



## **Consensus Report based on the NanoImpactNet workshop: Environmental fate and behaviour of nanoparticles - beyond listing of limitations**

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**Consensus Report based on the NanoImpactNet workshop:**

**Environmental fate and behaviour of nanoparticles  
– beyond listing of limitations**

**Bilthoven, October 7<sup>th</sup> 2009**

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### Executive Summary

This report summarizes the discussions that took place during the one-day workshop “*Environmental fate and behaviour of nanoparticles - beyond listing of limitations*” organized by NanoImpactNet on October 7, 2009, in Bilthoven, the Netherlands. The subject of the workshop was 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. Prior to the workshop participants were provided with a summary of what is currently known about the environmental fate and behaviour of nanomaterials as well as a summary analysis of the data and model input needed to complete an environmental exposure estimation according to the Technical Guidance Document, Chapter R.16. This former was prepared by Bryony Ross and Rob Aitken, IOM with contributions from Anders Baun and Steffen Foss Hansen, DTU Environment, Technical University of Denmark and Teresa Fernandes, Edinburgh Napier University. The latter was prepared by Steffen Foss Hansen and Anders Baun, DTU Environment, Technical University of Denmark. During the morning of the workshop the current state of knowledge - and especially the gaps in our knowledge - was discussed inspired by keynote presentations:

- 1) Detection and fate of engineered nanoparticles in aquatic systems by Dr. Karen Tiede (FERA, UK),
- 2) Probabilistic material flow modelling for assessing the environmental exposure to nanomaterials (TiO<sub>2</sub>, ZnO, Ag, CNT and fullerenes) by Dr. Fadri Gottschalk (EMPA, Switzerland) and
- 3) Getting exposure assessment for nanoparticles right: Is the standard exposure modelling methods for ordinary chemicals valid? by Dr. Dik van de Meent (RIWM, the Netherlands).

During the afternoon, two parallel break-out workshops were held under the supervision of Anders Baun and Steffen Foss Hansen. Participants were first asked to assess and discuss the mass balance approach and identify important inputs, processes and “receptors”/compartments. Then they were asked to assess and discuss model complexity in regard to the identification of distribution processes, distribution coefficients and appropriate estimation methods and/or inappropriate ones. Finally, the participants in each group were asked to evaluate and reflect on the relevance of the input data and model requirements, as well as the need to include new data and/or model parameters. In each of the sessions, lively discussions took place addressing both the possibilities of applying existing exposure assessment modelling and the need for adaptations, identification of the most important parameters and information needs.

In the field of detection and analysis of nanomaterials in aquatic systems it was found that a number of major issues remain to be addressed, e.g. how to ensure comparability and reproducibility in analytical determinations, how to adapt protocols to specific “nano” properties in contrast to “soluble” compounds. It was stressed that there are no

“generic” engineered nanomaterials but a way forward may be to look upon “classes of engineered nanomaterials” instead of following a substance-by-substance approach.

Discussions were also centred on the applicability of the [European Union System for the Evaluation of Substances \(EUSES\)](#) (the currently used model for environmental exposure assessment in the EU) (EC JRC 2010). It was found to be questionable whether EUSES can be used for predicting environmental concentrations, since nanoparticles are dispersed rather than dissolved and all approaches are based on dissolved chemicals. The tendency of nanoparticles to aggregate is also obviously not considered for conventional chemicals and it is unclear how to model partitioning of nanoparticles between the aqueous phase and solid surfaces. Focus should be on quantifying distributions e.g. for suspended:dissolved. In addition there is a need to focus on obtaining the fundamental understanding of distributions of nanomaterials between different environmental compartments. This knowledge can then be used to develop models. Much can be learned from colloid science, but additional research is needed as well.

Thus, EUSES was by most workshop participants deemed insufficient for nanoparticles for a number of reasons: a) the extent/rate of dissolution is unknown or not included in current models and the same goes for b) the extent / rate of aggregation / settling and c) the extent of association with sediment. It was discussed and 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, requirements mentioned included information on agglomeration, behaviour of agglomerates, sinks i.e. local accumulation, and understanding of what happens at the interfaces between water and sediments and water and biological surfaces.

It was generally agreed that diffusion from water and soil into air is unlikely for most nanoparticles, although it was argued that advection was likely. Degradation in air was also noted as unlikely. The possibility of emission from and between industrial, agricultural and natural soils (as defined in the EUSES approaches for chemical fate modelling) was likely.

In general the participants agreed that degradation and traditional transformation rates and characteristics as well as emission data were relevant for nanomaterials in general. However there was less agreement on whether and which physical-chemical properties were relevant. One of the most important issues discussed was that we probably need to change “degradation” to “disappearance” of NPs. “Disappearance” could be defined as either dissolved or irreversible aggregates bigger than what’s considered the nano-scale range. The need to find a replacement for the octanol-water partition coefficient ( $K_{ow}$ ) and for another parameter than  $K_{oc}$  (partition coefficient between organic carbon and water) for predicting solid phase-water partitioning was also discussed.

During the discussions in each workgroup a large number of properties relevant for fate modelling were mentioned and discussed, and some consensus developed around properties such as size distribution, shape, coating/surface chemistry, synthesis method,

state of agglomeration, shape, “pure” NPs vs. formulation/embedded NPs. Affinity for adsorption of natural organic matter (NOM) and zeta potential with NOM were also mentioned as well as dissolution rate and loads reported as tonnages volumes or as particle number.

There was general agreement on the statement that the limitations of the Technical Guidance Document on environmental exposure estimation fall into four overall categories:

1. Lack of information on physico-chemical properties relevant for nanoparticles;
2. Lack of access to information on production, emissions throughout the life-cycle, etc.;
3. Fundamental limitations of the various assumptions made such as  $K_{ow}$  as being a good descriptor for processes like sorption and bioconcentration;
4. Fundamental limitations of the various models of fate and degradation of nanoparticles since they are developed for organic chemicals and for non-particulates”.

It was concluded that while models developed for chemicals may be applied for nanomaterials with and without small adaptations, there is a need for developing other models and approaches. One suggestion was to focus on developing three interacting models: one for dissolved ions, one for nanoparticles and one for aggregates.

## 1. Background

During that last five years, a consensus seems to have been reached on the issue of using an incremental approach when performing risk assessments of nanomaterials in the EU (CEC 2008, SCENIHR 2007). In order to pursue such an incremental approach, alterations taking nano-specific properties/concerns into account may have to be implemented to the currently used guidelines for effects and exposure assessments. The current Technical Guidance Document (TGD), produced by the European Chemicals Agency on environmental exposure estimation (R.16) (ECHA 2008) provide guidance on how to assess the environmental exposure of “regular” chemical substances and will – following the incremental approach - also have to be applied to nanomaterials. In 2007, the EC’s Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) evaluated that TGD procedures were generally applicable to human risk assessment and less so for the environment risk assessment and argue that numerous adaptations are needed, but SCENIHR is less clear on what these should be (SCENIHR, 2007).

A number of scientific reviews have been published summarizing the current limitations of our knowledge on the environmental fate and transport behaviour of nanomaterials in air, water and soil (Boxall *et al.* 2008, Mueller and Nowack 2008, ENRHES 2010). These limitations include lack of knowledge about transport pathways, degradability, availability, accumulation of nanomaterials as well as toxic transformation products and interaction with known contaminants.

Models are often used to generate estimated data, but environmental fate and transport models used for chemicals are probably not applicable to nanomaterials. The question is which specific adaptations need to be made to existing models in regard to physico-chemical properties and/or transformation processes or which new models can be developed on the basis of current knowledge.

Based on the presentations of a limited number of invited speakers, the purpose of this workshop was to use "carrot and stick" approaches to push and pull participants to think beyond statements about the limitations of current models and important knowledge gaps and start a collaborative brain-storming about model adaptations, setting upper and lower estimates on key parameters and potential development of new models.

A background draft document was prepared and circulated among the participants before the conference (see Annex 2). The background paper was divided in two parts intended to serve as background documents for identifying discrepancies between what we currently know about the fate and behaviour of nanoparticles in the environment and what we need to know in order to apply the framework and the partitioning coefficients, equations and



exposure models described in the Technical Guidance Document on environmental exposure estimation (R.16).

The first part of Annex 2 is a recent review of the literature on the environmental fate and behaviour of nanoparticles. The review stems from a recent review performed by the FP7 project Engineered Nanoparticles - Review of Health & Environmental Safety (ENRHES) authored by Bryony Ross and Rob Aitken (IOM, UK) with input from Teresa Fernandes (Edinburgh Napier University, UK) and Steffen Foss Hansen & Anders Baun (DTU Environment, Technical University of Denmark).

The second part of the document is an extraction of key information needs and data requirements for applying the Technical Guidance Documents (R.16) for chemicals substances and - ideally - nanoparticles once adaptations have been implemented. This extraction was prepared by Steffen Foss Hansen & Anders Baun (DTU Environment, Technical University of Denmark).

In the following, we provided a short summary of the keynote presentations followed by a summary of the breakout sessions, as well as a number of final recommendations based on the discussions at the workshop.

## 2. Keynote presentations

### 2.1 Assessing the fate of engineered nanomaterials in aquatic and soil systems

In order to provide a solid background for discussion on how to assess the fate of engineered nanomaterials in aquatic and soil systems, Dr. Karen Tiede (The Food and Environmental Research Agency, UK) first presented and elaborated on the nature and format of the information required “in the ideal world” and the requirements for our analytical methods and instruments in such a world. She then presented what is known today and the challenges that have to be addressed under both laboratory and real life conditions in order to detect and quantify engineered nanomaterials in natural matrices.

One of the main points raised during Dr. Tiede’s presentation was, that it is not (yet) possible to detect and quantify engineered nanomaterials in the environment at low levels. This has also been identified by Benn & Westerhoff (2008) as a problem. However they also seem confident that advancement in technological development will eventually solve this problem: “The unknown risks are currently preventing scientists and the public from fully supporting the advancement of nanotechnology, but new analytical techniques can answer these questions, thus allowing nanotechnology to develop at a pace acceptable to all stakeholders.” (quote from Karen Tiede’s presentation)

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Ideally, the characteristics that affect environmental fate and behaviour should be known including chemical composition, mass concentration, surface area, charge, and chemistry as well as reactivity, particle number concentration, shape, structure, solubility, state of aggregation/agglomeration, size distribution as well as dissolution, stabilization, bioavailability, reactivity, sorption and mobility of nanoparticles.

An ideal analytical technique should enable *in situ* characterisation of nanoparticle aggregation state in water, soil, food etc., separate a wide range of particle sizes, deal with heterogeneous sample composition, be sensitive and robust at environmental concentrations, differentiate between natural and engineered NPs, determine speciation and allow high and fast sample through-put. However, the current abilities to determine these properties are limited.

Dr Tiede presented examples of conventional and more recently developed promising techniques for nanoparticle analysis in complex matrices. Here she focused on imaging and size fractionation techniques. Conventional atomic force microscopy (AFM) can be

used for 3-D surface profiling, whereas transmission & scanning electron microscopy in combination with EDX allows visualization and elemental analysis of nanomaterials. Dr. Tiede presented results and images showing examples of how this has been done on TiO<sub>2</sub> and ZnO engineered nanoparticles in lake water as well as studying the interaction of Au nanocolloids and NOM. She demonstrated the occurrence of imaging artefacts introduced by sample preparation, e.g. drying, which is necessary when working with conventional electron microscopes. These artefacts can be overcome by employing e.g. environmental SEM to study hydrated samples in a sample chamber featuring adjustable pressure and humidity. However, at the moment, only capsule-based technologies such as WetSEM can provide nanoparticle imaging under fully liquid conditions, thus avoiding imaging artefacts caused by sample preparation. Again, Dr. Tiede presented results and images of how this has been done for TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> engineered nanoparticles in lake water, imaged under fully liquid conditions. Dr. Tiede also presented on-going work on HDC-ICP-MS developed for simultaneous size & multi-element analysis of several inorganic ENPs in complex matrices (Tiede et al. 2009) and SPE extraction of fullerenes from tap water and analysis by LC/MS for analysis of carbon-based ENMs in complex matrices (Chen et al. 2008).

This work has underlined the importance of considering how to handle the nanoparticles tested including:

- Quality of nanoparticles (impurities, size distribution, shape), choice of nanoparticles (functionalisation, formulation, powder, commercial);
- Preparation of nanoparticles stock dispersion (sonic probe, stabilisation);
- Sample storage (where? how long?);
- Sample transportation (will changes occur due to transportation?).

Concentration of the tested nanoparticles need to be considered as well especially with regard to:

- What concentration should be tested?
- Are high concentrations worst case scenario?
- Real concentration of stock dispersion?
- How does exposure concentration and state of engineered nanomaterials change over time (e.g. aggregation, dissolution)?

Evidence was presented showing that results of size measurements depend and vary in regard to concentration, pH at the time of measurements, time of measurement and sample preparation. Therefore the use of multiple techniques is recommended. Also full

understanding of the size measurement techniques applied and correlation between different techniques is essential to for the interpretation of obtained sizing data.

Appropriateness of current test guidelines and procedures were also discussed. Many test guidelines prescribe the use of various labware, filtration and centrifugation techniques and Dr. Tiede presented results using different experimental approaches e.g., comparison of filtration and centrifugation to separate soil and supernatant, the performance of Teflon centrifuge tubes compared to disposable tubes and glassware as well as the effect of various matrices on particle behaviour, such as distilled water, lake water and CaCl<sub>2</sub>. It was found that the commercially available Au dispersions used in these experiments stuck to all labware but to a lesser extent to glass, whereas 0.4 µm filters retained nanoparticles, which might bias primary sampling results. The ionic background of 0.01M CaCl<sub>2</sub>, as recommended by the OECD guidelines for adsorption studies, was found to induce more aggregation of 20 nm Au particles compared to 20 nm Au particles suspended in distilled and lake water. Therefore it is questioned whether a CaCl<sub>2</sub> background will provide worst case scenario conditions.

