle sizes, the use of mass concentration data alone may be insufficient for NM, given that size-specific concentrations and surface area metrics may be more closely related to biological effects (OECD, 2012)58. The literature suggests a number of data characteristics that will need to be investigated and recorded when monitoring and/or modelling the concentrations of NM in environmental media in order to provide a complete picture, including:

- Mass concentrations in the range of µg L⁻¹–pg L⁻¹ and changes in concentrations over time;
- Particle size and shape and range of particle distribution: i.e. identifying and measuring the size fractions of different nanoforms;
- Available surface area;
- Distinguishing between NM and naturally occurring nanomaterials; and
- Data on the degree of aggregation and dissolution: i.e. ongoing fate and behaviour.

The characteristics of the resulting datasets on environmental exposure would therefore differ to those generated for bulk chemical substances (in terms of the scale of metrics, including info on particle

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distribution, and data on aggregation and dissolution). This will result in multi-metric reporting and will influence the methods through which data can be fed into risk assessments, possible demanding a revision of risk assessment tools.

2.5 Comparison with Other Chemicals

In terms of similarities with the “classic” chemicals and pollutants, there are a number of common points. Firstly, data scarcity is not limited to NM, rather chemical risk assessment is in general characterised by data limitations. The Regulation (EC) No. 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) is intended to address data scarcity for chemical substances, including NM.

Secondly, regarding the considerable uncertainties concerning the fate and behaviour of NM in the natural environment, it should be noted that similar issues exist for a number of conventional chemicals, including for example endocrine disrupting oestrogens (e.g. ethinyl oestradoil) and medicinal products and their residues. It will therefore be relevant to look at the regulatory approaches that are being considered for these other substances to inform a discussion of how to address limitations in exposure data for NM.

However, it can be said that the current uncertainties regarding the fate and behaviour of NM in the environment are particularly acute, due mainly to the extreme complexity of behaviour of nanomaterials in natural systems and the existence of multiple nanoforms of one EMN. The difference in physicochemical properties that result from small changes between nanoforms of the same parent material suggest that tools such as read across or reliance on Qualitative or Quantitative structure-activity relationship ((Q)SAR) are unlikely to be useful in assessing the hazards of ENM, which will instead require a case-by-case approach.

In addition, factors such as the abiotic and biotic composition of the environmental matrix may influence nanomaterials structure, form and behaviour by modifying the physic-chemical characteristics of the nanomaterials. This uncertainty makes the calculation of predicted environmental concentrations (PEC) extremely challenging. In particular, the receiving environments for NM may be highly complex in nature, such as complex industrial effluents, estuaries etc. As a consequence, uncertainties in predictions of exposure, or PEC, and indeed of hazard, or predicted no-effect

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concentrations (PNEC), will be propagated during characterisation of environmental risk, so amplifying overall uncertainties.
3. **Emissions Pathways for Nanomaterials**

3.1 **Introduction**

Completing a full exposure assessment requires extensive knowledge about the potential exposure scenarios for a specific substance. In sections 3.2 to 3.4 below, we briefly review discussions in the literature regarding possible emission pathways for NM, nanoparticles and UFP, including those that have been unintentionally produced.

3.2 **Emission Pathways for Nanomaterials**

Given the rapid increases in production volumes of ENM and their incorporation into multiple applications, it can be reasonably assumed that releases of ENM, as well as incidental nanoparticles, into the environment have increased accordingly.\(^{60}\) The figure below provides an overview of the different stages of a product life cycle at which ENM could enter the environment. The boxes in yellow represent the various stages in the life cycle of a product containing ENM, from the synthesis of the specific ENM, its incorporation into a product, the product use phase and final disposal. The boxes in blue all represent different waste management options, including incineration, landfill, waste water treatment and recycling. The boxes in green represent possible emissions to the environment, including emissions to air, releases of treated waste water effluent and leachate from landfills.

While it is not the focus of this study to identify exposure pathways, it is important to have a picture of potential exposure pathways when assessing the completeness of available exposure data and identifying gaps for future research efforts. In cases such as these where comprehensive and reliable data on concentrations of pollutants in the environment is absent, a classic approach is to estimate upstream emissions. These include point source emissions, such as those from industrial installations or from urban waste water treatment plants, and diffuse source emissions, i.e. emissions from products along their life cycle. Point source emissions and diffuse source emissions are considered in turn below.

\(^{60}\) Reijnders L "Cleaner technology and hazard reduction of manufactured nanoparticles" Journal of Cleaner Production (2006) 67(1) p87-108
Figure 2: Environmental exposure pathways for NM

As well as environmental exposure to NM, it is plausible to assume that the general public is being exposed to some extent via the environment, for example though inhalation of contaminated air and consumption of contaminated drinking water. In their 2009 report, SCENIHR reviewed available data on the release on NM into the environment and the subsequent exposure to humans via the environment. They concluded that “currently available knowledge of these processes is insufficient to allow quantitative predictions of the environmental fate of nanomaterials”.

3.3 Point Source Emissions of Nanomaterials

Point sources of emissions of NM are likely to include industrial emissions to air, water and soil, effluents released into surface waters from urban waste water treatment plants (UWWTP), emissions to air from construction sites, landfill leachates into soil and groundwater and direct releases of NM.

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61 Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) 2009 “Risk assessment of products of nanotechnologies” European Commission, January 19, Brussels
into soils and groundwater for remediation purposes. The evidence for each of these sources is briefly reviewed below.

Emissions to air are considered more likely to contain unintentionally-produced nanoparticles or ultrafine particle (UFP) than NM. Industrial sources of UFPs to air were reviewed by AMEC in their 2011 report “Industrial emissions of nanomaterials and ultrafine particles”62. Measurements of particulate matter (PM) will capture nanoscale particles such as air-borne nanoparticles and ultrafine particles, in particular the PM$_{0.1}$ range. Point sources were found to contribute 28% and 21% of total EU PM$_{10}$ and PM$_{0.1}$ emissions respectively, including industrial processes (13% and 5%), power generation (6% and 4%) and industrial combustion (9% and 12%).

Regarding industrial emissions of UFP (PM$_{0.1}$) by source type, the report identifies metals (3%), pulp and paper (9%), iron and steel (17%), heat and electricity (17%), chemicals (3%), petroleum refining (8%) and food and beverage (4%) as the most significant sources, with 39% of UFP from industrial processes emitted by other sectors.

Another source of UFP identified in the literature is construction activities using or breaking down cement structures. Recent trends to incorporate carbon nanotubes and plasticizers (e.g. nano–silica, Fe$_2$O$_3$, SiO$_2$, TiO$_2$) within a concrete mix to improve workability, pore structure, thermal behaviour, compressive and flexural strengths introduce additional sources of UFPs to the cement structure. Bystrzejewska–Piotrowska et al. (2009) therefore note that in addition to UFP emissions due to the fracture of conventional concrete, nanomodifications incorporated into the concrete mixes may also become airborne during construction, transport, storage or demolition$^{63}$. The size distributions, shape, morphology, chemical composition, oxidant potential and toxicity of UFPs produced during the processing of concrete structures are likely to differ from UFPs produced from the combustion of fossil fuels in vehicles or industries$^{64}$. Exposure to UFPs arising from building activities is therefore likely to have a different effect on both public health and the environment than UFP arising from combustion$^{65}$.

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62 AMEC (2011) Industrial emissions of nanomaterials and ultrafine particles, UK
Some evidence of emissions of NM from production plants is provided by Shinohara et al (2009), who measured fullerenes exposure 1-500m from a fullerene production installation.

Landfills may represent another potential point source of emissions to soil and water through leaching. The key source of nanomaterials into landfills is the disposal of nanoproducts by consumers at the end of life phase of those products, their subsequent entry into the municipal mixed waste stream, and the channelling of that waste stream into landfill. Recent life cycle analyses suggest over 50% of nanomaterials produced will eventually reside in landfills. An example of the introduction of nanowaste from industrial sources into landfills can be found in the disposal of production residues from the manufacturing of fullerenes.

In terms of point source emissions to water, effluent from UWWTP is considered a significant source. Regarding nanomaterials in urban wastewater, possible entry paths include cosmetics washed off the users’ body or face, used or spilt detergents, the release of nanomaterials from textiles during washing and from paints used on building facades, and the use of nanomaterials to disinfect water and in wastewater treatment.

In addition, ENPs are used to directly treat groundwater contamination, for example zero-valent iron nanoparticles (nZVI) are used in the environmental remediation of groundwater. Applications include their installation in permeable reactive barriers for the treatment of groundwater plumes, as well as direct injections or recirculation in contaminated source areas.

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68 Royal Commission on Environmental Pollution. 27th Report (2008) RCEP, UK


71 Benn, T. and Westerhoff, P. “Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics” (2008) Environmental Science and Technology, 42(11) p4133-4139


There are a number of specific applications of nanomaterials in the field of water purification that may involve the release of nanomaterials into drinking water, including the use of nano-filters, nanomaterials as absorbents, titanium dioxide photocatalysts and nanotechnology based sensors\textsuperscript{76}.

### 3.4 Diffuse Source Emissions of Nanomaterials

Possible examples of diffuse sources include nanomaterials leaching into groundwater and then into surface waters from landfills, run-off from agricultural land of pesticides that contain nanomaterials (these are known to be present in some pesticides in the US\textsuperscript{77} and may also potentially be present in pesticides in the EU, although no specific examples have been identified) and from sewage sludge, and spilt lubricants that are washed off roads into storm water discharges. Atmospheric deposition of nanomaterials is also likely to be relevant.

Emissions from products containing ENM over the product life cycle are thought to represent a significant source of ENM exposure pathways, with releases from products in the liquid form considered more likely than releases from products where the ENM are bound in a solid matrix. In the latter case, releases may still occur due to abrasion or resulting from grinding\textsuperscript{78} or shredding processes such as during recycling processes, or from incineration. Figure 2 below illustrates how emissions of ENM may arise from the use, recycling and final disposal of products containing nanomaterials.

In order to reliably estimate diffuse source emissions from products, data is required on:

- The volumes of each nanoform of specific ENM being placed on the market;
- The volume fraction of each nanoform incorporation into products and specific product types;
- The market penetration and use patterns for product types; and
- Emissions of ENM from products along the life cycle.


\textsuperscript{77} Nanotechnology and Pesticides, presentation by William Jordan (Office of Pesticide Programs, US EPA), Pesticide Program Dialogue Committee, April 29, 2010

Figure 3: A schematic diagram of possible emissions pathway over the nano-product life cycle

Source: Bystrzejewska-Piotrowska et al “Nanoparticles: Their potential toxicity, waste and environmental management” (2009) Waste Management 29, 2587-2595
Information on the volumes of nanomaterials being produced and placed on the market and the number and range of product application for nanomaterials should provide an insight into the scale of possible environmental exposure to nanomaterials. However, the availability of such information in the public domain remains limited, making an assessment of the volumes of nanomaterials entering product life cycles challenging. However, a number of databases have recently been established that include data on products containing ENM and on production volumes and the quality and usefulness of this data is considered in section 3.5 below.

### 3.5 Production Volumes for ENM

Despite the availability of estimates of market value, very little concrete data on production volumes for ENM is available in the public domain. What data are available are not broken down by specific nanoform of the ENM, but rather reference the bulk material.

A recent report by the NRC estimated nano-product sale of USD 250 billion in 2009\(^\text{79}\). Regarding future market estimates, an OECD report notes that the nanotechnology industry is still at an early phase of development, making its future hard to forecast\(^\text{80}\). A report published by Global Industry Analysts in 2010 forecasts that the global market for nanomaterials will reach US$6.2 billion (€4.26 billion) by 2015.\(^\text{81}\) In addition, the report predicts that the carbon nanotube industry in Western Europe will reach US$43.1 million (€29.64 million) by 2012.

### 3.6 Products Containing ENM on the EU Market

Available information sources that can contribute to a picture of what nanomaterials are on the market, in which products and in what volumes include product registers that list products that voluntarily declare a nano content and estimates of current market size and market forecasts. As an example, the Woodrow Wilson International Centre for Scholars has developed an online inventory of consumer products labelled as containing nanomaterials.\(^\text{82}\) As of March 10 2011 (last update), the nanotechnology consumer products inventory contains 1,317 products or product lines that voluntarily declare a nano content. A limitation with this database is that it relies on the producer to declare the content of NM, something that is not a legal requirement and may even be incorrect. In addition, the


\(^{82}\) Woodrow Wilson international Centre for Scholars, inventory of nanotechnology-based consumer products on the market, available at: http://www.nanotechproject.org/inventories/consumer
Woodrow Wilson inventory has been criticised as being limited to products that are advertised as containing nanomaterials in English, and hence excludes a large number of products on the EU market.

In 2010, the European Consumers’ Organisation (BEUC) in collaboration with ANEC developed an inventory of 475 products claiming to contain nanomaterials. Products fell into the categories presented in table 2 below.

<table>
<thead>
<tr>
<th>Categories</th>
<th>Number of products identified</th>
<th>Percentage of total products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appliances</td>
<td>27</td>
<td>5.67%</td>
</tr>
<tr>
<td>Automotive</td>
<td>72</td>
<td>15.13%</td>
</tr>
<tr>
<td>Cross Cutting</td>
<td>66</td>
<td>13.87%</td>
</tr>
<tr>
<td>Electronic and computers</td>
<td>6</td>
<td>1.26%</td>
</tr>
<tr>
<td>Food and drink</td>
<td>27</td>
<td>5.67%</td>
</tr>
<tr>
<td>Products for children</td>
<td>18</td>
<td>3.78%</td>
</tr>
<tr>
<td>Health and Fitness</td>
<td>199</td>
<td>41.81%</td>
</tr>
<tr>
<td>Home and garden</td>
<td>60</td>
<td>12.61%</td>
</tr>
<tr>
<td>Total</td>
<td>475</td>
<td>100%</td>
</tr>
</tbody>
</table>

Two government reports provide summaries of the NM of the EU market, including a Survey of Nanotechnological Consumer Products published in 2007 by the Danish Ministry for the Environment and Nanomaterials in Consumer Products published in 2010 by the Dutch national Institute for Public Health and the Environment (RIVM).

The 2007 Danish report reviewed products on the Danish market that claimed to contain nanomaterials and identified 243 products. Notable product categories included surface treatment (in liquid form), cosmetics and sports equipment (with the nanomaterials incorporated into a solid matrix).

The 2010 RIVM report, which was conducted on behalf of the European Commission, drew on existing databases, including the BEUC inventory and the Woodrow Wilson inventory. It identified 858 consumer products that claimed to contain NM as having been present on the EU market, with 805 on the market in 2010. The report built on equivalent data for 2007 from an earlier report, and found a six-fold increase in the number of products with a nano-claim on the EU market over the interim three years. Growth in the number of products on the market was particularly seen in the product category personal care products and cosmetics (mainly skin care products), as well as in the textiles category. Additionally, fast growth was seen in the market for coating products. A summary of the report’s finding is provided in table 3 below.

Table 3: Products claiming to contain NM as listed in the 2010 RIVM Report

<table>
<thead>
<tr>
<th>Product group</th>
<th>2007</th>
<th>2007 products withdrawn from the market</th>
<th>2007 products present without nano-claim</th>
<th>New products in 2010</th>
<th>Total products 2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appliances</td>
<td>5</td>
<td>1</td>
<td></td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>Electronics and Computers</td>
<td>7</td>
<td>1</td>
<td></td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Home Furnishings and Household Products</td>
<td>42</td>
<td>6</td>
<td>7</td>
<td>108</td>
<td>137</td>
</tr>
<tr>
<td>Motor Vehicles</td>
<td>13</td>
<td>2</td>
<td></td>
<td>103</td>
<td>114</td>
</tr>
<tr>
<td>Packages (Including those for food)</td>
<td>1</td>
<td></td>
<td>1</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Personal Care Products and Cosmetics</td>
<td>15</td>
<td>5</td>
<td>7</td>
<td>304</td>
<td>307</td>
</tr>
<tr>
<td>Health</td>
<td>6</td>
<td>1</td>
<td></td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>Sporting Goods</td>
<td>10</td>
<td>1</td>
<td>3</td>
<td>40</td>
<td>46</td>
</tr>
<tr>
<td>Textiles</td>
<td>15</td>
<td>12</td>
<td></td>
<td>81</td>
<td>84</td>
</tr>
<tr>
<td>Toys and Games</td>
<td>0</td>
<td></td>
<td>2</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Cross-cutting</td>
<td>28</td>
<td>3</td>
<td></td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>1</td>
<td></td>
<td></td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Total</td>
<td>143</td>
<td>36</td>
<td>17</td>
<td>715</td>
<td>805</td>
</tr>
</tbody>
</table>

The report also highlighted changes in the products on the market, with 36 of the 143 products identified as being on the market in 2007 having been withdrawn from the market by 2010 and 17 having lost their nano claim. Thus 30% of the products that were on the market in 2007 have been withdrawn or lost their claim. Regarding products that have lost their claim, it is not clear whether the

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change reflects a change in composition, or whether the claim was removed for marketing purposes as a possible response to negative publicity on NM.

The European Federation of Building and Woodworkers generated a report focussed on products containing nanomaterials in the construction industry\(^87\). Main product types included nanoparticle improved concrete and cement, nano-coatings and insulation materials.

The NANOWERK website,\(^88\) a commercially funded site that provides a searchable database of NM on the global market and provides links to producers. However, production volumes are not provided.

Regarding market estimates, an OECD report notes that the nanotechnology industry is still at an early phase of development, making its future hard to forecast.\(^89\) Research from UK consulting firm Cientifica Ltd. indicates that the market for nanotechnology-enabled products, excluding semiconductors and electronics due to uncertainties, will reach US$ 1.5 trillion (€1.03 trillion) in 2015.\(^90\) As mentioned in the introduction, Lux Research estimate that nanotechnology was incorporated into $254 billion worth of products globally in 2009 and forecasted that this will increase to $2.5 trillion worth of products globally by 2015\(^91\).

### 3.7 Action on Nano Registries by EU Member States

A number of EU Member States have taken recent action to establish product inventories that should led to the generation of valuable data on the volumes of ENM on the EU market and their application in consumer products. Activities are summarised in table 4 below.

In addition, the recent Commission Communication of 3 October 2012 on the “Second Regulatory Review on Nanomaterials”\(^92\) indicates that the Commission will create a web platform with references to all relevant information sources on NM, including existing registries on a national or sector level. The work towards a harmonized European web platform will draw on the recommendations of the

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\(^{90}\) [Industry Week.com, last accessed 07.06.11 at: http://www.industryweek.com/articles/nano-growth_14395.aspx](http://www.industryweek.com/articles/nano-growth_14395.aspx)


2010 RIVM project mentioned above\textsuperscript{93}. The Commission is to establish a first version mainly based on links to available information as soon as possible, and will assist in the development of harmonised data formats in order to facilitate information exchange.

At the same time, and in response to the call by the Parliament for an evaluation of the need for notification requirements for all nanomaterials, the Commission will be launching an impact assessment “to identify and develop the most adequate means to increase transparency and ensure regulatory oversight, including an in-depth analysis of the data gathering needs for such purpose”. The Communication notes that this analysis will include those nanomaterials currently falling outside existing notification, registration or authorisation schemes. Work on data gathering for NM in the form of an EU Registry is due to commence in the second half of 2013, with finalization foreseen for 2014 or early 2015. The Commission plans to draw on experiences gained with the implementation of the French Nano Registry.

In the following three sections, further detail is provided on actions to establish nano-product registers in France, Belgium and Denmark, those Member States for which more detailed information is publically available.

\textsuperscript{93} RIVM (2010) “Nanomaterials in consumer products: Update of products on the European market in 2010” RIVM Report 340370003/2010, the Netherlands
Table 4: Summary of activities regarding product registers for ENM in the EU

<table>
<thead>
<tr>
<th>Country</th>
<th>Summary of Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium</td>
<td>In Belgium, the Public Health, Food Safety and Environment Ministry has developed the</td>
</tr>
<tr>
<td></td>
<td>terms, conditions and methods for the establishment of a compulsory nanomaterials</td>
</tr>
<tr>
<td></td>
<td>database.</td>
</tr>
<tr>
<td>Denmark</td>
<td>In September 2012, the Danish Environment Minister announced a proposed Order to</td>
</tr>
<tr>
<td></td>
<td>establish a national database of mixtures and articles containing or releasing</td>
</tr>
<tr>
<td></td>
<td>nanomaterials. The order would also require producers and importers to report products</td>
</tr>
<tr>
<td></td>
<td>containing or releasing nanomaterials and generate information to allow for an</td>
</tr>
<tr>
<td></td>
<td>evaluation of the risks to consumers and the environment from nanomaterials in</td>
</tr>
<tr>
<td></td>
<td>products on the Danish market.</td>
</tr>
<tr>
<td>France</td>
<td>The French government has established a compulsory reporting scheme for nanomaterials</td>
</tr>
<tr>
<td></td>
<td>placed on the market by producers, importers or distributers. Information requirements</td>
</tr>
<tr>
<td></td>
<td>include an annual declaration of the identity, the quantity and the uses of the</td>
</tr>
<tr>
<td></td>
<td>nanomaterials, as well as the identity of recipients down the supply chain. The first</td>
</tr>
<tr>
<td></td>
<td>declarations are required in 2013 and will relate to nanomaterials manufactured, imported</td>
</tr>
<tr>
<td></td>
<td>or distributed in 2012. The objective to establish a reporting scheme was introduced</td>
</tr>
<tr>
<td></td>
<td>under Article 42 of Law No. 2009-967 of 3rd August 2009 on the programme relating to</td>
</tr>
<tr>
<td></td>
<td>the implementation of the Environment Round Table (Grenelle 1), with further details</td>
</tr>
<tr>
<td></td>
<td>provided under Article 185 of Law No. 2010-778 (Grenelle 2). Decree 2012-232 provides</td>
</tr>
<tr>
<td></td>
<td>requirements for the application of the reporting scheme, in terms of who has to report</td>
</tr>
<tr>
<td></td>
<td>and what data is required, and is due to enter into force on 1st January 2013.</td>
</tr>
<tr>
<td>Germany</td>
<td>The Federal Environment Agency and the Federal Ministry for the Environment, Nature</td>
</tr>
<tr>
<td></td>
<td>Conservation and Nuclear Safety (BMU) supported a legal feasibility study on the</td>
</tr>
<tr>
<td></td>
<td>introduction of a nano product register in Germany, which found the introduction of</td>
</tr>
<tr>
<td></td>
<td>such a register to be feasible and workable in practice. In its 2011 publication, the</td>
</tr>
<tr>
<td></td>
<td>NanoKommission notes that its members were unable to reach agreement on the function</td>
</tr>
<tr>
<td></td>
<td>and possible goals of a legally-binding nano-product register.</td>
</tr>
<tr>
<td>Italy</td>
<td>In Italy, a project to establish a nanomaterials database has been initiated and the</td>
</tr>
<tr>
<td></td>
<td>exact content of the database is currently under consideration. The Italian database</td>
</tr>
<tr>
<td></td>
<td>will be established on a voluntary basis, with the possibility that it may evolve into</td>
</tr>
<tr>
<td></td>
<td>a compulsory reporting system. Nanotec IT, the Italian Centre for Nanotechnology, was</td>
</tr>
<tr>
<td></td>
<td>established by the Italian Association for Industrial Research and has published the 3°</td>
</tr>
<tr>
<td></td>
<td>Edition of the Italian Nanotechnology Census providing an overview of the main public</td>
</tr>
<tr>
<td></td>
<td>and private players and the activity in the field. The information includes:</td>
</tr>
<tr>
<td></td>
<td>• Funding;</td>
</tr>
<tr>
<td></td>
<td>• Type and size of the organizations;</td>
</tr>
<tr>
<td></td>
<td>• Geographical distribution;</td>
</tr>
<tr>
<td></td>
<td>• R&amp;D activities;</td>
</tr>
<tr>
<td></td>
<td>• Publications and patents;</td>
</tr>
<tr>
<td></td>
<td>• Applications and products;</td>
</tr>
<tr>
<td></td>
<td>• initiatives related to regulation and safety issues;</td>
</tr>
<tr>
<td></td>
<td>• Education initiatives.</td>
</tr>
</tbody>
</table>

3.7.1 French Action to Establish a Nano Registry

The French model is considered first, given that it is the most advanced, mandatory and due for implementation in 2013. In France, Articles L523-1 to 4 of the Environment Code include the general legal provisions of the French nanoparticles mandatory reporting scheme. These general provisions
were recently complemented by Decree 2012-232\textsuperscript{94}, which provides detailed requirements for the conditions of application of this reporting scheme. The decree includes a number of definitions regarding nanoparticles and these are presented in Table 5 below.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles</td>
<td>Minute piece of matter with defined physical boundaries</td>
</tr>
<tr>
<td>Aggregate</td>
<td>A particle comprising of strongly bound or fused particles</td>
</tr>
<tr>
<td>Agglomerate</td>
<td>Collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components.</td>
</tr>
<tr>
<td>Substance with nanoparticle status</td>
<td>Substance as that defined in Article 3 of the Regulation (EC) No 1907/2006, intentionally manufactured to a nanometric scale containing particles non-bound or as aggregate or as an agglomerate where for a minimum amount of particles in the number size distribution, one or more external dimensions is in the size range 1nm-100nm. The Decree further mentions that this minimal proportion can be reduced in specific cases, when it can be justified for environmental or health protection reasons or for security and competitiveness reasons.\textsuperscript{95} It finally states that, in derogation to this definition, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm are considered substances with nanoparticle status.</td>
</tr>
<tr>
<td>Substances with nanoparticle status</td>
<td>Substances with nanoparticle status intentionally incorporated in a mixture from which it is likely to be extracted or released under normal or reasonably foreseeable conditions of use.</td>
</tr>
<tr>
<td>contained in mixture without being bound</td>
<td></td>
</tr>
</tbody>
</table>

In terms of who must declare, the target of the decree includes those who manufacture, import or distribute substances in the nanoparticle state, or contained in mixtures without being bound, or a material intended to eject such substances under normal or foreseeable conditions of use. Regarding the threshold above which a declaration must be made, those who manufacture, import or distribute \textbf{at least 100 grams per year} of the nanoparticles. Where the manufacture, import, and distribution takes place within the framework of a scientific research and development activity without being placed on the market, the registrant must only declare its identity and the sector of activity concerned.

The decree indicates that the declaration must include all available information related to the hazard of these substances and the exposure pathways or useful for the health and environmental risk assessment as well as information related to the identity, quantity and uses of these substances, and the identity of the professional users to whom it was sold or given. An implementing Order detailing the information

\textsuperscript{94} Décret n° 2012-232 du 17 février 2012 relatif à la déclaration annuelle des substances à l’état nanoparticulaire pris en application de l’article L. 523-4 du code de l’environnement, the original Decree of 17 February 2012 was modified on 20 February 2012, with the consolidated version available online at: \url{http://www.legifrance.gouv.fr}

\textsuperscript{95} This will be defined further by an Implementing Order not yet published
to be required in the declaration made by manufacturers, importers and retailers of these substances should be published in the following months. The proposed Order requires the following information:  

- Chemical identity of the substance
- Presence of impurity
- Particles size
- Size distribution of the particles
- Aggregation state
- Agglomeration state
- Shape
- Specific surface
- Cristal state
- Surface chemistry
- Surface charge
- Matrix where the nanoparticle is held or stabilised
- Commercial name of the mixture

The reporting obligation will enter into force as of 1 January 2013, with relevant dossiers to be submitted annually to the French Environment Ministry by 1 May. The French National Agency for Food Safety, Environment and Labour (Agence nationale de sécurité sanitaire de l’alimentation, de l’environnement et du travail) is then charged with the management and review of the dossiers. If the declaration is considered by the Agency to be incomplete, they shall demand additional specific information from the declarant to be submitted within two months of receipt of the request for additional information. The Starting on 1 July 2013, a penalty is also foreseen in cases where manufacturers, importers and retailers fail to submit their declaration to the Agency by the deadline, or where the request for additional information is not met within the two month deadline. The penalty is set at Euro 3,000, with a daily increase of Euro 300 until such time as the reporting obligation is met.

Following the requirement to make information available to the public under the French Environment Code, information is to be made public each year at the latest six months after the reporting deadline. Should the reported wish to request confidentiality, they should specifically identify the information for which they request confidentiality and justify the request on the basis of infringement of commercial secrecy or intellectual property rights. In particular, information contained in a patent application can remain confidential until the publication of that patent. The request for exemption

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must be sent to the Ministry within five days of the declaration. In the absence of explicit decision at the end of a period of three months from the receipt of the request, it shall be deemed rejected.

The French reporting obligation is therefore expected to yield extremely useful, high quality and reliable information on ENM available on the French market both in the raw form and in products, together with important data on physicochemical properties.

3.7.3 Belgian Action to Establish a Nano Registry

The proposed Belgian nano-products register applies to production with the purpose of placing on the market, and placing on the market for professional users, including importation, of substances, preparations and products that comply with the EU definition of nanomaterials. Professional users that fall within the scope are required to submit an annual declaration by email. No declaration is required for a company that places on the market annually a total amount of less than 100g of nanomaterials as a substance, or in preparations or products. Definitions that apply under the proposed Belgian system are provided in table 6 below.

Table 6: Definitions to apply to the proposed Belgian nano-product registry

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
<td>As defined in the Law of 21 December 1998 on product standards and its revisions, containing loose particles or particles in aggregate or agglomerate form, of which at least 50% of the particles, in size distribution according to amount, with one or several external dimensions ranging from 1 nm to 100 nm, with the exclusion of natural or accidentally formed substances. A declaration is also required for fullerenes, graphene flakes and single wall carbon nanotubes with one or several external dimensions smaller than 1 nm.</td>
</tr>
<tr>
<td>Preparation</td>
<td>As defined in the Law of 21 December 1998 and its revisions, containing one or several of the above mentioned substances likely to be extracted or released during normal or reasonably predictable conditions of use.</td>
</tr>
<tr>
<td>Products</td>
<td>As defined in the Law of 21 December 1998 and its revisions: - for which the above mentioned substances are used during their manufacturing process (at whatever stage) - or containing those substances in a loose state, in suspension in liquids or in gases, or linked to the surface.</td>
</tr>
<tr>
<td>Particle</td>
<td>Tiny piece of material with well-defined physical outlines</td>
</tr>
<tr>
<td>Agglomerate</td>
<td>Slightly tied cluster of particles or aggregates, the total external surface of which equals the sum of the surfaces of its individual components</td>
</tr>
<tr>
<td>Aggregate</td>
<td>Particle made of closely tied or melted particles</td>
</tr>
<tr>
<td>Professional user</td>
<td>Every person settled in Belgian territory, using for the purpose of his/her professional activities the above defined substances, preparations or products that are subject to declaration. The qualification as a professional user can be proven, for instance, by the awarding of a company registration number with the Banque-Carrefour des Entreprises</td>
</tr>
</tbody>
</table>

97 Details on the proposal Belgian national register are drawn from a draft from 20 September 2012, as set out in an invitation to tender for services provided to the Belgian Federal Public Service for Health, Food Chain Safety and Environment in Special Specifications No DGS/MR/JP/12026.
In terms of the information to be provided, declarations shall:

- identify the declarant;
- identify the substance and include specific details on physicochemical properties, including:
  - particle size;
  - particle size distribution;
  - aggregation and agglomeration state;
  - Shape; and
  - Particle coating, if any.
- state the total volume in kg produced, imported or placed on the market;
- identify uses, claimed properties and downstream users to which the substance, preparation or product is transferred.

In addition, when available the declaration shall determine whether the substances has been registered under REACH, and include data on impurities, crystalline state, specific surface area and surface load. Full details are provided in box 3 below.

While, the information mentioned in the declaration as described in Appendix III, is to be considered as confidential, the Belgian authorities will be able to use the data for the purpose of protecting workers, public health and environment, as well as for control purposes in different legislations including regional legislation, and for extracting aggregate information in order to write global reports destined to the public. These global reports will not mention any specific product or company.
**Box 3: Information requirements for the proposed Belgian nanomaterials registry**

### I. Declarant identification

I.1. The declarant shall provide specific identification information about the company having to make a declaration.
I.2. The declarant shall mention his company registration number and activity sector. Importers shall mention their qualification as a legal extranational entity or appointed representative.

### II. Substance identification

II.1 Information to be provided for each substance present as such, or in a preparation or product:

a) Chemical identification of the concerned substance. The substance is identified by:
   (i) its chemical name;
   (ii) its chemical formula, its CAS number and, if applicable, its EC number (EINECS or ELINCS);

b) When the substance is placed on the market as such under a registered trade mark, this trade mark must be mentioned;

c) Size of the particles: average and median size of the particles, in relation with a standard deviation, with mention of the determination method used together with facts explaining why this method is applicable to the substance, and with a description of the experimental conditions;

d) Particle size distribution according to amount: a size distribution curve according to amount is provided, with mention of the determination method used together with facts explaining why this method is applicable to the substance, and with a description of the experimental conditions;

e) Aggregation and agglomeration state: average amount of the aggregates and, if the substance is sold in agglomerate form, average size of the agglomerates, each of them in relation with a standard deviation when available. The declarant shall mention the determination method used, together with facts explaining why this method is applicable to the substance, and with a description of the experimental conditions;

f) Shape: qualitative description of the shape of the particle, with mention of the determination method used together with facts explaining why this method is applicable to the substance;

g) Qualitative description of the possible particle coating, if any;

h) The declarant shall specify whether it is a substance, or a substance in a preparation or a substance in a product according to the above mentioned definitions. If it is a preparation, the declarant shall mention the state in which the mixture containing the substance is offered (solid, liquid, gas, powder).

II.2 Information to be provided when available at the moment of the declaration:

a) If the substance has been registered by the declarant pursuant to EC Regulation "REACH" No 1907/2006, the registration number must be provided as well. The part of the registration number identifying the individual declarant may be omitted;

b) Possible presence of impurities: nature and amount of each impurity of which the mass concentration in the substance is equal to or higher than 0,1%, or lower when this information is required for the purpose of other regulatory provisions;

c) Crystalline state: nature of crystallographic phases and, in case of a mix of phases, proportion of each phase, including the amorphous phase if existing;

d) Specific surface: average specific surface, in relation with a standard deviation, with mention of the determination method used;

e) Surface load: zeta potential, with mention of the environment, pH conditions and ionic force.

### III Total amount of the substance(s) produced, imported and placed on the market, as identified under point II, expressed in kilograms annually. Depending on the case, these are amounts of substances which are declared as such, amounts in declared preparations and amounts in declared products.

### IV Uses

a) The declarant of a substance or mixture subject to declaration specifies what are all the scheduled uses.

b) He also mentions the registered trade marks of the declared preparations and products.

c) As an option, he mentions the claimed properties for which the substance is used in nanoparticles.

### V Identification of professional users to whom the declarant has transferred property of the substance, preparation or product
3.7.3 Danish Action to Establish a Nano Registry

In Denmark, plans for a nano register were recently announced by the Minister for the Environment. She explained that under a draft amendment to the Danish Chemicals Act, the Ministry of the Environment would write a detailed order establishing the rules for a national database of mixtures and articles containing or releasing nanomaterials. The order would also require producers and importers to report products containing or releasing nanomaterials. The information in the database is intended to form the basis of an evaluation of whether the content of nanomaterials in products on the Danish market poses a risk for consumers and the environment. The ministry plans for the first reports to be due in early 2014. A budget of DKK 24 million (Euro 3.2 million) has been allocated to the work over the next four years.  

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98 Announcement by the Danish Environmental Minister, Ida Auken and Per Clausen: Vi skal have bedre styr på nano, 17 September 2012, available in Danish at: http://www.mim.dk/Nyheder/20120917_nano.htm
4. Environmental Exposure data for Nanomaterials

4.1 Introduction

In this section we provide a short review of each of the studies identified as generating relevant environmental exposure data for NM. While there is scientific agreement that ENM production, use and disposal leads to releases of ENM to the environment, the total environmental load from current uses of nanomaterials is unclear. There is currently very limited information available to build well-informed and evidence based exposure scenarios covering the life cycle of ENMs for known uses. In addition, data regarding releases of incidental nanoparticles and UFP into air are very limited.

In their report on NM exposure scenarios, Gottschalk et al divide methods to assess NM releases into the environment into the following categories:

- Analytical in situ methods
- Experimental/simulation studies in laboratories
- Modelling/estimation
- Exploratory chemometric approaches, i.e. probabilistic mass flow analysis

In conducting our review of available methods, we build on this categorisation to include recent studies that use kinetic modelling. A brief description of each category is provided in the sections below, together with a discussion of our approach towards identifying and reviewing the methodologies that are available or under development.

In order to identify studies on environmental exposure assessment of nanomaterials an analysis of English language scientific articles and reports was conducted using Pubmed, ISI Web of Knowledge, SciFinder, Cambridge Abstract Service and the ICON Environmental, Health and Safety database available at http://www.icon.rice.edu/advancedsearch.cfm. Detailed literature searches and cross referencing was performed using the terms: Nanotechnology, nanomaterial, nanoscale material, nanoparticles, fullerenes, buckyballs, nanosized particles, nanotubes, nanowires, and quantum dots in combination with exposure and environment. We furthermore obtained copies of governmental and non-governmental reports including reports from research projects (including from the Nanosafety

Cluster under FP7\(^{10}\) dealing with nanoscience and technologies and the risks of nanotechnologies and scrutinized data from creditable websites and books.

In the following section, each of the studies identified as being relevant for this project are reviewed in turn with regards to the following criteria:

- Data gathering techniques, including: \textit{in situ} measurements, lab measurements and extrapolations, pure modelling, etc.;
- Metrics used;
- Environmental media;
- Exposure pathway (i.e. selected exposure scenario);
- Identifying and quantifying sources of uncertainty

In addition, a summary overview of the available exposure data for NM is provided in Annex I.

4.2 \textit{In situ Measurements}

A number of analytical measuring techniques are currently available to provide data on the concentrations of NM in the environment. The state of development and the reliability of the techniques vary according to the environmental media in which there are applied.

Techniques for measuring ultrafine particles (UFP) and nano-scale particles (aerosols) in air are most developed, although they have not yet been applied in a regulatory context. Over the past decade, much research has been done on urban particulate matter (PM) number size distributions, including long- and short-term measurements. The focus has been on PM generated through combustion processes in vehicle engines and resulting urban ambient air pollution levels, as well as research into secondary particle formation. As a result, over half of the studies identified here as taking \textit{in situ} measurement focus on PM in air samples, with a focus on urban settings and the contribution from traffic. Two studies have estimated concentrations of NM in air. Yang et al. (2012) measured nano-TiO\(_2\) inside a production plant, while Shinohara et al. (2009) modelled fullerene exposure in ambient air near to a production facility.

Researchers have started investigating NM in water samples more recently and, as a consequence, the application of these techniques remains at the laboratory scale. Both quantitative and qualitative

\(^{10}\) \url{www.nanosafetycluster.eu}
detection of NM in water samples remains challenging and distinguishing them from natural background nanomaterials presents problems. This becomes particularly difficult when background concentrations are higher than process-specific releases.\textsuperscript{101} However, researchers do report that progress is being made towards establishing methods for measuring NM in water samples\textsuperscript{102} and relevant studies are reviewed below. Still fewer studies have looked at NM in sludge and soils.

Those studies that have reported quantitative measurements of nanomaterials \textit{in situ} are summarised below in ascending chronological order.

4.2.1 Moore et al. (2007)

Moore et al. (2007)\textsuperscript{103} monitored summer air quality at an urban site in Los Angeles, USA during June-July 2006. They used a Micro-Orifice Uniform Deposition Impactor (MOUDI) and a Scanning Mobility Particle Sizer (SMPS) to measure the evolution of UFPs (<180 nm in diameter) concentrations. Their analysis of monthly data suggested that UFP concentrations were strongly influenced by traffic emissions in the morning, while during the afternoon UFP were thought to be predominantly generated through secondary photochemical reactions. They found UFP concentration to peak in the early afternoon.

4.2.2 Qian et al (2007)

Qian et al (2007)\textsuperscript{104} undertook continuous measurements of aerosol size distributions (3 nm – 2 µm) over a 26 month period (1 April 2001-31 May 2003) in an urban street in Louis, USA, in order to investigate secondary particle formation. The observed more frequent nucleation events in summer months than in winter, and nucleated particles grew faster in the summer than in winter. They found that the daily maximum in the number concentrations of UFP formed by nucleation (4.8 ± 3.5 X 104 cm\textsuperscript{-3}), as well as the maximum daily rates of 3 nm particle production (17 ± 20 cm\textsuperscript{3} s\textsuperscript{-1}) were highly variable and showed no clear seasonal dependence. They found that particle formation increased particle concentrations by an average factor of 3.1 ± 2.8.

\textsuperscript{102} Paul Westerhoff, Arizona State University, personal communication
\textsuperscript{104} Qian S, Sakuria H, McMurry PH (2007) Characteristics of regional nucleation evenings in urban East St. Louis, \textit{Atmospheric Environment} 41: 4119-4127
4.2.3 Kaegi et al. (2008)

Kaegi et al. (2008)\textsuperscript{105} compared the leaching of TiO\textsubscript{2} nanoparticles from a newly painted model facade and a real facade and traced leached nanoparticles from paint on house facades into receiving water bodies. Analytical transmission electron microscopy (TEM), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS analysis) were used. It was found that the leaching from a newly painted model facade resulted in a titanium concentration of 600 \(\mu g\) \(l^{-1}\) in receiving water bodies, with 90\% of the leached titanium nanoparticles being in the size range of 20 to 300 nm. Even after two years of exposure to weathering, the painted real facade resulted in a leaching of only 10 \(\mu g\) \(l^{-1}\) for titanium, while the urban run-off contained 8 \(\mu g\) \(l^{-1}\). For the real facade, the size of particles was similar to the newly painted facade and hence around 20-300 nm for 90\% of the particles, but for the urban run-off 50\% of particles were < 300 nm.

