

## A Review of the Properties and Processes Determining the Fate of Engineered Nanomaterials in the Aquatic Environment

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## **A Review of the Properties and Processes Determining the Fate of Engineered Nanomaterials in the Aquatic Environment**

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*Proper understanding of the basic processes and specific properties of engineered nanomaterials (NMs) that modify the fate and effects of NMs is crucial for NM-tailored risk assessment. This in turn requires developers of NMs and for regulators to consider the most important parameters governing the properties, behavior and toxicity of NMs. As fate and effect studies are commonly performed*

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*in laboratory settings, mimicking to a varying extent realistic exposure conditions, it is important to be able to extrapolate results of fate and effect studies in synthetic media to realistic environmental conditions. This requires detailed understanding of the processes controlling the fate and behavior of NMs in terrestrial and aquatic media, as dependent on the composition of the medium. It is the aim of this contribution to provide background reading to the NM and media specific properties and processes that affect the fate and behavior of NMs in aquatic environments, focusing on the specific properties of NMs that modulate the interactions in the aquatic environment. A general introduction on the dominant fate determining processes of NMs is supplemented by case studies on specific classes of NMs: metal NMs, stable oxides, iron oxides, and carbon nanotubes. Based on the synthesis of the current knowledge base toward essential data and information needs, the review provides a description of the particle specific properties and the water characteristics that need monitoring in order to allow for future quantification and extrapolation of fate and behavior properties of NMs in freshwater compartments of varying composition.*

**KEY WORDS:** nanomaterials, fate, behavior, environment, aggregation, transformation

## INTRODUCTION

Nanotechnology is a rapidly expanding domain of new sciences and technologies with the potential to revolutionize many aspects of modern society. So far, nanoscale properties have hardly been exploited to their full potential due to technological limitations. Recent developments, however, open up totally new possibilities for material scientists but also commit them to assure a safer production, handling and use of these materials. The novel properties of engineered nanomaterials (NMs) are not only advantageous, but also a potential concern for adverse health effects and environmental hazards that differ from those of corresponding materials at larger sizes. Proper understanding of the basic processes and chemical properties modifying the fate and effects of conventional, dissolved, chemicals has allowed the development of elaborated risk assessment approaches that provide the foundation of chemical legislation across the globe (REACH, USEPA). Despite the fact that the physical and chemical properties of NMs deviate fundamentally from the properties of conventional chemicals, there is no a priori ground for not applying the basic paradigm of environmental risk assessment of conventional chemicals, that is, risk being proportional to the extent in which (predicted) environmental concentrations in air, water, or soil exceed (predicted) effect thresholds in these media. To allow for NM-tailored

risk assessment it is crucial for the developers of NMs and for the regulators to know about the most important parameters governing the properties, behavior, and toxicity of NMs. In this respect, it is generally accepted that detailed understanding of the behavior of NMs in aquatic environments is crucial to allow for comprehensive assessment of the risks associated with the transport and ultimate fate of NMs following their release to the environment. As fate and effect studies are commonly performed in laboratory settings, which mimic the realistic exposure conditions to a varying extent, it is important to be able to extrapolate results in synthetic media to realistic environmental conditions. This in turn requires detailed understanding of the processes modifying the fate and behavior of NMs in terrestrial and aquatic media, and dependence on the composition of the medium. Among the important processes that have been identified to control NM behavior in synthetic media are dissolution and aggregation (Stumm and Morgan, 1996; Arvidsson, 2012; Batley *et al.*, 2012; Praetorius, 2012). However, it has also been recognized that NM fate in natural aquatic and terrestrial environments can differ significantly from that in synthetic media largely due to the dominant presence of natural nanoscale particles and colloidal materials (Klaine *et al.*, 2008). It is clear that the way particles move and interact with their biotic and abiotic environment among others depends on the size, surface chemistry, and composition of the NMs among other factors. In general, the interactions between similar NMs (homoaggregation) and between NMs and dissimilar natural colloidal materials (heteroaggregation) are not well understood, nor is there much direct data on the fate and behavior of NMs in the environment. In spite of the vast and well-established knowledge of the dynamics of colloidal particles, no comprehensive studies of the fate of NMs in the environment have been reported to date, and no generalized understanding of how exposure concentrations of dispersed NMs can be predicted from basic chemistry for risk assessment purposes. As reviewed by Klaine *et al.* (2008), by far the most information is available on the fate and effects of NMs in freshwaters, with exposure of benthic invertebrates being of major importance due to the general observation of instability of aqueous suspensions of NMs leading to sedimentation of aggregated clusters of particles. The authors stressed the importance of understanding the dynamics of the suspensions of NMs to which organisms are actually exposed. This understanding is specific for environmental conditions where natural colloids are present as well as numerous substances, such as humic and fulvic acids, which can act as natural dispersants.