Major issues that remain to be addressed are:

- How do we ensure comparability & reproducibility?
- How can we adapt protocols to specific “nano” properties in contrast to “soluble” compounds?
- There are no “generic” nanoparticles, but should “classes of nanoparticles” be investigated? Or does each nanoparticle need testing?

There is a need for the derivation of size, number & mass concentration standards, reference materials, cross-laboratory validation, multiple analytical method validation and for the determination of exposure concentrations.

While all of these issues are not only relevant for studies and validation performed under laboratory conditions, a number of additional challenges present themselves when it comes to studying the fate of ENMs in, for instance, waste water treatment plants (WWTPs) or in surface waters. Research was cited indicating that 70-90% of the particles are removed in WWTP (Benn & Westerhoff 2008, Kiser et al. 2009, Tiede et al. accepted). However, fractions remain in the aqueous phase in the nanoform and could survive sewage treatment processes. ENMs can furthermore be stabilised by natural organic matter (Navarro et al. 2009, Hyung et al. 2008), whereas aggregation and dissolution depends on ionic strength, pH, degradation and exchange of coatings (Baalousha 2009). Transport through soil could be possible (Fang et al. 2009).

Thus, moving from the laboratory to real-life experiences raises a number of additional questions such as:

- What do we measure?
- What is tested in studies?

- What are people/the environment exposed to?
- Are they the same?
- Does and if so, what concentration matters?
- Measurement in what units?
- How many measurements and which measurements are correct?

This also leads to a fundamental question of which data can we use in model predictions and how this should be done – a topic that was also addressed in the two subsequent presentations by Fadri Gottschalk and Dik van de Meent.

## **2.2 Probabilistic material flow modelling for assessing the environmental exposure to nanomaterials (TiO<sub>2</sub>, ZnO, Ag, CNT and fullerenes)**

Only some data on environmental behaviour and ecotoxicology of nanomaterials are available and analytical methods are not (yet) available for quantitative nanomaterial detection in the environment. There seems to be little doubt that nanomaterials will end up in the environment, but the question is at what concentrations? Fadri Gottschalk (Eidgenössisches Materialprüfungsanstalt (EMPA), Switzerland) presented recent work done at EMPA using Probabilistic Material Flow Analysis (PMFA) to assess the environmental exposure to nano-TiO<sub>2</sub>, ZnO, Ag, CNT and fullerenes. First, he presented the general concept and aim of PMFA and provided insight to PMFA via intermediate Monte Carlo iteration outputs. Finally, he presented the results of simulation studies on nano-TiO<sub>2</sub>, ZnO, Ag, CNT and fullerenes. PMFA consist of three steps: 1) material flow analysis (MFA), 2) emission estimates and 3) multimedia modelling. Model parameters can be revised and correlated with measured data once, and if, such data become available.

In practice, the current environmental concentrations of different nanomaterials TiO<sub>2</sub>, ZnO, Ag, CNT, and fullerenes for different regions were modelled through a three step process. First, the prior probability distribution was modelled for all input parameters via a Monte Carlo simulation whereas the posterior probability distributions were modelled via Monte Carlo Markov Chain algorithms. This led to a repeated computation of the linear equation system choosing randomly parameter values out of the modelled probability distributions.

Based on estimates on worldwide production volumes, distribution to product categories and material flow analysis, results were presented on the most sensitive transfer coefficients for concentrations in water, modelled yearly increase in soil and sediment concentrations in the EU and sludge treated soil in the US. Open points included:

1. better data on production and use needed;
2. release from products since only a few studies are available;
3. different forms and functionalizations of nanoparticles;

4. geographical and time-dependent differentiation, and;
5. lack of ecotoxicological data for some environmental compartments and nanoparticles.

### 2.3 Getting exposure assessment of nanoparticles right with a focus on aquatic ecotoxicology

Dr. Dik van de Meent (National Institute for Public Health and the Environment (RIVM), the Netherlands) gave a presentation on how to deal with exposure assessment in aquatic ecotoxicology. He indicated that the general environmental risk assessment paradigm based on no risk when  $RCR = PEC_{\text{water}}/PNEC_{\text{aquatic}} \ll 1$  is acceptable for nanomaterials. However, while most research efforts today are directed towards generating data on the ecotoxicity of nanomaterials (leading to  $PNEC_{\text{aquatic}}$ ), it is equally important to establish reliable estimates of  $PEC_{\text{water}}$ . In his presentation Dik van de Meent raised a number of concerns about whether the currently used programme for PEC estimation in the EU risk assessment of chemicals (EUSES) is fit for nanoparticles as they do not behave as conventional chemicals.

In EUSES models it is assumed that molecules in air, water and soil/sediment/biota are in a gas phase, dissolved state and sorbed state, respectively. It is furthermore assumed that the distribution among media can be predicted from Henry's law constant (measured, or depending on vapour pressure and aqueous solubility), partition coefficients ( $K_{ow}$ ,  $K_{oc}$ ) and bioconcentration factors (measured or estimated BCF-values). Using solid-water partitioning and QSAR modelling results of  $K_p = f_{oc} * K_{oc}$  as an example Dr. van de Meent raised doubt about the predictability of air/water/solid partitioning for nanoparticles. This is due to the fact that nanoparticles are primarily solid phase although dissolved atoms, ions and molecules might be present as well. Dispersed nanoparticles are not in solution, but are instead in suspension and dissolution is not considered/modelled for conventional chemicals. The tendency of nanoparticles to aggregate is furthermore a phenomenon 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 we would need to consider all chemical species i.e. dissolved, dispersed/suspended and aggregated/attached to solid surfaces as the relative toxicity of different size-classes and forms are often unknown.

Focus should be on quantifying distributions e.g. for suspended:dissolved the dissolution rate might be applicable, for air:water  $K_{\text{air-water}}$  could be set to be equal to 0 whereas (equilibrium) partitioning might apply for suspended:solid and uptake in biota. First we need to focus on obtaining a fundamental understanding of distributions and then use that information to develop models. Much can be learned from colloid science, but additional research is needed as well. A number of experiments are on-going at RIVM and in summary unpublished results indicate that NOM helps keeping nanoparticles such as CNTs and  $CeO_2$  suspended and less aggregated. This indicates that medium ionic

strength induces aggregation whereas high zeta potential causes stabilization and steric hindering, something which needs to be taken into account when developing models in the future. In conclusion, Dr. van der Meent argued that the overall risk assessment paradigm would be valid as long as the RCRs were derived for each chemical species and PEC and PNEC were measured correctly. EUSES however, was deemed insufficient for nanoparticles for a number of reasons: a) extent/rate of dissolution of nanoparticles is unknown or not included in current models and the same goes for b) the extent / rate of aggregation / settling of nanoparticles and c) the extent of association of nanoparticles with sediment.



### 3. Conclusions from breakout sessions

The NIN workshop on “Environmental fate and behaviour of nanoparticles - beyond listing of limitations” focused on concrete adaptation and/ or rejection of various aspects of the Technical Guidance Documents including new assumptions that need to be made, new aspects that need to be assessed and equations that need to be corrected so that they reflect what is currently known on the behaviour of nanoparticles.

Inspired by the mornings keynote presentations, the participants were given a total of five tasks. These tasks covered five overall subjects:

1. Mass balance model/material flow models
2. Environmental distribution models
3. Applicability of traditional input data for environmental modelling
4. Development of new input data for environmental modelling
5. General limitations of the Technical Guidance Document

#### **Task 1: Mass balance model/material flow model of the use of CeO<sub>2</sub> NP in diesel**

In the first task, the participants were asked to consider a conceptual mass balance model/material flow model of the use of CeO<sub>2</sub> nanoparticles in diesel (see Figure 1) and identify important inputs, processes and receptors/compartments for modelling. The participants were also asked to suggest sampling sites, if one were to do monitoring instead of modelling, or as input to models.



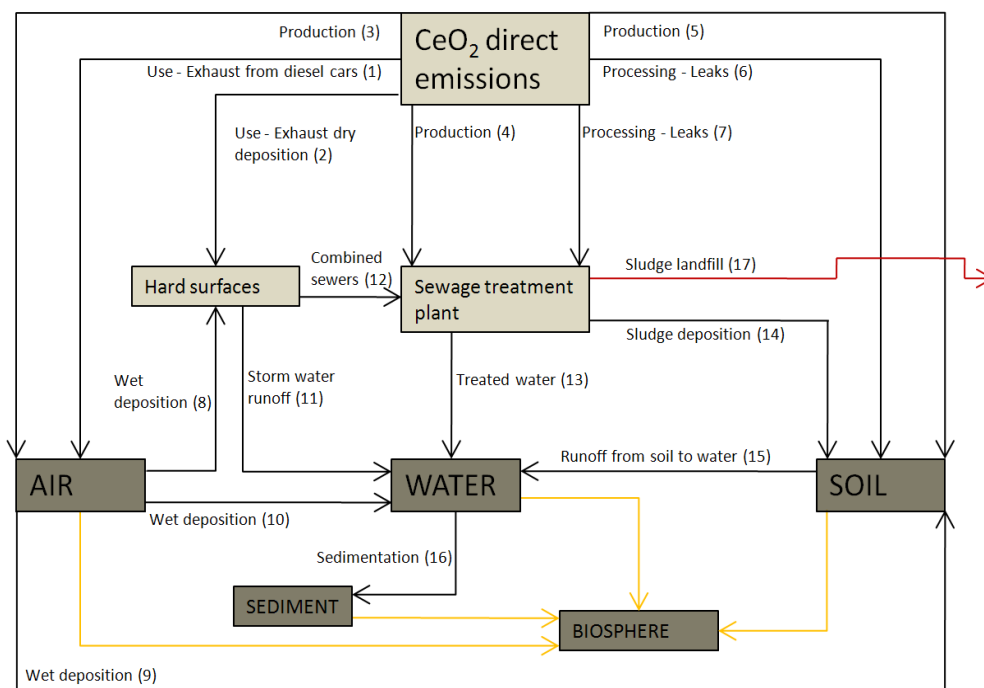


Figure 1: A mass balance approach for CeO<sub>2</sub> used as an additive to diesel fuel. Arrows indicate the different mass flows possible, numbers in brackets were used for identification of each flow in the discussions. The yellow arrows indicate that these flows were too uncertain to assign masses to. The red arrow indicate a mass flow over the model boundary (Hansen et al., 2009 unpublished).

In general, the participants were quite pleased with the mass balance approach for CeO<sub>2</sub> in diesel illustrated in Figure 1. Additional inputs identified included leaks during transport and processing, use in cars and spill of diesel at pumps whereas important processes identified included burning in cars and process in sewage treatment plants.

Monitoring was discussed especially in regard to what should be monitored and if the focus should be the exhaust. A possibility mentioned was the method/approach used by Park et al. (2009) to monitor CeO<sub>2</sub> in from buses in London, UK.

### Task 2: Developing and adapting environmental distribution models

The participants were first presented with a Mackay level 1 distribution model (i.e. no flow of water and air, no degradation, with equilibrium being assumed (see Figure 2a).

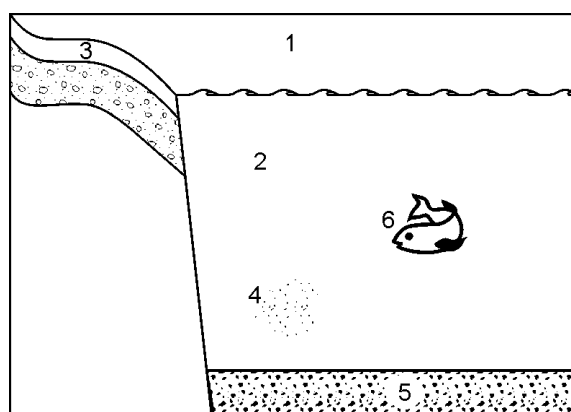


Figure 2a: A Mackay level 1 distribution model (numbers indicate the six different compartments usually included in Mackay level 1 models).

Based on the background paper provided in advance of the workshop and the keynote presentations, the participants were then asked to complete the following tasks:

- Insert arrows to identify distribution/equilibria
- Define relevant/irrelevant processes

The results of the discussion that took place during the afternoon session can be seen in Figure 2b.