4.2.4 Chen et al. (2008)

Chen et al (2008)\textsuperscript{106} developed methods to separate and concentrate fullerenes from water containing salts and organic matter and then quantify their concentrations using liquid chromatography coupled with mass spectrometry (LC/MS). The stable aqueous C\textsubscript{60} aggregates (nC60) prepared in the present study were approximately 60 to 70 nm in diameter and had an ultraviolet (UV) extinction coefficient of 0.0263 L/mg-cm at 347 nm, which equated to a UV detection limit of 0.4 mg/L based upon an absorbance of 0.01 cm\(^{-1}\). Ultraviolet analysis is not applicable to use in waters containing salts or organics (e.g., tap water) because of their interferences and potential to aggregate nC60. The LS/MS analysis detected C60 as single fullerene rather than aggregates. Three techniques were developed to separate and concentrate nC60 from ultrapure and tap water into toluene to facilitate LC/MS determination: Evaporation of sample to dryness; extraction using 20\% NaCl into toluene; and solid-phase extraction. The first two methods had limitations for use in complex water matrices, but aqueous nC60 concentration as low as 300 ng/L in water were quantified using solid-phase extraction (SPE) separation method. This is the first publication on the application of extraction methods for nC60 from ultrapure and tap waters and determination of detection limits by LC/MS.


4.2.5 Limbach et al. (2008)

Limbach et al. (2008)\textsuperscript{107} introduced nano-cerium oxide (nano-CeO\textsubscript{2}) into a model waste water treatment plant (WWTP) and went on to measure nano-CeO\textsubscript{2} in treated waste water and sludge. While the majority of the nano-CeO\textsubscript{2} was captured through adhesion to the sludge, a significant fraction escaped into waste waters. They measured concentrations of nano-CeO\textsubscript{2} in treated waste water of 2-5ppm using scanning electron microscopy. A centrifugation steps was used to distinguished unagglomerated particles and small agglomerates with a hydrodynamic aggregate diameter <200 nm.

4.2.6 Fushimi et al. (2008)

Fushimi et al. (2008)\textsuperscript{108} studied roadside particles and conducted qualitative analysis using carbon analysis and organic analysis to determine particle source. Measurements were taken during winter and roadside measurements showed a sharp peak in nucleation-mode particles not seen at a background site 200m away. Their results suggested that diesel contributed to roadside and background particles in the 0.030-0.060 \( \mu \text{m} \) size range.

4.2.7 Riddle et al. (2009)

Riddle et al. (2009)\textsuperscript{109} studied roadside particle concentrations in California, USA, and apportioned size fractions to sources. Size-resolved source profiles were combined to form an "on-road" profile for motor oil, diesel, and gasoline contributions to elemental carbon and organic carbon. The resulting equations were used to predict source contributions to the size distributions of elemental carbon and organic carbon in the roadside environment. The method successfully accounted for the majority of the carbonaceous material in particles with diameter < 0.18 microm, with significant residual material in larger size fractions. They found PM\textsubscript{0.18} to be dominated by diesel fuel and motor oil combustion products and PM\textsubscript{0.1} dominated by diesel fuel and gasoline fuel combustion products.


4.2.8 Kleeman et al. (2009)

Kleeman et al. (2009)\textsuperscript{110} studied a severe winter pollution episode in California, US, measured concentrations and determined the sources of fine particles (PM\textsubscript{1.8}) and ultrafine particles (PM\textsubscript{0.1}). They determined that concentrations of elemental carbon in the PM\textsubscript{0.1} size ranged from 0.03 ugm\textsuperscript{-3} during the day to 0.18 ugm\textsuperscript{-3} at night; while concentrations of organic carbon in the PM\textsubscript{0.1} size ranged from 0.2 ugm\textsuperscript{-3} during the day to 0.8 ugm\textsuperscript{-3} at night. Principle sources of PM\textsubscript{0.1} sized elemental carbon included gasoline fuel, diesel fuel and lubricating oil combustion products, with minor contributions from biomass combustion and meat cooking. Principle sources of PM\textsubscript{0.1} sized organic carbon included wood combustion and meat cooking, with minor input from gasoline fuel, diesel fuel and lubricating oil combustion products.

\textsuperscript{110} Kleeman MJ, Riddle SG, Robert MA, Jakober CA, Fine PM, Hays MD, Schauer JJ, Hannigan MP (2009) Source apportionment of fine (PM\textsubscript{1.8}) and ultrafine (PM\textsubscript{0.1}) airborne particulate matter during a severe winter pollution episode. Environmental Science and Technology 43(2): 272-279
4.2.9 Kiser et al. (2009)

Through field-scale investigation at a municipal WWTP, Kiser et al. (2009) quantified the concentrations of nanoTi at each point along the WWTP process train and although it was found that the majority of nanoTi sorbed to biomass, Kiser et al. (2009) found that 10-100 μg/L nanoTi still remained in effluents. At one WWTP raw sewage contained 100 to nearly 3000 μg Ti/L whereas Ti concentrations in effluents from this and several other WWTPs ranged from <5 to 15 μg/L. Ti larger than 0.7 μm accounted for the majority of the Ti in raw sewage, and this fraction was observed to be well removed by WWTP processes and a wastewater biomass concentrations of around 2000-3000 mg/L total suspended solid. In the effluent, nearly all Ti present was <0.7 μm - often observed to be aggregates of a few hundred nanometers composed of several primary particles less than 100 nm solely of TiO₂. Measurements were done in both June and January 2008 of the WWTP, and the average overall removal of Ti was 82 ± 21% by mass. Ti was found to accumulated in settled solids at concentrations ranging from 1 to 6 μg Ti/mg and the highest total Ti concentrations (2572 μg/L) were found within the activated sludge system (i.e. aeration basin), but Ti-containing solids were imaged in sewage, biosolids, and liquid effluent as well as in commercial products containing engineered TiO₂. Single nanoparticles plus spherical aggregates (50 nm to a few hundred nanometer in size) composed of sub-50 nm spheres of Ti and oxygen only (presumably TiO₂) were observed in all samples. Visual characterization of the Ti-bearing solids was conducted using the scanning electron microscopy/electron dispersive X-ray microanalysis (SEM/EDX) technique.

4.2.10 Geranio et al. (2009)

Geranio et al (2009) studied the amount and the form of silver (Ag) released during washing from nine fabrics with different ways of silver incorporation into or onto the fibers. The nine different fabrics included: a commercially available conventional antibacterial sock; a commercially available nanosock; six fabrics obtained directly from two companies; and one was a sample from an ongoing research Project.

Silver was quantified by ICP-OES as well as by X-ray fluorescence spectroscopy. Little dissolution of nano-Ag was found to occur under conditions relevant to washing (pH 10) with dissolved concentrations 10 times lower than at pH 7. The use of bleaching agents such as hydrogen peroxide or

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peracetic acid (formed by the perborate/TAED system) was however found to greatly accelerate the dissolution of Ag and the amount and form of Ag released from the fabrics depending on the type of Ag-incorporation into the textile.

As show in table 7, the percentage of the total silver emitted during one washing of the textiles varied considerably among products (from less than 1 to 45% by mass of the total silver). In the washing machine the majority of the particulate Ag (at least 50% but mostly >75% of the particulate silver) was released in the size fraction >450 nm, indicating the dominant role of mechanical stress. A conventional silver textile did not show any significant difference in the size distribution of the released silver compared to many of the textiles containing nano-Ag.

Table 7: Release of total Ag from textiles during washing in µg/g of textile

<table>
<thead>
<tr>
<th>Textile</th>
<th>1st cycle</th>
<th>2nd cycle</th>
<th>3rd cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Static</td>
<td>314</td>
<td>129</td>
<td>172</td>
</tr>
<tr>
<td>Plasma-NP</td>
<td>67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgCl</td>
<td>2.7</td>
<td>1.8</td>
<td>3.6</td>
</tr>
<tr>
<td>AgCl-Binder</td>
<td>2.4</td>
<td>0.9</td>
<td>3.2</td>
</tr>
<tr>
<td>NP-Pes-Surf</td>
<td>10.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NP-Pes</td>
<td>1.3</td>
<td>0.35</td>
<td>2.7</td>
</tr>
<tr>
<td>NP-Pes/Pa</td>
<td>4.3</td>
<td>1.6</td>
<td>10.2</td>
</tr>
<tr>
<td>AgKilBact</td>
<td>377</td>
<td>99</td>
<td>184</td>
</tr>
</tbody>
</table>

The total released Ag varied from 1.3 to 35% by mass of the total Ag in the fabric and the amount of Ag released per gram of textile varied about a factor of 300 between the different textiles and in general the textiles with Ag incorporated into the fiber matrix released only very small amounts of Ag. For all the fabrics used the Ag release decreased in the second wash. Particle analysis showed that the most significant particle size fraction in most of the samples was >450 nm as this fraction made up for from 75 to 100% of the silver release by particle.
4.2.11 Lin et al. (2009)

Lin et al. (2009)\textsuperscript{113} measured the average (mass) cumulative fraction of secondary inorganic aerosols ($\text{SO}_4^{2-}+\text{NO}_3^{-}+\text{NH}_4^{+}$) in PM$_{0.01-0.056}$ or PM$_{0.01-0.1}$ in roadside samples and in rural samples. The fraction of secondary inorganic aerosols was found to be three to four times higher in roadside samples. At both sites, evidence was found of NO$_3^{-}$/SO$_4^{2-}$ deposition in the nanoparticle fraction.

4.2.12 Wang et al. (2010)

Wang et al. (2010)\textsuperscript{114} investigated particle number concentration and size distribution of ultrafine particles (UFPs) at Montelibretti station, near Rome during October and November 2007. Measurements were made using SMPS. They then evaluated aerosol size distribution from 4 to 70 nm using scanning mobility particle size with a high resolution Nano Differential Mobility Analyzer (nanoDMA). They measured a daily average particle total number concentration of 19,000 cm$^{-3}$. They found concentrations on workdays to be 1.3 time higher than those on weekends.

Cluster analysis and factor analysis were used to analyze the correlation of different diameter particle fractions with related gaseous pollutants and meteorological parameters using an hourly data set. The analysis suggested that the $N_{30-50}$ (number concentration of particles with diameter between 30 and 50 nm) and the $N_{50-70}$ closely correlated to NOx and relative humidity, while the $N_{4-10}$, $N_{10-30}$ and $N_{4-70}$ consort with solar radiation, temperature and wind speed.

4.2.13 Kim et al. (2010)

Kim et al (2010)\textsuperscript{115} identified nanosized silver sulfide ($\alpha$- Ag$_2$S) particles in the final stage sewage sludge materials of a full-scale municipal wastewater treatment plant using analytical high-resolution transmission electron microscopy. Ag$_2$S nanocrystals were found to be in the size range of 5-20 nm with ellipsoidal shape, forming very small, loosely packed aggregates. Some of the Ag$_2$S nanoparticles were found to have excess S on the surface of the sulfide minerals under S-rich environments, resulting in a ratio of Ag to S close to 1. The study suggests that in a reduced, S-rich environment, such as the sedimentation processes during wastewater treatment, nanosized silver

\textsuperscript{113} Lin CC, Huang KL, Chen SC, Tsai JH, Lind YC, Lin WY (2009) NH$_4^{+}$, NO$_3^{-}$, and SO$_4^{2-}$ in roadside and rural size-resolved particles and transformation of NO$_2$/SO$_2$ to nanoparticle-bound NO$_3^{-}$/SO$_4^{2-}$, Atmospheric Environment 43: 2731-2736


sulfides are being formed. The study highlights the role of wastewater treatment processes on the transformation of nano-Ag and ionic Ag potentially released from them.

4.2.14 Farré et al. (2010)

Farré et al. (2010) investigated the release of fullerenes into the environment from wastewater treatment plants. Using ultrasonication extraction from suspended solids in wastewater and liquid chromatography (LC) coupled to a hybrid triple-quadrupole linear ion-trap mass spectrometer, Farré et al. (2010) reported the results of the determination of C60, C70, and functionalised C60 fullerenes in effluents of 22 wastewater treatment plants in Catalonia, Spain. In half of the cases fullerenes were detected, thereof some in the μg/L range e.g. a maximum C60 concentration of 19 μg/L. The upstream source of the fullerenes was not identified in the study.

4.2.15 Benn et al. (2010)

Benn et al. (2010) used ICP–OES to quantify (i) silver in 10 consumer products (shirt, medical mask and cloth, toothpaste, shampoo, detergent, towel, toy teddy bear, and two humidifiers) and (ii) the release of this silver into tap water, airborne water droplets, and simulated landfill leachate. Silver concentrations in the products ranged from 1.4 to 270,000 μg Ag g per product. Potential release of silver during wash in tap water showed that silver was released in quantities up to 45 μg Ag g per product. SEM/EDX and filtration techniques were used to investigate the form, shape, and size of the silver. Size fractions were both larger and smaller than 100 nm. SEM confirmed the presence of nanoparticle silver in most products as well as in the wash water samples (Benn et al. 2010).

4.2.16 Kaegi et al. (2010)

In a study similar to Kaegi et al. (2008), Kaegi et al. (2010) investigate the release of metallic silver nanoparticles from paints used for outdoor applications. A facade panel painted with nano-Ag containing paint was mounted on a model house was exposed to ambient weather conditions over a period of one year and a total of 65 runoffs events. The average silver concentration in the wet paint

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was 6.2 mg/kg (6.0-6.9, n = 6) whereas the amount of paint applied to the final rendering was 248 g/m² (wet basis) resulting in a calculated initial Ag concentration of 1.5 mg/m². The study did not attempt to determine the nano-specific concentration, nor did it look at particles numbers. A strong leaching of the nanosilver was observed during the initial runoff events with a maximum concentration of 145 m Ag/l. The Ag concentration in the runoff events strongly decreased during the first eight rain events and more than 80% by mass of the Ag released during the whole study was lost during the first eight rain events that occurred in the first two months. After half a year a plateau was reached indicating a total loss of Ag 0.5 mg/m and after a period of one year, more than 30% of the silver nanoparticles were released to the environment. The total amount of Ag released from the paint during one year of exposure determined as 0.5 mg/m² therefore corresponds to a loss of about 30% by mass of the initially applied Ag. Selected samples were prepared for electron microscopic analysis and using a combination of TEM and EDX, nanosilver particles were found to be mostly present as individual particles typically < 15 nm in size attached to the organic binder. Some aggregates were also observed consisting of up to several tens of nano-Ag particles.

4.2.17 NLP (2010)

The NPL (2010)\textsuperscript{119} measured particle size distributions by particle number counts in ambient air from 2007-9 at three sites in the UK: a rural site, an urban background site and a roadside site. Using a condensation particle counter (CPC), most measurements of total particle number concentrations for particles of 7 nm to several microns in diameter were found to be: 5,000-15,000 particles cm\(^{-3}\) at the rural site; 5,000-30,000 particles cm\(^{-3}\) at the urban site; and 20,000-60,000 particles cm\(^{-3}\) at the roadside site. They found a predominance of particles <0.1µm in diameter and a shift toward coarser particles going from roadside to urban background to rural, possible reflecting particle modification at distance from source and an increase in natural particles at the rural site. Corresponding information on mass concentrations is not available. Measurements with the SMPS were lower by factors of 1-5 (as a monthly average), however the techniques are not considered comparable.

4.2.18 Hays et al. (2010)

Hays et al. (2010)\textsuperscript{120} collected 24hr PM samples from July to August 2006, using a low-pressure impactor positioned 20m from an interstate highway in North Carolina with a traffic flow of 125,000


\textsuperscript{120} Hays MD, Cho SH, Baldauf R, Schauer JJ, Schafer M (2011) Particle size distribution of metal and non-metal elements n an urban near-highway environment, Atmospheric Environment 45:925-934
vehicles per day. The overall near-highway PM mass size distribution was trimodal with a major accumulation mode peak at 500-800 nm. They found that PM mass level correlated with daily traffic density. They measured PM$_{10}$ concentrations of $33 \pm 7.5 \mu g/m^3$, PM$_{2.5}$ concentrations of $29 \pm 6.8 \mu g/m^3$; and PM$_{0.1}$ concentrations of $1.4 \pm 0.3 \mu g/m^3$. The elemental composition of the impactor-collected PM was investigated using magnetic sector field inductively coupled plasma-mass spectroscopy (SF-ICP-MS) Hazardous metals were found to be concentrated in the PM$_{0.1}$ fraction.

4.2.19 Fernández-Camacho et al. (2010)

Fernández-Camacho et al. (2010)$^{121}$ measured concentrations of UFP in ambient air on a university campus in Huelva in south west Spain. They used an ultrafine condensation particle counter that detects particles larger than 2.5 nm and has a 50% counting efficiency for particles between 3 and 4nm and found concentrations of particles to be about 22,000 particles cm$^{-3}$. They identified vehicle exhaust and new particle formation due to photo-chemical activity as prominent processes contributing to UFP concentrations. The highest UFP concentrations were recorded from 11-17hr, under the sea breeze regime, when rates of secondary particle formation were greatest and it was estimated that approximately 80% of the particles were linked to sulphur dioxide emissions. The average overall contribution of secondary particles to total UFP was greater than 60%. Similar effects were reported in two other studies of areas affected by sea breezes.

4.2.20 Price et al. (2010)

Price et al. (2010)$^{122}$ investigated the heterogeneous and changing particle concentrations in urban air, in conjunction with gaining an understanding of the physicochemistry of the particles. They used a Dekati electrical low-pressure impactor to collect the particles and real-time data in a busy traffic corridor in Swansea, Wales, over a period of 10 nonconsecutive weeks. Particle concentrations in the street canyon were analyzed and particle physicochemistries investigated using a variety of techniques. Particle number concentrations were found to vary both diurnally and from day to day in the traffic corridor. Of all particles, the nano to fine size fraction was consistently identified in the highest concentrations (maximum: 140,000 particles cm$^{-3}$). Particle physicochemistry was found to

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vary as a function of size, with larger particles exhibiting a greater variety of morphologies (and consequently particle types) and associated metals.

4.2.21 Kaegi et al. (2011)

Kaegi et al. (2011) investigated the behaviour of metallic silver nanoparticles (Ag-NP) in a pilot wastewater treatment plant (WWTP) fed with municipal wastewater. The treatment plant consisted of a nonaerated and an aerated tank and a secondary clarifier and nanosilver were spiked into the nonaerated tank and samples were collected from the aerated tank and from the effluent. The average hydraulic retention time including the secondary clarifier was 1 day and the sludge age was 14 days. ICP-MS were used to determined Ag concentrations whereas TEM analyses confirmed that nanoscale Ag particles were sorbed to wastewater biosolids, both in the sludge and in the effluent. X-ray absorption spectroscopy (XAS) measurements indicated that most Ag in the sludge and in the effluent was present as Ag₂S.

4.2.22 Westerhoff et al. (2011)

Westerhoff et al. (2011) measured titanium concentrations in the raw sewage and treated effluent of ten representative WWTPs that use a range of unit processes. Raw sewage titanium concentrations ranged from 181 to 1233 µg L⁻¹ (median of 26 samples was 321 µg L⁻¹). The WWTPs were found to remove more than 96wt% of the influent titanium, and all WWTPs had effluent titanium concentrations of less than 25 µg L⁻¹. To characterize the morphology and presence of titanium oxide nanoparticles in the effluent, colloidal materials were isolated via rota-evaporation, dialysis and lyophilization. High resolution transmission electron microscopy and energy dispersive X-ray analysis indicated the presence of spherical titanium oxide nanoparticles (crystalline and amorphous) on the order of 4 to 30 nm in diameter in WWTP effluents.

4.2.23 Lonati et al. (2011)

Lonati et al. (2011) measured aerosol number concentration and size distributions in the 10–20,000 nm size range using a Differential Mobility Particle Sizer (DMPS) and an Optical Particle Counter

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(OPC) at an urban background site. Daily patterns of the total particle, ultrafine (UFP, $D_p < 100$ nm) and submicron ($100 < D_p < 1000$ nm) fine particle concentration were analysed both on seasonal (cold and warm season) and weekly (weekdays and weekends) basis. Total particle number concentrations are in the orders of $10^4$ cm$^{-3}$, with UFPs and submicron particles accounting for 80% and 20% of particles numbers respectively; the contribution of supermicron particles to total particle number was found to be negligible.

Aitken mode particles were found to increase simultaneously with primary traffic emissions, peaking on the morning rush hour and dominating the number size distributions during the afternoon and during the evening rush hour. The smaller accumulation mode particles are influenced by the condensation and coagulation processes induced by the daily patterns of the boundary layer and of ambient temperature, becoming more and more important from the evening rush hour throughout the night and providing the largest contribution to total particle number late at night.
Johnson et al. (2011) measured particulate (≥450 nm) and colloidal silver (2-450 nm) in the influents and effluents of nine separate sewage treatment plants and found that the mean effluent concentration of colloidal (including nano) silver was 6 ng/L whereas total particulate silver 78 ng/L. Overall silver removal in the sewage plants was 97% by mass, as larger particulate forms are in the majority, but colloidal silver removal was only 49% by mass. Effluent data was subsequently used to predict the silver concentrations throughout every reach of the rivers of England and Wales (21,452 km of river length) using the Low Flows 2000 (LF2000) WQX (Water Quality eXtension) water quality model assuming that the results from the nine sewage treatment plants could be taken as representative for all UK sewage treatment plants. LF2000-WQX is a decision support tool according to Johnson et al. (2011) and the model is designed to estimate river flow at gauged and ungauged sites and to assist regional water resources and catchment management. By combining hydrological models with water-quality models, the model makes predictions on the concentration of a given chemical originating from a point source, such as STPs. Effluent data was converted to a per capita effluent loading for total and colloidal silver and water concentrations were subsequently predicted on the basis of dilution under mean and 90%ile conditions. For the colloidal fraction, predicted concentrations in rivers were typically in the 0-3 ng/L range whereas the predicted mean concentrations for the larger particulate forms (>450 nm) were in the tens of ng/L and in 6% of locations exceeded the 50 ng/L.

4.2.25 Walser et al. (2012)

Walser et al. (2012) investigated the fate of nanomaterials during incineration and showed that cerium oxide nanoparticles introduced into a full-scale waste incineration plant bind loosely to solid residues from the combustion process and can be efficiently removed from flue gas using current filter technology. The nanoparticles were introduced either directly onto the waste before incineration or into the gas stream exiting the furnace of an incinerator that processes 200,000 tonnes of waste per year. Nanoparticles that attached to the surface of the solid residues did not become a fixed part of the residues and did not demonstrate any physical or chemical changes. The 10 kg nano-CeO$_2$ (case 1) and 1 kg nano-CeO$_2$ (case 2) that had been introduced to the process were mainly transferred to the slag (53wt%), fly ash (45wt%) and the quench water (1.7wt%). Along the cleaning steps, cerium mass decreased by orders of magnitude.

Their observations show that although it is possible to incinerate waste without releasing nanoparticles into the atmosphere, the residues to which they bind eventually end up in landfills or recovered raw materials, confirming that there is a clear environmental need to develop degradable nanoparticles. Uncertainties were generated through measurement uncertainty, heterogeneity of the samples and residue flow variability.

4.2.26 Kiser et al. (2012)

Building on their 2009 study and again through field-scale investigation at a municipal WWTP, Kiser et al. (2012) evaluated the use of a United States Environmental Protection Agency (USEPA) standard method (OPPTS 835.1110) for estimating soluble pollutant removal during wastewater treatment using freeze-dried, heat-treated activated sludge (FDH AS) that has been recently proposed for predicting NM fate in WWTPs. This study evaluated the use of FDH AS in batch experiments for quantifying NM removal from wastewater. While soluble pollutants sorbed equally to fresh and FDH AS, fullerene, silver, gold, and polystyrene nanoparticles’ removals with FDH AS were found to be approximately 60–100% by particle less than their removals with fresh AS. Unlike fresh AS, FDH AS had a high concentration of proteins and other soluble organics in the liquid phase, an indication of bacterial membrane disintegration due to freeze-drying and heat exposure. This cellular matter...
stabilized nanomaterials such that they were poorly removed by FDH AS. Therefore, FDH AS is not considered a suitable sorbent for estimating nanoparticle removal in WWTPs, whereas fresh AS has been shown to reasonably predict full-scale performance for titanium removal. The study indicates that natural or engineered processes (e.g., anaerobic digestion, biosolids decomposition in soils) that result in cellular degradation and matrices rich in surfactant-like materials (natural organic matter, proteins, phospholipids, etc.) may transform the surfaces of NM and significantly alter their fate in the environment.

4.2.27 Du et al. (2012)

Du et al. (2012) measured aerosol number size distributions between 10 nm and 10 μm in Shanghai, China. In situ measurements were conducted continuously on the roof of a 6-storey teaching building about 20 m above the ground within the campus of Fudan University from October 2008 to February 2009. The sampling site is located in an urban district with potential pollution sources including residential and traffic emissions. Du et al. used particle size-segregated monitoring to provide a quantitative measure of ambient aerosol number concentration in individual size stage and total particle size distribution. A set of Wide-range Particle Spectrometer (WPSTM, model 1000XP, MSP Corporation, USA) was used to measure the number size distribution of aerosols in diameter from 10 nm to 10 μm. The WPS consists of a high-resolution Differential Mobility Analyzer (DMA), a CPC and a wide-angle Laser Particle Spectrometer (LPS).

The averages of particle number, surface and volume concentrations were $1.3 \times 10^4$ cm$^{-3}$, $6.4 \times 10^2$ μm$^2$cm$^{-3}$ and $64$ μm$^3$cm$^{-3}$, respectively. Aitken particles prevailed in total particle number, and accumulation particles were the largest contributor to particle surface area. Particle size spectra were characterized successfully by integrating multi-lognormal functions, three-mode for number size distribution and two-mode for surface and volume size distributions. The average number size distributions of aerosols revealed a clear diurnal pattern of two peaks within 30–60 nm corresponding to the morning and afternoon traffic rush hours. All size particles demonstrated two peaks in mean number concentrations during the traffic rush times, and 10–20 nm and 20–50 nm particles demonstrated one additional peak in late morning.

4.2.28 Yang et al. (2012)

With a focus on occupational health and safety aspects rather than environmental exposure, Yang et al. (2012) measured nanoparticle number concentration distributions in samples taken from the pulverisation workshop of a plant manufacturing nano-sized titanium dioxide powder (nano-TiO$_2$). They found that aerosol nanoparticles were dispersed mainly out of the discharge port outlet of the jet mill by the compressed air. The discharge port, which was at a height of one meter above the ground, was therefore regarded as the source of aerosol nanoparticles. To suppress the influence of airflow and reduce uncertainties, all workplace windows and doors were closed during the sampling. Samplers were located at various distances from the discharge port and at various heights above the ground. Background tests were performed each morning before the working day began, and background corrections of the concentrations were carried out based on the referenced background data. To minimize experimental errors, each measurement was performed for 5 min at every sampling location.

In terms of analytical methods, a wide-range particle spectrometer (WPS 1000XP-A, MSP corp., USA) with a sampling flow rate of 1.0 L/min was employed to characterize the nano-TiO$_2$ nanoparticle number concentration in the workplace. N-butyl alcohol (butanol) was used as the working solvent for the condensation particle counter (CPC) in the instrument. The microstructure of the nano-TiO$_2$ was characterised using field emission scanning electron microscopy (FESEM, UltraPLus, Carl Zeiss, German). The commercial software ImageJ was used to measure the particle diameters from the FESEM images. A micrograph image of nano-TiO$_2$ is shown in figure 4 below.

**Figure 4: FESEM micrograph of nano-TiO$_2$ product**

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Yang et al. found that aerosol nanoparticles suspended in the air were mainly in the form of agglomerated particles, with average diameters of 124.2 nm for primary particles and 524.4 nm for agglomerations. The number concentration of aerosol particles increased with vertical distance from the source, but decreased with horizontal distance from the source. The concentration was highly affected by the dispersive forces of the discharging port, and the suspension and the agglomeration of particles. Fig. 3 shows the particle number concentrations for aerosols sampled at a fixed height of 1.0 m, at distances ranging from 1 to 5 m. All of the curves in Figure 5 exhibited the typical distribution of the nano-TiO$_2$ aerosol in the workplace. The inset in Figure 5 shows an enlargement of the size distribution of particles in the diameter range 0–200 nm.

Yang et al. went on to design and install an aerosol enclosure (dimensions: 2 m length × 1.5 m width × 2 m height) to control the suspension of aerosol nanoparticles, and to reduce their concentration in the workplace. The aerosol enclosure covered the discharging port in all directions, with the exception of one door that was used for the entrance and exit of the operating person. When the door was closed, the space within the enclosure became sealed. With the aerosol enclosure, most of the aerosol particles were limited to the space within the enclosure, rather than dispersing throughout the whole workplace. **Figure 5: Aerosol number concentration distributions, measured at a height of 1.0 m**
4.3 Extrapolation from laboratory measurements

Experimental studies have simulated various exposure scenarios in the laboratory in order to then apply analytical methods to measuring releases. For example, Hsu and Che (2007) stimulate releases of nano-titanium dioxide from coatings and both Geranio et al (2009) and Benn and Westerhoff (2008) investigated releases of nano-silver during washing.

In terms of study limitations, it can be argued that laboratory simulations do not represent the real operational conditions at building sites. However, such studies can be used to confirm release, generates a preliminary quantification of their concentrations and test analytical method for measurements. Release rates estimated through laboratory studies therefore offer a complimentary route to derive possible exposure to NM. Relevant studies are discussed in ascending chronological order below.

4.3.1 Hsu and Chein (2007)

Hsu and Chein (2007)\textsuperscript{131} evaluated TiO\textsubscript{2} nanoparticle emission from coated substrates including wood, polymer, and tile in a simulation box and measured with a SMPS. UV light, a fan, and a rubber knife were used to simulate the sunlight, wind, and human contacting conditions. Tile coated with 5 wt\%/T TiO\textsubscript{2} nanopowder was found to have the highest particle emission (22 #/cm\textsuperscript{3} at 55 nm) and UV light was shown to increase the release of particle below 200 nm from TiO\textsubscript{2} nanopowder coating materials. The results show that, under the conditions of UV lamps, a fan and scraping motion, particle number concentration or average emission rate decreases significantly after 60 and 90 min for TiO\textsubscript{2}/polymer and TiO\textsubscript{2}/wood, respectively. However, the emission rate continued to increase after 2 h of testing for TiO\textsubscript{2}/tile.

4.3.2 Park et al. (2008)

Park et al. (2008) completed a hazard and risk assessment of a nanoparticulate cerium oxide-based diesel fuel additive known as Envirox. Envirox is diluted with diesel to extend and improve fuel burn yielding a final concentration of CeO$_2$ in the diesel fuel of 5 mg/L. Park et al. (2008) estimated the ambient level of cerium by the use of modeling studies and drawing on historical data on atmospheric monitoring before and after Envirox was introduced into the diesel fuel used in buses in London and Newcastle in 2003 and 2005, respectively. A significant fourfold increase from 0.145 ± 0.064 to 0.612 ± 0.287 ng/m$^3$ was observed in the cerium concentrations in the ambient air in Newcastle following the introduction of Envirox whereas no increase was observed in the samples taken from London. The lack of increase observed in London might be reflected in the low percentage of buses using Envirox passing the sites in London where the samples were taken. Using various models, Park et al. (2008) also calculated the cerium emissions to the atmosphere for all EU Member States up to year 2020 for a baseline- and a diesel particulate trap application scenario under various best- and worst-case conditions – assuming a 5 ppm concentration of cerium oxide in the diesel fuel and that newly registered passenger cars, light- and heavy duty vehicles will be equipped with a filter operated on Envirox. Park et al. (2008) found that using traps to retain cerium emissions in conjunction with Envirox would reduce car emissions by more than 70%, buses by 85%, and heavy trucks by almost 90% by 2020 taking 1990 as a baseline. The introduction of traps will reduce particular matter by more than 70,000 tons per year whereas 75 tons of cerium would be emitted to the atmosphere. In the worst-case, assuming that all diesel fuel is doped with cerium and fully emitted to the atmosphere < 1255 tons would be emitted. The urban population of the EU will be exposed to about 0.2 g cerium oxide per year whereas the rural areas and the average emissions along the highways would be about 6.6 g and 0.3 kg cerium oxide per square kilometre per year. Park et al. (2008) also modelled the possible soil contamination along a typical highway assuming that all cerium oxide emissions would accumulate over a 40-year period and they found that estimated concentrations vary between 0.28 and 1.12 µg/g, depending on the soil depth at a distance from the edge of the highway.

4.3.3 Benn and Westerhoff (2008)

Benn and Westerhoff (2008) investigated silver content and release from six types of socks during wash and modelled the subsequent fate of silver in wastewater treatment plants (WWTPs). Socks were found to contain up to a maximum of 1,360 μg-Ag/g-sock and leached between 1.5 and 650 μg of silver in 500 mL of distilled water. One type of socks were found to leach a total of 1,245 and 1,020 μg after three washes during 24 hour and 1 hour washes, respectively whereas other types of socks only released only small percentages (<1% by mass) despite containing relatively large amounts of silver (31,242 and 2,105 μg, respectively). Scanning and transmission electron microscopy revealed the presence of silver particles from 10 to 500 nm in diameter and physical separation and ion selective electrode (ISE) analyses suggest the presence of both colloidal and ion silver leaching from the socks. Adsorption of the leached silver to WWTP biomass was used to develop a model which predicts that a typical wastewater treatment facility ability to cope with a high concentration of influent silver. Based on adsorption data from isotherm experiments using two wastewater biomass preparations from a full-scale WWTP and a laboratory-scale bioreactor, Benn and Westerhoff (2008) estimated the performance of a WWTP expressing the steady-state mass balance of a WWTP with nonlinear sorption of an adsorbate as:

\[ C = C_0 - \left( \frac{X_\tau KC^{1/n}}{\theta} \right) \]

where \( C \) is the effluent concentration of silver, \( C_0 \) is the influent silver concentration, \( K \) and \( 1/n \) are the Freundlich adsorption parameters, and \( X, \tau, \) and \( \theta \) are operational parameters of a WWTP (mixed liquor suspended solids (MLSS), hydraulic and solids retention time, respectively). Common values used for these model parameters are 2000 mg/L, 720 min and 7200 min.

Using a common municipal WWTP influent silver concentration of 5 μg/L, the model results in an effluent silver concentration of 0.01 μg/L and the wasted biosolids silver concentration is 2.8 mg-Ag/kg-biosolids.

Varying parameters such as mixed liquor suspended solids, hydraulic and solids retention time and using a Criteria Maximum Concentration of 1.9 ppb salt water as maximum allowable effluent concentration, it was found that a MLSS concentration of 2000 mg/L with a ratio between \( \theta:\tau \) of 20 would treat an influent silver concentration of 1460 μg/L. Similarly, a MLSS concentration of 4000

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mg/L with an $\theta:\tau$ ratio of 5 would treat an influent silver concentration of 11 600 μg/L. The model furthermore suggests at an influent silver concentration of 180 μg/L, the silver concentration in the biosolids would exceed the 5 mg/L Toxicity Characteristic Leaching Procedure (TCLP) by the USEPA.

4.3.4 Kobayashi et al. (2009)

In a study focused primarily on occupational exposure, Kobayashi et al. (2009) estimated exposure to CNT-containing dust during general waste treatment of CNT-containing products such as electric double-layer capacitor, lithium-ion battery, a conductive plastic, and CNT-reinforced plastic. The concentration of CNT was estimated to be 1.05 ppm in the total quantity of waste (10.2 tons CNTs in 9.7 million tons of waste). Within a crushing facility a dust concentration of 2.0–6.0 mg/m3 was observed at four measurement points in a general waste treatment facility. The maximum air concentration of CNTs was estimated to be 0.0064 μg/m3. Particle number concentrations were not reported.

4.3.5 Farkas et al. (2011)

Farkas et al. (2011) investigated the effluent from a commercially available washing machine described as “provided with silver solution supply device” and advertised to kill 99.9999% of the bacteria in the laundry. ICP-MS was used to analyze water and cotton samples for Ag concentration as well as to determine the number concentration of silver containing particles and obtain additional information about size single particle. Ion selective electrode (ISE) measurements and ultra-filtration were applied to determine whether the released Ag was in nanoparticulate or in ionic (Ag+) form.

A large variation in Ag concentration was observed between independent effluent samples with measured concentrations between 2.7 μg L$^{-1}$ and 25 μg L$^{-1}$. The average (n=10) effluent concentration was 10.9 (±7.1) μg L$^{-1}$. Water samples from washes containing cotton fabric and detergent were within the same concentration range as the pure water samples. Effluent from washes performed without the silver function activated, contained a mean Ag concentration of 3.1±1.5 μg L$^{-1}$ Ag (n=3) whereas the cotton T-shirts contained between 0.67 and 4.74 μg g$^{-1}$ Ag. Control T-shirts washed without the

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nanosilver function on or from the conventional washing machine contained 0.06 μg g$^{-1}$ and 0.007 μg g$^{-1}$ of Ag respectively. The presence of nAg in the control T-shirts shows that the deactivation of the silver wash function did not completely prevent release of silver release during wash. Ag$^{+}$ concentration in the washing water samples was below the detection limit of the ISE of 10 μg L$^{-1}$ and was found to give similar values (213.9±1.7 mV) compared to control water samples (213.6±4.5 mV). Less than 2 wt% (0.1 μg L$^{-1}$ of 5.1 μg L$^{-1}$) of the silver present in the effluent samples was found to pass through a 1.5 nm filter.

The majority of silver nanoparticles in the samples seem to be below 20 nm in size; however there are indications of the presence of a small amount of considerably larger particles in the sample. The average particle size in the effluent was about 10 nm measured with transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) and the particles were observed to be generally round with some having a more irregularly formed appearance.

For the whole of Norway, Farkas et al. estimate that the amount of Ag being released would increase to 98.5 kg per year at an average water consumption of 25 L per person per day for laundry if 20% of the Norwegian population would purchase a nanosilver producing washing machine that releases on average 11 μg L$^{-1}$ of Ag. It is currently unclear how much of this Ag would be retain in the STP, but as about 82% of the sewage sludge in Norway is used for agricultural purposes or otherwise applied to soil, Farkas et al. (2011) estimate that an additional 80.8 kg of silver would be applied to Norwegian soils per year.

### 4.3.6 Kaegi et al. (2011)

Kaegi et al. (2011)$^{136}$ investigated the behaviour of metallic silver nanoparticles (Ag-NP) in a pilot WWTP fed with municipal wastewater. The treatment plant consisted of a nonaerated and an aerated tank and a secondary clarifier and nanosilver were spiked into the nonaerated tank and samples were collected from the aerated tank and from the effluent. The average hydraulic retention time including the secondary clarifier was 1 day and the sludge age was 14 days. Inductively coupled plasma-mass spectrometry (ICP-MS) were used to determined Ag concentrations whereas TEM analyses confirmed that nanoscale Ag particles were sorbed to wastewater biosolids, both in the sludge and in the effluent. XAS measurements indicated that most Ag in the sludge and in the effluent was present as Ag$_2$S.

4.3.7 Kumar et al. (2012)

Kumar et al. (2012) investigated the release of particles in the 5–560 nm range from three simulated building activities: the crushing of concrete cubes, the demolition of old concrete slabs, and the recycling of concrete debris. A fast response differential mobility spectrometer (Cambustion DMS50) was used to measure particle number concentrations and particle size distributions at a sampling frequency of 10 Hz in a confined laboratory room providing controlled environment and near–steady background particle number concentrations. The sampling point was intentionally kept close to the test samples so that the release of new UFPs during these simulated processes can be quantified.

Tri–modal particle size distributions were recorded for all cases, demonstrating different peak diameters in fresh nuclei (<10 nm), nucleation (10–30 nm) and accumulation (30–300 nm) modes for individual activities. The measured background size distributions showed modal peaks at about 13 and 49 nm with average background particle number concentrations ~1.47x10^4 cm. These background modal peaks shifted towards the larger sizes during the work periods (i.e. actual experiments) and the total particle number concentrations increased between 2 and 17 times over the background particle number concentrations for different activities. After adjusting for background concentrations, the net release of particle number concentrations during cube crushing, slab demolition, and “dry” and “wet” recycling events were measured as ~0.77, 19.1, 22.7 and 1.76 (×10^4) cm, respectively. The particle size distributions were converted into particle mass concentrations. While majority of new particle number concentrations release was below 100 nm (i.e. UFPs), the bulk of new particle mass concentrations emissions were constituted by the particles over 100 nm; ~95, 79, 73 and 90% of total particle number concentrations, and ~71, 92, 93 and 91% of total particle mass concentrations, for cube crushing, slab demolition, dry recycling and wet recycling, respectively.

4.3.8 Kim et al. (2012)

Kim et al. (2012) conducted two field-scale investigations to describe how TiO_2 nano- and larger particles enter into the environment via the application of biosolids to soils. Firstly, they analyzed samples of three sewage sludge products from the US EPA TNSSS sampling inventory for the occurrence, qualitative abundance, and nature of TiO_2 nano- and larger particles using analytical scanning electron microscopy and analytical (scanning) transmission electron microscopy. Nano- and larger particles of TiO_2 were repeatedly identified across the sewage sludge types tested, providing
strong evidence of their likely concentration in sewage sludge products. The TiO₂ particles identified were as small as 40 nm, and as large as 300 nm, having faceted shapes with the rutile crystal structure, and they typically formed small, loosely packed aggregates.

Secondly, they examined surface soils in mesocosms that had been amended with nano-Ag spiked biosolids for the occurrence of TiO₂ particles. An aggregate of nano-TiO₂ with the rutile structure was again identified, but this time nano-TiO₂ were found to contain Ag on their surfaces. This suggests that nano-TiO₂ from biosolids can interact with toxic trace metals that would then enter the environment as a soil amendment.

4.3.9 Lowry et al. (2012)

Lowry et al (2012) used freshwater mesocosms to simulate an emergent wetland environment and determine the long-term behaviour of poly(vinylpyrrolidone)-coated silver nanoparticles (nanoAg). NanoAg were either applied to the water column or to the terrestrial soils. The distribution of silver among water, solids, and biota, and Ag speciation in soils and sediment was determined 18 months after dosing. Most (70wt%) of the added Ag resided in the soils and sediments, and largely remained in the compartment in which they were dosed. However, some movement between soil and sediment was observed. Movement of nanoAg from terrestrial soils to sediments was more facile than from sediments to soils, suggesting that erosion and runoff is a potential pathway for nanoAg to enter waterways. The nanoAg in terrestrial soils were transformed to Ag₂S (~52wt%), whereas nanoAg in the subaquatic sediment were present as Ag₂S (55wt%) and Ag-sulphydryl compounds (27wt%). Despite significant sulfidation of the nanoAg, a fraction of the added Ag resided in the terrestrial plant biomass (~3wt% for the terrestrially dosed mesocosm), and relatively high body burdens of Ag (0.5–3.3 μg Ag/g wet weight) were found in mosquito fish and chironomids in both mesocosms. Thus, Ag from the nanoAg remained bioavailable even after partial sulfidation and when water column total Ag concentrations are low (<0.002 mg/L).