This overview provides background reading to the NM and media specific properties and processes that may affect the fate and behavior of NMs in aquatic environments, and thus is complementary to a review paper on fate and bioavailability of engineered NMs in soils (Cornelis *et al.*, 2013). As general summaries on the current knowledge on this topic have been published before, the main merit of the present contribution is its focus

on the specific properties of NMs that can modulate the interactions in the aquatic environment. Apart from a general introduction on the dominant fate determining processes of NMs, more detailed information on each of the processes is summarized, backed up by the following case studies to which the knowledge on the basic processes has been applied and integrated:

- A – Metal engineered nanomaterials (MNMs) – Ag and Au
- B – Stable oxides: TiO<sub>2</sub> and CeO<sub>2</sub>
- C – Iron oxides
- D – Carbon nanotubes (CNTs): single-wall (SWCNTs) and multiwall (MWCNTs)

Based on the synthesis of the current knowledgebase in regard to essential data and information needs, the review lays down a description of the particle specific properties and the characteristics of the aquatic systems that need to be monitored in order to allow for future quantification and extrapolation of fate and behavior of NMs in freshwater compartments of varying composition. As deliberations are continuing on the definition of NMs, we will restrict to the use of current EU Recommendation for definition of nanomaterial (2011/696/EU):

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm to 100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%. By derogation from the above, fullerenes, graphene flakes and single wall carbon nanotubes with one or more external dimensions below 1 nm should be considered as nanomaterials.

## NANOMATERIALS IN THE AQUATIC ENVIRONMENT: GENERAL CONSIDERATIONS

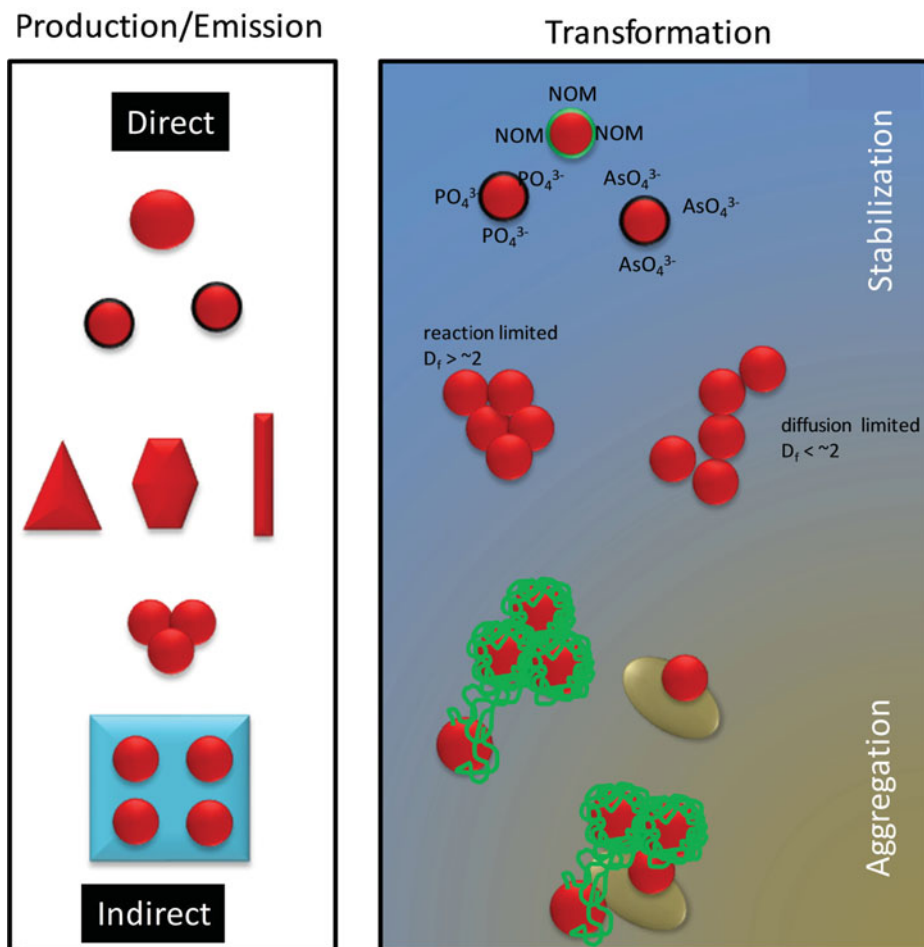
Environmental fate and transport models for organic and inorganic chemicals are well established tools (Mackay, 2001; Scheringer, 2002). They allow to estimate and to predict phase partitioning, transport, and transformation of chemicals at local to global scales (Scheringer, 2009). A number of platforms are available to model the fate of conventional chemical compounds in different environmental compartments, such as soils, surface- and groundwaters. Examples include FOCUS models such as PELMO, PRZM, PEARL, MACRO, and TOXSWA (Beulke et al., 2006), as well as more generalized models such