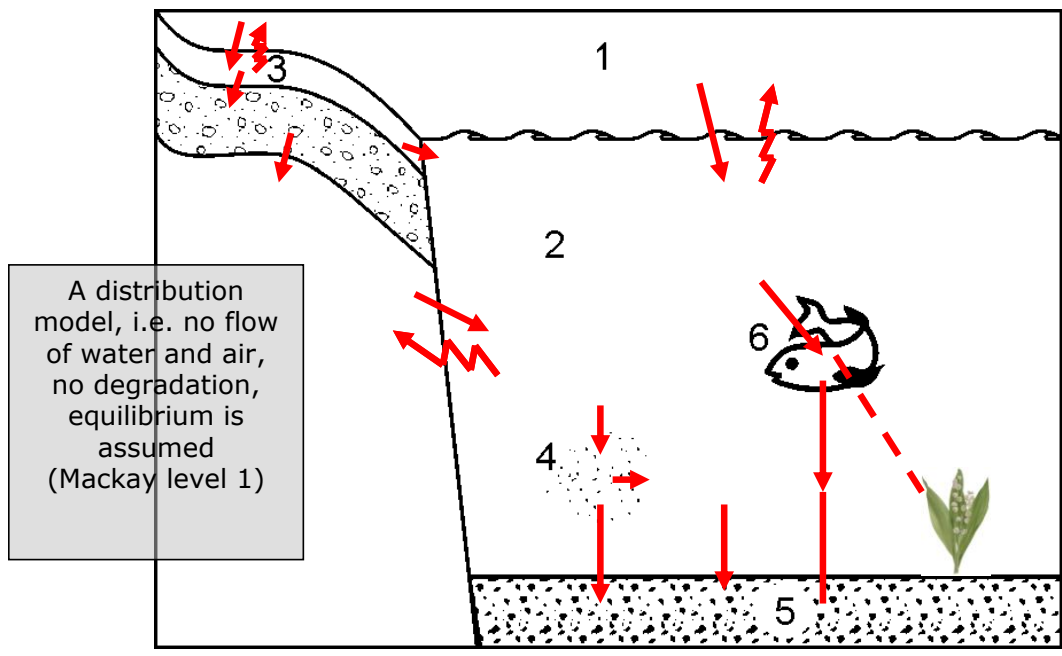


Figure 2b: A distribution model for nanomaterials. Straight arrows indicate likely fluxes, zig-zag arrows indicate that the flux is not likely to occur

In general fluxes (but not equilibria) were expected to occur from solid phases to water and in some cases vice-versa (see Figure 2b). Processes like deposition, sedimentation, and surface run-off were identified as important processes to be included for nanomaterials.

An extended distribution model showing inputs, processes, distributions, and degradation parameters was also presented to the participants (Figure 3) and the participants were asked to discuss whether presented and/or additional emission-, advection-, diffusion-, and/or degradation-patterns are relevant when it comes to nanomaterials. Specifically the participants were asked to:

- Identify the appropriate distribution coefficients
- List the needed input variables
- Assess if currently used approximations were valid – if not, which are the most crucial ones to address?

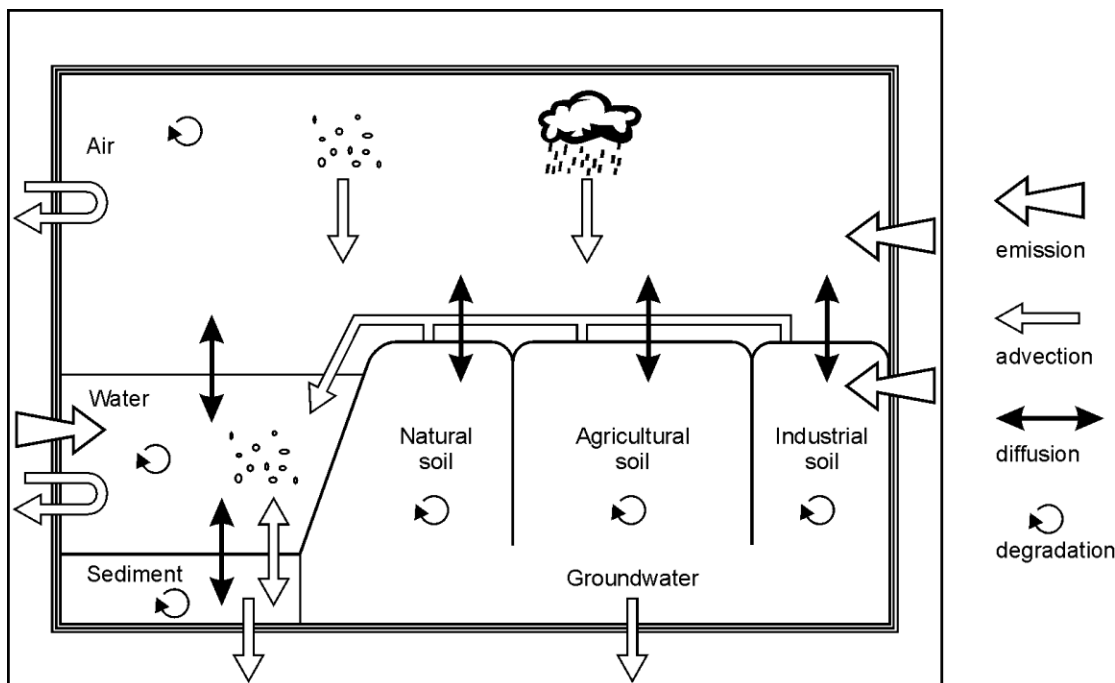


Figure 3: Distribution model showing inputs, processes, distributions and degradation parameters

The results of the discussions that went on in the two workgroups are illustrated in Figure 4. It was discussed and argued that we need 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, needs mentioned included information on agglomeration, behaviour of agglomerates, sinks i.e. local accumulation, and understanding of what happens at the interfaces between water and sediments and water and biological surfaces.

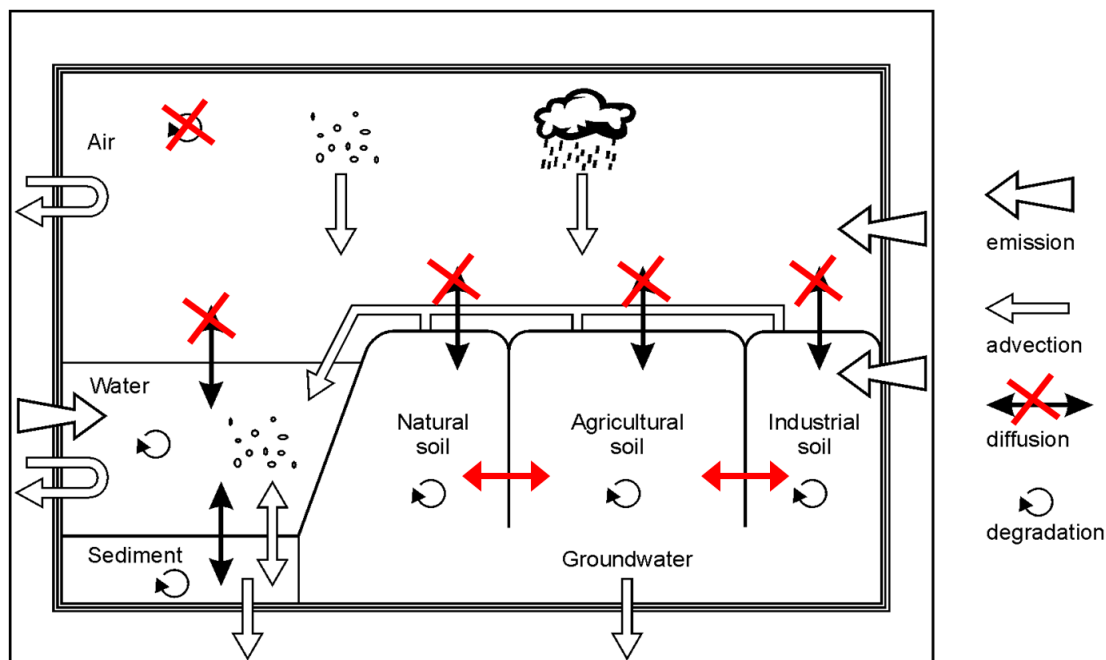


Figure 4: Distribution model showing inputs, processes, distributions and degradation parameters. Arrows indicate results of the discussion that went on in regard to adapting the distribution model showing inputs, processes, distributions and degradation parameters

It was generally agreed that diffusion from water and soil into air is unlikely for most nanoparticles, although it was argued that advection was likely. Degradation in air was also noted as unlikely. The possibility of emission from and between industrial, agricultural and natural soil was likely.

**Task 3: Evaluate the nano-relevance of the traditional input data for environmental modelling**

During task 3, the participants were presented with a table of the traditional input data for environmental modelling (see Table 1) and asked to evaluate the relevance of these parameters when it comes to nanomaterials in general and C<sub>60</sub> and TiO<sub>2</sub> in particular.

Table 1: Relevance of traditional input data for environmental modelling as evaluated by the two workgroups at the workshop. ■ = workgroup 1, ■ = workgroup 2. +: Relevant for nanomaterials; -: Irrelevant for nanoparticles.

<i><b>SUBSTANCE IDENTIFICATION</b></i>	<i><b>“Nanomaterials”</b></i>
General name	+/+
CAS no.	+
<i><b>PHYSICAL-CHEMICAL SUBSTANCE PROPERTIES</b></i>	
Molecular weight	-
Melting point	+
Vapour pressure at the temperature of the data set	-
Temperature at which vapour pressure was measured	-
Water solubility at the temperature of the data set	+/+
Temperature at which solubility was measured	+/+
Octanol-water partition coefficient	-/-
Chemical class for Koc-QSAR	-/-
Organic carbon - water partition coefficient	-/-
<i><b>DEGRADATION AND TRANSFORMATION RATES</b></i>	
<b>Characterization</b>	
Biodegradability test result	+/+
Rate constant for degradation in STP	+/+

Total rate constant for degradation in surface water	+/+
Total rate constant for degradation in marine	+/+
Total rate constant for degradation in bulk sediment	+/+
Rate constant for degradation in air	+/+
Total rate constant for degradation in bulk soil at env. temp	+/+
<b><i>EMISSIONS</i></b>	
<i>Tonnages</i>	+/+
Tonnage in EU	+/+
Fraction of EU production volume in Region	+/+
<i>Release fractions</i>	+/+
Fraction of tonnage released to air	+/+
Fraction of tonnage released to waste water	+/+
Fraction of tonnage released to surface water	+/+
Fraction of tonnage released to industrial soil	+/+
Fraction of tonnage released to agricultural soil	+/+
<i>Emission days</i>	+/+
Fraction of the main local source	+/+
Number of emission days per year	+/+
<i>Local release rates</i>	+/+
Local emission to air during episode	+/+

Local emission to wastewater during episode	+
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In general members of the two groups agreed that degradation and traditional transformation rates and characteristics as well as emission data were relevant for nanomaterials in general, however there was less agreement on which physical-chemical properties were relevant. One of the most important issues discussed in regard to task 3 was that we probably need to change “degradation” to “disappearance” of nanoparticles. It was suggested that “disappearance” could be defined as either dissolved or irreversible aggregates bigger than e.g. 300 nm (though this value was not discussed in detail it was suggested to indicate sizes above what normally defined as the nano-scale). The need to find replacement for the octanol-water partition coefficient, the chemical class for Koc-QSAR and the organic carbon - water partition coefficient was also discussed

**Task 4: Propose new input data needed to enable environmental models for NPs**

Subsequent discussion under completion of task 3 led to a debate about new input data needed to enable environmental models for NPs (task 4) and both workgroups were asked to fill out Table 2. The “X” indicates what the groups collectively identified as important.

Table 2: Proposed new input data needed to enable environmental models for NPs

<b><i>SUBSTANCE IDENTIFICATION</i></b>
Primary size distribution
Synthesis method
Coating
<b><i>PHYSICAL-CHEMICAL SUBSTANCE PROPERTIES</i></b>
Dissolution rate
Affinity for adsorption of NOM and
zeta potential with NOM
Size distribution
Agglomeration state
Shape



<b><i>DEGRADATION AND TRANSFORMATION RATES</i></b>
<b>Characterization</b>
Dissolution rate
<b>EMISSIONS</b>
Tonnages reported in particle number
Number of individual nanoparticles
Ratio between nanoparticles and nanoparticles embedded into other materials

During the discussions in each workgroup a large number of properties were mentioned and discussed, but some consensus developed around properties such as size distribution, shape, coating/surface chemistry, synthesis method, state of agglomeration, shape, “pure” NPs vs. formulation/embedded NPs. Affinity for adsorption of NOM to nanoparticles and NOMs impact on the zeta potential of nanoparticles were also mentioned as well as dissolution rate and exposure units reported as tonnages volumes or particle number

**Task 5: Current limitations of the TGD on environmental exposure**

As a final assignment, the participants were asked to discuss the following statements and add/delete claims in regard to:

*“The limitations of the Technical Guidance Document on environmental exposure estimation fall into four overall categories:*

- 1. Lack of information on physico-chemical properties relevant for nanoparticles*
- 2. Lack of access to information on production, emissions throughout the life-cycle, etc.*
- 3. Fundamental limitations of the various assumptions made such as  $K_{ow}$  as being a good descriptor for processes like sorption and bioconcentration*
- 4. Fundamental limitations of the various models on fate and degradation of nanoparticles since they are developed for organic chemicals and for non-particulates”*

In general, the four statements were supported by both workgroups although widely discussed and commented. Some of the comments included:

- If we have a model for chemicals that does not include physico-chemical properties relevant for nanoparticles, do we then need the model in the first place?
- Assumptions throughout the TGD need to be identified, verified and replaced where possible and appropriate
- How do we deal with the problem of information being available by some parts of society (industry and regulators), but not to modellers?
- Validation of models is key because if a given model is applied in a wrong way, it does not matter how much information is available.

One group also added a statement, which read:

- Fundamental limitation to the chosen modelling approach (static) since NPs behave dynamically and because this pathway through compartments/conditions affects the properties in a given compartment (along the way NPs change properties).

#### 4. Plenary discussion

During the final plenary discussion each of the two workgroups presented the results of their analysis and areas of dis-/agreement were discussed.