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4.4 Material mass flow analysis and simply modelling approaches

Given the lack of efficient, cost-effective analytical methods for monitoring the presence of nanomaterials in environmental media, estimates of occurrence in the environment have been based on other sources of information, namely the usage of nanomaterials in commercial products and modelling estimates of exposure over the life cycle of those products\textsuperscript{140}. Modelling methods have been used to make various estimates both for individual products, nanomaterials and applications as well as product types. Many of these have been able to apply fairly simple mathematical equations to estimate the current and future exposure. These studies are summarised below in ascending chronological order.

4.4.1 Blaser et al. (2008)

Blaser et al. (2008)\textsuperscript{141} estimated the silver emission into wastewater in Switzerland by multiplying the amount of silver in biocidal plastics and textiles with the release rate of silver ions from these products and the period the products are in contact with water. Assuming that the removal in the sewage treatment plant was assumed to range between 99-85wt\%, Blaser et al. (2008) found that the predicted environmental concentration (PEC) for the sewage treatment plant would be 18 $\mu$g/L, whereas PEC\textsubscript{water} and PEC\textsubscript{sediment} for the Rhine river stretch in Switzerland would be 320 ng/L and 14 mg/kg, respectively.

4.4.2 Boxall et al. (2008)

Based on available information about the applied concentration of nanoparticles in cosmetics, personal care products and paints, Boxall et al. (2008)\textsuperscript{142} used a long series of algorithms (for among other pesticides, medicinal products, and ultrafine particles) to estimate the predicted environmental concentrations of nanoparticles in soil and water. Although anticipating that 10% market penetration probably provides a conservative estimate (with the exception of sunscreens), Boxall et al. calculated the PEC for three scenarios assuming that 10%, 50% and 100% of the products on the market contained nanoparticles. The highest total predicted concentrations in water was found to be for latex product types.


nanoparticles (103-1025 μg/L) stemming from laundry detergents followed by zinc oxide (76.0-760 μg/L) and titanium oxide (24.5-245 μg/L) used in among others paints and sunscreens. The use of hydroxyapatite in toothpaste and fullerene in cosmetics is estimated to lead to an environmental concentration of between 10.1-101 and 0.31-3.13 μg/L, respectively. Predicted concentrations in soil range from 4.3-43 mg/kg for nanolatex to <0.01 mg/kg for CeO2.

Similar to Park et al. (2008), but ignoring that traps might capture much of the particulate emission, Boxall et al. (2008) also estimated the emission of cerium oxide in vehicle exhausts. Assuming that using cerium oxide as an additive in all diesel fuel at 10 ppm would lead to an emission rate of 10 ppm from diesel fuel vehicles, Boxall et al. found an emission of 0.0010 g/km for the passage of 1000 vehicles. The cerium oxide concentration at 50 m from the road would be 0.0002 μg/m³, whereas it would be three fold higher at 5 m. The annual emission of cerium oxide from all vehicles in the UK was estimated to be 161 kg based on the estimated vehicle emission rates and the total annual mileage for vehicles. Boxall et al. (2008) estimated the cerium oxide concentration in soil to be < 0.01 μg/kg.

4.4.3 Luoma (2008)

Luoma (2008) estimated mass release of silver from silver socks, silver wash machines and swimming pools assuming that 10 and 30% of the population in the U.S. use silver, that households that are wealthy enough will buy silver wash machines and that 1 million pools use silver as a biocide. Silver discharges from silver socks in the two scenarios were estimated to be in the range of 6-930 kg and 180-2790 kg respectively depending on the silver contents in the socks, whereas the contribution from silver wash machines was found to be 2850 kg. The contribution from the swimming pools was by far the largest found; it was estimated to be 30 tons. In another scenario, Luoma estimated the total future discharges to be 457 tons assuming that there will be 100, 10, and 5 products in the future that resemble the silver discharged from the socks, wash machines and the swimming pools, respectively. After waste treatment this could be reduced to 128 tonnes, provided that 80% of the discharges are treated sufficiently to remove 90% by mass of the silver.

4.4.4 Mueller and Nowack (2008)

Mueller and Nowack (2008)\textsuperscript{144} modelled the predicted environmental concentration for nano-Ag, nano-TiO\textsubscript{2} and CNTs for air, water and soil in Switzerland. The calculations by Mueller and Nowack (2008) were based on a quantitative substance flow analysis of how nanoparticles from various products categories such as textiles, cosmetics, coatings, plastics, sports gear, electronics, etc. enter the environment through abrasion, outlet from the sewage treatment plants and/or waste incineration plants and landfills. Given the lack of information, numerous assumptions and estimates had to be made about worldwide production volumes, concentration of the nanoparticles in the products, levels of incombustible nanoparticles and behaviour during wastewater treatment. For CNT, for example, it is estimated to be realistic that the worldwide production in 2007/2008 is 350 tons and that these are evenly incorporated into plastics and electronics. For the CNT that end up in the waste incinerator, it is furthermore assumed that 50wt\% will be burned, 25wt\% will end in the slag and 25wt\% will become airborne. Of the fraction that becomes airborne, it is assumed that 99.9wt\% of this fraction will be caught in the filters of the waste incineration plant, leaving only 0.1wt\% of the airborne fraction to enter the atmosphere. In a high exposure scenario, Mueller and Nowack (2008) assumed a worldwide production of 500 tons annually, with only 25wt\% of the CNT that end up in the waste incinerators being burned. The unburnt CNT is divided between the slag and the flue gases, with 37.5wt\% of the total CNT going to waste incinerators. Furthermore, in the high exposure scenario, they assume that on 99wt\% of the airborne CNT are caught by the filters of the incineration plant, leaving 1wt\% of the airborne fraction to enter the atmosphere.

Boxall \textit{et al.} (2008) estimated PECs for ENM in cosmetics and personal care products, whereas the analysis of Muller and Nowack include textiles, metal products, cosmetics and other products. However, Muller and Nowack estimated PECs to be lower, although in the same order of magnitude, as Boxall \textit{et al.} for Ag in water and soil, and for TiO\textsubscript{2} in air. This was the case even for the high exposure scenario. In contrast, estimates differ by several orders of magnitude for TiO\textsubscript{2} in soil. Some of the differences between the PECs could be related to the fact that Boxall \textit{et al.} (2008) assumed that no nanoparticles would be retained in the sewage treatment plants, whereas Mueller and Nowack (2008) assumed that 97wt\% and 90wt\% of the nanoparticles would be cleared in the realistic and the high exposure scenario, respectively.

4.4.5 Shinohara et al. (2009)

Shinohara et al. (2009)\textsuperscript{145} estimated the fullerene exposure levels within 500 m of a factory manufacturing 40 tons of fullerenes per year. Under normal functioning of the emission system, estimated fullerene concentrations would be $5.51 \times 10^{-7}$ µg/m$^3$ for all particle sizes, and $2.2 \times 10^{-9}$ µg/m$^3$ for particles <1000 nm. Assuming a worst-case scenario of unfiltered emission released from the factory due to malfunction of the emission system, the atmospheric concentrations of fullerenes of all particle sizes (10–10,000 nm) would be 0.0018 µg/m$^3$.

4.4.6 Robichaud et al. (2009)

Robichaud et al (2009)\textsuperscript{146} estimate an upper bound for the magnitude of potential exposure to nano-TiO$_2$ based on available production data. They combined knowledge of the existing bulk TiO$_2$ market with available nano-TiO$_2$ production data to estimate current nano-TiO$_2$ sources as a baseline. They then project the evolution of nano-TiO$_2$ production as a percentage of the total TiO$_2$ market based on material and market information using a method that combines observations from scientific articles and patents as predictive indicators of the rate of innovative transformation. They go to estimate various scenarios for the upper bound of cumulative release of nano-TiO$_2$ to the environment by summing the production amounts over time, as the nanoscale share of the TiO$_2$ market grows. Resulting values are presented in figure 2 below and are based on the nano-TiO$_2$ production portion of the life cycle.

The authors do not estimate nanomaterial release from products into which they are incorporated over the product life cycle, but rather examine the effects of broad, very explicit assumptions regarding nanomaterial exposure potential. While acknowledging this limitation, the authors assert that before detailed assessments exist to predict release mechanisms and quantities from nano-TiO$_2$ enabled products, taking the total amount produced as the upper limit of potential exposure provides another method of estimating potential environmental load. Multiple scenarios under which less than that full amount would be released can then be considered as the potential environmental load of the material.


4.4.7 Whiteley et al. (2011)

Whiteley et al. (2011)\textsuperscript{147} estimated the potential quantities of nanoAg released into sludge and water in the UK based on Kaegi et al.'s (2010) estimate that more than 30wt% of the total nanoAg is released to the environment from painted facades and assuming that a) the UK use 5wt% of the global nanoAg production in industrial application and b) that removal efficiencies of waste water treatment is 90wt%, with the remaining 10wt% potentially being released into water and aquatic environments. Based on these assumptions, Whitely et al. (2011) estimated that in the UK in 2009, 13.1 tonnes of nanoAg entered the waste water system, with 11.8 tonnes of NanoAg ending up in sludge and 1.3 tonnes of nanoAg entering water.

Whiteley et al. stress the importance, as well as the complexity, of the environmental form that nanosilver takes in studying its behaviour in the environment, noting that the transformation and speciation of silver in the environment is important for analysis, assessment of toxicity, and

understanding fate and behaviour. In addition, in their conclusions, they note that exposure scenarios for nanoAg can only be comprehensive if information on product types and use becomes available.

4.4.8 Tiede et al. (2011)

Tiede et al. (2011)\textsuperscript{148} estimated the risk of exposure to engineered nanoparticles via drinking water in the UK. The authors used information on the occurrence and quantities of NM in products, release scenarios and fate and behaviour in aquatic systems to categorise NM. A simple exposure model was then used to estimate worst-case concentrations of NM in raw water and treated drinking water. In terms of limitations, the study identifies the lack of available data on product usage, NM concentrations within a product and market penetration, as well as particle fate and behaviour in the aquatic environment and water treatment processes. This meant that the authors were obliged to rely upon a number of assumptions and employ a conservative approach that assumes that all NM in a product end up in the aquatic environment. A range of metal, metal oxide and organic-based NM were identified that have the potential to contaminate drinking waters. Worst case predicted concentrations in drinking waters in the UK were in the low to sub-μg/l range and more realistic estimates were tens of ng/l or less. Relevant NM include Ag, Al, TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} and carbon based materials.

4.4.9 Johnson et al. (2011)

As mentioned above, Johnson et al. (2011)\textsuperscript{149} measured particulate (≥450 nm) and colloidal silver (2-450 nm) in the influents and effluents of nine separate sewage treatment plants and used the effluent data to predict the silver concentrations throughout every reach of the rivers of England and Wales using the Low Flows 2000 (LF2000) WQX (Water Quality eXtension) water quality model. By combining hydrological models with water-quality models, the model makes predictions on the concentration of a given chemical originating from a point source.

4.5 Probabilistic mass flow analysis

Probabilistic mass flow analysis treats all parameters in the model as distributions. Monte Carlo and Markov Chain Monte Carlo computer simulations are used to generate estimates of sediment and

\textsuperscript{148} Tiede K, Westerhoff P, Hansen SF, Fern GJ, Hankin SM, Aitkin RJ, Chaudry Q and Boxall ABA (2011) Review of the risks posed to drinking water by man-made nanoparticles, DWI 70/2/246, FERA, UK
\textsuperscript{149} Johnson et al. 2011. Centre for Ecology and Hydrology (CEH) “Exposure assessment for engineered silver nanoparticles throughout the rivers of England and Wales” (2011) CEH, UK
groundwater concentration as well as emissions from production, manufacturing and recycling processes. This work has been undertaken by Gottschalk et al. and published in three studies that are reviewed in turn below.

4.5.1 Gottschalk et al. (2009)

Using a probabilistic material flow analysis model (PMFA) based on a Monte Carlo and Markov Chain Monte Carlo (MCMC) approach, Gottschalk et al. (2009) calculated the predicted environmental concentrations as probabilistic density functions for nano-TiO2, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes for the U.S., Europe and Switzerland (see table below).

All parameters were created as probability distributions in the light of the scarcity of data and model outcome represents a nanomaterial flow system, depicted by probability (or density) distributions. Model input and output distributions were derived from Monte Carlo (MC) and/or Markov Chain Monte Carlo (MCMC) simulations. The material flow model itself consists of 11 boxes representing all life-cycle stages engineered nanomaterials totalling 35 internal, 11 accumulation, one nanomaterial generation (within the first process), 11 elimination, and five system-leaving flows. The environmental compartments (lower atmosphere, soil, surface water, and sediments) were regarded as homogeneous and equally mixed for estimating a regional PEC for the U.S., Europe and Switzerland. PEC for sludge treated soils, sewage treatment plant effluent and sludge were also calculated. For each region, the corresponding geographic boundaries were used as the spatial system boundary.

Gottschalk et al. found that the most frequent PEC values range from 0.003 ng L-1 (fullerenes) to 21 ng L-1 (nano-TiO2) for surface waters and from 4 ng L-1 (fullerenes) to 4 μgL-1 (nano-TiO2) for sewage treatment effluents. Most prominent flows differed from nanoparticle to nanoparticle. For CNTs, the most prominent flows were from production, manufacturing, consumption (PMC) to the waste incineration plant and to the landfill whereas it for nano-ZnO was flows from PMC to the sewage treatment plant and the application of sewage sludge to soil were the most important. For nano-TiO2 and Ag the sewage treatment plant influent, the application of sewage sludge to soil, and the flow from PMC to the landfill were by far the predominant flows and for fullerenes it was flows from products to landfill and sewage treatment plant and from sewage treatment plant to waste incineration plant and surface waters. As note by Gottschalk et al. (2009) the probabilistic material flow analysis model (PMFA) assumes homogeneous and well-mixed compartments on a country or

Gottschalk F, Sonderer T, Scholz RW, Nowack B (2009) Modelled environmental concentrations of engineered nanomaterials (TiO2, ZnO, Ag, CNT, fullerenes) for different regions. Environmental Science and Technology, 43, 9216-9222
continent-wide scale and further modelling is needed in order to cover local conditions such as, e.g., those near factories, near sewage treatment outflows, etc.

4.5.2 Gottschalk et al. (2010a)

Building on the work of Mueller and Nowack (2008), Gottschalk et al. (2010)\textsuperscript{151} included estimates of sediment and groundwater concentration as well as production, manufacturing and recycling processes and used a probabilistic material flow analysis model, treating all parameters as probability distributions in the light of the scarcity of data. As in Gottschalk et al. (2009) the material flow model itself consists of 11 boxes representing all life-cycle stages engineered nanomaterials totalling 35 internal, 11 accumulation, one nanomaterial generation (within the first process), 11 elimination, and five system-leaving flows. The environmental compartments (lower atmosphere, soil, surface water and sediments) were regarded as homogeneous and equally mixed for estimating a regional PEC for the whole of Switzerland. PEC for sludge treated soils, sewage treatment plant effluent and sludge were also calculated. Accumulation in technical environments (production, manufacturing, and consumption processes [PMC], recycling process [R], sewage treatment plant [STP], waste incineration plant [WIP]) was not considered for steady-state calculations and all data and calculations refer to the base year 2008.

Using Monte Carlo and Markov Chain Monte Carlo computer simulations as well as a sensitivity and uncertainty analysis, Gottschalk et al. (2010) found that surface water concentrations (TiO\textsubscript{2} 0.02 mg/L; CNT 0.003 ng/L; Ag 0.72 ng/L) differed substantially from concentrations in the sewage treatment plant effluent (TiO\textsubscript{2} 4.3 mg/L; CNT 11.8 ng/L; Ag 38.7 ng/L) and sewage treatment plant sludge (TiO\textsubscript{2} 211 mg/kg, CNT 0.069 mg/kg; Ag 1.88 mg/kg). High rates of sedimentation led to remarkable annual deposition in sediment (TiO\textsubscript{2} 499 mg/kg; CNT 0.229 mg/kg; Ag 1.2 mg/kg).

Model input parameters were comprised by the annual nanomaterial input into the system, the mass distribution of nanomaterial to product categories, and the transfer coefficients that determined the nanomaterial flows between (emissions) and inside of the compartments (elimination and accumulation) as well as into and out of the system. Number of model input parameters considered was 104, 69, and 106 for nano-TiO\textsubscript{2}, CNT, and nano-Ag, respectively. Triangular distributions were chosen for the input parameters when the most probable outcome was known (guessed or measured) and this mode was assumed to be bounded between two parameter values. Uniform distributions were

\textsuperscript{151}Gottschalk F, Sonderer T, Scholz RW, Nowack B (2010a) Possibilities and limitations of modelling environmental exposure to engineered nanomaterials by probabilistic Material flow analysis, Environmental Toxicology and Chemistry 29(5): 1036-1048
used for parameters that had not yet been well studied, such as some TCs between the environmental compartments, and log normal distributions were applied where the input values ranged theoretically from 0 to an unlimited value.

4.5.3 Gottschalk et al. (2010b)

Gottschalk et al. (2010b)\textsuperscript{152} present a probabilistic method to compute distributions of PECs by means of a stochastic stationary substance/material flow modelling. Model input parameters and variables consider production, application quantities and fate of the compounds in natural and technical environments. Combined sensitivity and uncertainty analysis, i.e. Monte Carlo simulation and Markov Chain Monte Carlo modelling was used to cope with 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 (e.g. level of compound production and application) themselves. PECs for nano-TiO\textsubscript{2} in Switzerland were derived in the form of probability density distributions (see figure 2).

\textsuperscript{152} Gottschalk F, Scholz RW, Nowack B, (2010b) Probabilistic material flow modelling for assessing the environmental exposure to compounds: methodology and an application to engineered nano-TiO\textsubscript{2} particles, Environmental Modelling & Software 25: 320-332
Building on their earlier work, Gottschalk et al. (2011) combined probabilistic material flow analysis and graph theory to calculate PEC for nano-TiO$_2$, nano-Ag and nano-ZnO for 534 river sections in Switzerland with the aim of assessing geographical variability in PEC. Variability in PEC due to temporal variation was assessed using flow measurements over a 20-year period at 21 locations. In addressing uncertainties regarding removal rates for NM, an optimistic scenario assuming complete NM transformation/deposition was generated together with a conservative scenario, assuming no NM removal. The authors aimed to overcome one of the main limitations in generating PEC calculations.
at the regional scale, namely the assumption of homogenous materials distribution within aggregated environmental compartments. In doing so they modelled PEC at higher spatial and temporal resolutions, by including data on: total national NM emissions distributed according to spatial population density; geographical and temporal variation in river flow rates; and the transport and fate of NM within the real river system.

They found PECs to vary by a factor of 5 due to uncertain emissions and by a factor of 10 due to temporal river flow variations. For example, nano-TiO₂ PECs ranged from 11-1,623 ng/L (conservative scenario) and 2-1,618 ng/L (optimistic scenario). Equivalent values for nano-ZnO and nano-Ag were smaller by factors of 14 and 240 respectively. Their results indicate highly variable local PECs and a location and time dependent risk evaluation.

### 4.6 Kinetic modelling

Kinetic models specifically try to reflect the dynamic behaviour and fate of ENM in environmental media. The results of three relevant studies are summarised below.

#### 4.6.1 Koelmans et al. (2009)

Koelmans et al. (2009)\textsuperscript{154} calculated ranges of carbon nanoparticles (manufactured carbon-based nanoparticles and black carbon nanoparticles) surface sediments with a simple mass balance model that accounts for sedimentation fluxes, removal rates due to aggregation or degradation, and burial in deeper sediment layers. The model is based on three assumptions:

1. The sediment contains a surface mixed sediment layer with thickness L, which is homogeneously mixed due to bioturbation.
2. Carbon nanoparticles enter this sediment layer through sedimentation of particles from the overlying water column, with an average annual sedimentation rate SCNP.
3. Carbon nanoparticles are allowed to disappear in the uniformly mixed layer, following a first-order decay pattern, governed by an overall removal rate constant k (assumption 3). This removal could be due to degradation or aggregation to larger (nonnanosized) aggregates or particles.

\textsuperscript{154} Koelmans AA, Nowack B and Wiesner MR (2009) Comparison of manufactured and black carbon nanoparticle concentrations in aquatic sediments, Environmental Pollution 157, 1110-1116
These processes are combined in the following mass balance equation, where the three terms on the right-hand side relate to the three main processes sedimentation, burial and removal respectively:

\[
\frac{dC_{\text{CNP}}}{dt} = \frac{S_{\text{CNP}}}{L} - \frac{\Delta L}{L} C_{\text{CNP}} - kC_{\text{CNP}}
\]

with: \( C_{\text{CNP}} \) MCNP concentration in sediment (mgm\(^{-3}\)), \( S_{\text{CNP}} \) MCNP sedimentation flux (mgm\(^{-2}\) yr\(^{-1}\)), \( L \) thickness of mixed sediment layer (m), \( \Delta L \) sediment accumulation rate (myr\(^{-1}\)), \( k \) first-order removal rate constant (yr\(^{-1}\)).

The sedimentation flux (SCNP) is calculated as

\[
S_{\text{CNP}} = SS \times C_{\text{CNP,SS}}
\]

in which \( SS \) sedimentation flux of settling solids in the water column (gm\(^{-2}\) yr\(^{-1}\)), \( CCNP \), \( SS \) concentration of carbon nanoparticles in settling solids.

The concentration of in settling solids is calculated from the total concentration of carbon nanoparticles in the water column, the distribution of carbon nanoparticles between aqueous phase (MCNPs as dispersed particles) and settling solids (carbon nanoparticles in settling flocs or aggregates), and the concentration of settling solids:

\[
C_T = C_W + C_{\text{CNP,SS}}C_{SS}
\]

which can be rearranged to

\[
C_{\text{CNP,SS}} = \frac{C_T}{K_d + C_{SS}}
\]

in which \( C_T \) total concentration of MCNPs in the water column (mg/L), \( C_W \) aqueous non-settling MCNP concentration in the water column (mg/L), \( C_{SS} \) concentration of settling solids (kg/L), \( K_d \) conditional distribution ratio between MCNP concentration in settling particles and (dispersed) MCNP concentration in water (L/kg).

In the worst case scenario assuming 100% association of carbon nanoparticles with settling solids and zero removal in the sediment top layer, model calculation leads to steady state concentrations in sediment from 40 mg/kg (shallow lakes with high sedimentation fluxes) to 2000 mg/kg (large lakes).
4.6.2 Arvidson et al. (2011)

Arvidson et al. (2011) have developed a kinetic exposure model for the aquatic environment based on colloid chemistry principles. Based on the assumption that all particles are approximately spherical and that merging of two particles is an irreversible reaction, Arvidson et al. (2011) put for the following equation:

\[
\frac{dn_j}{dt} = \frac{1}{2} \sum_{i=1}^{i-j-1} \alpha_{i,j} \cdot K_{i,j} \cdot n_i \cdot n_{j-i} - n_j \sum_{i=1}^{i=\infty} \alpha_{i,j} K_{i,j} n_i - \frac{v_s}{d} \cdot j^\beta n_j + I_j
\]

where \( n_j \) is the particle number concentration of particle \( j \) (if \( j \) equals three, then particle \( j \) consists of three primary particles that have agglomerated), \( \alpha_{ij} \) and \( \alpha_{i,j-i} \) are collision efficiencies, \( K_{ij} \) and \( K_{ij,i} \) are rate constants, \( v_s \) is the sedimentation rate of primary particles, \( \beta \) describes the increase in sedimentation rate due to increased cluster size (2/3 for spherical particles), \( d \) is the depth of the water compartment and \( I_j \) is the inflow of particles.

The first term on the right side of the equation above describes the formation of particle \( j \) through agglomeration of particles \( i \) and \( j-i \) whereas the second term describes the loss of particle \( j \) through agglomeration with other particles \( I \). The third term accounts for the sedimentation and the last term for the inflow of particles.

A particle number based PEC can be derived from the equation above by solving the differential equation and summing the particle concentrations \( n_j \) at a time when the system has reached steady state.

Using data from Mueller and Nowack (2008) on inflow of 58.8 ton/year TiO\(_2\) to the Swiss water compartment, Arvidson et al. (2011) recalculated the inflow into primary 25 nm AEROXIDE\textsuperscript{®} P 25 particles to be \( 2.47 \times 10^7 \) particles s\(^{-1}\) m\(^{-3}\) of P 25 and use that number to derive at a PEC of approximately \( 2.5 \times 10^{12} \) particles m\(^{-3}\) for a 3 m deep lake with a bottom temperature of 4 °C, a water viscosity of 1.5 mPa x S, a water density of 1000 kg/m\(^3\). TiO\(_2\) nanoparticles density was set to be 4200 kg/m\(^3\) and a shear rate of 0.01 s\(^{-1}\) and a collision efficiency of 1 was used as a baseline.

A sensitivity analysis of the model using 21 nm TiO\(_2\) nanoparticles showed that the model output was mostly influenced by changes in inflow of nanoparticles to the water compartment and the collision efficiency.

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4.6.3 Quik et al. (2011)

Quik et al. (2011) evaluated the adequacy of the current guidance documents for use with NMs and concluded that nano-specific fate processes, such as sedimentation and dissolution need to be incorporated. After having reviewed the literature on sedimentation and dissolution of NMs in environmentally relevant systems, Quik et al. (2011) deduced that removal kinetics for dissolution and the overall kinetics of water–sediment transport of NMs should be close to first order. Based on limited data from literature, probable removal rates range from 0 to $10^{-4}$ s$^{-1}$ for sedimentation, and from 0 to $10^{-5}$ s$^{-1}$ for dissolution.

To assess exposure of aquatic organisms to nanomaterials, Quik et al. propose the model for chemical substances to be written as:

$$\frac{dC}{dt} = E - \Sigma k C \quad \text{with} \quad \Sigma k = k_{adv} + k_{vol} + k_{deg} + k_{sed} + k_{diss}$$

where

- $C =$ mass concentration of free nanoparticles in water (kg m$^{-3}$)
- $E =$ volume-specific release rate of NM to water (kg m$^{-3}$ s$^{-1}$)
- $k_{adv} =$ first order rate constant for removal via advection (s$^{-1}$)
- $k_{vol} =$ first order rate constant for removal via volatilization (s$^{-1}$)
- $k_{deg} =$ first order rate constant removal via (chemical) degradation (s$^{-1}$)
- $k_{sed} =$ first order rate constant for removal via aggregation/deposition and sedimentation (s$^{-1}$)
- $k_{diss} =$ first order rate constant for removal via dissolution (s$^{-1}$)

As noted by Quik et al. (2011), the challenge of modelling is placed entirely in assigning values to the various rate constants, which can be seen as strength and weakness at the same time. The obvious weakness is that a new removal rate needs to be measured for each individual NM. The advantage is that it provides one single approach to modeling of conventional chemical substances and NMs. Building on the this work, Quik et al. (2012) used sedimentation data of CeO$_2$ nanoparticles in natural river water to test their model and found that experimental data were in good compliance with the proposed model.

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4.6.4 Praetorius et al. (2012)

Praetorius et al. (2012) modelled the fate of nanoparticles using well-established multimedia box models for organic pollutants. In such box models, the environment is divided into compartments of different types and dimensions and processes that affect a chemical’s behaviour and transport in each compartment are parameterized and combined in a system of coupled mass-balance equations. Solving the equations yields the chemical concentration in each compartment at steady state or as a function of time.

Instead of transformation and degradation processes for organic chemicals, Praetorius et al. (2012) have used a transformation rate constant, \(k_{\text{trans}}\) as a general term for aggregation, dissolution or surface transformation in their box model. In order to describe the interaction of nanoparticles with naturally occurring suspended particulate matter, it is assumed that this interaction can be best described as a heteroaggregation process, where the nanoparticles collide with the suspended particulate matter on the basis of their respective diffusion velocities and will stick to the suspended particulate matter depending on the surface properties. Hence the heteroaggregation rate constant, \(k_{\text{het-agg}}\), is calculated by multiplying the collision rate constant, \(k_{\text{coll}}\), by the attachment efficiency for heteroaggregation, \(\alpha_{\text{het-agg}}\). Finally, Praetorius et al. (2012) characterized the transport processes of nanoparticles in environmental media as being dependent on advective transport with moving water (\(k_{\text{flow}}\)) or processes coupled with the movement of suspended particulate matter (sedimentation (\(k_{\text{sed SPM}}\)), sediment resuspension (\(k_{\text{resusp}}\)), horizontal bed load transfer (\(k_{\text{sed-transfer}}\)), or burial in the deep sediment (\(k_{\text{burial}}\)) in addition to the possibility that nanoparticles can be deposit to the sediment by gravity (\(k_{\text{sedNP}}\)).

In order to assess the environmental exposure concentration of TiO\(_2\) in the Rhine River, Praetorius et al. (2012) divided 700 km of the river into 520 boxes where each box again was divided into a compartment of moving water (w1), stagnant water (w2), and sediment (sed). Based on Gottschalk et al. (2011), Praetorius et al. (2012) assumed that the mass flow of TiO\(_2\) nanoparticles entering the Rhine River from the city of Basel in the first box of the model was 0.14 t a\(^{-1}\) (0.39 kg day\(^{-1}\)).

In all the simulations, it was found that the concentration of TiO\(_2\) nanoparticles was several orders of magnitude higher compared to the moving water. The TiO\(_2\) nanoparticles concentrations were found

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to be very depending on both the heteroaggregation attachment efficiency ($\alpha_{\text{het-agg}}$) and the characteristics of the suspended particulate matter in the Rhine River, such as their density and concentration.

In the extreme case, where all of these parameters were large, Praetorius et al. (2012) simulations show: that the TiO$_2$ nanoparticles would very quickly be removed from the water body; that they would move about 50 km away from the source before being completely deposited in the sediment compartment; and that the total flow of TiO$_2$ nanoparticles out of the last box of the model (700 km) would be $2.4 \times 10^{-4}$ kg day$^{-1}$. If all three parameters are very low, the TiO$_2$ nanoparticles would stay in their free form in the water compartment for a longer time and are still present 700 km away from the source and the total flow of TiO$_2$ nanoparticles out of the last box of the model would be 0.36 kg day$^{-1}$, which represents 92% of the input flow of 0.39 kg day$^{-1}$ into the first box.
5. **Set of Methodologies for assessing NM exposure**

5.1 **Introduction**

We systematically review the available methods for assessing NM releases into the environment used in the studies considered under section 4 above. We also briefly discuss proposed exploratory chemometric approaches as these have been proposed in the literature, but are yet to fully elaborated.

5.2 **Analytical in situ measurements**

Regarding available measurement techniques, there is a range of measuring techniques that can be applied under laboratory conditions to air and water samples and can provide resolution down to the sub-nanometre range, including microscopic methods, chromatography, filtration and centrifugation and spectroscopic techniques. However, there is currently a lack of cost-effective and reliable techniques for quantifying and characterising the release of nanomaterials into the environment in a regulatory context.

In the following discussion we review available analytical techniques for measuring nanomaterials in air and water samples and in soil and sediment. We then go on to consider how the diversity of NM affects the use of specific analytical methods and nanoforms, and the need for test protocols.

5.2.1 **Measuring Nanomaterials in Water**

Regarding the detection and analysis of NM in aquatic systems, researchers consistently report that undertaking reliable measurements of NM in natural waters is a challenging task. Analytical methods have been comprehensively reviewed by Tiede et al. (2008) and Tiede et al. (2009). All of these techniques exhibit specific disadvantages: some do not distinguish between ENPs and

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naturally occurring nanomaterials; some techniques require sample preparation approaches that can introduce artefacts and hence uncertainties. In their discussion of the application of analytical methods to environmental risk assessment, Tiede et al (2009) suggest that a combination of techniques is therefore needed.

Key methodological issues include how to ensure the comparability and reproducibility in analytical determinations and how to adapt protocols to specific “nano” properties in contrast to soluble compounds\textsuperscript{161}. Researchers report challenges in distinguishing NM from the high background of natural and incidental nanoparticles\textsuperscript{162}, problems with the insensitivity of current detection methods to the low concentrations of nanomaterials (relevant concentrations may be in the range of µg L\textsuperscript{-1}–pg L\textsuperscript{-1}), and difficulties in isolating the nanomaterials fraction in water\textsuperscript{163}. At the same time, the number of studies is increasing and some dedicated research teams are beginning to report successes with particular methods for specific classes NMs, rather than for generic NM.

In terms of available methods and techniques, given that natural nanoparticles in the colloidal state are easily disturbed in water, groundwater, soil and sediment during sampling\textsuperscript{164}, \textit{in situ} techniques that eliminate the separation between the sampling and the analysis stage are preferable. Light scattering methods (e.g. dynamic light scattering (DLS), turbidimetry and laser diffraction) have been found to be useful and can be used to determine size related properties and also concentrations. DLS has particular advantages including rapid analysis time, simple operation and is particularly useful in monitoring agglomeration. However, it has limitations when samples contain a non-homogenous composition of particles of varying sizes.

Microscopic methods for the analysis of nanoparticles include atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Such methods enable the investigation of properties at the level of individual particles as well as aggregates. Wet Scanning Electron Microscopy (WetSEM) is a method that addresses some of the shortcomings of

\textsuperscript{162} Baun A, Hartman NB, Grieger KD and Hansen SF (2009) Setting the limits for engineered nanoparticles in European surface waters – are current approaches appropriate? Journal of Environmental Monitoring 11 p1774-1781
\textsuperscript{164} Hassellöv, M., and Kaegi, R: Analysis and characterisation of manufactured nanoparticles in aquatic environments, chapter in Environmental and Human Health Impacts of Nanotechnology (Lead JR and Smith E (Eds), Blackwell, 2009.)
DLS\textsuperscript{165}. The technique uses capsules that comprise an electron transparent membrane enabling the imaging and analysis of liquid samples.

Hydrodynamic chromatography provides size separation ranges of 5-300 nm or 20-1200 nm and, combined with ICP-MS, can be used to detect multiple elements and isotopes. Only very few university laboratories currently possess the relevant equipment for the analyses described above\textsuperscript{166}. Other available methods include fractionation techniques and, finally, spectroscopic techniques that can be used to probe chemical entities on whole samples and on the nanoparticle ensembles in fractionated samples.

A number of analytical methods have been used for measuring exposure to nanomaterials from wastewater effluent and façade run-off. For instance, Kiser et al. (2009) used SEM and EDX analysis confirmed the presence of various sizes, shapes, and compositions of Ti-containing solids whereas Farre et al. (2010) used ultrasonication extraction from suspended solids in wastewater and liquid chromatography (LC) coupled to a hybrid triple-quadrupole linear ion-trap mass spectrometer to identify C60, C70, and functionalised C60 fullerenes in wastewater effluent. Analytical electron microscopy, optical emission spectrometry and mass spectrometry (TEM, ICP-OES and ICP-MS analysis) have also been used to determine TiO$_2$ and Ag nanoparticle façade runoff (Kaegi et al. 2008; Kaegi et al. 2010).

A research team at Arizona State University led by Paul Westerhoff are working to develop methods to quantify nanomaterials in matrices including drinking water, commercial products, blood and other biological matrices\textsuperscript{167}. They hypothesize that two basic instrumentation platforms (ion coupled plasma mass spectroscopy and liquid chromatography mass spectroscopy) can be developed in conjunction with sample pretreatment methods, involving extraction, separation and or concentration of ENM from environmental and biological samples, to quantify the size, number concentration and mass concentration of the currently most widely used inorganic nanomaterials (Ag, TiO$_2$, Au) and carbonaceous nanomaterials (fullerenes and functionalized fullerenes). The team has tested drinking water samples, as well as biological samples, for ENM, with the expectation that detection will not be possible. They have fortified samples with known and increasing concentrations of diverse ENM, until

\textsuperscript{165} Tiede K, Tear SP, David H, Boxall ABA (2009) Imaging of engineered nanoparticles and their aggregates under fully liquid conditions in environmental matrices, Water Research, 43(13):3335-3343

\textsuperscript{166} Agence Française de sécurité sanitaire des aliments (AFSSA) « Les nanoparticules manufacturées dans l’eau » (2008) AFSSA, France

detection becomes possible. This work will help to define what concentrations of ENM are required in order to achieve detection of engineered ENMs with state of the art techniques. Thus far, the research team has generated a number of publications and reported successes using the following methods:

- For metal/metallic nanoparticles in solution – detection and sizing using single particle inductively coupled plasma mass spectrometry (SP-ICP-MS)\(^{168}\);
- For TiO\(_2\) in raw sewage and treated effluent – characterisation using rota-evaporation, dialysis and lyophilisation and identification using high resolution transmission electron microscopy and energy dispersive X-ray analysis\(^{169}\);
- For C\(_{60}\) in ultrapure water and drinking water – separation and concentration via solid phase extraction (SPE) followed by quantification using liquid chromatography coupled with mass spectrometry (LC-MS)\(^{170}\);
- For C\(_{60}\)/C\(_{70}\) in wastewater - separation and concentration via liquid-liquid extraction (LLE) and SPE followed by quantification using HPLC-UV or LC/MS\(^{171}\); and
- For carbon nanotubes - combustion analysis\(^{172}\).

This supports suggestions by other researchers that testing methods will not be generic to all NM, but rather for “classes” of NM\(^{173}\).

5.2.2 Measuring Nanomaterials in Air

With regards to air, nanomaterials are too small to be effectively detected with instruments such as optical particle counters (OPCs) because the wavelength of light, around 400 to 700nm, is the limit of resolution. Also, unless they are abnormally high in density, they have insufficient mass to be detected, easily weighed or collected effectively by filtration involving mechanical capture mechanisms\(^{174}\). Particles smaller than 50nm may display quantum mechanical behaviour rather than...
obeying classical mechanics and in response may exhibit physico-chemically unique optical, magnetic, and electrical characteristics.\textsuperscript{175} Other key challenges include the need to differentiate NM from similarly sized natural materials, the need for sensitive and specific techniques to measure the required metrics, the need to measure NM properties in several media and the need to measure several properties in parallel. According to Baalousha and Lead, all current measuring methods and techniques fall some way short of addressing these requirements.\textsuperscript{176}

There are currently no standards or guidelines for the measurement of NMs and UFP in air emissions from industrial installations. However, there are several ISO standards that provide details on specific monitoring techniques. For instance, ISO 15900:2009 provides guidelines on the determination of aerosol particle size distribution by means of the analysis of electrical mobility of aerosol particles. This analytical method is applicable to particle size measurements ranging from approximately 1nm to 1μm. ISO 28439:2011 provides guidelines for the determination of the number concentration and size distribution of UFP and nanomaterial aerosols by use of mobility particle sizers. There is also an ISO standard (ISO/TR 27628:2007)\textsuperscript{177} that contains guidelines on characterizing occupational nanoaerosol exposures and with an emphasis on nanometre-diameter particles. The guidance discusses exposure metrics appropriate to nanoaerosols, and provides specific methods for characterizing exposures with reference to those metrics. Specific information is provided on methods for bulk aerosol characterization and single particle analysis.

5.2.4 Measuring Nanomaterials in soils and sediments

There are well recognized experimental difficulties associated with measuring NMs associated with soils, sediments and sewage sludges, including significant interference from naturally occurring nanoparticles, as well as issues with sample preparation and resulting artifacts\textsuperscript{178}. However, this represents an area of active research and a number of researchers have investigates ENM in sludges from WWTP. Methods used include analytical STEM, TEM combined with energy-dispersive X-ray spectrometry, and scanning electron microscopy/electron dispersive X-ray microanalysis (SEM/EDX).

\textsuperscript{175} Kreyling, W. G. 2006. Translocation and accumulation of nanoparticles in secondary target organs after uptake by various routes of intake, Toxicology Letters 164 (34)
5.2.5 Dealing with the Diversity of Nanomaterials

NM have heterogeneous distributions in size, shape, surface charge and composition leading to significant differences in intrinsic properties. In addition, properties are influenced by the presence of coatings or other functionalities added to the NM during production. Given the diverse range of intrinsic properties exhibited by nanomaterials and their effects on fate and behaviour in environmental compartments, environmental monitoring techniques need to be targeted towards specific NM, or groups of NM.

Future challenges for measuring techniques include allowing simultaneously sizing and analyzing particles in their original environmental media using size separation of the sample with quantitative and elemental evaluation of the size fractions in the sample.

5.2.7 The Need for Test Protocols for Nanomaterials

In measuring NM in samples a number of methodological questions have been found to significantly affect study results, including the choice of sample materials; pre-concentration/fractionation methods, and analytical methods to characterize and quantify collected particles. In achieving repeatability of results in testing for NM in environmental samples, variations between studies related to the quality of NM samples (i.e. impurities, size distribution and shape), as well as the choice of the specific nanoform (functionalization, formulation, powder, coating) serve to confound repeatability. Results will also vary depending on how the NM stock dispersion is prepared, be it through sonic probe or stabilisation. The location and duration of sample storage and sample transportation have also been found to influence results.

As such, careful consideration must there be given to the selection of the test material, the test system (including test vessels and study media) and the test exposure conditions. In order to maximise utility, measurement results must detail not only the concentration of the ENP in the sample, but also its

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180 Gottschalk F, Nowack B and Gawlik B (2010) op cit
characteristics (e.g. size, shape, degree of aggregation and dissolution). As mentioned above, several research teams are taking steps towards the development of test methods and protocols for certain classes of NM.

5.3 Laboratory measurements and extrapolations

A limited number of experimental or simulation studies have used analytical measurement methods to estimate an overall NM environmental exposure from specific applications under conditions that created and measured within the artificial setting of the laboratory. For instance, Farkas et al. (2011), Park et al. (2008) and Benn and Westerhoff (2008) investigated emissions of nanomaterials such as silver and CeO2 from effluent and diesel fuel, respectively. Subsequent they have used this data to derive estimation of how much silver, for instance, would be applied on Norwegian soil per year or the average emissions of CeO2 along the highways of UK and EU.

Such experimentally based simulation studies provide a valuable insight into releases of NM from products containing NM during the product life cycle, an area that is considered important in terms of overall emissions but where there is a severe lack of data. At the same time, data from simulation studies provide only a snapshot of environmental exposure under a specific set of conditions. A number of confounding factors need to be taken into account when using this data to make assumptions about the wider spectrum of environmental exposure scenarios, including:

- they are not representative of the whole spectrum of potential releases over the whole life cycle of a product that contains nanomaterials;
- studies tend to focus on one product make and product variability in release properties are generally not addressed;
- experiments suffer from a lack of repetition implying that resulting data is insufficient for statistical evaluation to test the robustness of results; and
- results reflect artificial laboratory conditions and may not be representative of releases under actual conditions.