as EXAMS, IMPAQT, IPX USEPA, MASAS, OMIVE, PEST, QWASI, SIMPLE-BOX, TOXIWASP, and TOXSWA (for a review, see Koelmans *et al.*, 2001).

Modeling the fate, behavior, and distribution of NMs throughout the lifecycle of a NM or NM-containing product, however, poses much greater challenges. It is important to note NMs have a dual nature—they are a chemical as well as a nanostructure. While some parallels to the chemical fate and behavior may be drawn from the existing knowledge on conventional equivalents (e.g., persistence, reactivity, degradation), the parameters that drive fate and behavior of the nanoparticulate forms in different environmental compartments are not yet fully understood.

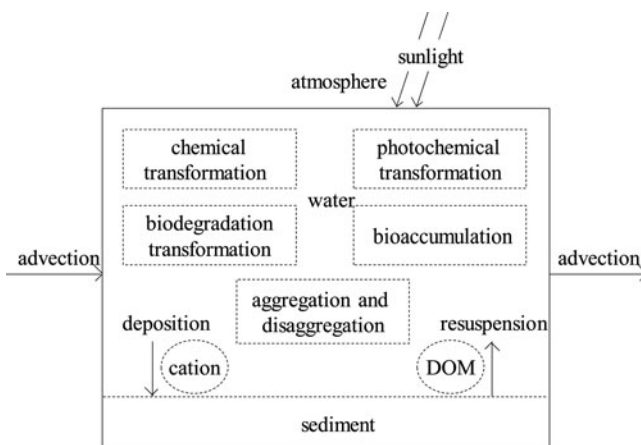
Modeling environmental distribution of NMs requires mass flows of NMs between different environmental compartments in a material-specific manner. The key factors to be considered include material-specific sorption of NMs to other particulate matter (e.g., natural organic matter, and other particulates suspended in water), soil solids, and vegetation. This also requires consideration of the processes that may lead to transformation and degradation of NMs in different environmental compartments. The models also need to consider the potential release of NMs from sewage treatment plants to surface water, downstream transport of NMs with flowing water, and transfer to sediments with settling particles (Nowack, 2012; Praetorius, 2012). Figure 1 schematically depicts the way NMs may be released in the environment (directly as pristine particles or embedded in a matrix) and the subsequent modes of stabilization and aggregation. The most important processes to be included in modeling are depicted in Figure 2.