Main issues discussed were:

- How many particles are produced and used?
- Should production and usage of nanoparticles be measured by mass per unit volume? If so, then do we need to consider other properties as well?
- Aggregation, nanoparticles interactions more important than other parameters?
- When does a NP stop being a NP?
- Is degradation important?
- Should we have and can we have the same models for carbon-based and metal-based particles?
- How do we move away from ratios and use rates (dynamics)?
- How do we ensure that the PEC units have the same units than the PNEC units used?

It was concluded that models developed for chemicals can and will be applicable with and without small adaptations in some cases. Other models and approaches, now used for chemicals, will have to be developed anew for nanomaterials and it was suggested to focus on developing three interaction models. One for dissolved ions, one for nanoparticles and one for aggregates (above 300nm)

## 5. References

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SCENIHR. 2007. Scientific Committee for Emerging and Newly-Identified Health Risks (SCENIHR) 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. Brussels: European Commission Health & Consumer Protection Directorate-General.

**Annex A: List of participants**

First name	Last name	Institute/Company	Country
Anders	Baun	DTU	Denmark
Carmen	Nickel	Air Quality and Sustainable Nanotechnology Unit- IUTA e.V.	Germany
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Fadri	Gottschalk	EMPA/ETH	Switzerland
Frans	Christensen	European Commission, DG Joint Research Centre	Italy
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Hans	Marvin	RIKILT- insitute of food safety; WUR	The Netherlands
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Jon	Mullinger	Napier University	UK
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Karen	Tiede	Fera	UK
Maria	Dusinska	NILU	Norway
Michael	Riediker	Institute for Work and Health	Switzerland
Nico	van den Brink	Alterra	The Netherlands
Paul	te Riele	Shell International Exploration and Production	The Netherlands
Ping	Luo	University of York	UK
Qinglan	Wu	DNV	Norway
Renaud	Vigneron	Fundp	Belgium
Socorro	Vázquez-Campos	LEITAT Technological Center	Spain
Steffen	Foss Hansen	DTU	Denmark
Susan	Dekkers	RIVM	The Netherlands

**Annex B. Background material delivered to participants before the workshop**

**NanoImpactNet – Environmental fate and behaviour of nanoparticles - beyond listing of limitations, 5-7 October 2009, Bilthoven, The Netherlands**

Steffen Foss Hansen and Anders Baun, Department of Environmental Engineering, Technical University of Denmark.

**Background**

During that last five years a consensus seems to have been reached on the issue of using an incremental approach when performing risk assessments of nanomaterials in the EU. In order to pursue such an incremental approach, alterations taking nano-specific properties/concerns into account may have to be implemented to the currently used guidelines for effects and exposure assessments. The current Technical Guidance Document (TGD) provided by the European Chemicals Agency (2008) on environmental exposure estimation (R.16) provide guidance on how to assess the environmental exposure of “regular” chemical substances and will – following the incremental approach - also have to be applied to nanomaterials. In 2007 EU’s Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) evaluated that TGD procedures were generally applicable to human risk assessment and less so for the environment risk assessment and argue that numerous adaptations are needed, but SCENIHR is less clear on what these should be (SCENIHR, 2007).

**Content of the background document for the NIN workshop**

The NIN workshop on “Environmental fate and behaviour of nanoparticles - beyond listing of limitations” focuses on concrete adaptation and/ or rejection of various aspects of the Technical Guidance documents including new assumptions that need to be made, new aspects that need to be assessed and equations that need to be corrected so that they reflect what we currently know about the behaviour of nanoparticles.

This paper is divided in two parts intended to serve as background documents for identifying discrepancies between what we currently know about the fate and behaviour of nanoparticles in the environment and what we need to know in order to apply the framework and the partitioning coefficients, equations and exposure models describes in the Technical Guidance Document on environmental exposure estimation.

*Part 1*

The first part of the document is a recent review of the literature on the environmental fate and behaviour of nanoparticles. The review stems from a recent review performed by the FP7 project ENRHES authored by Bryony Ross and Rob Aitken (IOM, UK) with input from Teresa Fernandes (Edinburgh Napier University, UK) and Steffen Foss Hansen & Anders Baun (DTU, DK). **Before the NIN workshop:** Take a look at the review to get an overview of the state-of-knowledge.

*Part 2*

The second part of the document is an extraction of key information needs and data requirements for applying the Technical Guidance Documents for chemicals substances and - ideally - nanoparticles once adaptations have been implemented.

**Before the NIN workshop:**

Please browse through these pages and make your own notes on where you would expect problems to occur if we apply the “standard TGD” approach to the management of nanoparticles.

**In preparation for the break-out sessions Wednesday afternoon we ask the participants to consider the gap between the TGD approach and the state-of-knowledge in NP fate and behaviour processes, as well as hazard assessment.**

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## **PART 1**

### **Review of the literature on the environmental fate and behaviour of nanoparticles**

**Review published in the report: Engineered Nanoparticles - Review of Health &  
Environmental Safety (ENRHES) available at  
<http://nmi.jrc.ec.europa.eu/project/ENRHES.htm>**



## Environmental Fate and Behaviour of Nanomaterials

By Bryony Ross and Rob Aitken, IOM. With contributions from Anders Baun and Steffen Foss Hansen, DTU Environment and Teresa Fernandes, Edinburgh Napier University.

Review published in the report: Engineered Nanoparticles - Review of Health & Environmental Safety (ENRHES) available at:

<http://nmi.jrc.ec.europa.eu/project/ENRHES.htm>

### Introduction

As the use of nanomaterials increases across a wide range of sectors, environmental release is an inevitable consequence. Nanomaterial introduction into the environment may occur both intentionally and non-intentionally throughout the life-cycle of nanomaterial production, use and disposal. For example, wastewater treatment streams, landfill leachates and waste incineration products are all likely to contain nanomaterials from within nano-enabled products disposed at the end of their useful life, accidental spills during production or later transport of nanomaterials, and release from wear and tear from materials containing NP may also lead to potential release. In addition, intentional release into the environment must be considered, such as via the use of nano-zero valent iron (nZVI) in the remediation of groundwater polluted with chemicals such as chlorinated solvents (Nowack and Bucheli, 2007).

Models and frameworks to describe the fate and distribution of nanomaterials are slowly being developed, some of which incorporate classical knowledge of colloid science (SCHENIHR, 2009) and others apply principles used for chemical fate modelling (Mueller and Nowack, 2008). Traditional predictions of fate and transport are based on inherent properties such as phase transfer properties (e.g. boiling point, vapour pressure, partition coefficients), reactivity (e.g. photo-reactivity and hydrolysis) and biological degradation behaviour (Mackay and Hendry, 2009). A major knowledge gap hampering the development of such model-based approaches is our current lack of understanding of the novel physico-chemical properties exhibited by many nanomaterials and the effect these have on particle behaviour. In addition, it is most likely that those nanomaterials released into the environment will also exist as modified forms of their primary counterpart (SCHENIR, 2009). Model-based approaches must be developed using empirical data as they becomes available, in order to ensure they form practical and accurate method for predicting nanomaterial fate and behaviour. As such, those models developed to date are still extremely primitive, and are not sufficient alone in developing an understanding of nanomaterial fate and transport, and it is likely to be some time before they will be so.

In order to develop a full understanding of the potential risks posed by nanomaterials, further examination of their environmental transport and fate within air, soil and water bodies is necessary. Although the current lack of quantitative exposure data hampers subsequent prediction of the environmental fate and thus concentration, the knowledge-base in this area continues to grow and develop fast, and much consideration has been given to extrapolating evidence from laboratory situations and from knowledge obtained with industrial chemicals. This chapter outlines some of the general principles of environmental fate and behaviour, and provides a summary of key knowledge to date.

Recently, several key reviews examining environmental fate and behaviour of nanomaterials have been published, including Klaine et al. (2008) and Nowack (2009). Knowledge from colloid science has also been used to provide useful additional information on the potential fate and behaviour of nanomaterials (Lead and Wilkinson 2006).

Behaviour of nanomaterials in the environment is dependant both on the physico-chemical characteristics of the nanomaterial in question, and those of the environment into which it is being received (Chen et al. 2008, Chen and Elimelech 2008, Saleh et al. 2008). Nanomaterial transport and distribution are influenced by a number of factors, such as Brownian diffusion, inertia effects, gravitational influences, thermal influences, pH, ionisation, and presence/absence of Natural Organic Matter (NOM). These interactions ultimately affect the processes the nanomaterial consequently undergoes in its transport and subsequent fate. Table 1 summarises some of the processes nanomaterials may undergo on entry into the environment.

Table 1. Processes that nanomaterials may undergo in the environment

<b>Process</b>
Dissolution
Settling / Sedimentation
Speciation (association with other molecular or ionic dissolved chemical substances)
Association with biotic/abiotic suspended particulate material (adherence, sorption)
Biological or chemical transformation e
Agglomeration / Disagglomeration
Complete mineralisation (conversion of a carbon-containing nanomaterial to an inorganic state via microbial decomposition)
Diffusion
Deposition(e.g. from an aerosolised form into water)
Re-suspension (e.g. from on a surface into gas or from sediment into water)

Knowledge to date leads toward the postulation that in many cases rather than remaining intact, nanomaterials will ultimately be aggregated, agglomerated or associated with other dissolved, colloidal or particulate matter present in the environment (SCHENIR, 2009). However, the novel physico-chemical characteristics which make nanomaterials desirable also present a challenge for determining how they interact with the environment, how, when and where they are distributed,

and in what form they ultimately end (Darlington et al. 2009). It is generally known that small particles tend to aggregate or agglomerate, and eventually become associated with other dissolved, colloidal and particulate matter present in the environment (SCHENIR, 2009).

To date, for the nanomaterials considered within this review there has only been one peer reviewed publication providing information on concentrations or amounts within environmental compartments such as soils or groundwater (Kaegi et al., 2008). Much of the current knowledge therefore lies within estimates on quantities of nanomaterials based on predicted use and calculated exposure scenarios (Boxall et al. 2007, Mueller and Nowack 2008), although these are based on simplified assumptions and scenarios of use and environmental transfer across media. Nevertheless, methods for measuring nanomaterials in specific environmental matrices are being developed for various materials (Christian et al. 2008, Hassellöv et al. 2008, Tiede et al. 2008). Most recently, Kaegi et al. (2008) published what may be the first paper offering quantitative information on transport of nanomaterials in the environment, tracing leached synthetic nano-TiO<sub>2</sub> from paint on house façades into receiving water bodies.

Appropriate metrics for measuring engineered nanomaterials in the environment are still subject to much discussion, and in particular those pertaining to exposure concentrations, or dose, are considered to be of high importance. Differences in behaviour across different physical and chemical species of the same nanoparticulate material must also be considered. In addition, their tendency to aggregate/agglomerate, adsorb to NOM and, in the case of wastewater treatment, potentially associate with the solid phase, must be taken in consideration, as all of these processes could lead to environmental ‘hot spots’ where concentrations of nano-particulates are particularly high.

Current knowledge indicates that nanomaterials are most likely to exist associated with sediments and soils in the environment (Baalousha et al. 2008, Klaine et al. 2008). However, the free dispersed forms of the material are of particular importance. In order to estimate possible presence of free nanomaterials within the environment, knowledge on release scenarios must be improved, as well as knowledge on exposure scenarios in which they may be found and the various processes which act on nanomaterials in the environment. Until such a time, assessment of exposure concentrations of dispersed nanomaterials remains a difficult task (SCENIHR, 2009).

### **Environmental fate and behaviour of nanomaterials in air**

Aerosol science is a well established and documented scientific field. However, there exist some major issues to be addressed in validation of definite hypotheses on behaviour, transport and fate of air-borne nanomaterials. For example, development of methods for accurate sampling or tracking of nanomaterials within the air compartment, elucidation of the effect of differing particle morphologies (of both nanomaterials and their agglomerates), and overcoming the issue of differentiating airborne manufactured nanomaterials from background nanoparticle levels in the atmosphere. As an illustration of the latter issue, investigations by Murr and colleagues (Murr et al. 2004, Murr and Guerrero 2006) suggest that carbon nanotubes (CNT) can originate from general combustion processes, and as such can be found in many ambient locations.

In addition, as nanomaterials may range from 1-100nm in size, the processes governing their transport are very diverse. Mädler and Friedlander (2007) illustrate that whilst transport of small nanoparticles (circa 1 nm) may have similarities to molecular transport, as the size of the

nanoparticle increases momentum exchange with the gas molecules and nanoparticle inertia are different and extend into the regime where corrections to the gas continuum model can be used.

To date, much of the available data in this context have been gathered so that exposure to workers can be adequately assessed (SCHENIR, 2009). This has provided preliminary information and data in relation to the determination and characterisation of nanomaterial distribution assessment of potential exposure, and effectiveness of personal protective equipment (EMERGNANO, 2009). Most of these studies relate to only one or two types of nanomaterials, and it is unclear whether it will be possible to extrapolate the results to other types. Studies focussing on workplace distributions of nanomaterials in air are summarised in the ENRHES report (available at <http://nmi.jrc.ec.europa.eu/project/ENRHES.htm>) on occupational and consumer exposure and will not be discussed further here. No quantitative or qualitative measurement of manufactured nanomaterials in ambient air have been reported. Simplified modelling work has been undertaken to predict nanomaterial distribution and concentrations in the environment. However, whilst these models are useful tools, they are very simple, and under development and do not include sufficient detail to allow the drawing of conclusions on environmental transport and behaviour of nanomaterials.