Nevertheless, in a context where data on environmental exposure is so limited, data from simulation studies provides a valuable indication of which exposure scenarios might be relevant for specific NM.

It can serve to direct further research towards determining whether the releases indicated have led to concentrations of specific NM in the environment, using both modelling and analytical techniques.

5.4 Material mass flow analysis and simple modelling approaches

In regard to studies that attempt to model environmental exposure, we distinguish between steady-state modelling studies and kinetic studies. Steady-state models assume that systems enter equilibrium whereas kinetic models try to include the fact that nanomaterials in environmental media undergo dynamic, non-equilibrium processes. In regard to the former, we again distinguish between studies that used material mass flow analysis followed by simple modelling approaches on the one hand and probabilistic mass flow analysis on other hand.

Examples of studies that use material flow analysis and simple modelling approaches include Boxall et al. (2008), Luoma (2008), and Mueller and Nowack (2008). Common amongst these studies is that calculations are based on a quantitative substance flow analysis of how nanoparticles from various products categories such as textiles, cosmetics, coatings, plastics, sports gear, electronics, etc. enter the environment through abrasion, outlet from the sewage treatment plants and/or waste incineration plants and landfills. Given the lack of information, numerous assumptions and estimates have to be made about worldwide production volumes, concentration of the nanoparticles in the products, levels of incombustible nanoparticles and behaviour during wastewater treatment. For instance, in the study by Mueller and Nowack (2008) it is estimated to be realistic that the worldwide production in 2007/2008 was 350 tons CNT and that these are evenly incorporated into plastics and electronics. For the CNT that end up in the waste incinerator, it is furthermore assumed that 50wt% will be burned, 25wt% will end in the slag and 25wt% will become airborne. Of the 25wt% that become airborne, 99.9wt% will be caught in the filters of the waste incineration plant leaving 0.1wt% to enter the atmosphere. In a high exposure scenario, Mueller and Nowack (2008) assumed a worldwide production of 500 tons annually and that only 25wt% are burned and that only 99wt% of the airborne CNT are caught by the filters of the incineration plant.

In terms of limitations and advantages of modelling, a number of points can be raised relating to the data upon which modelling studies are based, including:

- The complete lack of empirical quantitative data relating to releases along the product life cycle employed in the studies;
- The absence of reliable data on NM production volumes;
- The lack of data on the on volumes of NM incorporated into specific product categories;
- The combination of different product types under one category;
- Assumed steady-state approach for NM release and transmission-flow calculations.

One of the main limitations of PEC calculations at regional scale is the assumption of homogeneous material distribution within aggregated environmental compartments.\(^{184}\) In order to overcome this, the modelling of concentrations at higher spatial and temporal resolutions at a local level is required. In their 2011 study, Gottschalk et al have addressed this deficiency by incorporating spatial and temporal variability into their model of PEC in Swiss rivers. In order to serve in the regulatory context, models need not always provide full coverage but rather can provide representative data that can serve to inform decision making as to whether action is required.

### 5.5 Probabilistic mass flow analysis

In the light of the scarcity of data on, for instance, production volumes, product concentrations and distribution in the environment as noted above, probabilistic mass flow analysis treats all parameters in a mass flow analysis or model as probability distributions. Using Monte Carlo and Markov Chain Monte Carlo computer simulations as well as a sensitivity and uncertainty analysis, nanomaterial concentrations have been derived for surface water, sewage treatment plant effluent and sewage treatment plant sludge for the region of Switzerland.

Once more data become available to populate the probabilistic sub-models, probabilistic mass flow analysis provides a model approach that may prove very valuable (Quik et al. 2011).

Besides the general lack of access to data and information needed, one of the main limitations of PEC calculations at regional scale probabilistic mass flow analysis is the assumption of homogeneous material distribution within aggregated environmental compartments. Probabilistic mass flow analysis furthermore fails to acknowledge the particulate nature of the material. For instance, fate processes such as agglomeration and sedimentation have not been considered, despite the fact that agglomeration has been pointed out as an important fate mechanism that could affect the exposure and bio-availability of nanomaterials.

5.6 Kinetic modelling

In contrast to steady-state models developed so far, kinetic models try to include the fact that nanomaterials in environmental media undergo dynamic, non-equilibrium processes. The model developed by Koelmans et al. (2009) combines the material flow analysis performed by Mueller and Nowack (2008) with sedimentation and has been noted as one of the first attempts to incorporate a nanomaterial relevant fate process in the modelling of environmental exposure (Quik et al 2011, 2012).

Arvidson et al. (2011) have developed a kinetic exposure model for the aquatic environment based on colloid chemistry principles that accounts for agglomeration and sedimentation whereas Quik et al. (2011) included removal kinetics for dissolution and the overall kinetics of water–sediment transport of NMs in their exposure models to assess exposure of aquatic organisms to nanomaterials.

Besides sedimentation, a number of additional particle-specific behaviour properties will however need to be included in order to obtain nanomaterial relevant environmental exposure assessment. These include agglomeration and dissolution, which all are dynamic, non-equilibrium processes (Quik et al. 2011).

As noted by Quik et al. (2011), the challenge of modelling is in assigning values to the various rate constants, which can be seen as strength and weakness at the same time. The obvious weakness is that a new removal rate needs to be measured for each individual NM. The advantage is that it provides one single approach to modelling of conventional chemical substances and NMs.

5.7 Exploratory chemometric approaches

The possibility of developing so-called exploratory chemometric approaches has so far only been sketched as an idea and hence cannot be formally reviewed here, but in their report on exposure scenarios under the NANEX Project, Gottschalk, Nowark and Gawlik discuss the possibility of developing a chemometric approach for estimating NM exposure. In particular, they consider the use of a chemometric approach in combination with traditional analytical chemistry to determine the fraction of nano-silver in sewage sludge. This involves the application of multivariate mathematical models (cluster analysis, principle component analysis and positive matrix factorization) to data sets containing chemical/physical parameters in order to estimate the number and composition of pollutant

185 Gottschalk et al (2010) op cit
sources and identify trends and correlations. Such techniques are current used by the European Commission’s Joint Research Centre to extract data on the nano-Ag fraction in sewage sludge samples and to visualise the relationship between the NM and other parameters (i.e. ingredients of domestic washing powders). Identified correlations may allow for the identification of a marker for the nano fraction, which could then be used to predict the nano-Ag level ion sewage sludge samples. This approach is currently being tested in a EU-wide screening exercise on sewage sludge samples from approx. 100 wastewater treatment plants. If successful, it will be tested on other NM, such a cerium oxide, an NM used as a fuel additive.

5.8 Overall assessment of available methods

Each of the different methodologies for generating data and the resulting data sets have particular strengths and limitations. In addition, overall data is limited, although certain ENM have received more attention than others, in particular nano-Ag, nano-TiO₂, nano-CeO and C60. This suggests that data generated using different methods can be combined to provide a more comprehensive picture of overall exposure. Below, we identify the strengths and limitations of the different methods and consider how they might be usefully coupled with other methods.

Regarding analytical methods for measuring ENM, this represents a dynamic area where considerable research is ongoing to improve methods and develop and ultimately procedures, with a particular emphasis on the analysis of water and air samples and less focus on soils and sludge. With regards to ENM in aqueous samples, researchers have begun to identify methods, or combinations of methods for both quantification and qualitative analysis, that best suit particular “classes” of ENM (i.e. metal-based, fullerenes, CNT) and are developing suitable test protocols that can be applied across laboratories. Currently, the quantitative data generated using these methods are in the form of mass concentrations (µg/L), with mass concentrations for specific size fractions reported. Qualitative analysis has been used to characterize the specific morphology of ENM, in terms of form, shape and size, as well as to track transformation, including aggregation, and mobility over time resulting from interactions with other substances and particles.

At the same time, resulting data suffers from interference from naturally occurring nanoparticles, with particular problems during sampling whereby natural nanoparticles in the colloidal state are easily disturbed in water, groundwater, soil and sediment during sampling. In addition, the studies mentioned are not thorough in describing the quantities and quality (including the specific nanoform) of ENM released, reducing the relevance of cross-study comparisons and making it difficult to pool resulting datasets. Finally and in common with monitoring data for any pollutant, data from in situ analytical
studies will only ever be fully representative of that particular site and scale, and assumptions are involved in extrapolating to a wider range of exposure scenarios and upwards in scale.

Regarding measurements of nanoparticles and UFP in air, combinations of analytical techniques are available for qualitative and quantitative analysis, allowing particle number, mass, surface area and volume concentrations to be measured. Studies have also been able to attribute nanoparticles and UFP to particular sources, and distinguish between naturally-occurring nanoparticles and man-made nanoparticles including unintentionally-produced. However, the techniques required to generate such data are sensitive and specific and, as for water, are available only in specific research laboratories. Techniques allowing for the rapid assessment of a range of parameters of air-borne nanoparticles in parallel as would be required for the regulatory context are not yet available.

In general, existing studies suffer from a lack of coherence in terms of sampling strategies, metrics and other parameters used to describe exposure, as well as in the overall level of detail provided. As such, it is not currently possible to pool data or to make meaningful comparisons between data sets from different studies. Researchers have noted that these inconsistencies present barriers to the systematic use of available exposure data in risk assessments if actions to harmonize approaches are not taken.\textsuperscript{186}

In their recommendations for studies reporting on ENM exposure, Clark et al identify a set of minimum data requirements and these are presented in table 8 below.

Nevertheless, whilst acknowledging current data limitations in comparability and breadth in covering the wide range of nanoforms, it can be expected that the application of analytical techniques to a range of ENM and emission scenarios will begin to generate more comprehensive and comparable datasets. Given the limited application of analytical methods to within specialised research laboratories, it would seem useful to continue to draw on predictions from both models and simulation studies when selecting emissions scenarios and specific ENM for analysis. In this way, future data from analytical studies at the very local scale can be used in a complementary way to confirm the PEC predicted from models at a variety of scales and hopefully allow researchers to determine how robust models are and adjust them accordingly.

Table 8: Recommended minimum data requirement for studies on ENM exposure

<table>
<thead>
<tr>
<th>Description of physical and chemical form of the ENMs used (i.e., at source)</th>
</tr>
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<tbody>
<tr>
<td>- Chemical composition</td>
</tr>
<tr>
<td>- Size distribution (including dimensions for fibres)</td>
</tr>
<tr>
<td>- Whether MNM is bound in a matrix. If so, describe: The matrix itself (e.g., plastic, rubber, concrete, paint) Form of matrix (e.g., powder, liquid, solid, granules) Amount of MNMs used in the matrix</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Description of physical and chemical form of released/detected particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Embedded in a matrix, agglomerated, single particle</td>
</tr>
<tr>
<td>- Elemental composition by EDX/EDS or chemical analysis</td>
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</tbody>
</table>

Potential other sources of ultrafine and other particles

Exposure characterized using a combination of metrics and measurements, which could include, but are not limited to, mass, particle number, and particle size distribution.

Information on process:
- Description of the process and all activities included in the process;
- Typical duration and frequency of these activities; and
- Type of enclosure of process: if enclosed, provide frequency and duration of opening for maintenance, quality control and/or other manual operations.

Description of site:
- Room size, windows and other features that may affect exposure.

Risk management measures (RMM):
- For occupational studies, standardized description of RMM types (e.g. ventilation) and personal protective equipment present;
- For consumer studies, product design that affects the release (e.g., maximum volume released from one use of a spray) and description of other types other RMM applied during the measurement; and
- Other measures (e.g., administrative controls, additional engineering controls).

Environmental release information:
- Total volume of MNMs used on site;
- Amounts and processes for disposal and/or recycling;
- Volume of air flow and MNM concentrations in outlet air (emission to air after filters); and
- Volume of waste water flow and MNM concentrations in effluent (after treatment) (emission to surface waters).

Sampling and data analysis strategy:
- Location of samples/measurements relative to source and receptor (e.g., workers);
- Number of samples/measurements taken;
- Description of activities associated with each sample/measurement;
- Qualitative assessment describing how representative the measurements are for personal exposure;
- Description of data analysis, including the difference between background and activity, and how this was calculated, whether and how peaks were addressed, whether and how data were averaged.


Experimental/simulation studies generate data bodies that reflect artificial laboratory conditions and may not be representative of releases under actual conditions. They focus on one specific exposure scenario at a low scale and hence do not provide a picture of the whole spectrum of releases over the
life cycle and over larger scales. Studies tend to focus on one product make and product variability in release properties are generally not addressed. Despite these limitations, data from simulation studies can be extremely useful in validating exposure pathways for specific ENM predicted using models of exposure, and for providing indicative data of how ENM might behave in processes such as waste water treatment or incineration. These initial data can then be tested against data from in situ studies to corroborate results.

Modelling methods have effectively begun to address the gaps in empirical data regarding environmental exposure to nanomaterials. Estimates have been made from specific ENMs and their application/s, as well as wider ranges of ENM across ranges of uses, including one study modelling emissions from an ENM production installation. Researchers have been able to estimate PEC for water, sediment and air, for scales ranging from river stretches to individual countries and regions, including the EU. Importantly, in their 2011 study Gottschalk et al incorporated geographical and temporal variability in their model of PEC for three metal-based ENM in Swiss rivers, so generating data at the local level and overcoming a main limitation of PEC calculations at regional scale, i.e. the assumption of homogenous distribution\(^{187}\). As such, data from models are useful in providing a preliminary indication to regulators of which ENM might be a source of risk in the environment.

All modelling methods draw on production data and (in the cases of models at wider scales) on the volumes of ENM attributed to particular uses. The paucity of publically available data implies that numerous assumptions and estimates have to be made about worldwide production volumes, fractions attributed to particular product groups and concentrations of nanomaterials in the products. In addition, assumptions are made regarding the allocation of ENM to different fractions in different processes such as waste water treatment and incineration, as well as regarding diffuse emissions from products over the product life cycle. These assumptions introduce considerable uncertainty into resulting data. Researchers have sought to address these uncertainties by generating a range of scenarios, including optimistic and conservative (worst case) scenarios. Uncertainties regarding the behaviour and fate of ENM in specific processes can be addressed using simulation studies and analytical measurements of relevant waste flows (e.g. effluent vs. sludge).

Another significant challenge in developing model-based methods is incorporating the effects that the novel physico-chemical properties exhibited by many nanomaterials have on particle behaviour in environmental media, and in processes such as waste water treatment and incineration. This includes

\(^{187}\) Gottschalk F, Ort C, Scholz RW and Nowack B, 2011, Engineered nanomaterials in rivers – Exposure scenarios for Switzerland at high spatial and temporal resolution, Environmental Pollution 159: 3439-3445
the transformation of ENM away from their primary counterpart into nanoforms which may then exhibit different fate and behaviour, something dependent on the particular environmental conditions and the transformation history of the specific ENM. Nowack et al (2012) argue that the properties of nanomaterials released from point and diffuse sources, and hence subject to transformation reactions during use and processing, are more relevant for risk assessment that those of pristine ENM. They call for research to determine whether release and transformation processes result in a similar or more diverse set of ENM and how this in turn affects environmental behaviour. They also identify the need for a definitive classification scheme for ENM that reflects their surface condition, and hence reactivity and likely fate and behaviour.

The incorporation of colloidal mechanisms into the later kinetic models begins to reflect growing knowledge regarding the fate and behaviour of ENM in water, and as such these models hold significant promise. Model-based approaches should be tested against empirical data as they becomes available, in order to test their accuracy in predicting both emissions of ENM and the fate and behaviour of ENM in particular environmental media over time.

An overview of available methodologies for generating ENM exposure data is provided in table 9. In this table we review each method according to the following criteria:

- Scope of application of the methodology (exposure scenario/environmental media/specific ENMs)
- Key methodological steps
- Use to date (i.e. specific ENM, lab or in situ for measuring techniques)
- Possible application of data to EU environmental regulation (i.e. ambient measurements relevant to EQS or monitoring emissions relevant to controlling industrial emissions?)
- Availability and cost
- What are the main limitations?
- Can uncertainties be quantified?
- Are future developments/improvements foreseen?

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<thead>
<tr>
<th>Name of methodology</th>
<th>In situ measurements</th>
<th>Extrapolation from laboratory measurements</th>
<th>Material mass flow analysis and simple steady state modelling approaches</th>
<th>Probabilistic steady state mass flow analysis</th>
<th>Kinetic modelling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scope of application of the methodology (exposure scenario/environmental media/specific NMs)</strong></td>
<td>A series of fully developed methods have been used (e.g. analytical electron microscopy, optical emission spectrometry and mass spectrometry and optical particle counters) to estimate NP water effluent/runoff concentrations of specific exposure scenarios/applications</td>
<td>Individual product source estimates, outside air estimates near manufacturing sites, atmospheric air in large cities</td>
<td>Most NMs, air, water and soil</td>
<td>Water</td>
<td></td>
</tr>
<tr>
<td><strong>Key methodological steps</strong></td>
<td>Establishment of scenario involving NP release; detection and quantification of amount of NP by mass and by number</td>
<td>Analysis of one specific nanomaterial and application in a laboratory and investigation of, for instance, water effluent concentrations followed by extrapolation of exposure data onto a city, region or a country</td>
<td>Substance flow analysis with numerous assumptions and estimates made about worldwide production volumes, concentration of the nanoparticles in the products, levels of incombustible nanoparticles and behavior during wastewater treatment.</td>
<td>Estimates of sediment and groundwater concentration as well as production, manufacturing and recycling processes, etc. followed by Using Monte Carlo and Markov Chain Monte Carlo computer simulations</td>
<td>Determination of inflow, shear, collision, sedimentation and dissolution rates following by solving various equations to derive PEC</td>
</tr>
<tr>
<td><strong>Use to date (i.e. specific NM, lab or in situ for measuring techniques)</strong></td>
<td>C60, C70, TiO2, Ag in specific uses</td>
<td>Extrapolation from individual products (washing machine) that use NM to national regional PECs (Norway) as well as regional uses (CeO2 used in two UK cities) to EU regional PEC</td>
<td>Most NMs, most uses, air, water, soil</td>
<td>TiO2, Ag and CNT mainly at a regional scale</td>
<td>TiO2</td>
</tr>
<tr>
<td><strong>Possible application of data to EU environmental regulation (i.e. ambient measurements relevant to EQS or monitoring emissions relevant to controlling industrial emissions?)</strong></td>
<td>Due to the limitations in regard to air and water detection (see row 8), application of in situ measurements seems limited as they cannot consistently be used to monitor development of emissions over time</td>
<td>Might in theory be used to derive PEC from each specific use of NM, which again can be used to derive regional PECs. The validity of the derived PECs would be questionable given the limitations noted in row 8</td>
<td>Might in theory be used to derive PECs for NMs. These methods collectively hold a number of limitations such as for instance a complete lack of empirical quantitative data relating to releases along the product life cycle employed in the studies and often a combination of different product types are put under one overall category. Under various forms of EU</td>
<td>Might be used to derive PECs for NM, but current applicability is hampered by the need to establish new removal rate for each individual NM</td>
<td></td>
</tr>
<tr>
<td>Name of methodology</td>
<td>In situ measurements</td>
<td>Extrapolation from laboratory measurements</td>
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</tr>
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<td>-----------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>various forms of EU environmental legislation, regulators and industry might have access to such data, but the overall nanospecific relevance of the derived PECs would still be highly questionable as they are based on a mass-balance approach and steady-state NM release and transmission-flow calculations.</td>
<td>environmental legislation, regulators and industry might have access to such data, but the overall nanospecific relevance of the derived PECs would still be highly questionable as they are based on a mass-balance approach and steady-state NM release and transmission-flow calculations.</td>
<td></td>
</tr>
<tr>
<td>Availability and cost</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Algorithms used by, for instance, Boxall et al. (2008) and others, are readily available online as they funded and published by public institutions.</td>
<td>Software tools need seem readily available</td>
<td>n.a.</td>
</tr>
<tr>
<td>Inherent limitations</td>
<td>In regard to air, NM are often too small to be detected; hard to differentiate between NM and natural occurring particles; no standard for measuring NM emissions from industrial installations. In regard to water, detection limits are not sufficiently low; impossible to distinguish between NM and natural and incidental nanoparticles; choice of sample materials; pre-concentration/fractionation methods, and analytical methods need to be considered carefully as these affect results.</td>
<td>Artificial setting of the laboratory that are not representative of the whole spectrum of potential releases over the whole life cycle of a product that contains NM under actual conditions. Studies tend to focus on one specific product and product variability in release properties are generally not addressed. Furthermore, experiments suffer from a lack of repetition implying that resulting data is insufficient for statistical evaluation to test the robustness of results; and results reflect artificial laboratory conditions and may not be representative of releases under actual conditions.</td>
<td>These methods collectively hold a number of limitations such as for instance a complete lack of empirical quantitative data relating to releases along the product life cycle employed in the studies and often a combination of different product types are put under one overall category. Absence of reliable data on NM production volumes is furthermore a huge limitation and so is the lack of data on the on volumes of NM incorporated into specific product categories. Assumed steady-state approach for NM release and transmission-flow calculations.</td>
<td>One of the main limitations of PEC calculations at regional scale is the assumption of homogeneous material distribution within aggregated environmental compartments. These methods furthermore fail to acknowledge the particulate nature of the material. For instance, fate processes such as agglomeration and sedimentation have not been considered, despite the fact that agglomeration has been pointed out as an important fate mechanism that could affect the exposure and bio-availability of NPs. &quot;Summing up the key limitations of the results may be seen in the general lack of input data, the focus on one unique region (Switzerland) and the steady state calculations for</td>
<td></td>
</tr>
<tr>
<td>Name of methodology</td>
<td>In situ measurements</td>
<td>Extrapolation from laboratory measurements</td>
<td>Material mass flow analysis and simple steady state modelling approaches</td>
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<td>------------------------------------------------------------------------</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>only one time period (2008).” Gottschalk et al. 2010</td>
<td></td>
</tr>
<tr>
<td>Principle sources of uncertainty</td>
<td>Impact of sampling techniques on results; interference from naturally occurring nanoparticles in water; very difficult to repeat results</td>
<td>Results extrapolated from a single product and experiment not repeated multiple times</td>
<td>No reliable input data on production volumes and fractions attributed to specific products; no reliable data on point and diffuse emissions; assume steady state approach</td>
<td>No reliable input data on production volumes and fractions attributed to specific products; do not consider fate and behaviour of ENM</td>
<td>Removal rate must be established for ENM on a case by case basis; need to confirm results with in situ measurements</td>
</tr>
<tr>
<td>Can uncertainties be quantified?</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>The recent study by Gottschalk et al (2011) differentiates for the first time between uncertainty of input parameters and effects of measurable, natural variability (in this case, water flow in rivers).</td>
<td>No</td>
</tr>
<tr>
<td>Are future developments/improvements foreseen?</td>
<td>Work is on-going in regard to develop methods to simultaneously size and analyze particles in their original environmental media</td>
<td></td>
<td></td>
<td>One of the main limitations of PEC calculations at regional scale is the assumption of homogeneous material distribution within aggregated environmental compartments. In order to overcome this, the modelling of concentrations at higher spatial and temporal resolutions at a local level is required.</td>
<td></td>
</tr>
</tbody>
</table>
6. Assessment of Available Environmental Exposure Data for Nanomaterials against the Demand for Data under EU Environmental Legislation

6.1 Introduction

The assessment of the usefulness and comprehensiveness of the available NM exposure data starts with the identification of the of EU environmental legislation that uses exposure data. A list of legislation for analysis within the scope of this study is presented in table 10 below. However, it should be noted from the outset that none of these legislative acts currently demand exposure data specifically on NM. As such, this discussion of the possible value of exposure data for NM to EU environmental legislation is largely speculative. Possible exceptions include the Water Framework Directive and the Air Quality Directive, to be discussed below.

Table 10: EU environmental legislation demanding exposure data

<table>
<thead>
<tr>
<th>Scope</th>
<th>Legislative Acts</th>
</tr>
</thead>
</table>
| Water            | Directive 2000/60/EC establishing a framework for Community action in the field of water policy  
                   | Directive 2008/105/EC on environmental quality standards in the field of water policy  
                   | Directive 98/83/EC on the quality of water intended for human consumption  
                   | Directive 2006/118/EC on the protection of groundwater against pollution and deterioration |
                   | The list of waste decision 2000/532/EC  
                   | Urban waste water treatment Directive 91/271//EEC  
                   | Sewage Sludge Directive 86/278/EEC |
| Air              | Directive 2008/50/EC on ambient air quality and cleaner air for Europe |
| Industrial       | Directive 75/2010/EC on Industrial Emissions                                      |
| Emissions        |                                                                                 |

Under EU environmental legislation, exposure information is used to feed into risk characterisation and to trigger requirements to manage risks. An estimation of exposure is based upon exposure scenarios for a specific substance, with the nature of those exposure scenarios determined by the legislation, i.e. PEC in surface water for the Water Framework Directive.

Legislation currently uses a range of methods for estimating exposure, including direct measurements using sampling techniques and analytical methods set in legislation, as well as drawing in data from modelling.

Sections 6.2 to 6.5 provide a systematic overview of the demands for exposure data under EU environmental legislation on water, waste, air and industrial emissions against available data and methods for generating environmental exposure data for NM, airborne nanoparticles and UFP. An overall analysis is
then presented in section 6.6, including a preliminary consideration of how regulatory standards for NM airborne nanoparticles and UFP might be developed given the type of exposure data that is both available and relevant to ecotoxicological and toxicological effects.

6.2 Water Legislation

In this section we consider demands for exposure data under the Water Framework Directive, the Groundwater Directive and the Drinking Water Directive.

6.2.1 Water Framework Directive 2000/60/EC

Directive 2000/60/EC establishing a framework for Community action in the field of water policy \(189\) (hereafter the WFD) uses quality objectives to facilitate the management of concentrations of pollutants in surface waters and groundwater. These include the requirement for groundwater and surface waters to show good chemical status, the requirement for surface waters to also meet good ecological status, and the requirement for groundwater to also meet good quantitative status.

For surface waters chemical status is assessed with reference to EU Environmental Quality Standards for priority substances (individual or group of pollutants posing a risk to or via aquatic environment) and other pollutants (substances regulated under previous piece of legislations). As a first step, Decision 2455//2001/EC \(190\) established a list of 33 priority substances. In 2008, this was replaced by Annex II of Directive 2008/105/EC on environmental quality standards in their field of water policy (EQSD) \(191\) which sets EQS for the substances in surface waters (river, lake, transitional and coastal) and confirmed their designation as priority or priority hazardous substances \(192\). The Commission has subsequently reviewed the list and put forward a proposal for a Directive amending the WFD and the EQSD as regards priority substances in the field of water policy \(193\) (COM(2011)876).

According to Annex V, point 1.4.3 of the WFD and Article 1 of the EQSD, good chemical status is reached for a water body when it complies with the EQS for all the priority substances and other pollutants listed in Annex I of the EQSD. Compliance is determined through a programme of monitoring, as specified by the WFD.

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189 OJ L 327, 22.12.2000, p1-82
192 Priority Hazardous Substances are substances that have been selected from the priority substances due to their persistency, toxicity and liability to bioaccumulate (PTBs), or due to their exhibiting properties which give rise to "equivalent level of concern".
193 Proposal for a Directive amending the WFD and EQSD (COM(2011)876)
Exposure data plays a key role in the identification of priority substances. Although there are no nanomaterials specifically included as priority substances at this stage, it is relevant to consider whether the implementation tools used to select substances as priority substances and to then monitor environmental concentrations could be applied to NM. As such, in sections 6.2.1.1-2 we review the role played by environmental exposure data in identifying priority substances and describe how data is generated under monitoring programmes. In section 6.2.1.3 we then review available exposure data and associated methods for NM in surface waters and consider how they could feed into the implementation tools of the WFD.

### 6.2.1.1 Identifying Priority Substances

Directive 2000/60/EC introduces in Article 16(2) a scientifically based methodology for selecting priority substances on the basis of their significant risk to or via the aquatic environment. For instance, the risk-based assessment methodology takes particular account of:

- evidence regarding the intrinsic hazard of the substance concerned, and, in particular, its aquatic ecotoxicity and human toxicity via aquatic exposure routes;
- evidence from monitoring of widespread environmental contamination; and
- other proven factors which may indicate the possibility of widespread environmental contamination, such as production, use volume and use pattern of the substance concerned.

The 2008 list of priority substances was developed using the COMMPs\(^{194}\) procedure. This procedure was subsequently criticised by the Scientific Committee on Health, Toxicity, Ecotoxicity and the Environment (CSTEE) as relying too heavily on monitoring data, in a context where the available datasets are incomplete and cover only those substances that were considered historically relevant to monitor. As such, the CSTEE argued that the resulting list of priority substances cannot faithfully represent the current water pollution problems and that a second system should be incorporated “to allow inclusion in the final list of substances with a high potential risk for aquatic organisms for which no monitoring information is available to date”\(^{195}\). NM represent a set of emerging pollutants for which historical dataset are no available and hence this change is highly relevant.

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\(^{194}\) COMMPs stands for Combined Monitoring and Modelling based Priority Setting Scheme

In response to these criticisms, the approach adopted for the identification of priority substances for the 2012 Proposal was somewhat broader and is detailed in the accompanying Commission Staff Working Paper on the Technical Background to the Proposal\textsuperscript{196}. The overall approach was based on the Article 16(2) criteria and used a combination of different approaches to generate separate but complementary lists of substances, the highest priority substances on each list were then amalgamated and subject to a short listing procedure involving expert review. Short listed substances were subject to a detailed expert review in order to identify those substances that were then included in the final proposal. The various approaches to prioritising substances are set out in table 11 below, together with an indication of the relevance of each approach to NM.

Table 11: Approaches to identifying Priority Substances

<table>
<thead>
<tr>
<th>Approach</th>
<th>Relevance to NM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Targeted risk-based assessments focusing on aquatic ecotoxicity and on human toxicity via the aquatic environment</td>
<td>Currently specific to two substances, copper and PFOS. Not NM. Relevant bodies could choose to generate a targeted risk-based assessment for a NM.</td>
</tr>
<tr>
<td>Simplified risk-based assessment procedure, including:</td>
<td>Monitoring-based methodology: Monitoring data not currently available for NM, data is required from a minimum of 4 Member States. Future efforts may generate datasets, although there are currently significant challenges in generating comparable datasets using analytical methods. The modelling-based method is specifically designed for substances for which no monitoring data is available, hence relevant to NM. However, parameters are not currently calibrated for metals, or for the specific physic-chemical properties of NM.</td>
</tr>
<tr>
<td>• Monitoring-based methodology; and</td>
<td></td>
</tr>
<tr>
<td>• Modelling-based methodology.</td>
<td></td>
</tr>
<tr>
<td>Priority Hazardous Substances criteria (PBT or equivalent level of concern), including Substances of Very High Concern under REACH and POP criteria</td>
<td>No nanomaterial has been identified as a PBT or equivalent level of concern; Substances of Very High Concern or POP</td>
</tr>
<tr>
<td>Other sources of information, including: Substances of concern at Member State level; and Annex III of EQSD Directive 2008/105/EC</td>
<td>Not currently relevant – no NM identified as Substances of concern and no NM in Annex III of the EQD Directive (although nanoforms exist of the metals) Member States could choose to identify a NM as a substance of concern.</td>
</tr>
</tbody>
</table>

\textsuperscript{196} Commission Staff Working Paper, Technical Background, SEC(2011) 1544 final
The main method considered to have the potential to lead to the identification of nanomaterials under the current legislative framework (i.e. with no NM authorised as active substances in pesticides or biocides) is the use of a simplified risk-based assessment procedure. The assessment draws on:

- Evidence of intrinsic hazard of the substances; and
- Evidence from monitoring of widespread environmental contamination; and
- Other elements that may indicate widespread contamination such as production volumes and use patterns.

Regarding the exposure assessment, the simplified risk-based assessment procedure can accommodate exposure data generated either through monitoring or through modelling using two distinct approaches to assessing exposure data. Key steps and data requirements of the two approaches are considered below.

**Monitoring-based approach**

The methodology used to identify and rank priority substances on the basis of Member State monitoring data is described in a 2009 INERIS-IOW report entitled “Prioritisation process: Monitoring-based ranking”\textsuperscript{197}. The method uses direct evidence of the presence of substances in the environment by drawing on environmental exposure data from analytical measurement techniques applied to water, sediment and biota samples from rivers, lakes, transitional and coastal waters conducted by Member States in fulfilment of their requirements under the WFD. Raw monitoring datasets have been submitted by all Member States (except Malta). Submitted data had to be processed in order to consistently express results in comparable units, i.e. µg/l for water analyses and µg/kg for sediment and biota analyses.

Regarding the role played by exposure data, the monitoring-based approach uses both the availability and quantity of evidence of the contamination of EU water bodies with specific pollutants to priorities substances. As an initial ranking step and since the WFD intends that priority substances be of EU-wide concern, substances had to be monitored in at least four countries to be selected for further consideration.

The subsequent prioritization then generated relevant EU-wide exposure data from the amalgamated data sets, in the form of Predicted Environmental Concentration (PEC). Exposure data were calculated from the monitoring data as arithmetic means at the level of a single monitoring station for each analysed fraction (whole water, dissolved metals in water, sediment below 2mm, below 63µm, below 20µm, fish and

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invertebrates), and then as 90th percentiles of the means from all stations. If collected data are representative of the EU situation, 90% of the stations would be expected to experience average concentrations below this value, i.e. below the PEC. In terms of risk assessment, this implies that if the PEC is below the PNEC, 90% of the station locations are, on average, expected to present safe concentrations

In practice, difficulties arose because of measurements below the analytical determination limit. Two PEC calculations were consequently calculated, one using only quantified values (PEC1), the other using all available data (PEC2). In the latter, data below the determination limit was replaced by half its value, as recommended by Directive (2009/90/EC).

In their discussion of the pros and cons of the monitoring-based approach, INERIS recognise that while monitoring-based prioritisation provides an excellent basis for prioritisation, it overlooks substances that may pose a risk to or via the aquatic environment but that are not monitored. They note that the modelling approach (discussed below) is expected to fill in the gap for non-monitored substances. This would certainly apply to NM. They also note that the ongoing implementation of the WFD is expected to improve the availability of monitoring data. Monitoring requirements under the WFD are considered below, together with a discussion of technical progress towards measuring NM in water samples and key challenges in building a reliable and robust dataset.

**Modelling-based approach**

As mentioned above, the modelling-based approach was specifically designed to capture those substances for which monitoring data is not available, in particular emerging pollutants. As such, a discussion of the key elements and data demands and their application to ENM is highly relevant. The modelling-based approach to prioritising substances is described in a JRC report entitled “A modelling approach for the prioritisation of chemicals under the Water Framework Directive” and involves the identification of a starting list, data collection, risk ranking, and definition of a final list of substances.

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Exposure data plays a role in two stages: data collection and risk ranking. Regarding data collection, both hazard and exposure are assessed, scores are attributed to both and these scores are then combined. The assessment of exposure relies on the collection of data on substance use in products in the IUCLID database and SPIN. The IUCLID database\(^{202}\) contains data collected through an obligation on producers and importers of high-production-volume chemicals and low-production-volume chemicals. The SPIN database\(^{203}\) contains data from Nordic countries on the use of substances in products and is used when no data were found in IUCLID, applying an extrapolation factor to derive a European tonnage. Use patterns are applied to generate release indices. When several uses are possible, the most dispersive use is selected.

The risk ranking stages demands exposure data in the form of PEC. Two approaches were used to calculate PEC, namely a multimedia model and a tiered approach. These approaches were developed by ECETOC to calculate the exposure and related risks to consumers, workers and the environment. Data demands of the two approaches are summarised below in table 12.

<table>
<thead>
<tr>
<th>Modelling approach</th>
<th>Data demands</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multimedia modelling using OECD Pov and TRTP Screening tool</td>
<td>Industrial activity, use, type, use pattern and annual production volumes and tonnage fractions used in specific products (currently extracted from IUCLID and SPIN databases)</td>
</tr>
<tr>
<td>ECETOC TRA TOOL(^{204})</td>
<td>ECETOC TRA TOOL requires data on substance identification (including sector of use), physico-chemical properties and environmental exposure scenario (tonnage, fraction of tonnage to region and Environmental Release Category (ERC) Code(^{205}))</td>
</tr>
</tbody>
</table>

When applying this approach to the identification of priority substances for the 2012 proposal, a number of challenges were encountered. These include a complete lack of production volume data for some substances and difficulties in determining the Environmental Release Code (ERC). In addition, the age of production volume data extracted from IUCLID introduced uncertainties into the analysis. These data limitations would certainly also apply to NM, for which reliable production volume data and data product use fractions are not available.

In their discussion of the modelling-based approach, the authors of the JRC report stress that the approach is intended to take into account substances for which no monitoring data is available and which could pose


\(^{204}\) Downloadable from [http://www/ectoc.org/tra](http://www/ectoc.org/tra)

\(^{205}\) Environmental Release Categories (ERC) as described under REACH Guidance (Chapter R.16)
a risk to aquatic organisms and to human health. However, they note that the approach did not consider metals and organometallic compounds for which physic-chemical and toxicological data were absent. This is because the existing correlations and property predictors in the models are designed for organic chemicals and resulting predictions may not be valid for metals and organometallic compounds. This calls into question the applicability of the model to NM, the fate and behaviour of which is influenced by different physical forces to classical bulk chemicals due to their specific properties (e.g. small size, large surface area and the wide variation in physico-chemical properties across nanoforms). In addition, researchers suggest that it will be nanoforms of metal NM that pose the greatest risk to the aquatic environment\textsuperscript{206}. However, were specific aspects of fate and behaviour to be clearly understood, it is possible that with substantial efforts the model could be re-calibrated to serve specific nanoforms.

6.2.1.2 Monitoring NM in Water Bodies

In the WFD, requirements for monitoring are set out in Article 8 and Annex V and include the monitoring of surface water status, groundwater status and protected areas. Regarding chemical status, Member States must carry out surveillance monitoring and operational monitoring programmes and where relevant, investigative monitoring.

In terms of the quality elements to monitor, Article 8 and Annex V of the WFD require that Member States monitor all priority substances and other pollutants discharged in significant quantities. The application of these requirements to NM raises a number of challenges related to an understanding of what environmental exposure for NM might be considered “significant”, relevant metrics and interference from naturally occurring nanoparticles.

Given that there are currently no NM identified as priority substances, NM may fall under “other pollutants discharged in significant quantities”. This raises the question of what “significant quantities” might be and no guidance is provided in the WFD. We can proceed by assuming that significant implies that there may be some risk posed by resulting concentrations. For NM determining what discharge level might be significant, or entail risk, is complicated firstly by a lack of analytical data on emissions from point and diffuse sources (i.e. exposure) and secondly by uncertainties regarding the dose-response relationship between increased toxicity and increased concentration. In addressing the exposure data gap, models

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estimating exposure from both point and diffuse can serve and these are considered in section 6.2.1.3 below.

Interference from naturally occurring nanoparticles serves to confound results when seeking to measure NM in water samples. Although nanoparticles are known to occur naturally (e.g. nano-Ag), data regarding background levels is not available. Distinguishing between naturally occurring nanoparticles and NM in water samples is a key challenge facing scientists and this would need to be solved before threshold values could be established for those NM with naturally occurring nanoforms.

Looking back to the legal requirements for monitoring, the EQSD also requires Member States to arrange for the long-term trend analysis of concentrations of those priority substances that tend to accumulate in sediment and/or biota. The frequency of monitoring should provide sufficient data for a reliable long-term trend analysis and should as a guideline take place every three years.

Regarding the techniques and methods employed for monitoring, Articles 8(3) and 20 of WFD provide for the adoption of standardised methods for analysis and monitoring of water status and, where necessary, of guidelines on implementation, including monitoring. Guidance has subsequently been developed to assist stakeholders in implementing the WFD, namely “Guidance document No.7: Monitoring under the Water Framework Directive”207. The guidance does not currently address pollutants at the nano-scale.

Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water status208 establishes minimum performance criteria for methods of analysis to by applied by Member States when monitoring water, sediment and biota, as well as rule for demonstrating the quality of analytical results, with the aim of ensuring the comparability of chemical monitoring results. Methods of analysis should reflect EN ISO/IEC 17025:2005209 standard or other equivalent standards accepted at international level. No such accepted standards have yet been established for nanomaterials at international level, although work proceeds at OECD level. The Directive states that where there are no methods that comply with the minimum performance criteria, monitoring should be based on best available techniques not entailing excessive cost (BATNEC). This can therefore be assumed to apply to nanomaterials.

Article 2 of Directive 2009/90/EC also sets definitions relevant for the measurement of low concentrations of substances and these are presented in table 13 below. As mentioned above in the discussion on the use of

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monitoring data in identifying priority substances, measurements below the analytical detection limit pose a problem when being fed into data analysis. We can expect that for NM PEC are likely to be very low and possibly below analytical detection limits, with many measurements therefore categorised under uncertainty of measurement.

Table 13: Definitions relevant for conducting measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of detection</td>
<td>The output signal or concentration value above which it can be affirmed, with a stated level of confidence that a sample is different from a blank sample containing no determinand of interest</td>
</tr>
<tr>
<td>Limit of quantification</td>
<td>A stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank</td>
</tr>
<tr>
<td>Uncertainty of measurement</td>
<td>A non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used</td>
</tr>
</tbody>
</table>

Were NM to be monitored by Member States in the future, decisions would need to be taken regarding the parameters to be measured and the abovementioned definitions may no longer have relevance. Parameters proposed by Vonk et al (2009) as being relevant for the aquatic environment include: concentration (g/l), reactive surface area (m$^3$/l) and number of particles (#/l)$^{210}$. It is recommended that data be accompanied by information regarding the methods used and the test protocols (including sampling preparation) applied. Notwithstanding concerns regarding the comparability of data from analytical measurements, in the interest of generating comparable sets of monitoring data across the EU, parameters to measure should be decided at EU level and consistently applied.

6.2.1.3 NM in surface waters: Available Exposure Data and Data Generating Methods

At this point in time (November, 2012) Member States are not currently engaged in monitoring NM within the context of monitoring programme under the WFD. As such, no monitoring data is available to feed into an exposure assessment for NM in surface waters. Regarding the identification of priority substances using the monitoring-based method, monitoring data would be required from a minimum of four Member States to provide for consideration of a substance and this is not currently available.