An overview of relevant processes to be covered by environmental fate models for NMs is given by Nowack and Bucheli (2007). A key challenge in respect to NMs is that environmental fate models developed for traditional classes of micropollutants are not applicable to NMs as such, and need consideration of a number of particle-related adjustments so that they describe the relevant processes that govern their environmental fate (Scheringer, 2008). Modeling approaches have recently been used on these lines to estimate the potential environmental exposure to different NMs from manufacture, use, and disposal of materials and products of nanotechnologies (Hendren, 2013). The value derived from such modeling is the predicted environmental concentration (PEC). For example, a recent study modeled the emissions of silver from nanosilver containing biocidal products and compared the expected concentrations in the environment with a reference emission (Blaser *et al.*, 2008). The authors concluded that the contribution of nanosilver in the total silver flow in the environment is only small. The study, however, considered nanosilver as the  $\text{Ag}^+$ -ion and not in the form of particulate silver. Another study by Müller and Nowack (2008) used a life-cycle perspective to model the quantities of NMs released into the environment. The study modeled NMs of silver,  $\text{TiO}_2$ , and CNT, and based estimation on substance flow analysis from products to air, soil and water in Switzerland.



**FIGURE 1.** Schematic diagram showing the forms in which NMs are typically released in the environment and the subsequent modes of stabilization and aggregation in the aquatic environment.

The study used inputs such as estimated worldwide production volumes, allocation of the production volume to product categories, and particle release from products and flow coefficients within different environmental compartments. However, the study used similar generic flow coefficients for the three different NMs (i.e., it did not take into account the specific properties of the NMs, but assumed that different NMs will behave in the same way). The study compared PEC values with the predicted no effect concentrations (PNEC) derived from the literature for each NM. Because of different life cycles of the products studied, PECs of the three NMs studied varied in different environmental compartments. The results showed that currently nanosilver may not pose any significant risk to soil organisms (ratio of PNEC/PEC <0.001).



**FIGURE 2.** Schematic overview of the processes affecting the transport, behavior, and fate of nanomaterials in the aquatic environment.

Compared to this, PEC values for nano-TiO<sub>2</sub> in water were between 0.7–16  $\mu\text{g}\cdot\text{l}^{-1}$ , which suggests that it may pose a risk in the aquatic environment. A study by Boxall et al. (2007) used a different approach. The study used different hypothetical market penetration levels of nanoproducts, the concentration of different NMs in each product category and the likely usage of the products, and modeled PECs in water, air and soil. For the 10% market penetration model, which probably overestimated the expected exposure levels, PECs of most NMs (silver, aluminum, and fullerene) were predicted to be quite low (in the  $\text{ng}\cdot\text{l}^{-1}$  range), whereas nano-TiO<sub>2</sub> and ZnO (from use in cosmetics), hydroxyapatite (from use in personal care products) and latex (from use in laundry products) were predicted to be in the  $\mu\text{g}\cdot\text{l}^{-1}$  range. These modeling approaches, however, did not take into account the potential persistence, accumulation, and/or concentration of NMs in different environmental compartments. While these studies may be criticized in regard to some of the assumptions taken, or for not considering some of the essential underlying processes (Praetorius, 2012), it is worth noting that they nicely provide the current state of the art, as well as highlight the general lack of sufficient knowledge of the key parameters and/or quantitative data on NMs to fully assess their risks following emissions to the environment.

A comprehensive analysis of all the possible release pathways that can contribute to the human exposure to a particular chemical is a challenging task (Wormuth et al., 2007). The methodology for this type of analysis is still under development. For NM-containing products it is important to know in what form(s) the NM is present in the product and can potentially be released during different stages in the lifecycle of the product (Kohler et al., 2008). At the moment, information on potential releases of NMs is mostly



qualitative due to the lack of analytical methods to trace NMs and lack of info on the nature of the NMs in the products. But some recent work reported on the release of NMs into the environment through the use of NM-containing paints/coatings and socks (Benn and Westerhof, 2008). Kaegi et al. (2008) studied the presence of nano-TiO<sub>2</sub> in surface water, and traced their origin to leaching from facades that had been treated with nano-TiO<sub>2</sub> containing paint. Electron microscopy of the facades and the released particles showed that they were partially embedded in the organic binder, while some free NMs were observed from aged facades. Hsu and Chein (2007) showed the release of TiO<sub>2</sub> NMs from paints into the air, after mechanical stress. Kulthong et al. (2010) measured Ag NP release of fabrics, whereas Vorbau et al. (2008) showed that NM agglomerates embedded in a matrix were released after mechanical stress.