Aitken et al. (2004) provide a discussion of processes governing nanoparticulate behaviour in air with a particular focus on the workplace. Key processes governing nanomaterial behaviour include diffusion, agglomeration, and potential re-suspension of aerosol from deposited nanomaterials. The same authors report that in traditional aerosol science, the key process governing aerosol behaviour is particle size, whilst inertial, gravitational and diffusional forces are also 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 (ICRP, 1994).

*Particle diffusion* (governed by Brownian motion) is a process whereby particles suspended in gas are constantly and randomly bombarded from all sides by molecules of the gas, causing them to move in a seemingly random fashion. Particle diffusion coefficient (rate) is inversely proportional to particle diameter. Particles with a high diffusion coefficient (such as those on the nanoscale) therefore have high mobility and will mix rapidly in aerosol systems. Upon release into the environment, atmospheric diffusion will lead nanomaterials to migrate rapidly from a high concentration to a lower one, and thus resulting in rapid dispersion and potential for particles to travel a great distance from source (Aitken et. al., 2004).

*Agglomeration* is the process by which particles ‘coagulate’ or ‘stick together’ to form larger bodies (although these may still be on the nanoscale). It is in essence a by-product of the multiple collisions particles undergo during diffusion. Agglomeration rate is governed primarily by particle mobility and number concentration, both of which increase as particle size decreases (Aitken et. al., 2004). Thus, ‘aerosolised’ nanoparticles therefore tend to agglomerate rapidly, even at a low mass concentration. Kasper (2008) highlights that aged nanoparticle aerosols are also not recognisable by a specific particle size range, and tend to populate a size range almost indistinguishable from ubiquitous background aerosol by simple size distribution measurements. This means that tracking and measurement of ENP concentrations within the air is very difficult, unless measurements are taken close to a point source emission.

*Deposition* is a process by which nanoparticles may be removed from the atmosphere, for example onto soil, water or plants (Aitken et. al., 2004). Deposition of particles is dependent on the gravitational settling velocity, a characteristic which is proportional to the diameter of the

particle. Nanoparticulates within air will therefore deposit at a much slower rate than larger particles, and contribute to the potential for nanoparticles to be transported over great distances within the environment before being deposited.

*Potential re-suspension* of nanoparticles from deposits into the atmosphere is a complex concept, influenced by a number of factors including particle size, shape, charge and the energy applied to the potential re-suspension situation. Particles are held together in agglomerates (and to the surface on which they are deposited) by short-range attractions called Van der Waals forces (Aitken et. al., 2004). It is thus questionable how likely re-suspension would be once particles are deposited, a view supported by the work of Maynard et al. (2004) which indicated re-suspension of CNTs into aerosol was not easily achieved.

### **Summary & Recommendations**

The current lack of data in relation to the environmental fate and behaviour of nanomaterials in air represents a major gap in developing a holistic view on the fate and transport of nanomaterials within the environment. However, much work is underway, and it is likely that in the coming years more relevant scientific information will emerge on which to develop further understanding of the area (EMERGNANO, 2009; SCENIHR, 2009).

At the current time, most of our knowledge stems from aerosol science, which provides preliminary information from which to develop further understanding of nanoparticle fate and transport within air. To date, very little work has been undertaken in other environmental media which may assist further with this. As such, there is a need for systematic studies on different types of airborne NM 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. In concordance with this, development of more sophisticated predictive models is currently underway, especially for the workplace setting. The development of valid real-time methods by which to selectively detect and quantify specific aerosolized nanoparticles is also crucial, as is the characterisation of sources and release mechanisms for NM into the environment, according to source strength and nanomaterial physicochemical characteristics (NanoTransport, 2008). A final consideration which must be taken into account is the choice of suitable metrological strategies for monitoring transport and fate of NM within aerosols; this must be made carefully should, as is predicted, their size increase in size rapidly via agglomeration.

### **Take home messages:**

- *The lack of data represents a major gap in developing a holistic view on the fate and transport of nanomaterials within the environment.*
- *Much work is underway and it is likely that in the coming years more relevant scientific information will emerge within this area (EMERGNANO, 2009; SCENIHR, 2009).*
- *Most of our current knowledge stems from aerosol science, which provides preliminary information. Very little has been done in other environmental media.*
- *There is a need for systematic studies on different types of airborne NM using a range of physicochemical parameters (e.g. size, shape, form, surface area) to generate data and to support development of reliable models.*



- *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, and development of more sophisticated predictive models is underway, especially for the workplace setting.*
- *Development of valid real-time methods by which to selectively detect and quantify specific aerosolized nanoparticles is crucial.*
- *Characterisation of sources and release mechanisms for NM into the environment, according to source strength and nanomaterial physicochemical characteristics is also needed. (NanoTransport, 2008)*
- *If nanomaterials within aerosols increase in size rapidly via agglomeration, the choice of suitable metrological strategies must be made carefully for monitoring their transport and fate.*
- *Other issues relate predominantly to areas of characterising and monitoring NPs, both of which fall outwith the remit of this section*

### **Environmental fate and behaviour of nanomaterials in water**

There exists a body of knowledge on dispersal, accumulation, breakdown, persistence etc. of conventional chemicals in the environment. However, relatively little is known about the potential fate and behaviour of NM in aquatic environments. Development of a greater understanding of the mechanisms underlying NM fate and transport, and the influences which govern these, is imperative in order to assess risks associated with current and future environmental exposure to free NM (EMERGNANO, 2009).

It is generally expected that dispersed nanomaterials within water will behave according to the well-described and understood phenomena which govern colloid science (Jones 2002, Lyklema 2005). Colloidal suspensions of nanomaterials 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 (SCENIHR, 2009). Consequently particles may adhere to each other and then settle due to gravity (Baalousha et al. 2008, Ju-Nam and Lead 2008, Saleh et al. 2008). In accordance with this, it has been shown that suspensions of dispersed nanomaterials may only be stable under narrow ranges of well-defined environmental conditions (Baalousha et al. 2008).

Natural waters may contain other dissolved materials, both colloidal and solid (including natural nanomaterials). Thus, engineered nanomaterials introduced into water bodies usually can, and based on the knowledge to date, are expected to adhere to such materials (SCENIHR 2009).

In accordance with the principles of colloid science (under natural conditions), NM fate and transport may therefore be influenced by factors such as pH, ionic strength and presence of natural organic matter upon release into water (Lead and Wilkinson 2006). 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. In addition, the intrinsic properties and characteristics of the materials, including their specific chemistry, will influence their fate and behaviour. The surface properties of the nanomaterials are very important for their aggregation behaviour, and thus for their mobility in aquatic and terrestrial systems, and as such for their interaction with and general bioavailability to organisms.

Consequently, nanomaterials may undergo a number of processes, including partitioning to sediment and suspended particulate material, biological degradation and abiotic degradation (Boxall et al. 2007; Fortner et al. 2005).

Boxall et al. (2007) and Mueller and Nowack (2008) have provided estimates of nanomaterials present in surface waters and other media based on predicted use and calculated exposure scenarios. It is likely that in the future such models will be of valuable tools for providing quantitative estimates of environmental concentrations (EMERGNANO, 2009). Gao et al. (2009) recently published predictions on dispersion and toxicity of fullerenes, nano silver and nano copper in natural river water samples, but model approaches alone are not enough to make informed risk assessments and development of monitoring methods for environmental samples is crucial. While techniques for identification and quantification of nanomaterials in various environmental matrices are being developed it still remains a challenging task to attempt monitoring in real-world environmental samples (Christian et al. 2008, Hassellöv et al. 2008, Tiede et al. 2008).

In the following section, factors of importance for fate and behaviour in the aquatic environment will briefly be reviewed for the four groups of nanoparticles relevant for the ENRHES project.

## 1. Fullerenes

Fullerenes are of low solubility in water, hence much research has been undertaken into their behaviour in aqueous suspension/solution, their functionalisation and derivatives, all of which have unusual properties and characteristics (Wudl 2002). Fortner et al (2007) described the reaction of water stable fullerene aggregates with ozone in water. Their findings showed that presence of dissolved ozone in the aqueous phase led to fullerene aggregate dissolution, concurrent with formation of water-soluble fullerene oxide species, and thus highlighting the importance of considering the aqueous reactivity of fullerene-based nanomaterials in assessing their transport and fate.

Compared to the synthetic aqueous media used in most laboratory studies, the environmental behaviour of fullerenes may be significantly influenced by the presence of natural organic matter (NOM). This has been shown by several studies, including Xie et al. (2008) who examined the effects of aquatic NOM on the physicochemical properties of aqueous C<sub>60</sub> nanoparticles. The authors carried out thorough characterisation of the C<sub>60</sub> for particle size, morphology, and electrophoretic mobility in the absence or presence of two model NOM components, Suwannee River humic acid and fulvic acid. They reported that NOM caused disaggregation of C<sub>60</sub> crystals and aggregates, thus leading to significant alterations in particle size and morphology, and thus potential alterations in the transport and fate of the C<sub>60</sub> NPs in the aquatic environment. Another issue to consider is how to quantify the fullerene aggregates in water. Chen et al (2008) investigated methods for quantifying stable aqueous C<sub>60</sub> aggregates of approximately 60 to 70 nm in diameter in water. Of the three methods investigated, aqueous nC<sub>60</sub> concentration as low as 300 ng/L in water were quantified using solid-phase extraction separation method. The other methods (evaporation of sample to dryness and extraction using 20% NaCl into toluene) were less successful in complex water matrices.

### Summary of evidence – Fullerenes:

- *Fullerenes are of low solubility in water, therefore much research to date has focussed on their behaviour in aqueous suspension/solution, their functionalisation and derivatives (Wudl, 2002)*
- *Presence of NOM within the aquatic environment may significantly influence transport & behaviour of fullerenes (Xie et. al., 2008)*
- *Fullerenes may interact with other materials/chemicals within water bodies such as ozone (Fortner et. al., 2007)*

## 2. CNTs

In their 2008 review, Kennedy et al. (2008) discussed important factors affecting the partitioning and toxicity of nanotubes in the aquatic environment. The group considered that whilst the hydrophobicity and van der Waals interactions of NTs suggest aggregation and sedimentation in aquatic systems, engineered surface modifications may alter their environmental fate. Column stability and settling experiments carried out by the group indicated that un-functionalised or coated MWCNTs settled more rapidly than functionalised MWCNTs, although this would depend on type of functionalisation. In addition, the group observed that stabilisation of MWCNTs was especially notable in the presence of NOM. Their results highlight the importance of not classifying all NTs into one category in terms of their predicted environmental fate and transport.

In consideration of how Natural Organic Matter (NOM) present in the aquatic environment may affect CNT fate and transport, Hyung et al. (2007) investigated how the aqueous stability of



MWCNTs was altered by presence of NOM. Those MWCNTs tested were seen to be readily dispersed as an aqueous suspension in the presence of humic acids, remaining stable for over 1 month. Their findings indicate that through this association, dispersal of carbon based nanomaterials in the natural aqueous environment may occur to a greater extent than expected.

Further to Hyung et al. (2007), Hyung and Kim (2008) investigated the effect of NOM characteristics and water quality parameters (such as pH and ionic strength) on adsorption of NOM to MWCNTs. They reported that NOM adsorption to MWCNT varied greatly dependant on the type of NOM, and in direct proportion to the aromatic hydrocarbon content of NOM. In addition, water quality parameters greatly altered adsorption, which increased as pH decreased and ionic strength increased. Consideration of both the type of NOM present in any aquatic environment into which CNTs may be transported, and the effect that NOM may have on CNT dispersion and stability are therefore clearly important factors to take into account in the development of knowledge of CNT fate and transport.

The presence of other materials (e.g. mineral and other content) within the aquatic environment has also been investigated for MWCNT. In their work on the stability of MWCNT suspensions, Han et al. (2008) reported that the presence of the clay minerals montmorillonite and kaolinite resulted in deposition of some types of surfactant-facilitated MWCNT suspensions. These authors postulated that this effect could be due to either removal of surfactant from solution and MWCNT surface by the clay mineral, or bridging between the clay mineral and the MWCNTs via surfactant. This is therefore also an important consideration to take into account in relation to MWCNT transport and behaviour within aquatic bodies.

#### Summary of evidence – CNTs:

- *Functionalisation and Stabilisation of CNTs affects their fate and behaviour in water bodies Kennedy et al. (2008)*
- *To date, NOM has been found to have an effect on fate and transport of all CNT types tested (Hyung et al., 2007, Hyung and Kim, 2008)*
- *Characteristics of the NOM present and water quality parameters have been reported to affect this (Hyung and Kim, 2008)*
- *Mineral content was found to have an effect on NM dispersion and fate for CNT (Han et. al. 2008)*

### **3. Metal NPs**

The fate and behaviour of metal nanoparticles in aqueous solution/suspension is expected to be very dependent on each metals chemical identity and therefore no general conclusion can be made. Note that this would also be an impossible task for non-nanoscaled metals as e.g. the fate and behaviour of mercury, cadmium, or iron will be very different. In the following, a few studies dealing with metal nanoparticles will be mentioned in relation to important parameters shown to affect their behaviour in aqueous media.

Diegoli et al. (2008) investigated the interaction of manufactured gold nanoparticles and naturally occurring organic matter (NOM), by testing the effect of humic acid on citrate- and acrylate-stabilised gold nanoparticles. The group found that at high ionic strengths, the gold NPs

underwent extensive aggregation. Humic acid was found to enhance Gold NP stability at extremes of pH – probably by substituting for or coating the original stabiliser on the particles. As with CNTs, the presence of NOM is therefore most likely to be an influencing factor on the behaviour of metal NM within the environment.