In terms of available analytical techniques, these were reviewed under section 5.2.1 and are at the laboratory stage of development. While a number of techniques have been applied to water samples,

including drinking water and effluent from WWTP, no measurements have been made of NM in surface waters that are reported in the scientific literature. However, it can be assumed that the analytical methods that have been used to measure NM mass concentrations in drinking water and effluents may be relevant. These include:

- solid phase extraction, liquid chromatography coupled with mass spectrometry (LC/MS) used by Chen et al. (2009) to detect and measure mass concentrations of C60 in drinking water;
- high resolution transmission electron microscopy and energy dispersive X-ray analysis used by Westerhoff et al (2011) to measure nano-Ti mass concentrations in the influents and effluents of WWTPs;
- Ultrasonication extraction from suspended solids in wastewater and liquid chromatography (LC) coupled to a hybrid triple-quadrupole linear ion-trap mass spectrometer used by Farré et al. (2010) to measure mass concentrations of C60 and C70 in effluents from WWTPs; and
- Scanning electron transmission microscopy used by Limbach et al. (2008) to measure mass concentrations of nano-CeO from a model WWTP.

Key challenges in applying these techniques to surface waters include the impact of sampling techniques on results, and the very low concentrations falling below the detection limit of current apparatus. Research is ongoing to address these challenges and develop test methods and protocols.

Initial data on PEC for NM in surface waters is available from a number of published studies using modelling. In terms of available exposure data of relevance, the various sources of data are summarised in table 14 below.

The earliest data relied on mass flow analysis to model emissions of NM to the environmental compartments and estimate PEC in terms of mass concentrations (Mueller and Nowark, 2008). Gottschalk et al. subsequently built on this earlier work with a number of studies using probabilistic mass flow analysis to generate data in the form of mass concentrations, with their 2009 article providing the only EU-wide PEC estimates for a range of NM. Importantly, they refined their model in their later 2011 study to consider the influence of geographical variability and temporal variability, providing rich data sets at a localised scale. The 2011 study only provides data for Switzerland and as such is not relevant for the EU.

The work of Tiede et al. (2011) estimates emissions of NM from both point and diffuse sources and generated both mass concentrations and particle number concentrations of a wide range of NM in surface waters, found to be in the same order of magnitude of earlier estimates. The data is limited to the UK. Of particular interest is the study by Johnson et al (2011), who modelled nano-Ag mass concentrations in every reach of river in England and Wales based on measurements of colloidal and particulate Ag in the
influents and effluents of waste water treatment plants. This represents the only attempt to use data from analytical measurements in modelling when generating PEC for surface waters, rather than estimates of production volumes. Again, the geographical scope is limited.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NMs covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Praetorius et al.</td>
<td>2012</td>
<td>Nano-TiO₂</td>
<td>Modeled the fate of nano-TiO₂ in water, including:</td>
<td>Rhine river, Switzerland</td>
<td>Kinetic modelling using multimedia box models for organic pollutants</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Transformation;</td>
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<td></td>
<td></td>
<td></td>
<td>• Transport;</td>
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<td></td>
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<td></td>
<td>• Interaction with naturally occurring suspended particulate matter</td>
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<td></td>
<td></td>
<td></td>
<td>Estimated mass concentrations in moving water, stagnant water and</td>
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<td></td>
<td></td>
<td></td>
<td>sediment.</td>
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<tr>
<td>Arvidsson et al.</td>
<td>2011</td>
<td>Nano-TiO₂</td>
<td>PEC of approximately 2.5x10^{12} particles m⁻³ for a 3 m deep lake</td>
<td>Switzerland</td>
<td>Kinetic exposure model based on colloid chemistry principles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>with a bottom temperature of 4 °C, a water viscosity of 1.5 mPa x S,</td>
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<td></td>
<td>a water density of 1000 kg/m³. TiO₂ nanoparticles density was set to</td>
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<td></td>
<td></td>
<td></td>
<td>be 4200 kg/m³. Drew on data from Mueller and Nowark, 2008.</td>
<td></td>
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</tr>
<tr>
<td>Quik et al.</td>
<td>2011</td>
<td>General model</td>
<td>Developed a model to include nano-specific fate processes, such as</td>
<td>Hypothetical</td>
<td>Kinetic model that is tailored to individual NM with the inclusion of</td>
</tr>
<tr>
<td></td>
<td></td>
<td>that can be adapted to specific NM (and other chemicals)</td>
<td>sedimentation and dissolution. Estimated probable removal rates ranging</td>
<td></td>
<td>specific removal rates</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>from 0 to 10⁻⁴ s⁻¹ for sedimentation, and from 0 to 10⁻⁵ s⁻¹ for dissolution.</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Tested results against sedimentation data of CeO₂ nanoparticles in natural river water and found good compliance.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tiede et al.</td>
<td>2011</td>
<td>Wide range of NM</td>
<td>Modeled mass concentrations of a range of NM in surface waters (PEC_water - water treatment plant influent in the study) using algorithms. Mass concentrations presented in µg/L and particles number concentrations presented in #/L. Highest mass concentrations found for TiO₂, zinc and silicon-based NM, highest particles number concentrations found for silica-based ENP, TiO₂, Fe₂O₃ and ZnO. Includes an overview of the release pathways for NM into aquatic systems – including diffuse source along the product life cycle and point source releases from WWTPs.</td>
<td>UK</td>
<td>Adaptation of the CHMP surface water exposure model</td>
</tr>
<tr>
<td>Johnson et al.</td>
<td>2011</td>
<td>Colloidal and particulate Ag</td>
<td>Modeled nano-Ag mass concentrations in every reach of rivers based on measurements of WWTP influents and effluents and predicted concentrations as follows:</td>
<td>Rivers in England and Wales (21,452 km of river length)</td>
<td>Low Flows 2000 (LF2000) WQX (Water Quality eXtension) water quality model</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• for the colloidal fraction, in the 0-3 ng/L range</td>
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<td>• for the larger particulate forms (&gt;450 nm), PEC were in the tens of</td>
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<td>ng/L and in 6% of locations exceeded the 50 ng/L.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gottschalk et al.</td>
<td>2011</td>
<td>Nano-TiO₂, nano-ZnO, nano-Ag</td>
<td>Modeled PEC for surface waters and assessed geographical variability and flow measurements over a 20-year period at 21 locations. Found PECs to vary by a factor of 5 due to uncertain emissions and by a factor of 10 due to</td>
<td>Rivers (543 sections) in Switzerland</td>
<td>Probabilistic mass flow analysis and graph theory</td>
</tr>
<tr>
<td>Authors</td>
<td>Year</td>
<td>NM(s) covered</td>
<td>Summary</td>
<td>Geographical scope</td>
<td>Methods</td>
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<td>--------------------</td>
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<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Gottschalk et al</td>
<td>2010b</td>
<td>nano-TiO₂</td>
<td>Modelled PEC for nano-TiO₂ in surface waters were derived in the form of probability density distributions</td>
<td>Switzerland</td>
<td>Probabilistic mass flow analysis &amp; Monte Carlo simulation and Markov Chain Monte Carlo modelling</td>
</tr>
</tbody>
</table>
| Gottschalk et al   | 2010a| Nano-TiO₂, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes | Modelled PEC values for surface water, e.g.:  
- Nano-TiO₂ 0.02 mg/L;  
- CNT 0.003 ng/L;  
- Nano-Ag 0.72 ng/L                                                                                       | Switzerland        | Probabilistic mass flow analysis & Monte Carlo simulation and Markov Chain Monte Carlo modelling |
| Gottschalk et al   | 2009 | Nano-TiO₂, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes | Modelled PEC values for surface waters ranging from 0.003 ng L⁻¹ (fullerenes) to 21 ng L⁻¹ (nano-TiO₂)                                                                                                | US, Europe & Switzerland | Probabilistic mass flow analysis and Monte Carlo (MC) and/or Markov Chain Monte Carlo (MCMC) simulations |
| Koelmans et al     | 2009 | Carbon nanoparticles            | Calculated ranges of carbon nanoparticles surface sediments and found in the worst case scenario (assuming 100% association of carbon nanoparticles with settling solids and zero removal in the sediment top layer) steady state concentrations in sediment from 40 mg/kg (shallow lakes with high sedimentation fluxes) to 2000 mg/kg (large lakes). They found concentrations of manufactured carbon-based nanoparticles in aquatic sediments will be negligible compared to levels of black carbon nanoparticles. | Hypothetical scenario | Mass balance model                                                                           |
| Mueller and Nowark | 2008 | Nano-Ag, nano-TiO₂ and CNTs      | Modelled PEC for surface waters                                                                                                                                                                         | Switzerland        | Quantitative substance flow analysis                                                          |
Key limitations in these studies stem from their use of highly uncertain available production volume data for the main NM and volume allocations to specific products. Data on production volumes and volume attribution to specific product fractions to feed into models for NM overall, specific NM and specific nanoforms of NM are not publically available. The robustness of the results would therefore benefit significantly from an increase availability of accurate, up-to-date data on production volumes for NM and product allocation. Regulation action in some countries (notably France in the EU) will start to address this gap in the near future, although it will not be comprehensive for the EU or global market. In addition, emission rates from both point and diffuse sources are also based on estimates, with very little concrete data behind them.

More recently, researchers have developed kinetic models that incorporate the specific fate and behaviour mechanisms identified as influencing NM in water and have modelling PEC based on particle number concentrations. Both working with Nano-TiO₂, Praetorius et al. (2012) modelled the transport, transformation and interaction with naturally occurring particles, while Arvidsson et al (2011) modelled the influence of sedimentation and dissolution processes. Quik et al (2011) developed a model of fate and behaviour that can be tailored to the removal rates of specific nanoform (if known). These models represent the first attempt to draw in the different fate and behaviour mechanisms operating for NM in water resulting from their specific properties and as such are particularly interesting. They suggest a strong influence of collision efficiency on final PEC values that requires further investigation. Further work is required to refine these models and, in particular, to test their robustness against empirical data from analytical measurements before they can be applied on a wider scale. Current data is focussed on specific stretches of rivers in Switzerland.

Regarding its use under the Water Framework Directive, mass concentrations based PEC could theoretically be fed into a revised risk ranking system under the modelling-based exposure assessment step of the simplified risk-based assessment procedure used to identify priority substances. Models using material mass flow analysis are similar to the multimedia model and tiered approach already used in that they draw on production volume data and use allocation data. However, the use of available data is seriously hampered by the scale. Only one study to date (Gottschalk et al. 2009) provides EU-wide data, with the remaining data relevant to individual countries or limited stretches of rivers. The modelling method has subsequently been refined to incorporate geographical variation, although the resulting data is specific to Switzerland and nano-TiO₂, nano-ZnO and nano-Ag. Further studies could usefully expand the geographical scope to EU wide and include a wider range of NM. Chief limitations relates to uncertainties in the input data on production and use.

In terms of data from kinetic studies in the form of PEC based on particle number concentration, the risk-ranking step could presumably be adapted to accept these specific metrics for NM. This would however,
impact on the comparability of results with other non-nano pollutants and preclude effective ranking of NM against other pollutants.

Although data remain limited, a number of promising models are available and further refinement can be expected over the following years. In the meantime, available data from modelling suggests that the NM with the highest surface water mass concentration PEC are likely to be the metals, specifically nano-TiO2, nano-Ag, nano-ZnO and possibly silica-based NM. This initial data could be used to drive further investigations using modelling, as well as efforts to generate in situ data for surface waters using analytical measurements in order to test the robustness of results. Further work using kinetic models is required to develop PEC based on particle number concentrations for a wider range of NM and nanoforms.

6.2.2 Groundwater Directive 2006/118/EC

The Directive on the protection of groundwater against pollution and deterioration (the Groundwater Directive)\textsuperscript{211} works together with the WFD to control the pollution of groundwater. The Groundwater Directive sets the requirement for Member States to monitor the quality of groundwater in order to assess chemical status, and to respond with prevention measure should significant and sustained upward trends in any pollutant be detected.

As such, the Groundwater Directive uses exposure data in three possible scenarios: assessing chemical status; identifying upward trends in specific pollutants; and establishing starting points for trend reversal. These three demands are described in turn, followed by a discussion of the monitoring requirements for groundwater and whether they could be applied to NM in groundwater. Finally, we review available data on NM in groundwater and consider methods that might be used to generate data.

6.2.2.1 Assessing groundwater chemical status

In assessing the chemical status of groundwater, Member States shall use two criteria, namely:

- groundwater quality standards set out in Annex I for nitrates (50 mg/l) and active substances in pesticides, including their relevant metabolites, degradation and reaction products (0.1 µg/l or 0.5µg/l); and
- threshold values established by Member States for pollutants, groups of pollutants and indicators of pollution that have been identified as contributing to the characterisation of groundwater as being

at risk (under Article 5 and Annexes II and III of the Water Framework Directive), as a minimum, pollutants listed under Annex II, Part B.

Although NM are not currently included under Annex I and no Member States has set threshold values for NM in groundwater, NM are in principle captured under Annex II, Point 2, which refers to man-made synthetic substances. Should specific nanomaterials be identified as significant pollutants of groundwater in a Member State in the future, then threshold values would need to be established for those nanomaterials against which chemical status can be assessed. As discussed under the WFD, key challenges with threshold values include questions regarding dose-response and toxicity, metrics and interference from naturally occurring nanoparticles when measuring concentrations. Regarding metrics, while some researchers suggest that measurements of particle number concentrations are more relevant in determining toxicity, currently available data for analytical measurements of NM in water samples (drinking water and influent and effluent from WWTPs) are in mass concentrations.

The Groundwater Directive states that in establishing threshold values for specific pollutants, Member States should take into account background levels for substances that may occur both naturally and as a result of human activities. Background levels are defined as “the concentration of a substance or the value of an indicator in a body of groundwater corresponding to no, or only very minor, anthropogenic alterations to undisturbed conditions”. Background levels from nanoparticles in groundwater are as yet unknown, with efforts underway to refine techniques that can distinguish naturally occurring nanoparticles from NM in water samples.

6.2.2.3 Identifying upward trends in pollutants

In identifying upwards trends in pollutants, trend identification is to be calculated against a baseline level, defined as the average value of measured at least during the reference years 2007 and 2008. The calculation of trends shall be undertaken for a body or, where appropriate, group of bodies of groundwater. The Groundwater Directive states that trends that present a significant risk of harm to the quality of aquatic ecosystems or terrestrial ecosystems, to human health or to actual or potential legitimate uses of the water environment shall be reversed. Starting points for trend reversals are to be defined as a percentage of the level of groundwater quality standards set out in Annex I and the threshold values established by Member States, on the basis of the identified trend and the environmental risk associated therewith. Reversal of a trend shall be demonstrated statistically and the level of confidence stated.

Since there are currently no Member States testing for NM in groundwater, there is no body of historical data against which to assess trends. The Groundwater Directive states that for substances identified after
the reference years 2007 and 2008, the baseline level means the average value measured during the first period for which a representative period of monitoring data is available.

6.2.2.4 Determining starting points for trend reversal

Should exposure data reveal significant and sustained upward trends, the Member States is required to implement measures to reverse them. Annex IV Part B of the Groundwater Directive establishes the criteria that determine the starting point at which measures to reverse trends must be taken. As such, measures are to be taken when the concentration of the pollutant reaches 75% of the parametric values of the groundwater quality standards set out in Annex I and of the threshold values established pursuant to Article 3, unless:

(a) an earlier starting point is required to enable trend reversal measures to prevent most cost-effectively, or at least mitigate as far as possible, any environmentally significant detrimental changes in groundwater quality;

(b) a different starting point is justified where the detection limit does not allow for establishing the presence of a trend at 75% of the parametric values; or

(c) the rate of increase and the reversibility of the trend are such that a later starting point for trend reversal measures would still enable such measures to prevent most cost-effectively, or at least mitigate as far as possible, any environmentally significant detrimental changes in groundwater quality. Such later starting point may not lead to any delay in achieving the deadline for the environmental objectives.

Regarding NM in groundwater, the relevance of using 75% of a mass-based threshold value as a starting point may be called into question, given the difficulties involved in setting thresholds due to uncertainties regarding the nature of the dose-response relationship in the ecotoxicity of NM. As such, point (a) might be used to justify an earlier starting point, were evidence available to support this being a more cost effective route to prevent or mitigate detrimental changes. Alternatively, challenges regarding the detection of NM in groundwater at a concentration of 75% of the threshold value could justify an earlier starting point, should a threshold be set.

6.2.2.5 Monitoring Groundwater Chemical Status

As mentioned above, exposure data feeding into the assessment of chemical status, as well as the identification of upward trends in pollutants, is raw data generated by analytical monitoring of groundwater bodies.
Requirements for the type and frequency of groundwater monitoring are laid down in Annex V of the WFD. Annex V point 2.4 sets out the requirements for establishing a groundwater monitoring network, with the aim of meeting the objectives of Article 7 of the WFD on waters used for the abstraction of drinking waters and Article 8 on monitoring. The network should provide a coherent and comprehensive overview of groundwater chemical status and detect the presence of long term anthropogenically induced upward trends in pollutants.

Surveillance monitoring aims at assessing long term trends, including those resulting from anthropogenic activities. Where bodies of groundwater have been identified as being at risk of failing to achieve good status, they shall be monitored for those parameters that are problematic. Operational monitoring shall be undertaken, at a minimum, once per year in the periods between surveillance monitoring and shall establish the chemical status of those groundwater bodies determined as being of risk, as well as establishing any long term anthropogenically induced upward trends in pollutants.

The Groundwater Directive recognizes that reliable and comparable methods for groundwater monitoring are an important tool in assessing groundwater quality. As mentioned in the discussion of the WFD above, guidance is available on monitoring and Directive 2009/90/EC provides further specific requirements.

In analysing exposure data, the results of individual monitoring points within a groundwater body shall be aggregated for the body as a whole and mean values calculated. Given the challenges in generating coherent and comparable data sets measuring NM in water samples, this approach to aggregating data would need to be reviewed in order to deal with the considerable uncertainties associated with analytical data on NM concentrations in water samples.

On the basis of resulting exposure data, Member States are to provide colour-coded maps of groundwater chemical status, with good status marked in green and poor in red. Upward trends in pollution are to be marked by a black dot, with trend reversal marked by a blue dot.

6.2.2.6 NM in Groundwater: Available Exposure Data and Data Generating Methods

In terms of data generated through analytical measurements, no raw data on the concentrations of NM in groundwater could be found. However, as for surface waters, it can be assumed that the analytical methods that have been used to measure NM mass concentrations in water under other studies may be relevant. Again, particular challenges may arise due to the effects of sampling techniques and the very low concentrations of NM in groundwater, as compared to higher concentrations in effluents from WWTPs. As such, the work of Chen et al (2009) in measuring very low concentrations of C60 in drinking water is
particularly relevant. In addition and as mentioned above, interference from naturally occurring nanoparticles in groundwater would also pose challenges. The availability of these analytical techniques remains at the laboratory stage.

Regarding modelling, the probabilistic mass flow analysis model developed by Gottschalk et al (2009, 2010a, 2010b, 2011) included groundwater in its “geometry” – meaning in the multi-box map of materials flows, and showed groundwater receiving emissions of NM through infiltration from surface waters and leaching from soil and landfill. However, the authors have not yet gone so far as to calculate PECs for groundwater, limiting their analysis to surface water, soil and sediment, at least in the published data. It would seem possible for this research group to use the model to generate PEC for groundwater and this would provide a basis for assessing the need to pursue analytical monitoring of groundwater.

NM are in some cases directly introduced into groundwater during remediation. Grieger et al (2010) investigated the potential environmental risks associated with using nZVI in groundwater remediation, a point source emission identified in section 2.3, and in doing so review the potential for groundwater exposure. While they do not go so far as to estimate PECs in sites following nZVI application, they consider factors likely to influence PECs and highlight nZVI migration behaviour, transformation, degradation and the potential for bioaccumulation. Regarding migration, easy migration may lead to a wider distribution of nZVI at lower concentrations, whilst inhibited transport may lead to “hot spots” of nZVI at higher concentrations close to injection points. Migration is expected to be highly dependent on site characteristics such as ambient hydrological conditions and the specific surface properties of nZVI. Regarding the latter, they explain that bare nZVI is not expect to migrate more than a few centimetres due to collision and contact with surfaces of groundwater aquifers and retention, in a context where groundwater typically have ionic strengths greater than $10^{-4}$M. In contrast, in laboratory scale experiments, Saleh et al (2008) found surface coatings to significantly increase nZVI mobility. Regarding transformation and degradation, Grieger et al (2010) highlight a lack of data and note that this is compounded by the potential for significant variation depending on characteristics of the nanoform, i.e. oxidation of the Fe$^0$ to iron oxides or the presence of organic coatings. This example serves to support the discussion in section 1.3 regarding how the wide variety of nanoforms impacts on fate and behaviour and hence on NM exposure.

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213 Sahel NK, Phenrat T, Lowry GV, Tilton RD and Matyjaszewski K (2008) “Ionic strength and composition affect the mobility of surface-modified Fe0 nanoparticles in water-saturated sand columns” Environmental Science and Technology 42: 3349-3355
6.2.3 Drinking Water Directive 98/83/EC

Directive 98/83/EC on the quality of water intended for human consumption\textsuperscript{214} sets out parametric values for chemicals in drinking water and uses exposure data generated through monitoring to ensure compliance. Member States set quality standards for drinking water that cannot be less stringent than the parametric values under Annex I. Part B of Annex I includes several substances for which nanoforms are currently in use (i.e. nickel, cadmium and copper). Should the protection of human health require it, Member States must set values for additional parameters not included in Annex I. As such, theoretically Member States could set values for specific NM (or nanoforms thereof) if they were found to pose a danger to human health.

In implementing the Directive, exposure data is generated through monitoring and the specific requirements and their possible application to NM are discussed below.

6.2.3.1 Monitoring

Monitoring requirements are set out in Article 7, with minimum requirements on the frequency of sampling and analysis specified in Annex II and specifications for the analysis of parameters set out under Annex III. The requirements do not specifically mention NM, although again some NM could be captured under certain parameters (cadmium, nickel, copper, iron). Regarding the analysis of chemical parameters, Annex III specifies performance characteristics for methods of analysis, including trueness, precision and limit of detection as a percentage of the parametric value. In addition, Part 2.1 of Annex III notes that whatever the sensitivity of the method of analysis used, the result must be expressed using at least the same number of decimals as for the parametric value considered in Annex I. For the parameters identified as capturing NM, these are:

- cadmium - µg/l,
- nickel - µg/l,
- copper – mg/l, and
- iron - µg/l.

Article 7(6) states that additional monitoring should be carried out for substances for which no parametric value has been set if there is reason to suspect that they are present in volumes that constitute a potential

danger to human health. This affords a theoretical possibility for Member States to include NM, or specific nanoforms of certain NM.

Were monitoring of NM to be required, the Annex III specifications would need to be examined. The performance requirements would need to be revised in order to account for the state of development of analytical methods to measure NM in drinking water. Secondly, given uncertainties regarding dose-response, the use of mass-based thresholds against which to measure quality may not be appropriate or feasible, and as such other parameters (e.g. size-specific particle numbers and surface area metrics) with which to measure the presence of NM in drinking water may be required.

6.2.3.2 NM in Drinking Water: Available Exposure Data and Data Generating Methods

Very limited data on NM in drinking water from analytical measurements were found to be available with one study by Chen et al reviewed in table 15 below. Drinking water presents particular challenges since mass concentrations are expected to be very low, often below current detection limits for analytical techniques. As mentioned in section 4.2, research is on-going at Arizona State University to develop specific methods and test protocols for quantifying NM in water\textsuperscript{215}. As the results of this research become available, the methods can be picked up and applied by other researchers.

\textsuperscript{215} Global Institute of Sustainability, Arizona State University, see: \url{http://sustainability.asu.edu/research/project/671/detection-of-engineering-nanomaterials-in-drinking-water,-food,-commercial-product}
Table 15: Available data on NM in drinking water

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NMs covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tiede et al</td>
<td>2011</td>
<td>Ag, Al, TiO₂, Fe₂O₃</td>
<td>Predicted mass concentrations in µg/L of a range of NM in raw water and drinking waters treated by conventional, membrane and filtration methods, using algorithms. Predicted that nano-TiO₂ will be found in the highest mass concentrations in raw and drinking waters, followed by zinc and silicon-based NMs. Estimated particle number concentrations in #/L for water treatment plant influents and effluents.</td>
<td>UK</td>
<td>Material mass flow analysis</td>
</tr>
<tr>
<td>Chen et al</td>
<td>2008</td>
<td>C60</td>
<td>The authors sought to test methods for the detection of low quantities of NM in water. Measured aqueous C60 concentration as low as 300 ng/L in tap water and ultrapure water.</td>
<td>US tap water</td>
<td>Measured NM using liquid chromatography coupled with mass spectrometry (LC/MS). Separated out from the water samples using and solid-phase extraction (SPE) separation method</td>
</tr>
</tbody>
</table>

Regarding available data from modelling, Tiede et al, 2011 predicted mass concentrations and particle number concentrations for a range of NM in raw water and treated drinking water in the UK. This is the only study currently available that looks at a range of NM in drinking water and as such, the results must be used with caution. Uncertainties arise for the use of estimates of production volumes and use patterns in the modelling approach. However, the results have considerable value in directing further research, in particular the predictions that nano-TiO₂, followed by zinc and silicon-based NM will be found in the highest mass concentrations in drinking water. They also state that for the majority of product types, human exposure via drinking water is likely to be less important that exposure via other routes. Based on models of releases from products, they suggest that future work on the risk of ENM to drinking water focus on nano-AG, nano-Al/Al₂O₃, nano-TiO₂, and nano-Fe₂O₃.
6.3 Waste Legislation

6.3.1 Urban Waste Water Treatment Directive 91/271/EEC

The Directive concerning urban waste water\textsuperscript{216} regulates the collection, treatment and discharge of urban waste water and the treatment and discharge of waste water from certain industrial sectors, with the objective of protecting the environment from adverse effects. Exposure data is generated through monitoring of discharges, sludges disposed of to surface water, and waters receiving discharges in cases where the receiving environment is expected to be significantly affected. Monitoring requirements are considered below, followed by a review of available exposure data and of available methods.

6.3.1.1 Monitoring

Monitoring must comply with the requirements of Annex ID of the Directive, in terms of parameters measured, analytical methods and sampling frequency. Parameters to be measured include biochemical oxygen demand without nitrification, chemical oxygen demand, total suspended solids, total phosphorus and total nitrogen.

As such, the Directive does not require the monitoring of the concentration levels of any NM in treated urban waste water. This review of available exposure data against the exposure data demands of the Urban Waste Water Directive is therefore speculative. At the same time, the literature on NM emission pathways identify urban waste water emissions as a key source of NM into the environment\textsuperscript{217} and as such it may become relevant to monitor emissions in the future.

6.3.1.2 NM in Urban Waste Waters: Available Exposure Data and Data Generating Methods

As mentioned above, emissions of NM from treated waste water have been identified as a key exposure pathway and several studies have therefore sought to either measure or estimate concentrations of NM in effluents from WWPTs. These are presented in table 16 below.


\textsuperscript{217} Musee N. Nanotechnology risk assessment from a waste management perspective: are the current tools adequate? J Human Exper Toxicol (in press)
<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NMs covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kiser et al</td>
<td>2012</td>
<td>Fullerene, Ag, Au, polystyrene</td>
<td>Estimated removal during wastewater treatment using freeze-dried, heat-treated (FDH) activated sludge (AS)</td>
<td>Field scale WWTP</td>
<td>USEPA standard method (OPPTS 835.1110)</td>
</tr>
<tr>
<td>Tiede et al</td>
<td>2011</td>
<td>Wide range of NM</td>
<td>Modelled concentrations of a range of NM in influent and effluent from WWTPs using algorithms</td>
<td>UK</td>
<td>Adaptation of the CHMP surface water exposure model</td>
</tr>
<tr>
<td>Gottschalk et al,</td>
<td>2011</td>
<td>nano-TiO₂, nano-ZnO, nano-Ag,</td>
<td>Modelled emissions, including from WWTP in order to calculate PEC for 543 river sections</td>
<td>Switzerland</td>
<td>Probabalistic mass flow analysis &amp; graph theory</td>
</tr>
<tr>
<td>Westerhoff et al</td>
<td>2011</td>
<td>nanoTiO₂</td>
<td>Measured Ti mass concentrations in raw sewage and treated effluent:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• raw sewage Ti concentrations ranged from 181 to 1233 µg L⁻¹ (median of 26 samples was 321 µg L⁻¹);</td>
<td>for 10 representative WWTPs (US)</td>
<td>Colloidal materials: rota-evaporation, dialysis and lyophilisation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• all WWTPs had effluent titanium concentrations of less than 25 µg L⁻¹ (96% removal rate).</td>
<td></td>
<td>Nanoparticles: High resolution transmission electron microscopy and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Qualitative analysis found spherical titanium oxide nanoparticles (crystalline and amorphous) on the order of 4 to 30 nm in diameter in WWTP effluents</td>
<td></td>
<td>energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>Johnson et al</td>
<td>2011</td>
<td>Colloidal and particulate Ag</td>
<td>Measured Ag in influents and effluents of WWTPs, finding</td>
<td>WWTP located across southern, central and northern England</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• For colloidal Ag (2-450 nm) 12 ng/L in the influent and 6 ng/L in the effluent;</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• for particulate Ag (&gt;450 nm) 3.3 µg/L for influent and 0.08 µg/L for effluent.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gottschalk et al,</td>
<td>2010b</td>
<td>nano-TiO₂</td>
<td>Modeled emissions, including from WWTP in order to calculate PEC</td>
<td>Switzerland</td>
<td>Probabalistic mass flow analysis</td>
</tr>
<tr>
<td>Farré et al.</td>
<td>2010</td>
<td>C60, C70, and functionalised C60 fullerenes</td>
<td>Measured concentrations of C60, C70, and functionalised C60 fullerenes wastewater treatment plant effluent - a maximum C60 concentration of 19 µg/L</td>
<td>22 WWTP in Catalonia, Spain</td>
<td>Ultrasonication extraction from suspended solids in wastewater and liquid chromatography (LC) coupled to a hybrid triple-quadrupole linear ion-trap mass spectrometer</td>
</tr>
<tr>
<td>Gottschalk et al,</td>
<td>2009/2010a</td>
<td>nano-TiO₂, nano-ZnO, nano-Ag, CNT, and fullerenes</td>
<td>Modeled emissions, including from WWTP in order to calculate PEC. Highlighted the importance of flows from production, manufacturing and consumption to WWTPs and from WWTPs to water in effluents and to soil in sludges for specific NM. WWTP effluent identified as an important flow of fullerenes to surface</td>
<td>2009 – US, Europe &amp; Switzerland 2010a&amp;b - Switzerland</td>
<td>Probabalistic mass flow analysis</td>
</tr>
<tr>
<td>Authors</td>
<td>Year</td>
<td>NMs covered</td>
<td>Summary</td>
<td>Geographical scope</td>
<td>Methods</td>
</tr>
<tr>
<td>-----------------</td>
<td>------</td>
<td>---------------</td>
<td>------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>--------------------</td>
<td>--------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Kiser et al</td>
<td>2009</td>
<td>Nano-Ti</td>
<td>Quantified mass concentrations of nano-Ti at each point along the WWTP process train, finding the following mass concentrations: 100 to nearly 3000 μg Ti/L in raw sewage; 10-100 μg/L nano-Ti in effluent; 1 to 6 μg Ti/mg in settled solids; 1.1 ± 0.42 mg Ti/g in sludge; and 2572 μg/L in the activated sludge system. NM were sized and visually characterised as individual nanoparticles as well as spherical aggregates.</td>
<td>Field scale WWTP</td>
<td>Scanning electron microscopy/electron dispersive X-ray microanalysis (SEM/EDX) technique</td>
</tr>
<tr>
<td>Mueller and Nowark</td>
<td>2008</td>
<td>nano-Ag, nano-TiO2 and CNTs</td>
<td>Modelled emissions, including from WWTP Switzerland</td>
<td></td>
<td>Quantitative substance flow analysis</td>
</tr>
<tr>
<td>Limbach et al</td>
<td>2008</td>
<td>Nano-CeO</td>
<td>Measured concentrations of nano-CeO in treated waste water of 2-5ppm. Distinguished unagglomerated particles and small agglomerates with a hydrodynamic aggregate diameter &lt;200 nm using a centrifugation step.</td>
<td>Model sewage treatment plant</td>
<td>Scanning electron transmission microscopy Centrifugation for qualitative analysis</td>
</tr>
</tbody>
</table>
Analytical methods have been used to generate mass concentrations of specific NM in urban waste waters by Kiser et al (2012), Westerhoff et al. (2011), Johnson et al. (2011), Farré et al (2010) and Kiser et al (2009). Several of these studies focussed on the removal efficiency of the WWTP for NM, with Kiser et al (2009) specifically charting the allocation of nano-Ti at each point along the WWTP train and in all outputs.

Regarding data from modelling, studies have used material mass flow analysis to generate estimates of mass concentrations in the influent and effluent of WWTPs. Notably, in their macro-scale analysis of the flows of NM Gottschalk et al (2009) highlighted the importance of flows from production, manufacturing and consumption to WWTPs and from WWTPs to water in effluents and to soil in sludges for specific NM. In particular, fullerenes were identified as being channelled to surface waters in the effluent of WWTPs.

Given the limited requirements of the Urban Waste Water Directive on concentrations of pollutants in effluents, it would seem that the value of the exposure data generated under these studies lies in demonstrating the importance of treated urban wastewaters as an exposure pathway for specific NM, rather than feeding into implementation of the Urban Waste Water Directive. The data is particularly informative regarding the considerable efficiency of WWTPs in removing NM from wastewaters and their deposition in sewage sludge.

On the basis of this data combined with available ecotoxicology and toxicology data, regulators may choose to consider upstream controls for specific NM in products that have been or may be identified as significant diffuse sources over the product life cycle. The data is also informative for implementation of the Sewage Sludge Directive, discussed in the following section.

### 6.3.2 Sewage Sludge Directive 86/278/EEC

The aim of Directive 86/278/EEC\(^{218}\), the Sewage Sludge Directive, is to encourage the spreading of sewage sludge from waste water treatment plants\(^{219}\) in agricultural fields and to prevent harmful effects on soil, vegetation, animals and man of this use. In preventing harmful effects, limit values are set for heavy metals concentrations in soil (mg/kg of dry matter), for heavy-metal concentrations in

\(^{218}\) Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, OJ L 181, 4.7.1986, p. 6–12

\(^{219}\) Sewage sludge is defined under Article 2(a) as: i) residual sludge from sewage plants treating domestic or urban waste waters and from other sewage plants treating waste waters of a composition similar to domestic and urban waste waters, ii) residual sludge from septic tanks and other similar installations for the treatment of sewage; and iii) residual sludge other than the ones referred to in (i) (ii).
sludge for use in agriculture (mg/kg of dry matter), and for total volumes of heavy metals that may be added annually to agriculture land based on a 10-year average (kg/hectare/year). Limit values have been established for cadmium, copper, nickel, lead, zinc, mercury and chromium. There are no specific limit values for the nano-form of these heavy metals, or for any other specific nanomaterials. Sewage sludge is a residue of treated waste waters and is likely to contain NM that have sedimented out of waste waters in the waste water treatment plant, with modelling data supporting this assumption (see below).

Exposure data is required to ensure compliance with limit values and the Directive therefore sets requirements regarding analysis and sampling, reviewed below.

6.3.2.1 Analysis and Sampling

Article 9, read in conjunction with Annex II A, II B and II C, establishes criteria and a methodology to be followed by Member States for the analysis and sampling of sewage sludge and soil. Pursuant to Annex II A, chemical parameters for analyses include: cadmium, copper, nickel, lead, zinc, mercury, chromium. The methods of analysis for heavy metals are specified as atomic absorption spectrometry following strong acid digestion. The detection limit for each metal should be no greater than 10% of the appropriate limit value.

5.3.2.2 NM in Sewage Sludge: Available Exposure Data and Data Generating Methods

Following on from the discussion of available data on NM in effluent from WWTPs, many of the same studies are relevant and presented in table 17 below. In terms of analytical measurements, Kiser et al. (2012) estimated removal rates of Fullerene, nano-Ag, nano-Au, nano-polystyrene from wastewaters into sludge in WWTPs. Most recently, Kim et al (2012) identified and characterised nano-TiO₂ in sewage sludge products and went on to identify aggregates of nano-TiO₂ with the same structure in soil mesocosms, demonstrating the transfer of nano-TiO₂ from sludge to soil. In 2010 Kim et al identified and characterised nano-Ag in sewage sludge, while in 2009 Kiser et al measure mass concentrations of nano-Ti at each stage of the wastewater treatment process, including in sludge. Farkas et al (2010) measured nano-AG in sewage sludge and went on to model the annual application of nano-Ag to Norwegian soils. A number of studies have also modelled emissions of NM into soil through sludge. Collectively, these studies have effectively demonstrated the transfer of NM from wastewaters into sludges and from there into soils. These initial findings suggest that the spreading of sludges on soils may represent a significant environmental exposure route for specific NM and that further investigation is warranted.
### Table 17: Available data on NM in sewage sludge

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NM covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kiser et al</td>
<td>2012</td>
<td>Fullerene, nano-Ag, nano-Au, nano-polystyrene</td>
<td>Estimated removal during wastewater treatment using freeze-dried, heat-treated (FDH) activated sludge (AS).</td>
<td>Field scale WWTP</td>
<td>USEPA standard method (OPPTS 835.1110)</td>
</tr>
<tr>
<td>Kim et al</td>
<td>2012</td>
<td>Nano-TiO₂</td>
<td>Identified and characterised nano-TiO₂ in sewage sludge products - qualified their size as as small as 40 nm, and as large as 300 nm, having faceted shapes with the rutile crystal structure, typically forming small, loosely packed aggregates. Identified an aggregate of nano-TiO₂ with the rutile structure and with nano-Ag on their surface in soil mesocosms spiked with nano-Ag.</td>
<td>Field scale investigation and samples from mesocosms</td>
<td>analytical scanning electron microscopy and analytical (scanning) transmission electron microscopy</td>
</tr>
<tr>
<td>Tiede et al</td>
<td>2011</td>
<td>Wide range of NM</td>
<td>Modelled mass concentrations of a range of NM in sludge from WWTPs using algorithms.</td>
<td>UK</td>
<td>Adaptation of the CHMP surface water exposure model</td>
</tr>
<tr>
<td>Farkas et al</td>
<td>2011</td>
<td>Nano-Ag</td>
<td>Estimate the application of Nano-Ag to Norwegian soils per year at an additional 80.8 kg of silver due to releases into waste waters from nano-Ag containing products.</td>
<td>Norway</td>
<td>Lab measurements plus modelling</td>
</tr>
<tr>
<td>Kim et al</td>
<td>2010</td>
<td>Nano-Ag</td>
<td>Identified nano-Ag in sewage sludge and determined size, chemistry and atomic structure: size range of 5-20 nm with ellipsoidal shape, forming very small, loosely packed aggregates. Formation of Ag²⁺ nanoparticles in the sulphur rich environment.</td>
<td>Full scale WWTP</td>
<td>Analytical high-resolution transmission electron microscopy Energy-dispersive X-ray spectrometry was used to explore behaviour (formation of silver sulphide NP)</td>
</tr>
<tr>
<td>Gottschalk et al 2009/2010a</td>
<td>Nano-TiO₂, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes</td>
<td>Modelled emissions, including in sludge from WWTP.</td>
<td>2009 – US, Europe &amp; Switzerland 2010a Switzerland</td>
<td>Probabalistic mass flow analysis &amp; graph theory</td>
<td></td>
</tr>
<tr>
<td>Gottschalk et al 2010b</td>
<td>nano-TiO₂</td>
<td></td>
<td>Modelled emissions, including in sludge from WWTP.</td>
<td>Switzerland</td>
<td>Probabalistic mass flow analysis &amp; graph theory</td>
</tr>
<tr>
<td>Kiser et al</td>
<td>2009</td>
<td>Nano-Ti</td>
<td>Quantified the concentrations of nano-Ti at each point along the WWTP process train, finding 1.1 ± 0.42 mg Ti/g in sludge; and 2572 μg/L in the activated sludge system.</td>
<td>Field scale WWTP</td>
<td>scanning electron microscopy/electron dispersive X-ray microanalysis (SEM/EDX) technique</td>
</tr>
<tr>
<td>Mueller and Nowark</td>
<td>2008</td>
<td>Nano-Ag, nano-TiO₂ and CNTs</td>
<td>Modelled emissions, including in sludge from WWTP</td>
<td>Switzerland</td>
<td>quantitative substance flow analysis</td>
</tr>
</tbody>
</table>
6.3.3 Landfill Directive 1999/31/EC

Directive 1999/31/EC on the landfill of waste sets technical and operational requirements for dumping of waste in landfills with the aim of preventing or reducing negative effects on the environment, in particular the pollution of surface water, groundwater, soil and air.

Exposure data is generated under the Directive through two specific channels. Firstly, waste testing may be required in order to characterise waste and determine whether it can be accepted in relevant landfill types. Secondly, the Directive requires the monitoring of surrounding downstream and upstream surface waters and groundwater, as well as emissions from landfills in the form of leachate and gas, with the aim of identifying emissions of specific parameters. The requirements for these two processes and their potential application to NM are considered below, before a discussion of available data and methods for generating data on NM in landfill emissions.

5.3.3.1 Waste Testing and Acceptance Procedures

General procedures for the testing and acceptance of waste at landfills are detailed in Annex II (point 3) of the Landfill Directive, with more detailed provisions laid down in Council Decision 2003/33/EC. In characterising the waste, representative samples may be taken and subject to analysis on the basis of the three-level hierarchy presented in table 18 below.