In most parts of the world, wastewaters are collected and treated before channeling back to the aquatic environments (e.g., rivers and oceans). As a result, most NMs emitted to wastewaters will also undergo the water treatment processes that are generally considered to have a high efficiency (up to 99.9% depending on the type of the treatment process/plant) for removal of particulate materials. During water treatment, the addition of chemical coagulants further promotes the agglomeration of particulate materials, which also increases their sedimentation. The processes of coagulation, sedimentation, and filtration during water treatment are therefore likely to remove a large proportion of the NMs before the (treated) water enters other water bodies.

## EFFECT ASSESSMENT FOR NANOMATERIALS

The information on physicochemical properties contributes to the overall assessment of toxicological properties of chemical substances. It is, therefore, essential to ascertain how a substance will behave in a biological system by determining its ADME (absorption, distribution, metabolism, and excretion) properties. These properties are especially important in the case of NMs, because NMs are generally solid, poorly soluble, or insoluble materials that present similar safety considerations to those for fine dusts and fibers. It is also known that NMs may undergo certain transformations such as agglomeration, aggregation, adsorption and binding with other moieties in the surrounding, and lose their nano character. Depending on the surface chemistry, NMs can interact with different biological entities, and this may have a substantial effect on the distribution and excretion of an NM (Dobrovolskaia, 2007). In this regard, there is emerging evidence to suggest that NMs become coated with certain biomolecules, especially proteins, in biological environments, and such coatings can direct them to specific locations in the body (Lynch and Dawson, 2008). The protein corona is,

however, also reported to be changeable in different surroundings (Cedervall et al., 2010), suggesting that NMs can undergo complex and dynamic interactions in biological environments. Similar surface interactions of NMs may take place with other components of the environmental media (e.g., dissolved organic matter). Thus, studies carried out on pristine NMs under artificial experimental conditions may not always represent their true behavior and effects in real-life situations. It is therefore of utmost importance to establish the physicochemical nature of the NMs released into the environment in post-production stages, during use, or after final treatment of the NM-containing products—and whether they will pose a risk of exposure through the dermal, inhalation, or ingestion route. It also needs considering whether an NM released into the environment will persist, (bio)accumulate, or concentrate in solid inorganic phases over time. It should be noted that this section addresses effect assessment in terms of ADME on cellular and individual level. For traditional organic and inorganic chemicals, the attention has slowly shifted to higher levels of biological organization (community, ecosystem) to increase realism of the effect assessment. In future, a higher-tier shift in NM environmental risk assessment (i.e., community assessment) is also needed. Currently, insufficient insights to higher-tier responses to NM exposure and the lack of data hinder such attempts, although the first community effect studies have been published (Velzeboer, 2011, 2013).

Over the past decade, computational modeling has also emerged as a reliable tool to estimate the underpinning parameters that control properties and effects of chemical substances on the basis of (quantitative) structure-activity relationship (QSAR), and read-across from the available data on structurally- or functionally similar compounds that have already been tested. Combined with powerful data-mining tools, these computational methods offer a rapid way of filling knowledge gaps from the limited available datasets. The *in silico* models are now routinely used by researchers, industry, and regulators to estimate physicochemical and biological properties, and environmental behavior and fate of a wide range of chemical substances (e.g., Benfenati, 2007; Chaudhry et al., 2010c; Price and Chaudhry, 2011). Such *in silico* modeling approaches have, however, not yet been evaluated or applied to NMs to any significant extent so far. This presents a highly challenging task compared to chemical substances, because the parameters driving NM properties and effects may be different from those of conventional chemical substances, or altogether new.

The mechanistic interpretation for the (eco)toxic effects of NMs is also not yet available, although cell-based and cell-free *in vitro* models have started to generate some basic information. However, scientists have started to look into the possible links between physicochemical and structural aspects of NMs and their potential biological effects. A recent example is where structural similarities between MWCNT and asbestos fiber led to a pilot study,

which indicated that long MWCNTs introduced into the abdominal cavity of mice can manifest asbestos like pathogenic effects such as inflammation and formation of lesions (granulomas; Poland et al., 2008).