In considering the agglomeration behaviour of metal NM in water, Schrick et al (2004) demonstrated that unsupported iron nanoparticles within water rapidly agglomerate. However, association of the iron nanoparticles with delivery vehicles such as anionic hydrophilic carbon, and poly(acrylic acid) (PAA), led to formation of colloidal suspensions which settled very slowly (hours to days) in water.

A recently published paper by Gao et al. (2009) also considers dispersion and agglomeration of NM in water bodies. The study provides predictions on dispersion and toxicity of manufactured fullerenes, nano-silver and nano-copper in natural river water samples (from the Suwannee River Basin) and deionised water samples, in order to determine the effect of Dissolved Organic Carbon (DOC) concentration and solution ionic strength. The dispersion of all three nanoparticles tested varied significantly with solution chemistry: DOC, pH and concentrations of various electrolytes all had significant effects on the agglomeration pattern of all three NPs tested. It was observed that nanoAg had a considerably altered agglomeration pattern from nanoCu and C<sub>60</sub>, a difference potentially stemming from nanoAg's lower hydrophobicity. In contrast, presence of DOC (as with the Suwannee River water samples) brought about steric repulsion forces as the DOC adsorbed quickly onto the surface of the nanomaterial and stabilised the suspension, so much so that even a small DOC concentration was enough to prevent aggregation.

The effect of dispersant type, pH and concentration of NM has been investigated for nano copper by Li et al. (2007). Using zeta-potential, absorbency and sedimentation photographs, these authors showed that zeta-potential related well to absorbency. In addition, they showed that the higher the absolute value of the zeta potential and absorption, the better the nano-Cu is dispersed and the greater its stability is in liquid.

In a study which looked specifically at nanoparticulate silver within water bodies, Benn and Westerhoff (2008) investigated nano silver released from commercial clothing (socks) into water, and its fate in wastewater treatment plants (WWTPs). Using microscopic analysis, physical separation and ion-selective analysis, they found silver particles between 100-500nm in diameter of both colloidal and ionic forms leached from 6 sock samples tested. As the leaching varied between sock type tested, they postulated that the manufacturing process may control the extent to which silver was released. In addition, the researchers used the data gathered to build a basic model to predict how well a typical wastewater treatment facility could treat a high concentration of influent silver.

#### Summary of evidence – Metal NM:

- *As with CNT, NOM has been demonstrated to have an effect on metal NM fate and transport (Diegoli et al., 2008)*
- *Agglomeration patterns of metal NM within water vary greatly due to differences in their different physico-chemical properties.*
- *DOC, pH and concentrations of various electrolytes may all have significant effects on the agglomeration pattern of metal NPs (Gao et al., 2009)*

- Association of NM with delivery vehicles (e.g. iron nanoparticles) can lead to formation of steady colloidal suspensions (Schrack et. al., 2004)
- Zeta-potential has been demonstrated to be related to absorbency for nano copper (Li et. al., 2007)

#### 4. Metal Oxide NPs

As it is the case for nanometals, the fate and behaviour of metal oxide nanoparticles in aqueous solution/suspension is expected to be very dependent on the individual metal oxide's chemical identity. It is therefore difficult to draw any general conclusions about the environmental fate and behaviour of nano metal oxides. However, the following section provides a summary of relevant findings to date that may contribute to a general understanding of the phenomena involved in predicting the fate and behaviour of metal oxide nanoparticles in the environment.

As an initial consideration, it is important to note that the first paper which offered quantitative information on transport of nanoparticles into the environment deals with nano metal oxides. The paper, authored by Kaegi et al. (2008), traced leached synthetic nano-TiO<sub>2</sub> from paint on house façades into receiving water bodies; nano TiO<sub>2</sub> particles (in the size range of 20-300nm) were found in concentrations in the range of a few mg/l in a small stream. In an investigation of the influence of agglomeration and surfactants on the clearing efficiency of cerium oxide nanoparticles in a model wastewater treatment plant, Limbach et al. (2008) reported that whilst the majority of nanoparticles could be captured via adhesion to sludge, a significant proportion was recovered in the water effluent. In particular, up to 6% of the cerium oxide NPs tested were identified in the plant exit stream. These authors highlighted that clearance could also be significantly altered by surface charge and addition of dispersion stabilising surfactant. Further investigation into the agglomeration of those NPs found in wastewater streams revealed they carried a high stabilisation against clearance, due to adsorption onto the bacteria from the sludge.

After use and during emissions, but also during e.g. toxicity testing, the stability of metal oxide nanoparticles is of vital importance. This has been investigated in several studies. Zhang et al. (2008) studied the stability of various metal oxide nanoparticles in water. The group examined characteristics, dispersion, and stability of commercially available TiO<sub>2</sub> (two sizes), Fe<sub>2</sub>O<sub>3</sub>, ZnO, NiO, and silica NP in water as well as their removal by water treatment processes. Their results found that all nanoparticles apart from silica showed rapid aggregation in tap water due to electric double layer (EDL) compression. Silica remained stable in tap water due to its low Hamaker constant.

Ghosh et al. (2008) investigated whether the colloid-like behaviour of aluminium oxide nanoparticles was altered as a function of pH and the presence of natural organic matter (in the form of various humic acid types). The study found that surface charge of the NPs decreased with addition of humic acids, with increasing aggregation shown as the pH of the suspension approached zero charge (i.e. where van der Waals attraction forces dominate over electrostatic repulsion). At acid pHs in the presence of humic acid, NPs showed strong aggregation, whereas at alkaline pHs colloidal stability was enhanced. Ghosh et al. (2008) also observed that the hydrophobic state of the humic acid molecules had a strong influence on aggregation of NPs, something which they speculated may be due to their conformational behaviour in a particular solution condition.

Further investigation of both NOM and environmental conditions was undertaken by Baalousha et al (2008), who investigated interactions between manufactured iron oxide nanoparticles (~7nm in diameter) and humic acid, under varying environmental conditions. These authors reported that with increasing pH and humic acid concentrations, the NPs were seen to undergo increasing aggregation. Additionally, they observed that humic acid presence altered the type of aggregate formed: open, porous aggregates were formed in the absence of humic acid, whilst compact ones were formed in its presence.

Recently Baalousha (2009) published a further examination of the influence of particle concentration, pH and NOM on iron oxide aggregation and disaggregation. Increasing NP concentration was shown to concurrently increase aggregation, particularly at a pH close to the point of zero charge. However, a high concentration of NPs in the presence of a high humic acid concentration increased disaggregation of iron oxide NPs – an effect which was not seen at lower NP concentrations or without humic acid. Baalousha (2009) also highlighted the role of NOM in disaggregation of iron oxide NP aggregates, reporting that small iron oxide NP aggregates (of about 170nm) with a surface coating of humic acid were seen during the disaggregation process, an observation which indicates that NPs may mimic natural colloidal behaviour.

#### Summary of evidence - Metal Oxides:

- *Absorption of other materials present within water bodies (such as bacteria) has been shown to affect transport of metal oxide NM (Limbach et al. (2008))*
- *NM clearance within aquatic systems has been shown to be significantly altered by surface charge and addition of dispersion stabilising surfactant (Limbach et al. (2008))*
- *Several types of NM have been shown to undergo rapid aggregation in tap water as a result of electric double layer (EDL) compression (Zhang et al., 2008)*
- *As for metal NM and CNT, NOM has been found to have an effect on fate and transport of metal oxide NM (Ghosh, 2008)*
- *Characteristics of the NOM present and of the surrounding aquatic environment (e.g. pH level) have also been reported to affect metal oxide transport & behaviour (Ghosh, 2008; Baalousha et. al.; 2008)*

#### Conclusion & Recommendations

A number of important considerations for NM fate and transport within the aquatic environment has been highlighted to date. One consistent finding is that most NM interact with NOM, and that this will be of influence on the fate and transport of NM in water and may also be of significance for the biological effects. Absorption of other materials present within the aquatic environment has also been shown to have an impact on NM transport. Again however, the lack of extensive measured data in relation to the environmental fate and behaviour of nanomaterials in water represents a major gap in developing realistic prediction of fate and transport of nanoparticles in the aquatic environment. Most of our current knowledge stems from colloid science, which provides preliminary information, but there is a need for systematic studies on different types of NPs within aquatic bodies using a range of physicochemical parameters (e.g. size, shape, form, surface area) to generate data and to support development of reliable models. Predictive modelling of emission scenarios and subsequent transport pathways will also play an important role in furthering understanding in this area.

### **Environmental fate and behaviour of nanomaterials in soil and sediment**

As is described within the fate and transport in water sub-section, nanomaterials, if not degraded or dissolved and depending on receiving environment and material, will tend to aggregate and eventually settle onto the substrate (SCENIHR, 2009 Baalousha et al. 2008, Ju-Nam and Lead 2008, Saleh et al. 2008). Within soil and sedimentary systems it is expected that nanomaterials will adhere to solids. As such, a fundamental understanding of the transport properties of these materials in sediment and soil compartments is necessary not only to understand their potential environmental impact but also to develop nanomaterials specifically aimed at soil related applications such as remediation of contaminants (Leocanet and Wiesner 2004).

#### **1. Fullerenes**

Wang et al. (2008) described the influence of electrolyte species and concentration on aggregation and transport of nanoscale fullerene nanoparticles in water-saturated quartz sands. They found that as NaCl electrolyte concentration increased from 1-100mM, there was little change in particle diameter measured. However, when the same experiment was repeated using CaCl<sub>2</sub> electrolyte, the C<sub>60</sub> particle diameter increased over 7 fold. This effect was attributed to agglomeration of C<sub>60</sub> NPs, due to a net attractive force between particles and suppression of the electrical double layer. In relation to ionic strength, the group found that at low strengths (~3mM), C<sub>60</sub> NPs were readily transported through 40- to 50- mesh quartz sand. However, heightened ionic strength led to retention of C60 nanoparticles in sand column, regardless of electrolyte species present. Their findings clearly indicate that C60 NP transport and retention in water-saturated sand is strongly dependant on electrolyte conditions.

Li et al. (2008a) explored transport and deposition of nanoscale C<sub>60</sub> aggregate within water-saturated porous media. By comparing experimental column measurements to models based on clean-bed filtration theory, the group were able to show clearly that pre-existing models are not directly applicable to predict nanoparticle transport and fate. Li et al (2008b) reported that sorption capacity of C60 NPs to soil was strongly dependant on the soil's organic content; and that increased sorption reduced bioavailability.

Leocanet et al. (2004) investigated the mobility of nanomaterials in porous media. Eight nanomaterials were tested in a test system resembling a sandy groundwater aquifer. These included silica (2 sizes), anatase TiO<sub>2</sub>, fullerol (hydroxylated C<sub>60</sub>), clusters of C<sub>60</sub> referred to as *n*-C<sub>60</sub>, and single-wall carbon nanotubes. Of those tested, fullerene-based nanomaterials which had been functionalised to facilitate dispersal in water exhibited the highest mobility, colloidal aggregates of C<sub>60</sub> were amongst the least mobile and SWCNTs were between the two. The authors suggest that the same hydrophobicity that prevents fullerene dispersal in water is also anticipated to lead to relatively limited mobility in aquatic environments. However, as fullerene species may become more hydrophilic through manufactured or environmental modification (e.g. functionalisation) this principle cannot be applied across the board.

Leocanet and Wiesner (2004) investigated the effects of flow velocity on transport and deposition of three varieties of fullerene nanoparticles in porous media, against the colloid theory that 'particle deposition in porous media is a sequence of particle transport to the immobile surface or "collector" followed by attachment'. They reported that fullerene nanoparticles appear to share unique transport properties in porous media, which span a range of fullerene preparations.

Wang et al. (2008) conducted experimental and mathematical modelling studies to investigate the transport and retention of nanoscale  $C_{60}$  aggregates in water-saturated porous media (glass beads and Ottawa sand). They observed that up to 77% of the mass of  $C_{60}$  introduced was retained in columns filled with Ottawa sand. Furthermore, they found that both the retention profile and the effluent concentrations could be accurately simulated when the numerical model accounted for the  $C_{60}$  attachment kinetics and a limiting retention capacity of the solid phase.

## **2. CNTs**

Only one study into the transport of single walled carbon nanotubes in soil was identified. Jaisi et al. (2008) investigated the transport and deposition of carboxyl-functionalised SWCNT in quartz sand over a range of solution chemistries. The group reported that increasing solution ionic strength or addition of calcium ions resulted in increased SWNT deposition (filtration), a finding consistent with conventional colloid deposition theories and confirming the importance of CNT physico-chemical characteristics in their transport. The group proposed that SWCNT shape and structure, particularly the very large aspect ratio and its highly bundled (aggregated) state in aqueous solutions, contribute considerably to straining in flow through porous media. In addition, the group showed that deposited SWCNTs could be mobilised from quartz sand upon introduction of low ionic strength solution (KCl).



### **3. Metal NPs**

Darlington et al. (2009) recently published a study investigating characteristics affecting fate and transport of aluminium nanoparticles through a soil column system containing white quartz sand and soil (collected from an area of Florida USA known to have routine use of devices containing Al NPs). The type of solution and surface functionalisation had marked effect on the charge, stability and agglomeration state of the Al NPs, which in turn altered transport through the soil matrix. In particular, it was found that electrostatically induced binding effects of the Al NPs to the soil matrix were greater in positively charged than negatively charged particles, and that salts found within the environment greatly impacted on Al NP transport, causing agglomeration and potentially reducing bioavailability.

Yang et al. (2007) found that poly-acrylic acid (PAA) modified nano-iron slurry was able to travel through silica sand easily, but not through loamy sand, a finding the authors attributed to varying characteristics of the soil matrix between the two.