<table>
<thead>
<tr>
<th>Level 1: Basic characterisation</th>
<th>This constitutes a thorough determination, according to standardised analysis and behaviour-testing methods, of the short and long-term leaching behaviour and/or characteristic properties of the waste.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 2: Compliance testing</td>
<td>This constitutes periodical testing by simpler standardised analysis and behaviour-testing methods to determine whether a waste complies with permit conditions and/or specific reference criteria. The tests focus on key variables and behaviour identified by basic characterisation.</td>
</tr>
<tr>
<td>Level 3: On-site verification</td>
<td>This constitutes rapid check methods to confirm that a waste is the same as that which has been subjected to compliance testing and that which is described in the accompanying documents. It may merely consist of a visual inspection of a load of waste before and after unloading at the landfill site.</td>
</tr>
</tbody>
</table>

Basic characterisation involves, amongst other things, both determining the composition of the waste and assessing the waste against leachate limits for chemical parameters set out for specific classes of landfill (i.e. inert, non-hazardous and hazardous landfills) in Decision 2003/33/EC. These include:

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- Leaching limit values for waste acceptable at landfills for inert waste;
- Leaching limit values for non-hazardous waste accepted at landfills for non-hazardous waste;
- Leaching limit values for hazardous waste acceptable at landfills for non-hazardous waste; and
- Leaching limit values for waste acceptable at landfills for hazardous waste.

Leaching limit values for a range of parameters are calculated at liquid to solid ratios (L/S) of 2 l/kg and 10 l/kg for total release to give mg/kg dry substance; and expressed in mg/l for $C_0$ (the first eluate of percolation test at L/S = 0.1 l/kg). The use of CEN methods for sampling and testing is required, with the leaching test methods being EN 14405 (leaching behaviour test - up-flow percolation test for inorganic constituents) and EN 12457/1-4 (Leaching – compliance test for leaching of granular waste materials and sludges). These test methods are not designed to capture NM. Decision 2003/33/EC identifies cases where testing is not required, including “where appropriate testing procedures and acceptance criteria are unavailable”. Nanowastes currently fall within this category.

### 5.3.3.2 Monitoring of Surface Water, Groundwater, Leachate and Gas

The requirements for generating emission data on water, leachate and gas control through monitoring are set out under Point 3 of Annex III. Sampling and measuring the volume and composition of leachate must be performed separately at each point at which leachate is discharged from the site, following the general guidelines on sampling technology, ISO 5667-2 (1991). Parameters to be measured in leachate vary according to the composition of the waste deposited and must be laid down in the permit to reflect the characteristics of the wastes. Should industrial waste consisting of NM be sent to landfill, this composition could make monitoring of NM in leachate relevant, depending on an understanding of the fate and behaviour of the specific NM.

Regarding monitoring of surface water, this must be performed at not less than two points, one upstream from the landfill and one downstream. Parameters to be measured and methods to be used as not specified. Gas emissions are to be monitored for parameters related mainly to the organic content of the waste.

Requirements for groundwater sampling and analysis are set out under Point 4, with sampling to be based on ISO 5667, Part 11 (1993)\(^\text{221}\). The parameters to be analysed must be derived from the expected composition of the leachate and the groundwater quality in the area, and should take account

of mobility in the groundwater zone. Trigger levels are to be laid down in permits that identify significant changes in groundwater quality that may lead to significant adverse effects.

5.3.3.3 NM in Landfills: Available Data and Methods for Data Generation

Data on potential emissions of NM from landfill is limited. A number of studies modelling PEC have included leachate from landfills as an exposure pathway, with Gottschalk et al. (2009) finding prominent flows of CNT and fullerenes to landfill. One analytical study by Benn et al (2010) measured releases of nano-Ag through leaching in a simulated landfill scenario.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NM(s) covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benn et al.</td>
<td>2010</td>
<td>Nano-Ag</td>
<td>Subjected four products to a toxicity characterization leaching procedure to assess the release of nano-Ag in a landfill. Found medical cloth to release an amount of silver comparable to the US toxicity characterization limit.</td>
<td>Lab simulation</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Gottschalk et al</td>
<td>2009</td>
<td>Nano-TiO2, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes</td>
<td>Predicted PEC based on a modelled flow system for NM. Found prominent flows of CNTs from production, manufacturing and consumption sites to landfill and from fullerenes in products to landfill.</td>
<td>US, Europe and Switzerland</td>
<td>Probabilistic mass flow analysis</td>
</tr>
<tr>
<td>Mueller and Nowark</td>
<td>2008</td>
<td>Nano-Ag, nano-TiO2 and CNTs</td>
<td>Modelled emissions, including from landfills</td>
<td>Switzerland</td>
<td>Quantitative substance flow analysis</td>
</tr>
<tr>
<td>Blaser et al</td>
<td>2008</td>
<td>Nano-Ag</td>
<td>Estimated nano-Ag leaching from landfills in modelling PEC for the Rhine river</td>
<td>Switzerland</td>
<td>Mass flow analysis</td>
</tr>
</tbody>
</table>

Further research on the fate and behaviour of NM in landfills is required before any decision can be taken on the need to monitor NM in landfill leachate. This is particularly relevant for landfills that may be receiving industrial waste containing a high proportion of NM, such as can be found in the disposal of production residues from the manufacturing of fullerenes.222

222 Royal Commission on Environmental Pollution. 27th Report (2008) RCEP, UK
6.3.4 Waste Framework Directive 2008/98/EC

Directive 2008/98/EC on waste\textsuperscript{223} (hereafter the Waste Framework Directive) establishes the general framework for waste policies, including the definition of concepts such as waste, recovery and disposal and key requirements for waste management. Requirements include the obligation for waste management operations to be permitted or registered, and the obligation for Member States to draw up waste management plans, treat waste in line with the waste hierarchy and ensure that waste management is not harmful to human health or the environment.

No specific demand for exposure data was identified under the Waste Framework Directive. Article 4 requires application of the waste hierarchy to waste prevention and management, (a) prevention; (b) preparing for re-use; (c) recycling; (d) other recovery, e.g. energy recovery; and (d) disposal. Member States shall take measure to encourage the options that deliver the best overall environmental outcome. With regards to the impact of NM in waste on application of the waste hierarchy, further understanding of the behaviour of NM within the various processes involved is required in order to deduce which options delivery the best environmental outcome. Key questions concern the effect of NM on the integrity of waste management processes and their release into the environment.

The behaviour of different nanomaterials in waste management processes and the degree of release into the environment is not yet fully understood. Initial results suggest that behaviour within process is determined by the specific properties of the nanoparticles in question, with different nanoparticles exhibiting a wide range of behaviours, making the determination of the best option specific to certain NM and to nanoforms of those NM.

6.3.4.3 NM in Waste: Available Data and Methods for Data Generation

Again, both data on NM in waste and data on emissions of NM from waste treatment processes are limited, with relevant studies presented in table 19 below.


### Table 19: Available data on NM in wastes and waste management processes

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NMs covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
</table>
| Walser et al     | 2012 | CeO₂        | CeO₂ was artificially introduced into a municipal waste incineration plant and CeO₂ was measured in fly ash, slag, slag water and flue gas, as well as in the quench water of the wet scrubber. Ce inhalable dust and UFP were measured in indoor locations as well as outdoors. Results include:  
  - Size characterisation;  
  - Ce concentrations in slag water, quench water extracts, fly ash and slag (µg/g);  
  - extracted mass in flue gas and clean gas (µg);  
  - % recovery rates for quench water fly ash and slag; and  
  - Inhalable dust in mg/m³, µg/m³ and ppm w/w and number concentrations #/cm³ and mean diameter for UFP. Residues found predominantly in the slag, fly ash and quench water. | Emmenspitz, Zuchwil, Switzerland | Quantitative analysis to measure concentration: in solid and liquid samples, ICP-MS; in air, GSP-10, EDB, ICP-MS, mobility spectrometer and condensation particle counter  
Particle number measured in air with optical devices Grimm 1.108, TSI DustTrak  
Qualitative analysis of structure, morphology and chemical composition: STEM, TEM, HAADF, EDXS  
Size characterisation: LUMISizer  
Elemental flow analysis |
| Mueller and Nowack | 2008 | Ag, TiO₂, CNT | Modelled PEC for air water and soil. Estimated worldwide production and product fractions and assumed flows through a waste incinerator with partitioning of 25% incinerated, 25% in the slag and 25% in flue gases, of which 0.1% will enter the atmosphere. | Switzerland          | Quantitative material flow analysis |
| Kobayashi et al  | 2009 | CNT         | Estimated exposure to CNT-containing dust during a general waste treatment process of CNT containing products. Maximum CNT air concentration: 0.0064 µg/m³ | Laboratory scale     |                                                                                              |
| Gottschalk et al | 2008 | TiO₂, ZnO, Ag, CNT, fullerene s | Calculated PEC as probabilistic density functions for nano-TiO₂, nano-ZnO, nano-Ag, carbon nanotubes (CNT), and fullerenes for the U.S., Europe and Switzerland. Includes estimated emissions from waste incinerators as one of 10 stages in the life cycle of the NM. | U.S., Europe and Switzerland | Probabilistic material flow analysis model based on a Monte Carlo and Markov Chain Monte Carlo approach |
| Gottschalk et al | 2010a| Ag, TiO₂, CNT | Modelled PEC for air, water soil, sediment and groundwater. Included emission estimated from waste incinerators as one of 10 stages in the life cycle of the NM. | Switzerland          | Probabilistic material flow analysis model based on a Monte Carlo and Markov Chain Monte Carlo approach |
| Gottschalk et al | 2010b| TiO₂        | Calculated PEC for nano-TiO₂ for Switzerland. Includes estimated emissions from waste incinerators as one of 10 stages in the life cycle of the NM. | Switzerland          | Stochastic stationary substance/material flow modelling. Monte Carlo simulation and Markov Chain Monte Carlo modelling |
In terms of modelling studies, Mueller and Nowack (2008) used quantitative substance flow analysis to model emissions of CNT from incinerators, while Gottschalk et al (2009) used a probabilistic material flow analysis model to estimate emissions from waste incinerators. As mentioned above, Gottschalk et al (2009) identified prominent flows of CNT and fullerenes to landfill.

6.4 Air Legislation

6.4.1 Air Quality Directive 2008/50/EC

Directive 2008/50/EC\(^{224}\) defines and establishes objectives for ambient air quality designed to avoid, prevent or reduce harmful effects on human health and the environment. It sets common methods and criteria for assessing the ambient air quality in Member States. It establishes requirements for obtaining information on ambient air quality in order to help combat air pollution and nuisance and to monitor long-term trends and improvements.

The Directive also establishes risk management for specific pollutants, namely sulphur dioxide, nitrogen dioxide and oxides of nitrogen, lead, benzene, carbon monoxide and particulate matter (PM\(_{10}\) and PM\(_{2.5}\)). Definitions of PM\(_{10}\) and PM\(_{2.5}\) under this Directive read as follows:

- **PM\(_{10}\)** shall mean particulate matter which passes through a size-selective inlet as defined in the reference method for the sampling and measurement of PM\(_{10}\), EN 12341, with a 50 % efficiency cut-off at 10 μm aerodynamic diameter;

- **PM\(_{2.5}\)** shall mean particulate matter which passes through a size-selective inlet as defined in the reference method for the sampling and measurement of PM\(_{2.5}\), EN 14907, with a 50 % efficiency cut-off at 2.5 μm aerodynamic diameter.

The following definitions of nanomaterials and ultrafine particles were applied in a 2011 AMEC study on industrial emissions of nanomaterials and ultrafine particles\(^{225}\):

- **NM** means a material in which one or more properties are determined to a significant degree by the presence of nanoscale\(^{226}\) structural features.

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\(^{226}\) Nanoscale means a scale at which the surface or interfacial properties of a material become significant compared with those of the bulk material. The term nanoscale is generally used to refer to the dimensions of the order of 1 nm to 100 nm.
Ultrafine particles (UFP) are defined as particles that have at least one dimension between 1 and 100 nm or have an aerodynamic diameter between 1 and 100 nm. Structures of larger dimensions, such as aggregated nanomaterials,\textsuperscript{227} are included provided that they have retained properties and/or functionalities.

As such, both airborne NM and UFP may constitute part of the PM\textsubscript{10}/ PM\textsubscript{2.5} size fraction, based on the definitions above. For the purpose of air emissions, nanomaterials and ultrafine particles in air emissions are likely to have been generated in some kind of combustion process, as opposed to NM. Significant sources of nanomaterials and UFP (as PM\textsubscript{0.1}) were estimated in the 2011 AMEC report and include: road and other transport; residential/commercial combustion; industrial combustion and industrial process emissions; power generation; and agriculture. The relative importance of each source type in terms of contribution to total emissions is likely to be different to that for coarser particles (such as PM\textsubscript{10}) because there are differences in particle size distributions amongst sources. As mentioned in section 3.3, building activities have also been identified as a source of UFP emissions.

The role of exposure data in implementing Directive 2008/50/EC is to monitor compliance with limit and target values for pollutants in ambient air, including the particulate matter PM\textsubscript{2.5} and PM\textsubscript{10}. The demand for monitoring data set by limit values and the reference methods for monitoring air quality for PM\textsubscript{2.5} and PM\textsubscript{10} are discussed below.

### 6.4.1.1 Limit Values for PM\textsubscript{2.5} and PM\textsubscript{10}

According to Article 13 read in conjunction with Annex XI, levels of PM\textsubscript{10} in the zones and agglomerations defined by Member States shall not exceed the limit values set out in table 20 for the protection of human health.

<table>
<thead>
<tr>
<th>Averaging period</th>
<th>Limit value</th>
<th>Margin of tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>One day</td>
<td>50 µg/m\textsuperscript{3}, not to be exceeded more than 35 times a calendar year</td>
<td>50 %</td>
</tr>
<tr>
<td>Calendar year</td>
<td>40 µg/m\textsuperscript{3}</td>
<td>20 %</td>
</tr>
</tbody>
</table>

\textsuperscript{227}NMs have specific properties and/or functionalities and can be nano-objects (sheets, tubes or particles) that may have respective one, two or three dimensions at the nanoscale, or nano-structured materials which have an internal or a surface structure at the nanoscale both of which lead to these specific functionalities. The definition of NMs therefore explicitly also covers in nanostructured materials, agglomerates or aggregates of parts which have internal or surface structures at the nanoscale, but which are larger than nanoscale and retain properties and/or functionalities that lead to specific properties that are characteristic to the nanoscale.
According to Article 16 read in conjunction with Annex XIV Member States shall take all necessary measures not entailing disproportionate cost to ensure that concentration of PM$_{2.5}$ in ambient air do not exceed the targets for the protection of human health set out in table 21 below.

Table 21: Limit and target values for PM$_{2.5}$

<table>
<thead>
<tr>
<th>Averaging period</th>
<th>Value</th>
<th>Margin of tolerance</th>
<th>Date by which limit value is to be met</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calendar year</td>
<td>Limit value: 25 $\mu$g/m$^3$</td>
<td>Decreasing from 20% in June 2008 to 0% in 2015.</td>
<td>1 January 2015</td>
</tr>
<tr>
<td>Calendar year</td>
<td>Limit value: 20 $\mu$g/m$^3$ (indicative, to be reviewed by the Commission)</td>
<td></td>
<td>1 January 2020</td>
</tr>
<tr>
<td>Calendar year</td>
<td>Target value: 25 $\mu$g/m$^3$</td>
<td></td>
<td>1 January 2010</td>
</tr>
</tbody>
</table>

The Directive also includes a national exposure reduction target and an exposure concentration obligation for PM$_{2.5}$.

There is probably insufficient reliable information at present to define comparable limit values for the protection of human health specifically from airborne NM or UFP. As mentioned under section 2.4, other metrics such as particle number and surface area are likely to be more appropriate in reflecting potential risk. Furthermore, factors such as chemical composition become increasingly important at the nano-scale, meaning that qualitative characteristics may need to be considered.

6.4.1.2 Monitoring Air Quality

Checking exposure data against these limit values therefore sets a demand for data on ambient air concentrations expressed in $\mu$g/m$^3$. Application of assessment thresholds requires data on a 24hr average and an annual average for PM$_{10}$ and an annual average for PM$_{2.5}$. Article 8 read in conjunction with Annex VI of the Directive set reference measurement methods for monitoring PM$_{10}$ and PM$_{2.5}$ as follows:

- PM$_{10}$: EN 12341:1999 ‘Air Quality — Determination of the PM$_{10}$ fraction of suspended particulate matter — Reference method and field test procedure to demonstrate reference equivalence of measurement methods’
- PM$_{2.5}$: EN 14907:2005 ‘Standard gravimetric measurement method for the determination of the PM$_{2.5}$ mass fraction of suspended particulate matter’

These methods are unlikely to be sufficient for nanomaterials and ultrafine particles, which will be captured in the fractions but not specifically identified and measured. However, it is of note that the
technical standards report ISO/TR 27628 does include guidelines on measuring occupational nano-aerosol exposure against a range of metrics. It includes methods to measure mass concentration, surface-area concentration, number concentration, size-resolved characterisation, on-line chemical analysis and single particle analysis (e.g. electron microscopy and scanning force microscopy). Similar approaches could also presumably be adopted for measuring environmental concentrations, and a number of examples of the use of analytical techniques to measure UFP in ambient air are presented in section 6.4.1.2 below.

There are naturally occurring UFP generated through natural processes such as forest fires and volcanoes. It is thought that the proportion of total ultrafine particle (PM$_{0.1}$) emissions from natural sources is much lower than that for coarser particulates (PM$_{10}$). According to Article 20 of the Directive, Member States must transmit to the Commission, for a given year, lists of zones and agglomerations where exceedances of limit values for a given pollutant are attributable to natural sources. They shall provide information on concentrations and sources and the evidence demonstrating that the exceedances are attributable to natural sources. Techniques such as elemental analysis of composition might provide options for attributing nanomaterials to natural sources, though it is currently unclear how feasible it would be to apply such techniques in practice.

6.4.1.3 Directive 2004/107/EU

It is also important to mention daughter Directive 2004/107/EU which sets target values for arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air with the aim of avoiding preventing or reducing harmful effects on the environmental and human health. Following Article 3, Member States shall take all necessary measures not entailing disproportionate costs to ensure that, as from 31 December 2012, concentrations of arsenic, cadmium, nickel and benzo(a)pyrene, used as a marker for the carcinogenic risk of polycyclic aromatic hydrocarbons, in ambient air do not exceed the target values laid down in Annex I. The target values for arsenic, cadmium, nickel and benzo(a)pyrene apply to the total content of these elements and compounds in the PM$_{10}$ fraction averaged over a calendar year. As mentioned above, airborne NM and UFP may constitute part of the PM$_{10}$ fraction and as such airborne NM or UFP of these substances would be covered.

228 Workplace atmospheres — Ultrafine, nanoparticle and nano-structured aerosols — Inhalation exposure characterization and assessment, 2007.
As a result of the requirements in the Air Quality Directive, concentrations of particulate matter in ambient air within the PM$_{10}$ and PM$_{2.5}$ size ranges are measured across the EU and these data are available on the website of the European Environment Agency. Airborne nanoparticles and UFP will be captured under these size fractions and hence included in these data. However there are no specific EU wide data available with a specific focus on nanoparticles (i.e. PM$_{0.1}$) and UFP in air.

At the same time, a fairly large number of research studies have employed analytical techniques to identify, quantify and qualitatively describe nanoparticles and UFP in ambient air. The majority of these studies have focused on the effects of traffic emissions on urban air quality by sampling ambient air in urban areas. These studies have demonstrated the importance of traffic emissions as a source of UFP in ambient air, with evidence from Europe, the USA and China. Studies have found daily variation in UFP total particle number concentrations linked to daily variation in traffic density. Limited data suggests that the size distribution of particles originating from vehicle exhausts evolves with distance from the source (NPL, 2010). Many of these studies have successfully characterised UFP by particle size and quantified the contribution of each particle size to total particle concentrations. Several studies have investigated the contribution of secondary particle formation to total particle number concentrations and identified associations with weather conditions.

Studies with a specific focus on NM are less common, although one study by Shinohara et al. modelled NM in ambient air near to a fullerene production installation.

Also using modelling, AMEC (2011) modelled mean EU-27 population mean exposure levels to UFP (as PM$_{0.1}$) in urban areas. They also estimated exposure to UFPs by source. While this data is modelled and subject to considerable uncertainties, it is the only available data that is EU-wide and has value in providing an overview.

Available data and associated methods are presented by study in table 22 below.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NM covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Du et al.</td>
<td>2012</td>
<td>PM 10nm-10μm</td>
<td>Measured in situ PM (aerosol) number size distributions between 10 nm and 10 μm on the roof of a 6-storey teaching building about 20 m above the ground within the campus of Fudan University, from October 2008 to February 2009. Used particle size-segregated monitoring to provide a quantitative measure of ambient aerosol number concentration in individual size stage and total particle size distribution. Found: • Averages of particle number concentrations to be $1.3 \times 10^4$ 1/cm$^3$; • Averages of surface area to be $6.4 \times 10^7$ μm$^2$/cm$^3$; and • Averages of and volume concentrations to be $64$ μm$^3$/cm$^3$.</td>
<td>Fudan University, Shanghai, China</td>
<td>Wide-range Particle Spectrometer (WPSTM, model 1000XP, MSP Corporation, USA), including a high-resolution Differential Mobility Analyzer (DMA), a Condensation Particle Counter (CPC) and a wide-angle Laser Particle Spectrometer (LPS)</td>
</tr>
<tr>
<td>Lonati et al.</td>
<td>2011</td>
<td>PM in the 10–20,000 nm size range</td>
<td>Measured aerosol number concentration and size distributions in the 10–20,000 nm size range at an urban background site. Daily patterns of the total particle, ultrafine (UFP, $D_p &lt; 100$ nm) and submicron (SMP, $100 &lt; D_p &lt; 1000$ nm) fine particle concentration were analysed both on seasonal (cold and warm season) and weekly (weekdays and weekends) basis. Total particle number concentrations are in the orders of $10^4$ cm$^{-3}$, with UFPs and SMPs accounting for 80% and 20%, respectively; the contribution of supermicron particles to total particle number was found to be negligible.</td>
<td>Urban background site in Milan, Italy</td>
<td>Differential Mobility Particle Sizer (DMPS) and an Optical Particle Counter (OPC)</td>
</tr>
<tr>
<td>AMEC</td>
<td>2011</td>
<td>PM$^{0.1}$</td>
<td>Estimated population mean exposure levels to UFP (as PM$^{0.1}$) on the basis of estimates of population mean exposure to PM$^{10}$ in urban areas. Mass contributions of each source to total PM$^{10}$ and PM$^{0.1}$ emissions across the EU were used to estimate exposure to UFPs by source. Population mean exposure to UFPs in ambient air from all sources as about 3 μg/m$^3$, or total particle number concentration of 6,000-35,000 particles cm$^{-3}$.</td>
<td>EU-27</td>
<td>Modelling</td>
</tr>
<tr>
<td>NPL</td>
<td>2010</td>
<td>PM</td>
<td>Measured particle size distributions by particle number counts in ambient air for 2007-9 in rural, urban background and roadside sites in the UK and found a predominance of particles &lt;0.1μm in diameter. Found a shift toward coarser particles going from roadside to urban background to rural, possible reflecting particle modification at distance from source and an increase in natural particles at the rural site. Most measurements of total particle number concentrations for particles of 7 nm to several microns in diameter using the CPC were found to be: • 5,000-15,000 particles cm$^{-3}$ at the rural site; • 5,000-30,000 particles cm$^{-3}$ at the urban site; and • 20,000-60,000 particles cm$^{-3}$ at the roadside site. Measurements with the SMPS were lower by factors of 1-5.</td>
<td>Rural, urban background and roadside sites in the UK (Harwell, North Kensington and Marylebone Road)</td>
<td>Condensation particle counter (CPC) Scanning mobility particle sizer (SMPS)</td>
</tr>
<tr>
<td>Hays et al.</td>
<td>2010</td>
<td>PM$^{10}$, PM$^{2.5}$ and PM$^{0.1}$</td>
<td>Collected 24hr PM samples from July to August 2006 20m from an interstate highway in North Carolina with a traffic flow of 125,000 vehicles/day. The overall near-highway PM mass size distribution was trimodal with a major accumulation mode peak at 500-800 nm. PM mass level correlated with daily traffic density. PM$^{10}$ concentrations were $33 \pm 7.5$ μg/m$^3$, PM$^{2.5}$,</td>
<td>North Carolina, USA</td>
<td>Samples collected using a low-pressure impactor Particle characterisation: SF-ICPMS analysis</td>
</tr>
<tr>
<td>Authors</td>
<td>Year</td>
<td>NMs covered</td>
<td>Summary</td>
<td>Geographical scope</td>
<td>Methods</td>
</tr>
<tr>
<td>--------------------------</td>
<td>------</td>
<td>-------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>--------------------------</td>
<td>----------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Price et al.</td>
<td>2010</td>
<td>Nanoparticles/UFP</td>
<td>Collected and characterised nanoparticle and UFP concentrations in heavy traffic in Swansea, Wales, and found maximum concentrations of 140,000 particles cm$^{-3}$. Qualitative analysis found the larger particles to exhibit a greater variety of morphologies and associated metals.</td>
<td>Swansea, Wales</td>
<td>Pm collection: Dekati electrical low-pressure impactor</td>
</tr>
<tr>
<td>Fernández-Camacho et al.</td>
<td>2010</td>
<td>UFP</td>
<td>Measured concentrations of UFP in ambient air and found concentrations of particles &gt;2.5 nm to be about 22,000 particle cm$^{-3}$. Vehicle exhaust and new particle formation due to photo-chemical activity were identified as contributing to UFP concentrations. Highest UFP concentrations were recorded from 11-17hr, under the sea breeze regime, when rates of secondary particle formation were greatest and it was estimated that approx. 80% of the particles were linked to sulphur dioxide emissions. The average overall contribution of secondary particles to total UFP was &gt;60%.</td>
<td>University campus, Huelva, Spain</td>
<td>Ultrafine condensation particle counter that detects particles &gt;2.5 nm with a 50% counting efficiency for particle of 3-4nm</td>
</tr>
<tr>
<td>Wang et al.</td>
<td>2010</td>
<td>PM 4 - 70 nm</td>
<td>Measured particle total number concentrations during October and November 2007. Found a daily average particle total number concentration of 19,000 cm$^{-3}$ for particles between 4 and 70 nm.</td>
<td>Montelibretti station, near Rome</td>
<td>Measurements used a Scanning Mobility particle Sizer System (SMPS) Evaluated aerosol size distribution using scanning mobility particle size with a high resolution Nano Differential Mobility Analyzer (DMA)</td>
</tr>
<tr>
<td>Lin et al.</td>
<td>2009</td>
<td>PM$<em>{0.01}$-0.056 or PM$</em>{0.01-0.1}$</td>
<td>Measured the average (mass) cumulative fraction of secondary inorganic aerosols (SO$_4^{2-}$+NO$<em>3^{-}$+NH$<em>4^+$) in PM$</em>{0.01-0.056}$ or PM$</em>{0.01-0.1}$ in roadside samples and in rural samples. The fraction of secondary inorganic aerosols was found to be three to four times higher in roadside samples. At both sites, evidence was found of NO$_3^{-}$/SO$_4^{2-}$ deposition in the nanoparticle fraction.</td>
<td>Roadside location, Taiwan</td>
<td>Not known</td>
</tr>
</tbody>
</table>
| Shinohara et al.         | 2009 | Fullerenes   | Estimated fullerene exposure levels <500 m of a factory manufacturing fullerenes under normal functioning of the emissions system at:  
• 5.51 $\times$ 10$^{-7}$ µg/m$^3$ for all particle sizes, and  
• 2.2 $\times$ 10$^{-9}$ µg/m$^3$ for particles <1000 nm. | Factory manufacturing fullerenes | Material mass flow analysis                                                                 |
| Fushimi et al.           | 2008 | PM          | Studied roadside particles and conducted qualitative analysis. Measurements taken during winter showed a sharp peak in nucleation-mode particles not seen at a background site 200m away. Diesel thought to contribute to roadside and background particles in the 0.030-0.060 µm size range. | Kawasaki City, Japan      | Qualitative analysis: carbon analysis; organic analysis                                           |
| Riddle et al.            | 2008 | PM$_{0.18}$ and PM$_{0.1}$ | Studied roadside particle concentrations and apportioned size fractions to sources. Qualitative analysis found PM$_{0.18}$ to be dominated by diesel fuel and motor oil combustion products and PM$_{0.1}$ dominated by diesel fuel and gasoline fuel combustion products. | California, USA           | Not known                                                                                         |
| Johansson et al.         | 2007 | PM$_{2.5}$ and PM$_{1}$ | Measured personal exposure for 30 Swedish adults and found: 
• Median levels of PM$_{2.5}$ were 8.4 µg m$^{-3}$ (personal), 8.6 µg m$^{-3}$ (indoor) 6.4 µg m$^{-3}$ | Gothenburg, Sweden, 30   | EPA WINS impactor                                                                                  |
<table>
<thead>
<tr>
<th>Authors al.</th>
<th>Year</th>
<th>NMs covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(residential outdoor) and 5.6 ug m⁻³ (urban background)</td>
<td>adults</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Personal exposure to PM₁ was 5.4 ug m⁻³, with indoor levels of 6.2 ug m⁻³ and outdoor levels of 5.2 ug m⁻³</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• PM₁ made up 70-80% of PM₂.₅ in each environment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qian et al.</td>
<td>2007</td>
<td>UFP</td>
<td>Continuous measurements of aerosol size distributions (3 nm – 2 µm) over a 26 month period (1 April 2001-31 May 2003) in an urban street in, in order to investigate secondary particle formation. Daily maximum in the number concentrations of UFP formed by nucleation (4.8 ± 3.5 X 10⁴ cm⁻³) as well as the maximum daily rates of 3 nm particle production (17 ± 20 cm⁻³ s⁻¹) were highly variable and showed no clear seasonal dependence. They found that particle formation increased particle concentrations by an average factor of 3.1 ± 2.8.</td>
<td>Louis, USA</td>
<td>Sunset Labs ECOC Field Analyzer, HSPH thermal/catalytic sulfate monitor, Georgia Tech / BNL Particle-into-Liquid Sampler (PILS-IC)</td>
</tr>
<tr>
<td>Moore et al.</td>
<td>2007</td>
<td>UFP</td>
<td>Monitored summer air quality June-July 2006 and measured the evolution of UFPs (&lt;180 nm in diameter) concentrations. Found UFP concentrations to be strongly influenced by traffic emissions in the morning, while during the afternoon UFP were predominantly generated through secondary photochemical reactions. They found UFP concentration to peak in the early afternoon.</td>
<td>Urban site in Los Angeles, USA</td>
<td>Micro-Orifice Uniform Deposition Impactor (MOUDI) and a Scanning Mobility Particle Sizer (SMPS)</td>
</tr>
<tr>
<td>Pakkanen et al.</td>
<td>2003</td>
<td>PM₁</td>
<td>Collected five pairs of simultaneous 24hr atmospheric aerosol samples in June 1997 at 3.5 m and 20 m at an urban site in Helsinki. Average concentrations of particles of submicron size were 11 ug m⁻³ at both heights. Identified five principle sources, including: long-range transport; mainly long-range transport with some local contribution; local oil combustion; vehicle exhaust and brake wear; and various local sources and long-range transport.</td>
<td>Urban site, Helsinki</td>
<td>Sample collection: Berner low-pressure impactors</td>
</tr>
<tr>
<td>Kellman et al.</td>
<td>2009</td>
<td>PM₀.₁</td>
<td>Studied a severe winter pollution episode in California and determined that; concentrations of elemental carbon in the PM₀.₁ size ranged from 0.03 ug m⁻³ during the day to 0.18 ug m⁻³ at night; and concentrations of organic carbon in the PM₀.₁ size ranged from 0.2 ug m⁻³ during the day to 0.8 ug m⁻³ at night. Identified the principle sources of elemental and organic carbon PM.</td>
<td>California, USA</td>
<td>GC-MS</td>
</tr>
</tbody>
</table>

6.5 **Industrial Emissions Directive 2012/75/EU**

The Industrial Emissions Directive 2010/75/EU (IED) acts to control and minimise pollution from industrial installations. The IED incorporates the previous IPPC Directive (2008/1/EC), as well as other sectoral directive addressing industrial emissions, notably the large combustion plant and waste incineration directives. The IED replaces the IPPC Directive and the sectoral directives as of 7 January 2014, with the exemption of the LCP Directive, which will be repealed with effect from 1 January 2016.

The IED operates along the same principles as the IPPC Directive, by requiring operations listed under Annex I to obtain an integrated permit from the competent authority. The IED sets a demand for exposure data generated though analytical monitoring, and more specifically, data on emissions to air and water, in order to determine compliance with emission limit values (ELVs) set out for certain types of installations. Where ELVs are not included in the Directive, the exposure data is to be compared against the emission levels associated with Best Available Techniques (BAT) for each specific sector, as set out in the BAT Reference Documents (BREFs) 231.

In addition, the IED specifies that local environmental quality standards (EQS) shall not be transgressed, and in cases where air and water standards are above EQS, stricter emissions limit values are to be set in the permits of installations emitting relevant pollutants.

A 2011 report by AMEC232 reviewed the extent to which the IED covers emissions of NM and UFP to air from industrial sources. The report identifies relevant categories of installations that may emit NM and UFP and that are covered by the IED and highlights relevant ELVs and BAT-AELS. As discussed under section 3.3. on point source emissions of NM, relevant industrial sectors include combustion installations for heat and electricity generation, as well as installations producing ferrous and non-ferrous metals, pulp and paper, chemicals, petroleum refining and food and beverage. Here, we draw on the AMEC review and go on to ask whether data and methods are available to support an assessment of emissions against IED requirements, currently limited to emissions to air of dust (PM). We also consider whether data and methods are available to support requirements for measuring emissions of NM to water and soil and in waste, were such requirements to be set in the future.

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231 For copies of the BREF documents see: [http://eippcb.jrc.es/reference/](http://eippcb.jrc.es/reference/)

The emissions monitoring data that is currently required to ensure compliance with ELV and to allow for comparison with BAT-Associated Emission Levels (BAT-AELS) is identified below, followed by a discussion of the role of the BREFs in ensuring that the IED keeps pace with innovation.

6.4.2.1 Emissions Monitoring

As mentioned above, emissions data is required in order to check compliance with ELV in the IED, or to compare with BAT-AELs in the sector specific BREFs. Following Article 14(c), suitable emission monitoring requirements are to be included in the permit conditions for Annex I installations, including requirements for measurement methodology, frequency and evaluation procedures. These are to be based on the horizontal BREF on “General Principles on Monitoring”233 published in 2003 and for which a review has just been initiated. Periodic monitoring shall be carried out at least once every 5 years for groundwater and 10 years for soil, unless based on a systematic appraisal of the risk of contamination.

Currently, particles at nano-scale may be covered by ELV and BAT-AELs set for emissions to air of dust (or particulate matter) for specific sectors. Sectors for which there is coverage of dust are set out in table 23 below. The ELVs and BAT-AELs are almost all based on units of mass concentration, with a limited number based on mass emissions per unit of production. ELVs for air emissions generally expressed in terms of mass concentration g/m³ - mg/Nm³. The mass metric may not be the most relevant for NM, rather metrics such as particle number and surface area concentration may be more important.

Within the IED, certain sectors receive specific attention. Specific requirements are set for monitoring air emissions from combustion plants (Annex V) and from waste incineration plants and waste co-incineration plants (Annex VI) in order to verify compliance with relevant ELVs. Sampling an analysis shall be carried out according to CEN standards, or when not available to ISO, national or other international standards which ensure the provision of data of an equivalent scientific quality.

233 JRC (2003) General guidance on monitoring, JRC, Sevilla
### Table 23: IED Annex I sectors with ELV and/or BATAELs for dust or particulates

<table>
<thead>
<tr>
<th>IED Activity</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Combustion of fuels in installations with a total rated thermal input of 50MW or more</td>
<td>ELVs for dust in the IED</td>
</tr>
<tr>
<td></td>
<td>BAT-AELS in the LCP BREF</td>
</tr>
<tr>
<td>1.2 Refining of mineral oil and gas</td>
<td>BAT-AELS for dust in the refineries BREF</td>
</tr>
<tr>
<td>2.1 Metal ore (including sulphide ore) roasting or sintering</td>
<td>BAT-AEls for dust set out in the BREFs on:</td>
</tr>
<tr>
<td>2.2 Production of pig iron or steel (primary or secondary fusion) including</td>
<td>• Ferrous metals processing</td>
</tr>
<tr>
<td>continuous casting, with a capacity exceeding 2,5 tonnes per hour</td>
<td>• Non-ferrous metals industry</td>
</tr>
<tr>
<td>2.3 Processing of ferrous metals: (a) operation of hot-rolling mills with a capacity</td>
<td>• Iron and steel production</td>
</tr>
<tr>
<td>exceeding 20 tonnes of crude steel per hour; (b) operation of</td>
<td>• Smelteries and founderies</td>
</tr>
<tr>
<td>smelters with hammers the energy of which exceeds 50 kilojoule per hammer, where the</td>
<td></td>
</tr>
<tr>
<td>calorific power used exceeds 20 MW; (c) application of</td>
<td></td>
</tr>
<tr>
<td>protective fused metal coats with an input exceeding 2 tonnes of crude</td>
<td></td>
</tr>
<tr>
<td>steel per hour.</td>
<td></td>
</tr>
<tr>
<td>2.4 Operation of ferrous metal foundries with a production capacity extending 20 tonnes per day</td>
<td></td>
</tr>
<tr>
<td>2.5 Processing of non-ferrous metals</td>
<td></td>
</tr>
<tr>
<td>3.1 Production of cement, lime and magnesium oxide: (a) production of cement clinker</td>
<td>BAT-AELs in cement and lime BREF</td>
</tr>
<tr>
<td>in rotary kilns with a production capacity exceeding 500 tonnes per day;</td>
<td></td>
</tr>
<tr>
<td>(b) production of lime in kilns with a production capacity exceeding 50</td>
<td></td>
</tr>
<tr>
<td>tonnes per day; (c) production of magnesium oxide in kilns</td>
<td></td>
</tr>
<tr>
<td>with a production capacity exceeding 50 tonnes per day.</td>
<td></td>
</tr>
<tr>
<td>4.1 Production of organic chemicals</td>
<td>BAT-AEls for dust in BREFs for:</td>
</tr>
<tr>
<td></td>
<td>large volume organic chemicals and manufacture of organic fine chemicals</td>
</tr>
<tr>
<td>4.2 Production of inorganic chemicals</td>
<td>BAT-AEls for dust in BREFs on:</td>
</tr>
<tr>
<td></td>
<td>• Chlor-alkali manufacturing industry</td>
</tr>
<tr>
<td></td>
<td>• Large volume inorganic chemicals:</td>
</tr>
<tr>
<td></td>
<td>• ammonia, acids, and fertilizers</td>
</tr>
<tr>
<td></td>
<td>• Large volume inorganic chemicals:</td>
</tr>
<tr>
<td></td>
<td>• solids and others industry</td>
</tr>
<tr>
<td></td>
<td>• Speciality inorganic chemicals</td>
</tr>
<tr>
<td>4.3 Production of phosphorous-, nitrogen- or potassium-based fertilisers</td>
<td>BAT-AELs for dust in BREFs on large volume</td>
</tr>
<tr>
<td>(simple or compound fertilisers)</td>
<td>inorganic chemicals: ammonia, acids, and</td>
</tr>
<tr>
<td>4.4 Production of plant protection products or of biocides</td>
<td>fertilizers</td>
</tr>
<tr>
<td>4.5 Production of pharmaceutical products including biocides</td>
<td></td>
</tr>
<tr>
<td>4.6 Production of explosives</td>
<td></td>
</tr>
<tr>
<td>5.2 Disposal or recovery of waste in waste incineration plants or in waste co-incineration plants:</td>
<td>ELVs for dust in the IED</td>
</tr>
<tr>
<td>(a) for non-hazardous waste with a capacity exceeding 3 tonnes per hour;</td>
<td>BAT-AELS in the WI BREF</td>
</tr>
<tr>
<td>(b) for hazardous waste with a capacity exceeding 10 tonnes per day.</td>
<td></td>
</tr>
<tr>
<td>6.1. Production in industrial installations of: (a) pulp from timber or other fibrous</td>
<td>BAT-AELS for dust in the pulp and paper</td>
</tr>
<tr>
<td>materials; (b) paper or card board with a production capacity exceeding 20 tonnes per day;</td>
<td>BREF</td>
</tr>
<tr>
<td>(c) one or more of the following wood-based panels: oriented strand board, particleboard or</td>
<td></td>
</tr>
<tr>
<td>fibreboard with a production capacity exceeding 600 m3 per day.</td>
<td></td>
</tr>
<tr>
<td>6.4. (a) Operating slaughterhouses with a carcass production capacity greater than 50 tonnes per day;</td>
<td>Suggested techniques in the BREF on</td>
</tr>
<tr>
<td>(b) Treatment and processing, other than exclusively packaging, of the following raw materials,</td>
<td>slaughterhouses</td>
</tr>
<tr>
<td>whether previously processed or unprocessed, intended for the production of food or feed; (c)</td>
<td>BAT-AEls for dust in the BREF on food,</td>
</tr>
<tr>
<td>Treatment and processing of milk only, the quantity of milk received being</td>
<td>drink and milk industries</td>
</tr>
<tr>
<td>greater than 200 tonnes per day (average value on an annual basis).</td>
<td></td>
</tr>
</tbody>
</table>
Currently therefore, the IED only addresses emissions of dust (or particulate matter) to air from specific industrial sectors. As mentioned in the section above, the particulate matter fraction will contain NM and UFP (as PM$_{0.1}$), as well as the coarser fractions, and to this extent they are covered.

Were emissions of NM from IED Annex I activities to be identified as contributing significantly to environmental exposure to NM as point source emitters of NM to water, soil or in wastes, it would then become relevant to target those point sources for emissions controls. For example, the IED covers installations producing titanium dioxide, therefore including those installations producing the nano-form and it is possible that such installations represent point source emitters of nano-TiO$_2$. Requirements for monitoring and ultimately controlling NM in waste waters or in solid wastes could then be included in the permit conditions for relevant installations, based on the performance of BAT as listed in the BREF. The role of the BREF in pulling in substances identified as pollutants, in this case NM, is discussed below.

6.4.2.2 Role of the BREFs

In their 2011 report, AMEC reviewed the coverage of NM/UFP in the BREFs and found coverage to be limited. Relevant coverage focuses on the efficiency of air emission control techniques in collecting particulates, namely ESP, bag filters and wet scrubbers. There are no specific provisions for NM/UFP in a number of relevant BREF, including those for the pulp and paper industry, tanneries, refineries and LCPs. The pulp and paper BREF is currently under revision and the most recent 2012 draft only mentions nano in terms of the possible application of nano-filtration to water treatment$^{234}$.