In response to the observation that Fe/C and Fe/PAA nanoparticles settle very slowly in water, Schrick et al. (2004) found nanoparticle diffusion to be the dominant filtration mechanism of transport through soil and sand packed columns. In clay-rich soils, the sticking coefficient of zero-valent iron nanoparticles associated with PAA was greater than that of Fe/C particles, whilst non-associated Fe nanoparticles agglomerated quickly and were thus efficiently filtered by all soils tested except clay (where clay-rich platelets act as an anionic support material).

Doshi et al. (2008) investigated transport of two sizes of nano-aluminium particles (nAl) through sand columns with either aluminium oxide, or carboxylate ligand coatings (Alex and L-Alex respectively). As pH controls solubility and electrostatic interactions between the nAl and porous media, it was found to be a major determinant of Al transport. In addition, surface characteristics of the particles were also shown to be of importance.

Saleh et al. (2008) investigated the effect of ionic strength and composition on mobility of surface-modified nanoscale zerovalent iron. The group tested a number of bare, polymer- and surfactant- modified zerovalent iron NPs in water-saturated sand columns at low particle concentrations (where filtration theory is applicable). They concluded that electrosteric stabilization of nanoparticles provides the best resistance to altered transport caused by changing electrolyte conditions likely to be encountered in groundwater aquifers.

### **4. Metal Oxide NPs**

Leocanet and Wiesner (2004) investigated the effects of flow velocity on transport and deposition of metal oxide nanoparticles in porous media against the colloid theory that 'particle deposition in porous media is a sequence of particle transport to the immobile surface or "collector" followed by attachment'. Anatase (TiO<sub>2</sub>) and silica (SiO<sub>2</sub>) nanoparticles were found to pass through the test system as a function of velocity with a constant attachment efficiency factor.

### **Summary**

- *As for the previous section, there is a general lack of data, in particular for metal oxide and CNTs*
- *Much of what has been done is not really comparable e.g. different functionalisation on the NPs, different experimental approaches, different levels of attention to characterisation of the NPs used etc.*
- *Lack of analytical tools for detection and quantification of NPs in soil matrices is a problem*
- *There seem to be many studies addressing various aspects at remediation – these can offer some information on transport*
- *Due to the use of ENPs for remediation purposes there is a strong incentive to gain knowledge on transport properties of selected nanomaterials*
- *Work is ongoing to assess transport of NMs in soil (EMERGNANO, 2009) from which output should be valuable.*
- *EMERGNANO (2009) notes however that of the work ongoing there is much overlap and as such the scope of outcomes will be lesser than had the research effort been a little more coordinated.*

### **Conclusion & Recommendations**

As for the previous section, there is a general lack of data in relation to the environmental fate and behaviour of nanomaterials in soil and sediment. It may even be stated that the paucity in data relevant for soil and sediment behaviour of NM is so pronounced, particularly for metal oxides and carbon nanotubes, that no general conclusions can be drawn. In addition, 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 NPs used etc. The current lack of analytical tools for the detection and quantification of NPs in soil matrices is also a problem.

There seem to be many studies addressing various aspects at remediation. These can offer some information on transport and, due to the use of ENPs for remediation purposes, there is a strong incentive to gain knowledge on transport properties of selected nanomaterials. Work is ongoing to assess transport of NMs in soil (EMERGNANO, 2009) from which output should be valuable. EMERGNANO (2009) notes, however, that of the work ongoing there is much overlap and as such the scope of outcomes will be lesser than had the research effort been a little more coordinated.



### Environmental exposure – modelling approaches

It is clearly conceivable that fugitive emission from processes in which nanomaterials are produced, could potentially lead to increased air concentration of these nanomaterials. As well as environmental exposure in these circumstances, it is plausible that the general public would become exposed.

In their 2009 review, SCENIHR consider what is known regarding the release on NM into the environment and the subsequent exposure to humans from that route. In their view, there was no suitable information available on this topic. Examples of exposure routes for nanomaterials via the environment are inhalation by humans, and other air-breathing species, and uptake by aquatic organisms from water or sediments, or via surfaces and roots, by primary producers. Assessment of exposure concentrations of dispersed nanomaterials requires detailed insight into the processes that act on these materials in the environment. However, they conclude that “currently available knowledge of these processes is insufficient to allow quantitative predictions of the environmental fate of nanomaterials”.

Some attempts at modelling this have been carried out, most notably by Boxall et al (2007) and by Mueller and Nowack (2008), although these were very preliminary studies.

One interesting application which could lead to increased exposure of the general population is the use of nanomaterials as a fuel additive, since this application has now become widespread, and inhalation, as well as environmental deposition, are likely to be extensive. Boxall *et al.* (2007) have estimated potential concentrations of cerium oxide in air, based on assumptions about the quantity of cerium oxide present in fuel, the market penetration of fuel containing cerium oxide. These authors used dispersion models developed and validated by the UK Highways Agency. In their assessment, using a mix of traffic type with traffic flow at 40km/h and at 1000 vehicles per day, they estimated a cerium oxide concentration at a distance of 5 meters from the road of 0.0006mg/m<sup>3</sup>. In relation to occupational exposure this is very low. Their estimate, however, did not take into account standing traffic in congested city centre streets. In these circumstances, it is likely that concentrations would be perhaps several orders of magnitude higher than that that reported. Clearly however, the potential for exposure scenarios of this type to result in significant exposures needs to be further evaluated.

In the paper by Mueller and Nowack (2008) the quantities of engineered nanoparticles released into the environment was estimated throughout the expected product life-cycle. Three types of nanoparticles were included: nano silver (nano-Ag), nano TiO<sub>2</sub> (nano-TiO<sub>2</sub>), and carbon nanotubes (CNT). The quantification was based on a substance flow analysis from products to air, soil, and water in Switzerland. The model inputs used were: estimated worldwide production volume, allocation of the production volume to product categories, particle release from products, and flow coefficients within the environmental compartments. The predicted environmental concentrations (PEC) were then compared to the predicted no effect concentrations (PNEC) derived from the literature to estimate a possible risk. The expected concentrations of the three nanoparticles in the different environmental compartments vary widely, caused by the different life cycles of the NM containing products.

In this study full dispersion of NM was considered within the different media and transfer across media was considered to follow a specific pattern. The authors note that the lack of information concerning NM usage in consumer products is a limitation to their work. For nano-Ag and nano-TiO<sub>2</sub> the range between the estimations for worldwide production is wide. In order to address the uncertainty of data in this thesis, two scenarios were modelled: a realistic exposure scenario based

on the most reliable data and a high exposure scenario including the worst-case assumptions. A future scenario was not conducted, as the predictions for the development of the production volumes of the NM are too vague. It seems to be realistic, though, that the production volumes of all three materials will increase significantly in the coming years.

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## **PART 2: Environmental exposure estimation according to the TGD**

**PART 2:**

**Environmental exposure estimation according to the TGD**

In the following section we provide an extract of key information needs and data requirements for applying the Technical Guidance Documents on environmental exposure estimation (R.16) for chemicals substances and - ideally - nanoparticles once adaptations have been implemented.

In Appendix 1 we have provided a list of equations needed for the derivation of  $PEC_{local}$  air, water and soil.

*2.1 Calculation of  $PEC_{local}$  and  $PEC_{regional}$*

The purpose of completing environmental exposure estimations is to derive a Predicted Environmental Concentration (PEC). Two types of PEC-values are derived to be in the further risk assessment: the local and regional concentration.

The local concentration is calculated for each identified local point source and is normally reported in terms of the discharged daily average concentration. In principle, a local assessment has to be performed for each relevant application and each relevant life-cycle step based on the calculation of the concentrations in air, surface water, soil, sediment and groundwater.

$$PEC_{local,air,ann} = C_{local,air,ann} + PEC_{regional,air} \quad \text{EQUATION R.16-33}$$

$$PEC_{local,water,ann} = C_{local,water,ann} + PEC_{regional,water} \quad \text{EQUATION R.16-40}$$

$$PEC_{local,seawater,ann} = C_{local,seawater,ann} + PEC_{regional,seawater} \quad \text{EQUATION R.16-45}$$

$$PEC_{local,soil} = C_{local,soil} + PEC_{regional,natural\ soil} \quad \text{EQUATION R.16-62}$$

$$PEC_{local,soil} = \frac{K_{susp-water}}{RHO_{susp}} \cdot PEC_{local,water} \cdot 1000 \quad \text{EQUATION R.16-41}$$

$$PEC_{local,grw} = PEC_{local,agr.soil,porew} \quad \text{EQUATION R.16-64}$$

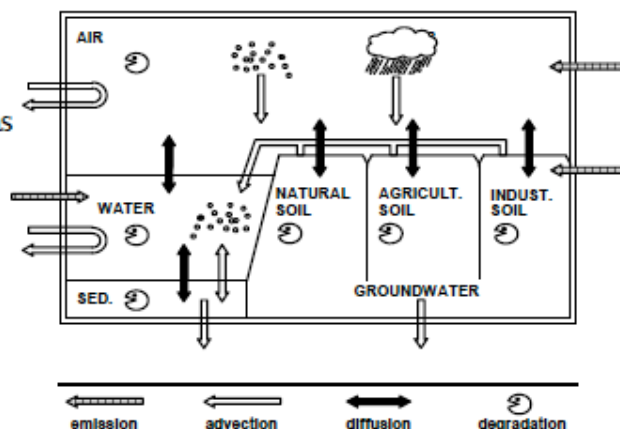
For more on the derivation of these  $PEC_{local}$  equations for air and water see Appendix 1.

Regional exposure concentrations in all environmental compartments are based on regional computations by means of multimedia fate models based on the fugacity concept (SimpleBox).

These models are box models that consider each to box to be homogenous and well

mixed and a substance released into the model scenario is distributed between the compartments according to the properties of the both the substance and the model environment (see figure R.16-11).

**Figure R.16-11 Regional calculations**



The regional concentration will be used as estimates for background levels. These are so-called steady-state concentrations, i.e. the concentrations obtained at emissions and fate processes taking place over infinite time. Therefore, the estimated PECs are considered worst-case estimates.

The choice of modelling parameters and which fraction of the total emissions is used as emission to the region is important when calculating the  $PEC_{\text{regional}}$ . As a first approach  $PEC_{\text{regional}}$  should be calculated on basis of a standardized regional environment with agreed model parameters (see table R.16-14). More specific information can be applied to refine the regional assessment by using country model parameters, which might provide a better estimation of the concentrations for a specific country.

**Table R.16-14 Proposed model parameters for regional model**

Parameter	Value in regional model
area of the regional system	4.104 km <sup>2</sup>
area fraction of water	0.03
area fraction of natural soil	0.60
area fraction of agricultural soil	0.27
area fraction of industrial/urban soil	0.10
mixing depth of natural soil	0.05 m
mixing depth of agricultural soil	0.2 m
mixing depth of industrial/urban soil	0.05 m
atmospheric mixing height	1000 m
depth of water	3 m
depth of sediment	0.03 m
fraction of the sediment compartment that is aerobic	0.10
average annual precipitation	700 mm · yr <sup>-1</sup>
wind speed	3 m · s <sup>-1</sup>
residence time of air	0.7 d
residence time of water	40 d
fraction of rain water infiltrating soil	0.25
fraction of rain water running off soil	0.25
EU average connection percentage to STP	80%

*2.2 Intermedia mass transfer coefficients*

In addition to the environmental characteristics of the region, selected intermedia mass transfer coefficients are required in the multimedia fugacity model to ensure comparability of the outcome with other models. These are summarized in table R.16-15.