While this may currently be the case, the BREFs are subject to review in order to keep pace with technological innovation in the field of pollution control and industrial processing. Emerging techniques are also listed in the BREF and their status checked at the next review in order to determine whether they may be brought in as BAT. As the efficiency of emission control techniques in industrial processing in controlling emissions of UFP and, eventually, NM, these developments will be picked up under the Sevilla Process and brought into the BREF. IED permits may then start to include requirements with a specific focus on NM.

While it might be thought that in the absence of current EQS for NM pressure is limited for the development of emission control techniques, investigation is being driven in some cases by occupational health and safety concerns. For example, Shiue et al. (2012) investigated the removal

efficiency of fan dry coil units (FDCUs) return system for 0.1–5 μm particles and found removal rates of 61 to 67%\textsuperscript{235}. Some of these control techniques may be transferrable to controlling emissions to the environment.

6.4.2.2 NM in Industrial Emissions: Available Data and Methods for Data Generation

The IED takes an integrated approach to managing emissions from industrial installations and as such demands data on emissions to air, water and soil, as well as for wastes generated at Annex I industrial sites. In terms of available analytical data to feed into an assessment of the overall emissions from an installation, there are limited data available, with the majority of data focussed on emissions to air of particulates and UFP in flue gases from combustion processes. Available data and possible methods for data generation are discussed below for emissions from industrial installations to air, water and soil, as well as in wastes.

Emissions to Air

Available data on emissions of NM and UFP to air are presented in table 24 below and are very limited. Notable is a 2009 study undertaken by Shinohara et al.\textsuperscript{236}, who modelled the fullerene exposure levels within 500 m of a factory manufacturing fullerenes, although they did not actually measure concentrations in flue gases from the installation. Another study of relevance is by Kumar et al. (2012)\textsuperscript{237}, who measured releases of particles from simulated building activities in a lab simulation. Although construction is not an IED activity, the analytical method (fast response differential mobility spectrometer) may be relevant for monitoring releases of NM and UFP from industrial sources and provides the only analytical data on air emissions from a specific activity available.

Most recently, AMEC estimated population mean exposure to PM\textsubscript{0.1} in EU urban areas on the basis of the mass contribution of each type of source to total emissions of PM\textsubscript{0.1} and PM\textsubscript{10} across the EU27. In isolating emissions for specific sources, they estimated that total emissions of PM\textsubscript{0.1} from industrial sources estimated to account for <5% of total emissions of PM\textsubscript{0.1}, small compared to emissions from

\begin{footnotesize}
\begin{itemize}
\item 237 Kumar, P., Mulheron, M., Claudia, S., 2012, Release of ultrafine particles from three simulated building activities, Journal of Nanoparticle Research 14, 771
\end{itemize}
\end{footnotesize}
other sources, in particular road transport. In addition, they argue that emissions of NM (i.e. not resulting from combustion processes) from industrial sources are likely to represent a very small fraction (<1-2%) of emissions from industrial sources, given that NM are manufactured in modern installations and are valuable materials. They therefore estimate population mean exposure to NM in ambient air >1.3 µg/m³, if not less, and suggest that this will be an extremely small proportion of any future health risk.

The paucity of data on emissions of nanoparticles and UFPs in the PM₀.₁ range is partly due to difficulties in measuring air quality in conditions found in most industrial installations, including high temperatures, semi volatile flue gas components (driving particle nucleation and/or condensation phenomena and as such affecting particle number concentrations) and dynamic physicochemical processes. Another explanation is the lack of regulatory requirements for routine monitoring of emissions to air of NM or UFP specifically (i.e. not as a component of the dust fraction). While there are currently no relevant standards or guidelines, a number of studies have measured nanoparticles and UFP in air, as discussed in the section above on air quality. In terms of available analytical techniques for measuring nanoparticles in air, a range of methods are available for measuring particles number, surface area, size and mass and these methods are summarised below:

- Surface area: TEM, SED, diffusion charger, ELPI, MOUDI
- Size: AFM, DMA, photon correlation spectroscopy, X-ray diffraction
- Number: CPC, OPC, SEM/TEM, SMPS
- Mass: size-selective static sampler, TEOM, filter collection with elemental analysis

More data has been generated for occupational risk assessments, with a focus on exposure through air, and the analytical methods may in some cases be applicable to measuring concentrations in the surrounding environment. An example of a relevant study by Yang et al. (2012) is included in table 24 below, where they measured particle number concentrations inside an industrial installation manufacturing nano-TiO₂.

In their 2011 report, AMEC consider the possible use of fingerprinting techniques to determine the source of emissions measured in ambient air. Such techniques rely on Transmission Electron Microscopy (TEM) plus energy-dispersive X-ray spectroscopy (EDX) and are at the early stages of development.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Year</th>
<th>NMs covered</th>
<th>Summary</th>
<th>Geographical scope</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yang et al.</td>
<td>2011</td>
<td>nano-TiO$_2$</td>
<td>Measured nanoparticle number concentration distributions in samples taken from the pulverisation workshop of a plant manufacturing nano-TiO$_2$. Found aerosol nanoparticles were mainly agglomerated particles, with average diameters of 124.2 nm for primary particles and 524.4 nm for agglomerations. The number concentration of aerosol particles increased with vertical distance from the source, but decreased with horizontal distance from the source.</td>
<td>Industrial installation in China</td>
<td>Measuring particle number: Wide-range particle spectrometer (WPS 1000XP-A, MSP corp., USA), sampling flow rate of 1.0 L/min Characterisation: Field emission scanning electron microscopy (FESEM, UltraPLus, Carl Zeiss, German) Measuring particle diameters: ImageJ</td>
</tr>
</tbody>
</table>
| AMEC | 2011 | PM$_{0.1}$ | Mass contributions of each source to total PM$_{10}$ and PM$_{0.1}$ emissions across the EU were used to estimate exposure to UFPs by source.  
- Population mean exposure to UFPs in ambient air from all sources as about 3 $\mu$g/m$^3$;  
- Population mean exposure to NM in ambient air >1.3 $\mu$g/m$^3$;  
- Total emissions of PM$_{0.1}$ from industrial sources estimated to account for <5% of total emissions of PM$_{10}$ | EU-27 | Modelling |
| Kumar et al. | 2012 | UFP | Measured the release of particles in the 5–560 nm range from three simulated building activities: the crushing of concrete cubes, the demolition of old concrete slabs, and the recycling of concrete debris. measure particle number concentrations (PNC) and size distributions (PNDs) | Lab simulation | Fast response differential mobility spectrometer (Cambustion DMS50) |
| Shinohara et al. | 2009 | Fullerenes | Estimated fullerene exposure levels <500 m of a factory manufacturing fullerenes under normal functioning of the emissions system at:  
- $5.51 \times 10^{-7}$ $\mu$g/m$^3$ for all particle sizes, and  
- $2.2 \times 10^{-9}$ $\mu$g/m$^3$ for particles <1000 nm. | Factory manufacturing fullerenes | Material mass flow analysis |
**Emissions to Water**

Regarding emissions of NM to water from IED Annex I industrial installations, no analytical data is currently available. No analytical studies were found that sought to identify or measure NM in industrial effluent. In reviewing the list of Annex I industries, a number are known to use nanotechnology in their production processes, including for example the pulp and paper sector and the food and beverages sector, as well as installations producing NM themselves that would fall under Annex I for the production of organic or inorganic chemicals.

Despite the current lack of data, we can presume that the analytical methods discussed under the water legislation in section 6.2 and in particular under the Urban Waste Water Directive in section 6.3.1 would serve equally for identifying and determining NM concentrations in industrial effluent, with all the identified limitations applying (impacts of fate and behaviour, influence of sampling techniques, etc.). As such, it should be possible to identify and measure emissions of NM in the effluent of industrial installations, should the IED require this in the future.

In terms of modelling data, the probabilistic material based mass flow analysis model developed by Gottschalk et al and applied in their 2009, 2010a, 2010b and 2011 studies estimates emissions of NM from production, manufacturing and consumption facilities to air water and soil, as one of the boxes in the multi-box geometry of the model. In their 2009 article, Gottschalk et al identify emissions from PMC as a significant flow for nano-TiO\(_2\) and nano-Ag. The data on emissions from this box could, in theory, be used to identify those NM for which emissions from industry are expected to be significant. This raw data is not publically available in the published articles on these studies, but was generated to feed into the PEC predictions.

**Emissions to Soil**

No data are available on emissions of NM from industrial installations to soil. Possible emission pathways to soil from Annex I installations include for example, the spreading of sludges on land and possible leaching into soils from on-site landfills.
**Industrial Wastes**

No data are available on NM in industrial. However, the absence of evidence should not be taken as the absence of NM in industrial emission streams. Rather ever increasing applications of NM in industrial processes suggest that NM will increasingly be found in industrial waste. For example, given the use of NM in the pulp and paper industry, as well as in inks, it can be assumed that sludges from pulp and paper making installations and from paper recycling installations would contain NM.

### 6.6 Overall Analysis of Available Data and Methods Against the Demand for Exposure Data in EU Environmental Legislation

As noted in the introduction, no environmental legislation currently sets specific demands for NM exposure data and hence the term “demand” is used speculatively, meaning were legislation to include specific requirements for nano-scale particles, be they nanoparticles, UFP or NM, what exposure data would then be required. Possible exceptions to this include the Water Framework Directive and the Air Quality Directive.

The Water Framework Directive requires Member States to monitor priority substances, as well as “other pollutants discharged in significant quantities” in surface waters. Setting aside the considerable challenges in determining what significant qualities are for NM, if an NM were to be identified as a pollutant of a particular river basin by a Member State authority, exposure data would be required for the relevant river basin. However, this is a chicken and an egg scenario, whereby an NM could only be identified as a pollutant if data were available to support this. Data is not available, since analytical methods for application in a regulatory context are not available and NM are not currently being monitored in surface waters by any Member State. So the absence or presence of NM in surface waters is unknown.

Demands under the Air Quality Directive are limited to the monitoring of the particulate matter fractions PM$_{10}$ and PM$_{2.5}$ under the air legislation, and while these fractions will capture UFP and aerosol nanoparticles (including airborne NM), they are not specific to this smaller fraction.

The analysis of available NM exposure data against demands is therefore essentially speculative. At the same time, available exposure data for NM serve as a key element in wider decision-making as to whether NM in the environment require regulatory attention.
Table 25 provides an overview of available data broken down into analytical, simulation and modelling data, against potential legislative demand under EU environmental legislation. A cross indicates the availability of data specific to that medium or emission pathway generated under one study or more.

Table 25: Summary of available data against legislative demand for exposure data

<table>
<thead>
<tr>
<th>Legislation</th>
<th>Analytical data</th>
<th>Simulation studies</th>
<th>Modelling data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Framework Directive</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Groundwater Directive</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drinking Water Directive</td>
<td>X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Drinking Water Directive</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Urban Waste Water Directive</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Sewage Sludge Directive</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Landfill Directive</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Waste Framework Directive</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Air Quality Directive</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial Emissions Directive</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Regarding data for implementation of the Water Framework Directive, all available data is generated using models, with no analytical data from monitoring surface waters available. The primary use of exposure data is for the identification of priority substances, and their subsequent monitoring. The current lack of cost-effective analytical techniques that can be applied in a regulatory context has significant implications for the implementation of water legislation, specifically for the detection of pollutants in surface waters. Regarding the usefulness of data from modelling, key issues include questions of scale, metrics and how knowledge regarding the fate and behaviour of NM in aqueous media are dealt with.

In terms of scale, the identification of priority substances using modelling data demands EU wide estimates of PEC. Only one study (Gottschalk et al, 2009) provides EU wide PEC for a number of metal-based and carbon-based ENM. The authors have subsequently refined their model (Gottschalk et al, 2011) to incorporate spatial and temporal variability and hence yield localised data over a wide region, but this more recent data is limited to Switzerland. Further studies at the wider EU scale using this model may serve to provide useful mass concentration exposure data that could be fed into the identification of priority substances. Uncertainties in the data relate to the robustness of input data on ENM production values and emissions of ENM from diffuse and point sources.
Regarding metrics, the majority of the available data is provided in mass concentrations, in some cases complemented by particle number concentrations. The most recent kinetic models have generated data in the form of particle number concentrations. The risk ranking system under the modelling-based exposure assessment step of the simplified risk-based assessment procedure used to identify priority substances would require adaptation in order to incorporate data in the form of particle number concentrations. Such adaptations would then affect the comparability of results against non-nano pollutants.

A number of authors have stressed the importance of fate and behaviour in affecting environmental exposure to NM and ultimate risk. The most recent kinetic models seek to incorporate growing knowledge about the importance of collision efficiency. Currently, resulting data is limited to particular river stretches and cannot currently serve the specific needs of the Water Framework Directive. The data can be used more broadly to fill in the gaps of understanding regarding the behaviour of NM in aqueous media.

Available data on NM in surface waters from modelling could serve to direct further investigation of the presence and concentrations (mass and/or particle number) of specific NM in water. While available monitoring techniques do not readily provide for the detection of the very low concentrations of NM expected in surface or groundwater, research is ongoing. In particular, the research team at Arizona State University led by Paul Westerhoff have proposed particular analytical methods for certain classes of NM, namely metal-based, C60/C70, and CNT. Further progress is therefore expected at the laboratory scale in the development and validation of methods and text protocols for classes of NM in water samples. Future efforts could usefully build on data from modelling by seeking to investigate and possibly validate data from modelling.

Regarding NM exposure data to serve the Groundwater Directive, no data is currently available. A study by Chen et al (2009) measured very low concentrations of C60 in drinking water using LC/MS and suggests that this method may hold promise for this particular ENM and could be applied to groundwater.

For the Drinking Water Directive, data is limited to the results of the abovementioned study on C60 in drinking water and data from a modelling study conducted by Tiede et al (2011). Tiede et al estimate very low concentrations of ENM in drinking water. They also state that for the majority of product types, human exposure via drinking water is likely to be less important than exposure via other routes. Based on models of releases from products, they suggest that future work on the risk of ENM to drinking water focus on nano-AG, nano-Al/Al2O3, nano-TiO2, and nano-Fe2O3. While from one study only, this data can be useful in directing future research concerning which ENM might appear in
drinking water and the source products. The parameters to be measured in monitoring the quality of drinking water are limited and the scale of the mass concentrations metrics unlikely to be relevant for NM (based on the results of Tiede et al, 2011). Future exposure data on NM in drinking water may more profitably serve to inform ideas concerning upstream controls on products identified as significant diffuse sources of particular ENM, in order to address pollution at source, rather than servicing the Drinking Water Directive itself.

Regarding data to service the Urban Waste Water Treatment Directive, this exposure pathway has received considerable attention and NM exposure data is available from a range of studies, including those using analytical techniques, simulation and modelling. Analytical data provides evidence of the removal efficiency of particular NM from waste waters and fractions deposited in sludge, while Gottschalk et al provide a picture of flows of particular ENM to UWWTP. The monitoring requirements for UWWTP effluents under the Urban Waste Water Directive are very limited and it is considered unlikely that NM would be included in the list of parameters to be monitored and that data from analytical monitoring would be demanded. Instead, and as for the Drinking Water Directive, exposure data may serve to inform possible upstream controls on ENM in products, in order to address pollution at source.

Many of the same studies serve to provide exposure data on NM in sewage sludge, with a fairly clear picture emerging of the transfer of NM from wastewaters into sludge and thence into soils. Much of the available data focuses on nano-TiO₂, with some data on other metal-based ENM, fullerenes and CNT. Again, the parameters to be controlled in sludges and receiving soils under the Sewage Sludge Directive are limited and it is considered that data on NM exposure could more readily feed into thoughts regarding upstream controls on key emission pathways.

The Landfill Directive demands data for waste acceptance and for monitoring the surrounding environment. Regarding waste acceptance, only one study by Benn et al (2010) has sought to characterise the leaching behaviour of an ENM, with a focus on nano-Ag. Considerably further research is required before the leaching behaviour of NM can be considered under waste testing and acceptance procedures for landfills. Data from modelling studies can serve to inform wider thinking, by providing quantitative estimates of flows of particular ENM to landfill. Regarding monitoring of the surrounding environment using analytical techniques, the limitations considered under the discussion of the Water Framework Directive and the Groundwater Directive apply.

Although no specific demand for exposure data was identified under the Waste Framework Directive, data on the fate and behaviour of ENM in waste treatment processes and resulting emissions of ENM and unintentionally produced NM would serve to inform application of the waste hierarchy. One study
has specifically investigated the fate and behaviour of an ENM (CeO$_2$) in a waste incineration plant, and this provides the only data available from analytical studies. As above, data from modelling studies can serve to inform wider thinking on flows of ENM to waste, by providing quantitative estimates of flows of particular ENM to different waste treatment processes.

As mentioned above, the Air Quality Directive currently demands exposure data for UFP and airborne NM, in so far as they are captured under the PM$_{10}$ and PM$_{2.5}$ size fractions. As such, mass concentrations of PM$_{10}$ and PM$_{2.5}$ are measured across the EU, with data available on the website of the European Environment Agency.

When we shift down a scale to look specifically for data on airborne NM and UFP, although there are a large number of relevant studies using analytical techniques, data become much patchier and issues arise according to scale and metrics. Regarding scale, data is specific to individual sites, mainly urban sites with the aim of linking variation in UFP concentrations to traffic density. However, the number of studies means that overall conclusions can be drawn regarding the generation of UFP in the internal combustion engine and associations with weather conditions and this can feed into regulatory decision-making. EU-wide data on the PM$_{0.1}$ fraction is available from one modelling study, and is subject to considerable uncertainties.

In terms of metric, particle total number concentrations and particle size distribution are important metrics, and current risk assessment model for air quality would require adjustment to incorporate this multi-metric data. While these studies are conducted by specialised research groups, the analytical techniques used for conducting measurements are more widely available than those discussed under water legislation, in particular due to parallel pressures from occupational health and safety concerns.

In providing permits under the IED, competent authorities require data on the overall environmental performance of an industrial installation, and in particular emissions to air, water and soil, as well as in wastes. This assessment is based on requirements, including ELV, for specific sectors in the IED, and BAT and associated BAT-AELs in the BREF. While some sectors have ELV or BAT-AELs for dust in the form of mass concentrations, there is no other specific mention of the need to control emissions of NM in the IED or BREF to date.

In terms of available data on emissions of NM to air, water and soil from industrial installation, emissions to air have received the most attention. Modelling data from AMEC provides a picture of emissions by industrial sector at the EU-wide scale and can be used by regulators to identify those particular industries with significant emissions at the PM$_{0.1}$ scale. Currently, taking online measurements of flue gas emissions are confounded by the conditions in emission stakes and data from analytical studies are not available to validate estimated emissions.
AMEC estimate total emissions of PM$_{0.1}$ from industrial sources at <5% of total PM$_{0.1}$ emissions. They find emissions of ENM to represent a very small fraction of PM$_{0.1}$ emissions from industrial sources. In terms of other data on airborne ENM, Yang et al (2011) measured particle number concentrations of nano-TiO$_2$ inside a production plant, while Shinohara et al (2009) modelled ENM in ambient air near to a C60 production facility.

In terms of NM emissions to water from industrial processes, the only available data comes from the numerous materials mass flow analysis undertaken Gottschalk et al, which identify prominent flows of particular ENM for nano-TiO$_2$ and nano-Ag. This data can serve in helping to identify particular ENM that may be being released from industrial installations for further analysis. No data is available on emissions of NM to soil or in industrial wastes.
7. **Application of Existing Chemical Risk Assessment Tools to NM**

7.1 **Introduction**

A number of authors have looked at available models for undertaking chemical risk assessment in general, and environmental exposure assessment in particular, and assessed their applicability to NM. In sections 7.2 to 7.4 we review the chemical risk assessment models under EU legislation and consider their application to NM and likely future yields of useful data on NM to feed into environmental exposure assessment. In section 7.5 we discuss the European Union System for the Evaluation of Substances (EUSES), the model for environmental exposure assessment currently used in the EU, and draw on available literature to consider its applicability to NM.

7.2 **REACH**

The EU regulatory framework for chemical risk assessment for manufacturers and importers of chemical substances is set under Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)\(^{239}\), and the Commission clarified in a 2008 Communication that provisions of this regulation apply to engineered nanomaterials\(^{240}\). The Guidance Document\(^{241}\) provided by ECHA on the preparation of a Chemical Safety Assessment (CSA, REACH terminology for a risk assessment) includes very limited reference to substances in nanoforms. Despite a number of important concerns regarding its coverage of NM that are considered to be outside of the scope of this Study, REACH is likely to represent a future source of environmental exposure data on NM.

A CSA is only required for substances placed on the market at volumes of 10 tonnes or more per year, implying that not all nanomaterials will be captured. It can therefore be assumed that while it will not be performed for all NM on the EU market. Nevertheless, a CSA will be required for those NM that are manufactured at higher volumes, such as CNTs, nano-Ag and nano-TiO\(_2\).

The environmental assessment of the CSA starts with an assessment of the hazards of the substance, including establishing the level of exposure to a substance below which no ill-effects occur on the

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\(^{241}\) ECHA, 2008, REACH guidance on information requirements and chemicals safety assessment. European Chemicals Agency, Helsinki
environment (Predicted No-Effect Concentration/PNEC). If the substance is classified as dangerous or is bioaccumulative and toxic (PBT) or very persistent and very bio-accumulative (vPvB), then an exposure assessment and risk characterisation must be performed to demonstrate that the risks are adequately controlled. This involves the development of exposure scenarios and an estimate of the exposure or Predicted Environmental Concentration (PEC) for each environmental compartment (air, water, soil). The PEC is based on models for the degradation or distribution of the substance in the environment (between water, air and solids) using physico-chemical and biodegradation data. As well as the test data, other key factors include how the substance is manufactured, formulated or used and the dilution factors from use. The conclusions of an environmental risk assessment is to compare the estimated exposure with the estimated effects for the environment, this is expressed as the ratio of PEC / PNEC.

The ultimate goal of the environmental exposure assessment is to define the production, use and disposal conditions that will ensure that emissions to the environment are limited at each stage of the life cycle of the substance to ensure that resulting concentrations are below the PNEC and risks to the environment are controlled (Aschberger et al, 2011).

REACH is considered to provide a future source of exposure data for NM. The application of current methodologies for estimating exposure to NM is considered in the 2011 publication “Specific Advice on Exposure Assessment and Hazard/Risk Characterisation for Nanomaterials under REACH (RIPoN3)”,242 and further discussed in the Final Report of the NANEX project.243

RIPoN3 provides advice on the development of exposure scenarios for NM and products containing NM and includes a number of exposure scenario case-studies that were provided by industry. Several of the exposure scenarios address environmental release/exposure scenarios for specific nanomaterials, namely: nano-TiO2; nano-TiO2 (Mn-doped); nano-Ag; Multi-walled Carbon Nanotubes (MWCNTs). Some Case-Study providers conducted state-of-the-art detection and measurement approaches using multi-instrument, multi-metric measurement studies, while others used models (e.g. Consexo, ECETOC TRA) to estimate exposure.

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Participants at a 2009 workshop entitled “Environmental fate and behaviour of nanoparticles – beyond listing of limitations”\textsuperscript{244} reviewed the Technical Guidance Document on environmental exposure estimation and identified and number of limitations with respect to NM, including:

a) A lack of information on physico-chemical properties relevant for nanoparticles;

b) A lack of access to information on production, emissions throughout the life-cycle, etc.;

c) Fundamental limitations of the various assumptions made such as $K_{ow}$ as being a good descriptor for processes like sorption and bioconcentration;

d) Fundamental limitations of the various models of fate and degradation of nanoparticles since they are developed for organic chemicals and for non-particulates.

A 2009 JRC study (Stone \textit{et al}, 2009, summarised in Aschberger \textit{et al}, 2011)\textsuperscript{245} sought to apply the REACH CSA to four different classes of nanomaterials based on available information in the literature. The classes were: metals, with a focus on nano-silver; metal oxides, with a focus on nanotitanium dioxide and nano-zinc oxide; fullerenes; and carbon nanotubes (CNT). The authors found that due to data limitations regarding inherent properties, use, exposure and risk management measures the approach could not be followed in all details. In dealing with the resulting uncertainties under the environmental exposure assessment, the authors chose to use the term Indicative No-Effect Concentrations (INEC) rather than PNEC in identifying potential risks to environmental compartments. In addition, they proposed a qualitative ranking of the NM, based on available exposure, use and hazard data. The study concludes that the main risk to the environment is expected from metals and metal oxides, especially for algae and \textit{Daphnia}, due to exposure to both particles and ions. At the same time, the authors highlight considerable uncertainties in any conclusion on risk, due to data limitation, and urge that the results should not be used for regulatory decision-making.

As noted by Hankin \textit{et al.} (2011)\textsuperscript{246} in the REACH Implementation Project 2 \textit{in situ} approaches for environmental hazard and exposure assessment of nanomaterials are not validated, nor are solid quantitative structure activity relationships (QSARs) for nanomaterials on which to base such models.

\textsuperscript{244} NanoImpactNet Workshop “Environmental fate and behaviour – beyond listing of limitations” held in Bilthoven on October 7th 2009


Several studies have highlighted the needs for such approaches, but they have yet to suggest a validated approach.

7.3 Regulation (EU) No 528/ 2012 on Biocidal Products

On 22 May 2012, the revised regulation concerning the placing on the market and use of biocidal products was adopted247. The regulation will take effect from September 1, 2013, with a transitional period for certain provisions. The regulation is the first piece of legislation to incorporate Commission Recommendation 2011/696/ EU on the definition of a nanomaterial248. In implementing this definition, Member States may request that the Commission deciding whether a substance is a nanomaterial by means of an implementing act. In addition, the definition can be adapted on the basis of scientific progress using delegated acts.

Importantly, the Regulation requires that, where nanomaterials are used in a product, the risk to human health, animal health and the environment be assessed under a separate risk assessment specific to the nanoform. Approval of active substance does not automatically cover the nanoform of that substance (Article 4(4)), except when explicitly mentioned. Biocidal products that contain nanomaterials are not eligible for authorisation via the simplified authorisation procedure set out under Article 25. The regulation states that “approval of an active substance shall not cover nanomaterials except where explicitly mentioned.”

Rather, Article 19 requires that a separate dossier be prepared for nanoforms of active substances and formulants. In undertaking the risk assessment, all data requirements apply equally to nanomaterials. Annex II/III notes that where established test methods are used for the nanoform, an explanation of their scientific appropriateness, as well as any technical adaptations or adjustments, should be provided. In addition, following Annex IV, the principles for the evaluation of dossiers both in the Regulation and in technical guidance must be adapted to nanomaterials. This legislative change will therefore generate impetus for the development and validation of new test methods specific for nanomaterials.

In the interest of generating information on what is placed on the market, Member States will monitor biocidal products and treated article placed on the market based on records kept and maintained by manufacturers. This documentation shall include information on the use of nanomaterials in biocidal

248 Commission Recommendation of 18 October 2011 on the definition of nanomaterial, OJ L275/38
products and the potential risks thereof. The information will be included in reports submitted to the Commission and subsequently made public, with the first reports due in 2020. As such, this will serve to generate publically-available EU-wide information on the use of nanomaterials in a particular product group, and the associated risks, although the time-lag until 2020 is rather long.

In addition, biocidal products and treated articles must be labelled with the name of all nanomaterials therein, followed by the word “nano” in brackets.

**7.4 Food and Feed Chain**

In 2011, the European Food Safety Authority (EFSA) published a scientific opinion entitled “Guidance on the risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain”\(^{249}\). The guidance provides practical guidance for the risk assessment of applications involving NM in the food and feed chain, noting that the existing risk assessment paradigm is appropriate for these applications. EFSA identifies uncertainties relating to the identification, characterisation and detection of NM related to the lack of suitably validated test methods and notes that the guidance will require updating in response to developments in the field.

The guidance considers possible exposure scenarios and notes that exposure characterisation will contribute to decisions on the extent of hazard characterisation and the exposure assessment. Key questions regarding exposure scenarios include:

- Whether the NM are directly added to food or feed, and if so, in what type and quantity and what is their solubility;
- When NM are present in an indirect manner, e.g. due to migration or transfer of non-nanoform degradation products, the type and amount should be determined.

In undertaking exposure assessment, the guidance states that the principles will be the same as in for non-nanoform materials. Anticipated average and high intakes in various population groups on the NM in food/feed must be estimated on the basis of available consumption data, with populations with an expected high exposure identified. The guidance suggests that probabilistic methods may be used to determine ranges on plausible values rather than specific point estimates.

\[^{249}\text{EFSA 2011 Scientific Opinion: Guidance on the risk assessment of the application of nanoscience and nanotechnologies in the food and feed chain, EFSA Journal 9(5): 2140}\]
The starting point for determining the amount of ENM in food/feed relies on information on ENM added or in contact with food/feed. The guidance notes that it is not currently possible to routinely determine ENM in situ in the food or feed matrix using analytical methods. Ideally, the exposure assessment should also consider any possible transformations and migrations of the ENM resulting from processing, storage, interactions with other substances and degradation of the food/feed matrix. In the absence of data and where it is not possible to determine the nanoform in the food/feed matrix, the guidance states that it should be assumed that all added ENM is present, ingested and absorbed in the nanoform.

The guidance also discusses the characterisation of EENM in food/feed and identifies key physicochemical parameters for which data is required to feed into exposure assessment, presented in table 26 below.

In addition, the guidance calls for non-nanoform specific information such as: name (generic or proprietary); CAS number; production method (e.g. precipitation, gas phase); details on intended uses and reasons for use in food/feed applications; batch to batch variation and stability/shelf life. The identification of these parameters is relevant since this data would be very useful to feed into environmental exposure assessments. The demand for data on the physicochemical properties of ENM under food/feed safety legislation adds weight to the demands generated under environmental legislation.

With regards to available methods for detecting and characterising ENM in the food/feed matrix, the guidance identifies a similar range of methods to those discussed under section 5.2.1, and notes that analysis is made challenging due to the presence of complex matrices, the low concentrations of ENM and the wide range of natural structures, including some in the nanoscale range. These echo the challenges experienced by researchers working to measure ENM in natural matrices. Similarly to the recommendations of Tiede et al (2009) regarding the use of analytical methods to measure ENM in aquatic samples, the guidance recommends the use of a combination of methods to detect and characterise ENM in food/feed. They also note similar problems with sampling techniques resulting in alterations in the ENM structure or properties.
Table 26: Physicochemical parameters for characterisation and identification of NM to feed into exposure assessment of NM in food/feed

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Requirements</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical composition/identity</td>
<td>Essential</td>
<td>Information on chemical composition of the NM – including purity, nature of any impurities, coatings or surface moieties, encapsulating materials, processing chemicals, dispersing agents and/or other formulants e.g. stabilisers.</td>
</tr>
<tr>
<td>Particles size (primary/secondary)</td>
<td>Essential (two methods, one being electron microscopy)</td>
<td>Information on primary particle size, size range and number size distribution (indicating batch to batch variation – if any). The same information would be needed for secondary particles (e.g. agglomerates and aggregates) if present.</td>
</tr>
<tr>
<td>Physical form and morphology</td>
<td>Essential</td>
<td>Information on the physical form and crystalline phase/shape. The information should indicate whether the NM is present in a particle-, tube-, rod-/shape, crystal or amorphous form, and whether it is in free particulate form or in an agglomerated/aggregated state as well as whether the preparation is in the form of a powder, solution, suspension or dispersion.</td>
</tr>
<tr>
<td>Particle and mass concentration</td>
<td>Essential for dispersions and dry powders</td>
<td>Information on concentration in terms of particle number and particle mass per volume when in dispersion and per mass when as dry powder.</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>Essential for dry powders</td>
<td>Information on specific surface area of the NM.</td>
</tr>
<tr>
<td>Surface chemistry</td>
<td>Essential (for NM with surface modifications)</td>
<td>Information on NM surface – including any chemical/ biochemical modifications that could modify the surface reactivity, or add a new functionality.</td>
</tr>
<tr>
<td>Surface charge</td>
<td>Essential</td>
<td>Information on zeta potential of the NM.</td>
</tr>
<tr>
<td>Redox potential</td>
<td>Essential for Inorganic NMs</td>
<td>Information on redox potential. Conditions under which redox potential was measured need to be documented.</td>
</tr>
<tr>
<td>Solubility and partition properties&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Essential</td>
<td>Information on solubility of the NM in relevant solvents and their partitioning between aqueous and organic phase (e.g. as log Kow if appropriate).</td>
</tr>
<tr>
<td>pH</td>
<td>Essential for Liquid dispersions</td>
<td>pH of aqueous suspension.</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Essential for Liquid dispersions</td>
<td>Information on viscosity of liquid dispersions.</td>
</tr>
<tr>
<td>Density and pour density</td>
<td>Essential for granular materials</td>
<td>Information on density/porosity of unformulated NM and pour density.</td>
</tr>
<tr>
<td>Dustiness</td>
<td>Essential for dry powders</td>
<td>Information on dustiness of powder products – such as spices, creamers and soup powders.</td>
</tr>
<tr>
<td>Chemical reactivity/catalytic activity&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Essential</td>
<td>Information on relevant chemical reactivity or catalytic activity of the NM and of any surface coating of the NM.</td>
</tr>
<tr>
<td>Photocatalytic activity</td>
<td>Essential for photocatalytic materials</td>
<td>Information on photocatalytic activity of relevant materials used in food packaging, coatings, and printing inks and internal reactions.</td>
</tr>
</tbody>
</table>

<sup>a</sup> Dispersions, solution, dissolved: An insoluble NM introduced to a liquid form a ‘dispersion’ where the liquid and the NM coexist. In a true solution the NM is dissolved (and thus not present) (see OECD ENV/JM/MONO(2010)25)

<sup>b</sup> If an NM has catalytic properties, it may catalyse a redox or other reaction that may perpetuate resulting in a much larger biological response even with small amounts of the catalytically active NM. Thus, compared to a conventional biochemical reaction that uses up the substrate, NM reaction centres may perpetuate catalytic reactions.
7.5 Cosmetics

In 2011, the European Commission Scientific Committee on Consumer Safety (SCCS) published “Guidance on the safety assessment of nanomaterials in cosmetics”\(^{250}\). The document is intended to provide guidance on how to consider the specific properties, interactions with biological systems, and/or effects of ENM that are different from conventional or bulk ingredients when testing and reporting data for ENM. The guidance draws on experience gained with risk assessments being carried out by SCCS on three specific manufactured nanomaterials for their inclusion in Annex VII (ultraviolet (UV) filters) of the Cosmetics Directive 76/768/EEC\(^{251}\).

The guidance notes that the exposure assessment for ingredients in cosmetic products as described in the SCCS Notes of Guidance is a general approach that applies to nanomaterials. It states that the risk assessment of cosmetic nanomaterials is likely to be driven by considerations of exposure. Regarding the application of existing methods, the SCCS is of the view that the method for calculating dermal and oral exposure to nanomaterials will not be very different from the calculation of exposure to conventional cosmetic ingredients. It recognises that certain assumptions that are used for estimation of dermal absorption of conventional chemical ingredients are not applicable to nanomaterials, and as such dermal absorption of nanomaterials will need to be determined experimentally. The guidance notes that the calculation of exposure to nanomaterial containing aerosols is likely to be more challenging and will need determination of the generated droplet size distribution as well as size distribution of the dried residual aerosol particles.

7.6 European Union System for the Evaluation of Substances

European Union System for the Evaluation of Substances (EUSES) is a decision-support instrument used to carry out rapid and efficient assessments of the general risks posed by chemical substances to man and the environment. EUSES is intended mainly for initial and refined risk assessments rather than for comprehensive assessments. The system is fully described in the extensive EUSES documentation and is based on the EU Technical Guidance Documents (TGD) on Risk Assessment for New Notified Substances, Existing Substances and Biocides. The latest version of EUSES, version 2.1.2, was made available in 2012 and can be downloaded from the JRC website.\(^{252}\)

\(^{250}\) SCCS (2011) Guidance on the safety assessment of nanomaterials in cosmetics, SCCS/1484/12


At a 2009 workshop on ENM fate and behaviour, a number of researchers in the field examined the applicability of the EUSES to ENM. A presentation was provided at the workshop by Dr van der Meent, who questioned whether EUSES can be used for PEC, since nanoparticles are dispersed rather than dissolved and the EUSES approach is based on dissolved chemicals. To expand a little, the EUSES model assumes that molecules in air, water and soil/sediment/biota are in a gas phase, dissolved state and sorbed state, respectively. It also assumes that the distribution among media can be predicted from Henry's law constant (measured, or depending on vapour pressure and aqueous solubility), partition coefficients (Kow, Koc) and bioconcentration factors (measured or estimated BCF-values). However, the predictability of air/water/solid partitioning for nanoparticles was doubted by Dr van der Meent, since nanoparticles are primarily solid phase. Dispersed nanoparticles are not in solution, but are instead in suspension and dissolution is not considered/modelled for conventional chemicals. In addition, the tendency of nanoparticles to aggregate is not observed for conventional chemicals and it is unclear how to model partitioning of nanoparticles attached to solid surfaces.

Dr van der Meent argued that the focus should be on quantifying distributions e.g. for suspended:dissolved the dissolution rate might be applicable, for air:water Kair-water could be set to be equal to 0 whereas (equilibrium) partitioning might apply for suspended:solid and uptake in biota. He prioritised obtaining a fundamental understanding of distributions and then using that information to develop models.

Thus, EUSES was deemed insufficient for nanoparticles given that a number of key mechanisms are unknown and not reflected in the model, including:

a) the extent/rate of dissolution;

b) the extent / rate of aggregation / settling; and

c) the extent of association with sediment.

Given the dynamic nature of ENM, it was argued that knowledge is required on fluxes or rates instead of distribution coefficients on which models for chemicals are often dependent. Important rates include rates of sedimentation, resuspension, bioaccumulation, deposition and runoff fluxes. Besides information on these fluxes and rates, information is required on agglomeration, behaviour of

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agglomerates, sinks i.e. local accumulation, and an understanding of what happens at the interfaces between water and sediments and water and biological surfaces.

7.7 Risk Forecasting for NM

A group of researchers have stepped back from existing risk assessment model to speculate on possible approaches that could begin to cope with the current uncertainties resulting for data scarcity on NM and in particular ENM. Wiesner and Bottero (2011)\textsuperscript{254} considered the application of available chemical risk assessment tools to ENM and conclude that currently a traditional risk assessment on nanomaterials is not possible. They argue that the enormous variety of nanomaterials makes a case-by-case risk analysis impossible. In forecasting risk, they identify key challenges, including high uncertainty concerning production amounts, ENM characteristics and uses and exposure pathways, as well as data scarcity regarding the relationship between ENM characteristics and their (eco)toxicity. They call for an evolving process to allow for the risks associated with emerging nanomaterials-related industries and propose that such a process should:

- generate forecasts and associated levels of uncertainty for questions of immediate concern;
- consider of all pertinent sources of nanomaterials;
- consider the impacts of activities stemming from nanomaterial use and production that extend beyond the boundaries of toxicology and include full life cycle impacts;
- adapt and update risk forecasts as new information becomes available;
- feedback to improve information gathering; and
- feedback to improve nanomaterial design.

They suggest that the potential risks of ENM will ultimately be determined as a function of fundamental, quantifiable properties of nanomaterials, implying that these properties can be recognized as indicators of risk in a novel ENM.

In a subsequent publication, Money et al (2012)\textsuperscript{255} describe the use of Bayesian networks in NM risk forecasting and develop a baseline probabilistic model using expert elicitation techniques called Forecasting the Impacts of Nanomaterials in the Environment (FINE). The model incorporates


nanoparticle specific characteristics (particle behaviour) and environmental parameters, along with elements of exposure potential, hazard, and risk related to NM. The Bayesian nature of FINE allows for updating as new data become available, a critical feature for forecasting NM risk, and allow for the incorporation of expert judgment when other knowledge bases are lacking. This may provide a practical option for conducting risk assessments for ENM in the absence of comprehensive data on exposure and hazards.
8. Chemical risk assessment and the precautionary principle

In the absence of concrete evidence regarding current concentrations of ENM in environmental compartments, trends in concentrations and any related negative environmental impacts in situ, traditional chemical risk assessment cannot be conducted. The precautionary principle provides the legal basis in EU legislation for decision-making in the absence of comprehensive data to feed into a traditional risk assessment.

The precautionary principle is mentioned in the context of environmental protection in Article 191 (2) of the Treaty on the Functioning of the European Union256 (ex Article 174 of the Treaty establishing the European Community) In 2000, the Commission issued a Communication (2000)1 on the precautionary principle,257 with the aim of outlining the Commission’s approach to using the precautionary principle. In addition, the Communication aims to build a common understanding of how to assess, appraise, manage and communicate risks that science is not yet able to evaluate fully, as such its content is relevant to the question of whether or how to regulate environmental releases of nanomaterials.

The Communication clarifies that, in practice, the scope of the precautionary principle is “specifically where preliminary objective scientific evaluation, indicates that there are reasonable grounds for concern that the potentially dangerous effects on the environment, human, animal or plant health may be inconsistent with the high level of protection chosen for the Community”. In addition, the Communication notes that the precautionary principle is to be used by decision-makers in the management of risk to inform two aspects: the political decision of whether to act or not; and how to act.

Regarding recourse to the precautionary principle when taking the decision whether to act to manage a potential risk, the Commission explains that the precautionary principle specifically applies in cases where “potentially dangerous effects deriving from a phenomenon, product or process have been identified” and where “scientific evaluation does not allow the risk to be determined with sufficient certainty”.

The scientific evaluation should entail a risk assessment, which consists of four components, namely: hazard identification, hazard characterisation, appraisal of exposure and risk characterisation. In the

256 Treaty on the Functioning of the European Union, OJ C 115/47, 9.5.2008, 47-199
257 Communication from the Commission on the Precautionary Principle, COM(2000)1,
case of nanomaterials, the scientific knowledge needed to inform each of these components is currently limited, with evidence for hazard identification existing for some specific nanomaterials. These knowledge limitations serve to increase the overall level of uncertainty and ultimately affect the foundation for preventative action.

In informing how to act, the Commission Communication notes that recourse to the precautionary principle does not necessarily mean adopting legal instruments. Rather, a whole range of actions are available to policy makers, including funding research to increase the availability of information.

In the case of ENM, information is required on which ENM (and nanoforms thereof) are being sold on the EU market, the volumes produced and sold, volumes attributed to specific products and the market penetration of those products. Additional information would include data on emissions of nanomaterials (including ENM and unintentionally-produced nanoparticles) from both diffuse and point sources, as well as data on the fate and behaviour of nanomaterials in the environment and in waste management processes, such as in WWTP and incinerators. Relevant measures to generate this information could include reporting schemes for producers and manufactures, monitoring requirements to generate exposure data for ENM, and scientific researcher to elucidate the fate and behaviour of ENM.

The precautionary principle could be applied to the management of the potential risks of nanomaterials in general, or to the management of potential risks from specific nanomaterials. In the case of some specific nanomaterials (i.e. carbon nanotubes, nano titanium dioxide), the available body of evidence that could feed into a risk assessment may be somewhat larger and more targeted, possibly creating a foundation for more stringent preventative action, such as product controls.

The procedures surrounding application of the precautionary principle set a framework for assessing available exposure data, as well as possible gap-filling techniques.
9. **Possible Future Approaches to Regulating ENM**

The review of exposure data generates a number of questions regarding possible future approaches to regulating NM under environmental legislation. These questions concern which NM (chiefly ENM) might be prioritised for regulatory action, how to consider nanoform, metrics and the use of mass-based thresholds.

9.1 **Targeting Specific ENM**

A key question concerns whether certain ENM should be prioritised for regulatory action on the basis of higher levels of environmental exposure, either measured using analytical techniques or, more likely given current data, modelled using data on production volumes and fraction attributable to particular products. Regarding the ENM that are being modelled and/or measured in environmental media, studies tend to focus on the metal-based ENM, in particular nano-TiO\textsubscript{2} and nano-Ag, with a lesser focus on the carbon-based ENM and a couple of studies on airborne CeO\textsubscript{2}. Some studies go so far as to identify those ENM that are considered to be of key concern, with general agreement that the metal-based ENM are a focus of concern for the aqueous environment.

9.2 **Targeting nanoforms**

Secondly, it should be considered how to address the variation in nanoforms of an ENM. In terms of identifying particular nanoforms of the metal-based ENM, data from analytical studies suffers from a lack of precise detail meaning that it is not possible to distinguish particular nanoforms of concern based on the available dataset. Researchers report that when receiving samples, the purity of the nanoform varies considerably and that this confounds results. While studies do report on size and size fractions are measured, few studies provide additional data to characterise the specific properties of the ENM under examination. Modelling data is also presented at the level of the ENM, rather than for specific nanoforms, since available data on production volumes is at the level of the ENM, not the specific nanoform or mix of nanoforms in a production batch.

9.3 **Metrics**

The literature suggests a number of data characteristics that will need to be investigated and recorded when monitoring and/or modelling the concentrations of NM in environmental media in order to provide a complete picture, including:
• Mass concentrations in the range of µg L\(^{-1}\)–pg L\(^{-1}\) and changes in concentrations over time;
• Particle size and shape and range of particle distribution: i.e. identifying and measuring the size fractions of different nanoforms;
• Available surface area;
• Distinguishing between NM and naturally occurring nanomaterials; and
• Data on the degree of aggregation and dissolution: i.e. ongoing fate and behaviour.

9.4 Relevance of Mass-Based Thresholds

Another key question concerns the relevance of applying mass-based threshold to NM. There are several ways in which mass-based threshold values are used in legislation, including EQS, the transgression of which trigger controls, and ELV that set a cap on the concentrations of a specific substance that can be emitted in effluent or flue gas. As mentioned previously, the relevance of mass-based thresholds to nanomaterials has been questioned in a context where research suggests that ecotoxicity does no correlate with mass concentration for nanomaterials in the same way as for non-nano chemical substances. In considering the issues of metrics, the October 2012 Commission Communication states that “as risk characterisation may depend on particle size or surface functionalization, it is anticipated that setting the precise scope, dose metrics and value of any thresholds employed under environmental legislation, if necessary, would be more challenging than for conventional pollutants”.

In thinking about how threshold values could be adapted to apply to ENM, a number of issues require consideration. Firstly, thresholds would need to include multiple metrics, including data on particle number concentrations, broken down by particle size and particle shape to provide a picture of the size fractions of different nanoforms. The large variety of nanoforms (NM of different sizes and shapes) and the large and highly variable multi-metric dataset that would result from monitoring generates practical challenges in developing and applying thresholds. Therefore, thresholds would not include a single value, but rather it might be possible to envisage ranges of values for particular metrics to capture groups of nanoforms. The development of threshold would require considerable input from toxicity studies to identify those particular characteristics that influence toxicity and could serve as a basis for grouping nanoforms of a particular ENM.

9.5 Accounting for Fate and Behaviour

A number of researchers in the field have stressed the importance of fate and behaviour in influencing how ENM, as well as naturally occurring nanoparticles and incidental nanoparticles behave in the
environment. In particular, a clearer understanding of the fate and behaviour of specific ENM, and nanoforms thereof, in products, emission pathways and in the relevant environmental media is required to inform possible regulatory action.

Kinetic models specifically try to reflect the dynamic behaviour and fate of ENM in environmental media, including modelling processes such as sedimentation flux (Arvidson et al (2011), removal kinetics for dissolution and the overall kinetics of water–sediment transport of nanomaterials (Quik et al (2011) and the heteroaggregation process whereby ENM collide and interact with suspended particulate matter (Praetorius et al (2012). With regards to the latter, Praetorius et al. found that the distance that nano TiO₂ would travel before being deposited in sediment was highly dependent on both the heteroaggregation attachment efficiency (describing the interaction of nanoparticles with naturally occurring suspended particulate matter) and the characteristics of the suspended particulate matter, such as their density and concentration. The model suggested that high estimates for these parameters would result in short transport distances in water and rapid deposition in sediment, while low parameters would result in longer transport in water and slower deposition in sediment.

Of particular importance for aquatic compartments, soil and waste water treatment plants, and somewhat in contrast to the suggestions of the model above, is the conclusion of Kiser et al (2012) based on in situ measurements regarding the stabilising effect of proteins and other soluble organic in holding ENM in solution. The study indicated that natural or engineered processes (e.g., anaerobic digestion, biosolids decomposition in soils) that result in cellular degradation and matrices rich in surfactant-like materials may transform the surfaces of ENM and significantly alter their fate in the environment.

The Trojan function of ENM as potential carriers of trace metals on their surfaces was highlighted by Kim et al (2012) and is important for regulators, since it provides evidence that trace metals can be picked up and may enter environmental compartments on amended ENM. Kim et al found nano-TiO₂ from biosolids to interact with and carry toxic trace metals on their surface.

In addition, a number of recent studies have demonstrated the importance of surface chemistry, including hydrophobicity, of ENMs in determining their fate, transport and toxicity (Xiao and Wiesner, 2012, Lin et al, 2012 and Lin et al, 2011). The results of these studies imply that information on the surface chemistry of ENM is crucial to allow regulators to undertake a risk assessment, with an influence on both hazard and exposure.
10. Conclusions and Recommendations

In this final section, we identify some of the key data gaps in available environmental exposure data for ENM. We then present some regulatory options that can be used to increase the availability of information on ENM, and outline the kinds of information that would usefully serve methods for generating ENM environmental exposure data.

10.1 Key Data Gaps

This review of available environmental exposure data for NM and, in particular, the examination of available methods has thrown up a number of gaps in currently available data. Gaps can be considered at two levels, firstly gaps in available exposure data and secondly gaps in available information to feed into exposure assessment methods for NM. These are addressed in turn below.

In terms of gaps in available exposure data, a key area of concern is the complete lack of analytical data on NM in surface waters. This gap results from major challenges in measuring NM in surface water samples, due to the very low concentrations of NM in such samples, as well as interference from naturally occurring nanoparticles and the introduction of artefacts during samples techniques. Likewise, for groundwater, there is no analytical data available, while for drinking water there is one study focussing on one NM. While analytical methods are under development to redress this data deficit, it is expected to be some time before EU-wide analytical data is available on NM in surface waters and groundwater.

Emissions of NM in effluent from UWWTP and in sewage sludge are perhaps the best addressed in both analytical and modelling data, although studies have tended to focus on nano-Ag and nano-TiO$_2$. Further analytical work could usefully seek to validate evidence of the deposition of NM in sludges and subsequent transfer to soils through the spreading of sewage sludge. Knowledge regarding the fate and behaviour of NM in soils is extremely poor.

Regarding possible emissions of NM from landfills, only one study looks at the leaching behaviour of a particular NM, and as such the fate and behaviour of NM in landfills is very poorly understood. Landfills are included as a box in several materials mass flow analysis models, providing very initial data on possible flows to landfill for specific NM.

Regarding air pollution, comprehensive EU-wide data on concentrations of airborne NM and incidental nanoparticles (UFP) is also lacking, although analytical data is available for a large number
of site-specific studies. Data on emissions from industrial installation is very limited, with one modelling study seeking to attribute the PM$_{0.1}$ fraction to particular industrial sectors. Analytical measurements of incidental nanoparticles and NM in flue gases are required and could focus on those industries identified as main contributors (iron and steel, heat and electricity, pulp and paper), although online monitoring is hampered by the unfavourable conditions in the smoke stack.

Finally, there is virtually no data on emissions of NM to water, soil and in wastes from industrial installations, although they are included in some of the large scale material flow models.

In terms of the availability of data to feed into methods for generating exposure data, there are also major gaps. These gaps significantly affect the robustness of data generated using models that rely on input data on production volumes, fractions attributable to specific products and emissions from those products over the life cycle. In order to provide reliable, consistent data sets on NM exposure, the following knowledge gaps require immediate attention:

- worldwide production volumes of ENM;
- type of use on the life cycle stage, in particular during manufacturing;
- what ENM are being used in which products, which qualities and nanoforms are being used;
- allocation of production volumes amongst these products;
- current and future market penetration of these products;
- release from products throughout the life-cycle of the products by mass or other relevant metric(s);
- waste management of products containing ENM, including whether they are incinerated, landfilled, channelled to sewage treatment plants, or end up directly in the environment;
- releases from waste incinerators and removal efficacy in the sewage treatment plants; and
- distribution in time and space of the emissions; and
- empirical data on releases through specific emission pathways.

In addition, in order to effectively model exposure data, a more complete understanding of the fate and behaviour of ENM along the product life cycle, including in any waste management processes, and in environmental media is required. Key areas where data on nanomaterials is required to feed into an exposure assessment, including:

- Knowledge of the degradation mechanisms of the nanoproduc ts in aquatic media, in terms of kinetics and chemical change;
- The quantities that are distributed in the different ecosystems compartments; and
• Biological effects on various target organisms.

The first area related to the physic-chemical properties of the nanomaterials and how it is embedded in the product, the second to environmental exposure and the third to hazards associated with the specific nanomaterials. As such, we are concerned with the first two data areas, since the physico-chemical properties will affect fate and behaviour in the environment and hence exposure over time.

A number of the studies reviewed in this project have focused in particular on aspects of fate and behaviour in determining environmental exposure to NM and incidental nanoparticles, in particular transport and transfer between water and soil compartments. One kinetic model suggested that transport distance and deposition rates for nano TiO₂ would be influenced by NM interaction with suspended particulate matter, as well as the density and concentration of suspended particulate matter. An *in situ* study found that natural or engineered processes (e.g., anaerobic digestion, biosolids decomposition in soils) that result in cellular degradation and matrices rich in surfactant-like materials may transform the surfaces of NM and significantly alter their fate in the environment. A number of recent studies have looked at the surface chemistry of an NM, including their hydrophobicity, and identified surface chemistry as an important determinant of their fate, transport and toxicity. In particular, the Trojan capacity of NM to transport trace metals is of concern.

At a workshop in 2009 held under NanoImpactNet, a Coordinated Action under the EC 7th Framework Programme, researchers focused on the gap that exists between what we know *now* about the environmental fate and behaviour of nanomaterials and what we *need to know* in order to apply the Technical Guidance Documents for Risk Assessment of Chemicals, especially Chapter R.16: Environmental exposure estimation. In the workshop report, Hansen et al (2011)²⁵⁸ proposed new input data to enable environmental models for NM. These data needs are presented in table 27 below.

---

Table 27: Data input needs to enable environmental exposure models for NM

<table>
<thead>
<tr>
<th>Substances identifications:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Primary size distribution</td>
<td>• Synthesis methods</td>
</tr>
<tr>
<td>• Coating</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physicochemical substance properties:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Dissolution rates</td>
<td>• Size distribution</td>
</tr>
<tr>
<td>• Affinity for adsorption of NOM</td>
<td>• Agglomeration state</td>
</tr>
<tr>
<td>• Zeta potential with NOM</td>
<td>• Shape</td>
</tr>
<tr>
<td>Size distribution</td>
<td></td>
</tr>
<tr>
<td>Agglomeration state</td>
<td></td>
</tr>
<tr>
<td>Shape</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Degradation and transformation rates:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Dissolution rate</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Emissions:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Tonnages reported in particle number</td>
<td>• Ratio between nanoparticles and nanoparticles embedded into other materials</td>
</tr>
<tr>
<td>• Number of individual nanoparticles</td>
<td></td>
</tr>
</tbody>
</table>


Nowack et al (2012) have emphasised that in modelling fate and behaviour in environmental media it is more important to know the properties of transformed NM than it is to know the properties of pristine ENM.259

10.2 Regulatory Options for Data Generation

This section provides a number of recommendations for options to address the information gaps identified above as limiting the generation of exposure data.

10.2.1 Information requirements under REACH

REACH aims to provide a high level of protection of human health and the environment through the better and earlier identification of the intrinsic properties of chemicals and their uses, while at the same time enhancing the innovative capability and competitiveness of the EU chemicals industry. The regulation applies to substances manufactured, placed on the market and used in the EU either on their own, in mixtures or in articles and its coverage of nanomaterials has been explicitly clarified by the Commission. REACH is based on the principle that it is for industry to ensure that they manufacture, place on the market or use such substances that do not adversely affect human health or the environment. Its provisions are underpinned by the precautionary principle.

REACH establishes obligations for the registration of substances manufactured or imported in amounts starting at 1 tonne per year (per manufacturer or importer). The information requirements for the registration of substances manufactured or imported vary according to the quantity per registrant. The lack of production volume data for the majority of ENM means that their tonnage band cannot be precisely determined. Nevertheless, the standard information on the physicochemical properties of a substances that registrants are obliged to report in registration dossiers are set out in Annex VII and presented in table 28 below.

Table 28: Information on the physicochemical properties of the substances, as required under Annex VII

<table>
<thead>
<tr>
<th>Physicochemical Endpoints</th>
<th>Adaptations to Requirements¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Physical state of substance (at 20 °C and 101.3 kPa)</td>
<td>None specified</td>
</tr>
<tr>
<td>7.2 Melting/ freezing point</td>
<td>Only above -20 °C</td>
</tr>
<tr>
<td>7.3 Boiling point</td>
<td>Not required for gases or for solids that melt above 300 °C or any substance which decomposes before boiling. Boiling point at reduced pressure may be used</td>
</tr>
<tr>
<td>7.4 Relative density</td>
<td>Where the substance is only stable in solution in a particular solvent and the solution density is similar to that of the solvent, an indication of whether the solution density is higher or lower than the solvent density is sufficient. For gases, an estimation is required based on molecular weight and the Ideal Gas Laws</td>
</tr>
<tr>
<td>7.5 Vapour pressure</td>
<td>Not required for solids that melt above 300 °C (if between 200 °C and 300 °C, a limit value based on measurement or a recognised calculation method is sufficient)</td>
</tr>
<tr>
<td>7.6 Surface tension</td>
<td>Not required where water solubility is below 1 mg/l at 20 °C, otherwise only when:</td>
</tr>
<tr>
<td></td>
<td>• based on structure, surface activity is expected or can be predicted; or</td>
</tr>
<tr>
<td></td>
<td>• surface activity is a desired property of the material</td>
</tr>
<tr>
<td>7.7 Water solubility</td>
<td>Not required if hydrolytically unstable at pH 4.7 and 9 (half-life &lt; 12 hours) or readily oxidises in water. Insoluble substances require a limit test up to the analytical detection limit</td>
</tr>
<tr>
<td>7.8 Partition coefficient (at least n-octanol/ water ratio)</td>
<td>Not required for inorganic substances. Calculated log P may be provided where direct measurement cannot be performed</td>
</tr>
<tr>
<td>7.9 Flash-point</td>
<td>Not required for inorganic substances, or where:</td>
</tr>
<tr>
<td></td>
<td>• the substance only contains volatile organic components with flash-points above 100 °C for aqueous solutions, or</td>
</tr>
<tr>
<td></td>
<td>• the estimated flash-point is above 200 °C, or</td>
</tr>
<tr>
<td></td>
<td>• the flash-point can be accurately predicted by interpolation from existing characterised materials</td>
</tr>
<tr>
<td>7.10 Flammability</td>
<td>Not required for solids that are explosive, pyrophoric or spontaneously ignite when in contact with air. Also not for gases if the concentration of the flammable gas in a mixture with inert gases is so low that, when mixed with air, the concentration is all times below the lower limit or for substances which spontaneously ignite in contact with air</td>
</tr>
<tr>
<td>7.11 Explosive properties</td>
<td>Not required where:</td>
</tr>
<tr>
<td></td>
<td>• there are no chemical groups associated with explosive properties present in the molecule;</td>
</tr>
<tr>
<td></td>
<td>• the substance contains chemical groups associated with explosive properties which include oxygen and the calculated oxygen balance is less than -200;</td>
</tr>
<tr>
<td></td>
<td>• an organic substance or a homogenous mixture of organic substances contains chemical groups associated with explosive properties but the exothermic decomposition energy is less than 500 J/g and the onset of exothermic decomposition is below 500 °C; or</td>
</tr>
<tr>
<td></td>
<td>• a mixture of inorganic oxidising substances (UN Division 5.1) with organic materials, the concentration of the inorganic oxidising substance is: less than 15 %, by mass if assigned to UN Packaging Group I (high hazard) or II (medium hazard); or less than 30 %, by mass if assigned to UN Packaging Group III (low hazard).</td>
</tr>
</tbody>
</table>

Neither a test for propagation of detonation, nor a test for sensitivity to detonative shock, is required if the exothermic decomposition energy of organic materials is less than 800 J/g.
<table>
<thead>
<tr>
<th>Physicochemical Endpoints</th>
<th>Adaptations to Requirements</th>
</tr>
</thead>
</table>
| 7.12 Self-ignition temperature | Not required where:  
• the substance is explosive or ignites spontaneously with air at room temperature;  
• a liquid is non-flammable in air, e.g. no flash point up to 200 °C  
• a gas has no flammable range; or  
• a solid has a melting point ≤ 160 °C, or if preliminary results exclude self-heating of the substance up to 400 °C |
| 7.13 Oxidising properties | Not required where the substance is:  
• explosive;  
• highly flammable;  
• an organic peroxide;  
• is incapable of reacting exothermically with combustible materials, for example on the basis of the chemical structure; or  
• a solid if the preliminary test clearly indicates that the test substance has oxidising properties.  
Note that as there is no test method to determine the oxidising properties of gaseous mixtures, the evaluation of these properties must be realised by an estimation method based on the comparison of the oxidising potential of gases in a mixture with that of the oxidising potential of oxygen in air |
| 7.14 Granulometry | Only for substances marketed in solid or granular form |

**Note 1:** Where these conditions are met, the registrant must clearly state this fact and the reasons justifying this statement.

In terms of how this compares against the data on the physicochemical properties of NM identified as important by researchers in the field, key omissions include the following:

- Data on particle size, size range and number size distribution, for both primary particles and secondary (i.e. agglomerates);
- Physical form and morphology, including surface area;
- Surface chemistry; and
- Surface charge.

Guidance on information requirements could suggest that these additional data be included for registrations concerns with the nanoform of substances.

Regarding exposure data generated under REACH, studies conducted under the CSA are likely to represent a main future source of data. As mentioned under section 7.2, an assessment of exposure scenarios over the life cycle of possible uses of a substance is included in the CSA. While, it can be assumed that the CSA will not be performed for all ENM on the EU market as production volumes will be below the 10 tonne threshold, the requirements of the CSA as set out in Annex I of REACH could be adapted to specify that uses of the nanoform be identified and that a separate exposure assessment be conducted where data indicate different exposure scenarios as compared with the other forms addressed under the dossier. This is in line with recommendations made in a Commission
10.2.2 EU-Wide Nano-Product Register

The development of nano registers in a number of Member States was considered under section 3.7, with France having made the most significant process in establishing an obligation to report commencing in September 2013. To recap, the data requirements of the French registry include all available information related to the hazard of these substances and the exposure pathways or useful for the health and environmental risk assessment as well as information related to the identity, quantity and uses of these substances, and the identity of the professional users to whom it was sold or given. Specific data on physicochemical properties includes the following:

- Chemical identity of the substance
- Presence of impurity
- Particles size
- Size distribution of the particles
- Aggregation state
- Agglomeration state
- Shape
- Specific surface
- Cristal state
- Surface chemistry
- Surface charge
- Matrix where the nanoparticle is held or stabilised
- Commercial name of the mixture

In addition, both Belgium and Denmark have proposed nano registries, with work proceeding towards their legal establishment. Data emerging from these registries is expected to make a useful contribution to researchers working to model and measure environmental exposure to NM over the next few years, as well as providing data to feed into hazard assessments.

The recent Commission Communication of 3 October 2012 on the “Second Regulatory Review on Nanomaterials”\(^\text{261}\) indicates that the Commission will, as soon as possible, create a web platform with

references to all relevant information sources on NM, including existing registries on a national or sector level. At the same time, the Commission will be launching an impact assessment on an EU Nano Registry with the aim of gathering the data required for regulatory purposes, and capturing those nanomaterials that currently fall outside existing notification, registration or authorisation schemes. Work on the EU Nano Registry is due to commence in the second half of 2013, due for completion in late 2014 or early 2015.

The development of an equivalent EU-wide product register would serve to significantly increase the availability and importantly the quality of data to be fed into models used to estimate environmental exposure to NM. This would serve to considerably reduce the uncertainties surrounding data emerging from such models and make resulting data more robust. Researchers would then be in a position to more confidently make EU-wide PEC estimates of specific nanoforms for environmental media. Remaining uncertainties would relate to the fate and behaviour of NM over the product life cycle, including in waste treatment processes. On-going analytical research can serve to address these uncertainties in parallel. The increased availability of data on physicochemical properties would serve the needs of analytical researchers, and contribute towards studies on fate and behaviour.

### 10.2.3 Monitoring Requirements for Nanomaterials

Another option for galvanising the production of environmental exposure data for NM would be for regulators to establish monitoring requirements for NM in environmental media, in particular surface waters and air.

With regards to monitoring NM in surface waters, analytical methods and test protocols are not yet validated and monitoring NM would present considerable challenges to Member States, who would be obliged to employ research laboratories to undertake testing of surface waters. It may therefore be more constructive to work in parallel with Member States in sharing ongoing research and developments and in doing so to support ongoing efforts.

With regards to air, monitoring is already undertaken in the framework of the Air Quality Directive, although this is not specific to the nano-scale fraction. The introduction of monitoring requirements for the PM$_{0.1}$ fraction in urban areas could be considered, although this would need to be supported by a process of standardisation of available methods and test protocols.

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### Annex I: Overview table of NM environmental exposure data

The table below provides an overview of available exposure data for NM generated through the range of methods considered in this report. The table includes data from studies where media were deliberately spiked with NM in order to test the efficiency of methods. In such cases, this is explicitly stated under the column on exposure scenarios.

<table>
<thead>
<tr>
<th>Specific ENM/NMs</th>
<th>Results</th>
<th>Data gathering methodology</th>
<th>Environmental media</th>
<th>Exposure scenario</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C60, C70, and functionalised C60</td>
<td>≤19 μg/L</td>
<td>In situ measurement</td>
<td>Water</td>
<td>Wastewater effluent</td>
<td>Farré et al. (2010)</td>
</tr>
<tr>
<td>Ag</td>
<td>Varied from 1.3 to 35% up to 377 μg/g</td>
<td>In situ measurements</td>
<td>Water</td>
<td>Washing of 9 different fabrics</td>
<td>Geranio et al. (2009)</td>
</tr>
<tr>
<td>TiO2</td>
<td>Newly painted model façade: 600 μg l-1; painted real façade: 10 μg l-1; urban run-off: 8 μg l-1</td>
<td>In situ measurement</td>
<td>Water</td>
<td>Leaching from house facades into receiving water bodies</td>
<td>Kaegi et al. (2008)</td>
</tr>
</tbody>
</table>

---


<table>
<thead>
<tr>
<th>Specific ENM/NMs</th>
<th>Results</th>
<th>Data gathering methodology</th>
<th>Environmental media</th>
<th>Exposure scenario</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag Painted façade: ≤ 145mg/l</td>
<td>In situ measurement</td>
<td>Water</td>
<td>Leaching from house</td>
<td>Kaegi et al. (2010)</td>
<td></td>
</tr>
<tr>
<td>Ag 90% of the spiked Ag ended in excess sludge, 2.5% in effluent, 7% remaining in WWTP</td>
<td>In situ measurement</td>
<td>Water</td>
<td>Ag-spiked wastewater</td>
<td>Kaegi et al. (2011)</td>
<td></td>
</tr>
<tr>
<td>Ti 16 μg/L</td>
<td>In situ measurement</td>
<td>Water</td>
<td>Wastewater effluent</td>
<td>Kiser et al. (2009)</td>
<td></td>
</tr>
<tr>
<td>Ag 45 μg Ag g per product</td>
<td>In situ measurement</td>
<td>Water</td>
<td>Release from products during wash</td>
<td>Benn et al. (2010)</td>
<td></td>
</tr>
<tr>
<td>nC60 As low as 300ng/L</td>
<td>In situ measurement</td>
<td>Water</td>
<td>Pure water and water containing salts spiked with nC60</td>
<td>Chen et al (2008)</td>
<td></td>
</tr>
<tr>
<td>CeO 2-5ppm in treated waste waters</td>
<td>In situ measurement</td>
<td>Water</td>
<td>CeO introduced into a WWTP</td>
<td>Limbach et al (2008)</td>
<td></td>
</tr>
<tr>
<td>Titanium Raw sewage titanium concentrations ranged from 181 to</td>
<td>In situ measurement</td>
<td>Water</td>
<td>raw sewage and treated effluent of ten</td>
<td>Westerhoff et al. (2011)</td>
<td></td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Specific ENM/NMs</th>
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<th>Data gathering methodology</th>
<th>Environmental media</th>
<th>Exposure scenario</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effluent titanium concentrations of &lt;25 µg L(^{-1})</td>
<td></td>
<td></td>
<td></td>
<td>representative WWTPs</td>
<td></td>
</tr>
<tr>
<td>Ag: particulate (≥450 nm) and colloidal (2-450 nm)</td>
<td>mean effluent concentration of colloidal (including nano) silver was 6 ng/L</td>
<td></td>
<td></td>
<td>Johnson et al. (2011)(^{272})</td>
<td></td>
</tr>
<tr>
<td>ultrafine (UFP, (D_p &lt; 100) nm) and submicron (100 &lt; (D_p &lt; 1000) nm)</td>
<td>Total particle number concentrations in the order of (10^4) cm(^{-3})</td>
<td>In situ measurements</td>
<td>Air</td>
<td>Urban site</td>
<td>Lonati et al. (2011)(^{273})</td>
</tr>
<tr>
<td>UFP 3nm particles</td>
<td>Daily max. number concentrations of UFP formed by nucleation: 4.8 ± 3.5 (\times) (10^4) cm(^{-3}), maximum daily rates of 3 nm particle production:</td>
<td>In situ measurement</td>
<td>Air</td>
<td>Urban street, USA</td>
<td>Qian et al. (2007)(^{274})</td>
</tr>
</tbody>
</table>


\(^{273}\) Lonati G, Crippa M, Gianelle V and Dingenen RV (2011) Daily Patterns of the Multi-modal Structure of the Particle Number Size Distribution in Milan, Italy, Atmospheric Environment 45: 2434-2442

\(^{274}\) Qian S, Sakuria H, McMurry PH (2007) Characteristics of regional nucleation evenings in urban East St. Louis, Atmospheric Environment 41: 4119-4127
<table>
<thead>
<tr>
<th>ENM/NMs</th>
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<th>Data gathering methodology</th>
<th>Environmental media</th>
<th>Exposure scenario</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>UFP</td>
<td>daily average particle total number concentration of 19,000 cm$^{-3}$</td>
<td>In situ measurement</td>
<td>Air</td>
<td>Urban site, Italy</td>
<td>Wang et al. (2010)$^{275}$</td>
</tr>
<tr>
<td>PM 7nm</td>
<td>total particle number concentrations for particles of 7 nm to several microns in diameter were found to be: 5,000-15,000 particles cm$^{-3}$ at the rural site; 5,000-30,000 particles cm$^{-3}$ at the urban site; and 20,000-60,000 particles cm$^{-3}$ at the roadside site</td>
<td>In situ measurement</td>
<td>Air</td>
<td>3 sites in the UK: urban, rural, roadside</td>
<td>NPL (2010)$^{276}$</td>
</tr>
<tr>
<td>PM$_{0.1}$ elemental and organic carbon</td>
<td>PM$<em>{0.1}$ elemental carbon: 0.03 ug m$^{-3}$ during the day to 0.18 ug m$^{-3}$ at night; organic carbon PM$</em>{0.1}$ size from 0.2 ug m$^{-3}$ during the day to 0.8 ug m$^{-3}$ at night</td>
<td>In situ measurement</td>
<td>Air</td>
<td>Severe winter pollution, USA</td>
<td>Kleeman et al. (2009)$^{277}$</td>
</tr>
<tr>
<td>PM$_{0.1}$</td>
<td>PM$_{0.1}$ concentrations of 1.4 ± 0.3</td>
<td>In situ measurements</td>
<td>Air</td>
<td>20m from an interstate</td>
<td>Hays et al. (2010)$^{278}$</td>
</tr>
</tbody>
</table>

$^{277}$ Kleeman MJ, Riddle SG, Robert MA, Jakober CA, Fine PM, Hays MD, Schauer JJ, Hannigan MP (2009) Source apportionment of fine (PM1.8) and ultrafine (PM0.1) airborne particulate matter during a severe winter pollution episode. Environmental Science and Technology 43(2): 272-279
<table>
<thead>
<tr>
<th>Specific ENM/NMs</th>
<th>Results</th>
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<th>Environmental media</th>
<th>Exposure scenario</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>aerosol 10 nm - 10 μm</td>
<td>particle number: 1.3 × 10⁴ 1/cm³, surface: 6.4 × 10⁷ μm²/cm³, volume concentrations: 64 μm³/cm³</td>
<td>In situ measurements</td>
<td>Air</td>
<td>highway in North Carolina with a traffic flow of 125,000 vehicles per day, US</td>
<td>Du et al. (2012)²⁷⁹</td>
</tr>
<tr>
<td>nano to fine size PM fraction</td>
<td>nano to fine size fraction 140,000 particles cm⁻³</td>
<td>In situ measurements</td>
<td>Air</td>
<td>Urban site, China</td>
<td>Price et al. (2010)²⁸⁰</td>
</tr>
<tr>
<td>Ag</td>
<td>PEC 0-3 ng/L; predicted mean concentrations (&gt;450 nm) tens of ng/L</td>
<td>Extrapolation from laboratory measurements</td>
<td>Water</td>
<td>Wastewater effluent</td>
<td>Johnson et al. (2011)²⁸¹</td>
</tr>
<tr>
<td>PM 5-560 nm</td>
<td>release of particle number concentrations during: Laboratory measurements and extrapolations</td>
<td>Air</td>
<td>3 simulated building activities: the crushing of</td>
<td>Kumar et al. (2012)²⁸²</td>
<td></td>
</tr>
</tbody>
</table>

²⁸² Kumar, P., Mulheron, M., Claudia, S., 2012, Release of ultrafine particles from three simulated building activities, Journal of Nanoparticle Research 14, 771
<table>
<thead>
<tr>
<th>Specific ENM/NMs</th>
<th>Results</th>
<th>Data gathering methodology</th>
<th>Environmental media</th>
<th>Exposure scenario</th>
<th>Reference</th>
</tr>
</thead>
</table>
| cube crushing: ~0.77 ($\times 10^4$) cm
slab demolition: 19.1 ($\times 10^4$) cm
“dry” recycling events: 22.7 ($\times 10^4$) cm
“wet” recycling events: 1.76 ($\times 10^4$) cm | | | concrete cubes, the demolition of old concrete slabs, and the recycling of concrete debris | | |
| Ag | 2.7 $\mu$g L$^{-1}$ and 25 $\mu$g L$^{-1}$ | Laboratory measurements and extrapolations | Water | Washing machine effluent | Farkas et al. (2011) $^{283}$ |
| | 98.5 kg per year | | | 20% market penetration in Norway | |
| | 80.8 kg per year | | | | |
| CNT | Total CNT conc.: 1.05 ppm | Laboratory measurements and extrapolations | Waste | Waste treatment CNT-products | Kobayashi et al. (2009) $^{284}$ |
| | Dust CNT conc.: 2.0–6.0 mg/m3; Max air conc.: 0.0064 $\mu$g/m3 | | Air | | |
| Ag | 1.5 and 650 $\mu$g in 500 mL of distilled water
WWTP effluent Ag 0.01 $\mu$g/L
Sludge Ag 2.8mg/Kg | Measurement of Ag released in wash and modelling Ag in effluent | Water | Release during wash and fate in WWTP | Benn and Westerhoff (2008) $^{285}$ |
| CeO2 | 0.612 ± 0.287 ng/m3 | Modeling studies, historical data | Ambient air | CeO2 emissions from diesel | Park et al. (2008) $^{286}$ |


<table>
<thead>
<tr>
<th>Specific ENM/NMs</th>
<th>Results</th>
<th>Data gathering methodology</th>
<th>Environmental media</th>
<th>Exposure scenario</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO2</td>
<td>&lt; 1255 tons</td>
<td>Modeling</td>
<td>Atmospheric outlet</td>
<td>Worst-case scenario for EU Member States assuming 5 ppm CeO2 in diesel fuel</td>
<td>Park et al. (2008)</td>
</tr>
<tr>
<td>CeO2</td>
<td>0.2 g/ year</td>
<td>Modeling</td>
<td>Ambient air</td>
<td>Exposure to urban EU population assuming 5 ppm CeO2 in diesel fuel</td>
<td>Park et al. (2008)</td>
</tr>
<tr>
<td>CeO2</td>
<td>6.6 g/ year</td>
<td>Modeling</td>
<td>Ambient air</td>
<td>Exposure to rural EU population assuming 5 ppm CeO2 in diesel fuel</td>
<td>Park et al. (2008)</td>
</tr>
<tr>
<td>CeO2</td>
<td>0.3 kg/ year</td>
<td>Modelling</td>
<td>Ambient air</td>
<td>Average emissions along the EU highways assuming 5 ppm CeO2 in diesel fuel</td>
<td>Park et al. (2008)</td>
</tr>
<tr>
<td>CeO2</td>
<td>0.28-1.12 µg/g</td>
<td>Modelling</td>
<td>Soil</td>
<td>40-year accumulation period depending on the soil depth at a distance from the edge of the highway</td>
<td>Park et al. (2008)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Specific ENM/NMs</th>
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<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>PEC&lt;sub&gt;water&lt;/sub&gt;=320 ng/L</td>
<td>Material mass flow analysis and simple modelling approaches</td>
<td>Water</td>
<td>Biocidal plastics and textiles</td>
<td>Blaser et al. (2008)(^{287})</td>
</tr>
<tr>
<td></td>
<td>PEC&lt;sub&gt;sediment&lt;/sub&gt;=14 mg/kg</td>
<td></td>
<td>Sediment</td>
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<tr>
<td></td>
<td>PEC&lt;sub&gt;STP&lt;/sub&gt;</td>
<td></td>
<td>STP</td>
<td></td>
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<tr>
<td>Latex</td>
<td>103-1025 μg/L</td>
<td>Material mass flow analysis and simple modelling approaches</td>
<td>Water</td>
<td>Laundry detergents</td>
<td>Boxall et al. (2008)(^{288})</td>
</tr>
<tr>
<td>Latex</td>
<td>4.3-43 mg/kg</td>
<td></td>
<td>Soil</td>
<td></td>
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<tr>
<td>ZnO</td>
<td>76.0-760 μg/L</td>
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<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>3194 μg/kg</td>
<td></td>
<td>Soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2</td>
<td>7 mg/m(^3)</td>
<td></td>
<td>Air</td>
<td></td>
<td></td>
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<tr>
<td>TiO2</td>
<td>24.5-245 μg/L</td>
<td></td>
<td>Water</td>
<td></td>
<td></td>
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<tr>
<td>TiO2</td>
<td>1030 μg/kg</td>
<td></td>
<td>Soil</td>
<td>Paints, sunscreens, etc.</td>
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<tr>
<td>Hydroxyapatite</td>
<td>10.1μg/L</td>
<td></td>
<td>Water</td>
<td>Toothpaste</td>
<td></td>
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<tr>
<td>Hydroxyapatite</td>
<td>422 μg/kg</td>
<td></td>
<td>Soil</td>
<td></td>
<td></td>
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<tr>
<td>Organo-silica</td>
<td>0.0005 μg/L</td>
<td></td>
<td>Water</td>
<td>Cosmetics</td>
<td></td>
</tr>
<tr>
<td>Organo-silica</td>
<td>4307 μg/kg</td>
<td></td>
<td>Soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>0.0007 μg/L</td>
<td></td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO2</td>
<td>0.03 μg/kg</td>
<td></td>
<td>Soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>6,00E-07</td>
<td></td>
<td>Air</td>
<td>Fuel additive</td>
<td></td>
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</tbody>
</table>


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<tr>
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<tbody>
<tr>
<td>CeO2</td>
<td>&lt;0.0001</td>
<td></td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CeO2</td>
<td>&lt;0.01</td>
<td></td>
<td>Soil</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2850 kg[^3]</td>
<td></td>
<td></td>
<td>Wash machine</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 tons[^6]</td>
<td></td>
<td></td>
<td>Swimming pools</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>1.7e-3 - 4.4e-3 µg/m³</td>
<td>Material mass flow analysis and simple modelling approaches</td>
<td>Air</td>
<td>Textiles, cosmetics, etc.</td>
<td>Mueller and Nowack (2008)[^90]</td>
</tr>
<tr>
<td></td>
<td>0.03-0.08 µg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02-0.1 µg/kg</td>
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<tr>
<td>TiO2</td>
<td>1.5e-3 - 4.2e-2 µg/m⁴[^7]</td>
<td></td>
<td>Air</td>
<td>Sporting good, cosmetics, etc.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7-16 µg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4-4.8 µg/kg</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CNT</td>
<td>1.5e-3 - 42.3e-3 µg/m⁵[^5]</td>
<td></td>
<td>Air</td>
<td>Plastics and electronics</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5e-3-0.8e-3 µg/L</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01-0.2 µg/kg</td>
<td></td>
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<tr>
<td>C60</td>
<td>All NP emission: $5.51 \times 10^{-7}$ µg/m³; NP &lt;1000 nm: $2.2 \times 10^{-9}$ µg/m³</td>
<td>Material mass flow analysis and simple modelling approaches</td>
<td>Air</td>
<td>500 m of a C60 manufacturing factory</td>
<td>Shinohara et al. (2009)[^91]</td>
</tr>
<tr>
<td></td>
<td>NP: 10-10,000 nm: $0.0018$ µg/m³</td>
<td></td>
<td>Atmospheric air</td>
<td>500 m of a C60;</td>
<td></td>
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<tbody>
<tr>
<td>Ag</td>
<td>13.1 tonnes</td>
<td>Material mass flow analysis and simple modelling approaches</td>
<td>Waste water system</td>
<td>Release into UK sludge and water in 2009</td>
<td>Whiteley et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>11.8 tonnes</td>
<td></td>
<td>Sludge</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.3 tonnes</td>
<td></td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02 mg/L</td>
<td>Probabilistic mass flow analysis</td>
<td>Water</td>
<td>Sediment and groundwater concentrations stemming from production, manufacturing and recycling processes</td>
<td>Gottschalk et al. (2010a)</td>
</tr>
<tr>
<td></td>
<td>4.3 mg/L</td>
<td></td>
<td>STP effluent</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>211 mg/kg</td>
<td></td>
<td>STP sludge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT</td>
<td>0.003 ng/L;</td>
<td></td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11.8 ng/L</td>
<td></td>
<td>STP effluent</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.069 mg/kg</td>
<td></td>
<td>STP sludge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>0.72 ng/L</td>
<td></td>
<td>Water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.7 ng/L</td>
<td></td>
<td>STP effluent</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.88 mg/kg</td>
<td></td>
<td>STP sludge</td>
<td></td>
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</tbody>
</table>

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<tbody>
<tr>
<td>25 nm TiO2 NP</td>
<td>Approximately $2.5 \times 10^{12}$ particles m$^{-3}$</td>
<td>Kinetic modelling</td>
<td>Water</td>
<td>3 m deep lake; bottom temperature 4 °C, water viscosity 1.5 mPa·S, water density 1000 kg/m3, TiO2 NP density 4200 kg/m3, shear rate 0.01 s$^{-1}$, collision efficiency 1</td>
<td>Arvidson et al. (2011)</td>
</tr>
<tr>
<td>Carbon nanoparticles</td>
<td>PECsediment 40 -2000 mg/kg</td>
<td>Kinetic modelling</td>
<td>Sedimentation from the water column</td>
<td></td>
<td>Koelman et al. (2011)</td>
</tr>
</tbody>
</table>

$^a$ Particle number retention were betw. 97-100%; $^b$ Sun lotion contains 2% TiO2; $^c$ Assuming that 10 and 30% of the population in the U.S. use silver; $^d$ Households in the U.S. that are wealthy enough will buy silver wash machines; $^e$ 1 million pools in the U.S. use silver as a biocide; $^f$ Removal in the STP was assumed to range between 99-85% wastewater; $^g$ 10 and 100% market penetration; $^h$ All diesel fuel doped with 10 ppm will lead to emission rate of 10 ppm

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295 Koelmans AA Nowack B and Wiesner MR (2009) Comparison of manufactured and black carbon nanoparticle concentrations in aquatic sediments, Environmental Pollution 157, 1110-1116