Table R.16-15 – ADD TITLE

Parameter	Value
air-water interface: air side partial mass transfer coefficient	Equation R.16-75
air-water interface: water side partial mass transfer coefficient	Equation R.16-76
Aerosol deposition rate	0.001 m.s-1
air-soil interface: air side partial mass transfer coefficient	1.39.10-3 m.s-1
air-soil interface: soil side partial mass transfer coefficient	Equation R.16-66
sediment-water interface: water side partial mass transfer coefficient	2.78.10-6 m.s-1
sediment-water interface: pore water side partial mass transfer coefficient	2.78.10-8 m.s-1
net sedimentation rate	3 mm.yr-1

### 2.2.1 Air-water interface

$$k_{aw\_water} = 0.01 \cdot (0.0004 + 0.0004 \cdot WINDSPEED^2) \cdot \left(\frac{0.032}{MOLW}\right)^{0.25} \quad \text{EQUATION R.16-75}$$

#### Explanation of symbols

MOLW	molecular weight of the substance	[kg·mol <sup>-1</sup> ]	
WINDSPEED	average windspeed	[m·d <sup>-1</sup> ]	<a href="#">Table R.16-14</a>
k <sub>aw<sub>air</sub></sub>	partial mass-transfer coefficient at the air side of the air-water interface	[m·d <sup>-1</sup> ]	
k <sub>aw<sub>water</sub></sub>	partial mass-transfer coefficient at the water side of the air-water interface	[m·d <sup>-1</sup> ]	

### 2.2.2 Calculation of a predicted environmental concentration in food

$$PEC_{oral\_predator} = PEC_{water} \cdot BCF_{fish} \cdot BMF \quad \text{EQUATION R.16-76}$$

#### Explanation of symbols

PEC <sub>oral<sub>predator</sub></sub>	Predicted Environmental Concentration in food	[mg·kg <sub>wet fish</sub> <sup>-1</sup> ]
PEC <sub>water</sub>	Predicted Environmental Concentration in water	[mg·l <sup>-1</sup> ]
BCF <sub>fish</sub>	bioconcentration factor for fish on wet weight basis	[l·kg <sub>wet fish</sub> <sup>-1</sup> ]
BMF	biomagnification factor in fish	[-]

### 2.2.3 Substance-dependent penetration depth

$$d_p = \frac{V_{eff\ soil} + \sqrt{V_{eff\ soil}^2 + D_{eff\ soil} \cdot 4 \cdot k_{deg\ soil}}}{2 \cdot k_{deg\ soil}} \quad \text{EQUATION R.16-66}$$

**Explanation of symbols**

MOLW	molecular weight of the substance	[kg·mol <sup>-1</sup> ]	
kdeg <sub>soil</sub>	rate constant for degradation in bulk soil	[d <sup>-1</sup> ]	
RAINRATE	average daily rate of wet precipitation	[m·d <sup>-1</sup> ]	Table R.16-14
Finf <sub>soil</sub>	fraction of precipitation that penetrates into the soil	[-]	Table R.16-14
d <sub>p</sub>	substance-dependent penetration depth	[m]	Equation R.16-67
Veff <sub>soil</sub>	effective advection (with penetrating porewater)	[m]	Equation R.16-68
Deff <sub>soil</sub>	effective diffusion coefficient	[m <sup>2</sup> ·d <sup>-1</sup> ]	Equation R.16-69
FRa.soil	mass fraction of the substance in the air phase of soil	[-]	Equation R.16-72
FRw.soil	mass fraction of the substance in the water phase of soil	[-]	Equation R.16-70
FRs.soil	mass fraction of the substance in the solid phase of soil	[-]	Equation R.16-71
Fair <sub>soil</sub>	volume fraction of air in the soil compartment	[m <sub>air</sub> <sup>3</sup> ·m <sub>soil</sub> <sup>-3</sup> ]	Table R.16-11
Fwater <sub>soil</sub>	volume fraction of water in the soil compartment	[m <sub>water</sub> <sup>3</sup> ·m <sub>soil</sub> <sup>-3</sup> ]	Table R.16-11
Fsolid <sub>soil</sub>	volume fraction of solids in the soil compartment	[m <sub>solid</sub> <sup>3</sup> ·m <sub>soil</sub> <sup>-3</sup> ]	Table R.16-11
K <sub>air-water</sub>	air-water partitioning coefficient	[m <sup>3</sup> ·m <sup>-3</sup> ]	Equation R.16-12
K <sub>soil-water</sub>	soil-water partitioning coefficient	[m <sup>3</sup> ·m <sup>-3</sup> ]	Equation R.16-13
DIFF <sub>gas</sub>	molecular diffusivity of the substance in the gas phase	[m <sup>2</sup> ·d <sup>-1</sup> ]	Equation R.16-73
DIFF <sub>water</sub>	molecular diffusivity of the substance in the water phase	[m <sup>2</sup> ·d <sup>-1</sup> ]	Equation R.16-74
SOLID <sub>adv.soil</sub>	rate of advective downward transport of soil particles	[m·d <sup>-1</sup> ]	6.34·10 <sup>-12</sup>
SOLID <sub>diff.soil</sub>	solid phase diffusion coefficient in the soil compartment	[m <sup>2</sup> ·d <sup>-1</sup> ]	6.37·10 <sup>-12</sup>
kas <sub>soil</sub>	partial mass-transfer coefficient at soil side at the air-soil interface	[m·d <sup>-1</sup> ]	

### 2.3 Release estimation

Exposure is a result of the release of substances which may be partly degraded/removed due to treatment facilities and the subsequent distribution and degradation within the environment. Hence, input needed to do exposure estimation calculations are substance properties and emissions rates, removals and distribution in waste treatment systems and partition coefficients and degradation rates.

Release estimation is the procedure whereby releases to the environment are quantified during the life cycle stages of a chemical, taking into account the different types of uses during these life cycle stages, the different emission pathways and receiving environmental compartments and the spatial scale of the emissions.

The information that needs to be considered for the release estimation is:

- Tonnage

- Life Cycle Stage
- Type of use in the life cycle stage
- Distribution of production volume in the market
- Emission Pattern – Distribution in time and space
- Emission Pathways (Air, Soil, Water)
- Multiple emissions
- Emission factors
- Risks management measures to reduce emissions.

Based on this information the local releases from single point sources and can be estimated by using equation R.16-1.

$$E_{local_{i,j,u}} = \frac{Q_{chemical} \cdot F_{emission} \cdot (1 - F_{abatement})}{T_{emission}}$$

**EQUATION  
R. 16-1**

with:

i: environmental compartment (water, air, soil)

j: life cycle stage (from production to waste treatment/recovery)

u: use or process in a specific life cycle stage

$Q_{chemical}$ : quantity of the substance of concern that is applied in a use or a process and life cycle stage per year [mass per year]

$F_{emission}$ : emission factor: the fraction of the substance emitted from the process or use considered to (waste) water, (waste) air, soil, or (solid) waste before onsite or offsite abatement measures [dimensionless]

$F_{abatement}$ : efficiency of any abatement or control technology (onsite or offsite) that reduces the emission to air, water, soil or (solid) waste [dimensionless]

$T_{emission}$ : duration of emission (e.g. working days per year) [days per year]

The regional background release for each environmental compartment can then be calculated from the sum of releases from all uses in all life cycle stages of the substance in a particular region.



$$E_{regional\_background_{i,j,u}} = \frac{\sum_{i,j,u} [Q_{chemical} \cdot F_{emission} \cdot (1 - F_{abatement})]}{365d}$$

EQUATION  
R.16-1

### 2.5 Partitioning and degradation within the environment

To assess the environmental exposure, the following processes should be considered:

- Adsorption to aerosol particles (gas-aerosol partitioning)
- Partitioning between air and water (volatilisation)
- Partitioning between solids and water in soil, sediment and suspended matter (adsorption and desorption)
- Partitioning between water/solids and biota (bioconcentration and biomagnification)
- Transformation processes in the environment. Both biological and abiotic should be considered. If stable and/or toxic degradation products are formed, these should be assessed as well.

According to the TGD the following information is required as a minimum:

- molecular weight
- water solubility
- vapour pressure
- octanol-water partition coefficient
- information on ready biodegradability for the substance

For an inorganic substance, it is also advised to provide information on the abiotic degradation, and solid-water partition coefficients and the water-biota partition coefficients.

#### 2.5.1 Adsorption to aerosol particles (gas-aerosol partitioning)

The fraction of the substance associated with aerosol particles can be estimated using the following equation:

$$F_{ass_{aer}} = \frac{CON_{junge} \cdot SURF_{aer}}{VPL + CON_{junge} \cdot SURF_{aer}} \quad \text{EQUATION R.16-8}$$

Explanation of symbols			
CON <sub>junge</sub>	constant of Junge equation	[Pa · m]	*
SURF <sub>aer</sub>	surface area of aerosol particles	[m <sup>2</sup> · m <sup>-3</sup> ]	*
VP	vapour pressure	[Pa]	data set
F <sub>ass<sub>aer</sub></sub>	fraction of the substance associated with aerosol particles	[-]	

\* as a default the product of CON<sub>junge</sub> and SURF<sub>aer</sub> is set to 10<sup>-4</sup> Pa (Van de Meent, 1993; Heijna-Merkus and Hof, 1993).

Alternatively, the octanol-air partition coefficients could be used. For solids, a correction of the vapour pressure is required to drive the sub-cooled liquid vapour pressure using:

$$VPL = \frac{VP}{e^{6.79 \cdot (1 - \frac{TEMP_{melt}}{TEMP})}} \quad \text{EQUATION R.16-9}$$

Explanation of symbols			
TEMP	environmental temperature	[K]	285
TEMP <sub>melt</sub>	melting point of substance	[K]	data set
VPL	sub-cooled liquid vapour pressure	[Pa]	
VP	vapour pressure	[Pa]	data set

### 2.5.2 Partitioning between air and water (volatilisation)

The transfer of a substance from the aqueous phase to the gas phase can be estimated by means of its Henry's Law constant. If the value is not available in the input data set, the required Henry's Law constant and the *K<sub>air-water</sub>* (also known as the "dimensionless" Henry's Law constant) can be estimated from the ratio of the vapour pressure to the water solubility (Equation R.16-11).

$$HENRY = \frac{VP \cdot MOLW}{SOL} \quad \text{EQUATION R.16-10}$$

$$K_{air-water} = \frac{HENRY}{R \cdot TEMP} \quad \text{EQUATION R.16-11}$$

Explanation of symbols

VP	vapour pressure	[Pa]	data set
MOLW	molecular weight	[g · mol <sup>-1</sup> ]	data set
SOL	solubility	[mg · l <sup>-1</sup> ]	data set
R	gas constant	[Pa · m <sup>3</sup> · mol <sup>-1</sup> · K <sup>-1</sup> ]	8.314
TEMP	Temperature at the air-water interface	[K]	285
HENRY	Henry's law constant	[Pa · m <sup>3</sup> · mol <sup>-1</sup> ]	
K <sub>air-water</sub>	air-water partitioning coefficient	[-]	

2.5.3 Partitioning between solids and water in soil, sediment and suspended matter (adsorption and desorption)

The solid-water partition coefficient  $K_p$  can be calculated for soil, sediment and/or suspended matter from the  $K_{oc}$  value, and the fraction of organic carbon in the compartment in the standard environment given in table R.16-11

$$K_{p_{comp}} = F_{oc_{comp}} \cdot K_{oc} \quad \text{with } comp \in \{soil, sed, susp\} \quad \text{EQUATION R.16-12}$$

Explanation of symbols

K <sub>oc</sub>	partition coefficient organic carbon-water	[l · kg <sup>-1</sup> ]	data set/Ch. 4
F <sub>oc<sub>comp</sub></sub>	weight fraction of organic carbon in compartment <i>comp</i>	[kg · kg <sup>-1</sup> ]	<a href="#">Table R.16-11</a>
K <sub>p<sub>susp</sub></sub>	partition coefficient solid-water in suspended matter	[l · kg <sup>-1</sup> ]	
K <sub>p<sub>sed</sub></sub>	partition coefficient solid-water in sediment	[l · kg <sup>-1</sup> ]	
K <sub>p<sub>soil</sub></sub>	partition coefficient solid-water in soil	[l · kg <sup>-1</sup> ]	

2.5.4 Partitioning between water/solids and biota (bioconcentration and biomagnification)

Bioconcentration and bioaccumulation may be of concern for lipophilic organic chemicals and some metals compounds as both direct and indirect toxic effects may be observed upon long-term exposure. Bioaccumulation in aquatic species is described by the Bioconcentration Factor (BCF), which is the ratio between the concentration in the organism and the concentration in water in a steady-state situation. BCF can be calculated from the quotient of the uptake and depuration rate constants:

$$BCF_{org} = \frac{C_{org}}{C_{water}} \text{ or } \frac{k_1}{k_2} \qquad \text{EQUATION R.16-14}$$

Explanation of symbols		
$C_{org}$	concentration in aquatic organism	$[mg \cdot kg^{-1}]$
$C_{water}$	concentration in water	$[mg \cdot l^{-1}]$
$k_1$	uptake rate constant from water	$[l \cdot kg^{-1} \cdot d^{-1}]$
$k_2$	Elimination rate constant	$[d^{-1}]$
$BCF_{org}$	bioconcentration factor	$[l \cdot kg^{-1}]$

2.5.5 Transformation processes in the environment.

The degradation in all environmental compartments and the sewage treatment plant can be predicted using information on the ready biodegradability of the substance, however such calculations are very conservative. Actual degradation rates in the environmental can be used as a part of an iteration strategy. The hydrolysis half-life (DT50) of a hydrolysable substance (eq. R. 16-16) and half-life for photolysis in water (Eq. R.16-17) can be converted to degradation rate constants which again can then be used to in the models for calculating PEClocal and PECregional. Finally, the photochemical reactions in the atmosphere can be accounted for by determining the degradation rate constant of a substances with OH-radicals (Eq. R.16-18).

$$k_{hydr_{water}} = \frac{\ln 2}{DT50_{hydr_{water}}}$$

EQUATION R.16-16

Explanation of symbols

DT50hydr <sub>water</sub>	half-lifetime for hydrolysis in surface water	[d]	data set
khydr <sub>water</sub>	first order rate constant for hydrolysis in surface water	[d <sup>-1</sup> ]	

$$k_{photo_{water}} = \frac{\ln 2}{DT50_{photo_{water}}}$$

EQUATION R.16-17

Explanation of symbols

DT50photo <sub>water</sub>	half-lifetime for photolysis in surface water	[d]	data set
kphoto <sub>water</sub>	first order rate constant for photolysis in surface water	[d <sup>-1</sup> ]	

$$KDEG_{AIR} = K_{OH} \cdot OHCONC_{AIR} \cdot 24 \cdot 3600$$

EQUATION R.16-18

Explanation of symbols

k <sub>OH</sub>	specific degradation rate constant with OH-radicals	[cm <sup>3</sup> · molec <sup>-1</sup> · s <sup>-1</sup> ]	data set/Ch.4
OHCONC <sub>air</sub>	concentration of OH-radicals in atmosphere	[molec · cm <sup>-3</sup> ]	5 · 10 <sup>5</sup> *
kdeg <sub>air</sub>	pseudo first order rate constant for degradation in air	[d <sup>-1</sup> ]	

\*The global annual average OH-radical concentration can be assumed to be 5.105 molecules.cm-3 (BUA, 1992).

## References

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