The limited available data on NMs indicate that physicochemical properties likely to influence ADME characteristics include parameters like size, surface charge, and functional groups (Florence, 2005; Roszek et al., 2005; Singh et al., 2006). Other aspects that have been considered to influence physicochemical properties of NMs include solubility, size, surface chemistry, form, degree of agglomeration/aggregation, surface modification or reactivity, number concentration, mass, and volume (e.g., BAuA, BfR, and UBA Report, 2007). The influence of these variables on the toxicological dose-response relationships of NMs has not yet been assessed in a holistic manner, and there are most likely to be other yet-unidentified parameters that are also important. For example, there is an emerging scientific evidence to suggest that exposure to some NM may lead to an increased generation of oxyradicals (Oberdörster, 2000; Donaldson et al., 2002; Donaldson et al., 2004). It is also known that not all NMs are more harmful compared to their corresponding larger forms (Oberdörster et al., 2000b; Warheit, 2004). This clearly indicates that there are other parameters, additional to size and surface area, that play a role in determining the effects and interactions of NMs in biological systems. This presents a perfect challenge for applying modeling approaches to identify the most important parameters that determine properties, behavior and effects of NMs.

## LIFE-CYCLE CONSIDERATIONS

The life-cycle analysis (LCA) is essentially an environmental tool, which is complementary to risk assessment. An LCA addresses the whole life cycle of a product or a service, and would therefore consider all the stages from production of NMs, transportation, manufacture of NM-containing product(s), use of the product(s), to end-of-life treatments and final disposal. The protocols established by the International Organization for Standardization (ISO) provide recommendations on how a life cycle can be defined and what can be considered in the definition. The general aim of an LCA is to inform and complement risk assessment, by estimating the potential exposure to NMs throughout the lifecycle of the selected products. The conventional LCA, however, does not cover two issues so well—the occupational exposure and the consumer exposure. This is primarily due to difficulties in collecting the data and modeling the exposure. The ISO protocols do not specify or restrict what can be included or excluded in an LCA. So far, nanotechnology products and processes have only scarcely been studied from LCA perspective, and there is little information in relevant databases on the LCA unit processes to inform a full-scale LCA for most NM-containing products.

The application of LCA at early stages of a nanoproduct development can inform the manufacturers to design products such that they are safe to consumer health and/or devise the postproduction processes to mitigate any potential risks they may pose to the environment from use and disposal (Som *et al.*, 2010).

## FATE AND BEHAVIOR IN THE AQUATIC ENVIRONMENT

The environmental fate and behavior of NMs are controlled by physical, chemical and biological transformations of NMs (Lowry *et al.*, 2012) as depicted schematically in Figure 2. Physical factors include formation, replacement, or degradation of surface coating, advection, dispersion, aggregation, agglomeration, disaggregation, disagglomeration, deposition, and resuspension. Chemical factors include complexation with other chemicals, sorption, oxidation, and reduction reactions (redox), dissolution, sulfidation, and phase transformation. Biological factors include degradation of the capping agent or phase transformations.

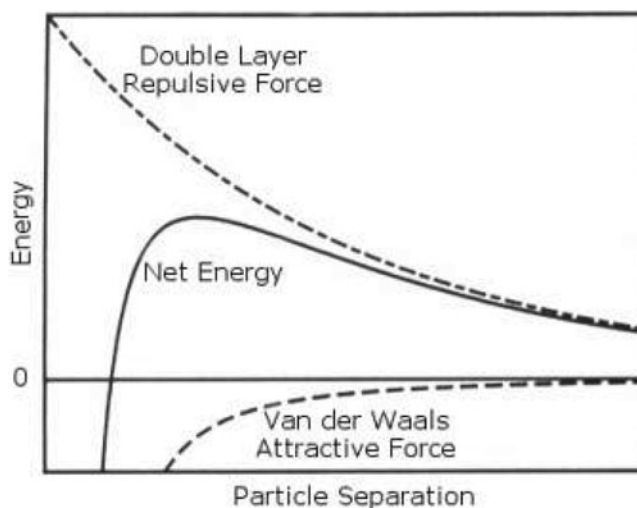
Sorption is a key process that governs the transport, behavior, and fate of dissolved chemicals as well as NMs in the environment. Sorption behavior also plays an important role in altering NM reactivity. NMs have significant adsorption capacities because of their relatively large surface area, thereby they are able to bind or carry other molecules such as dissolved organic matter, surface-active dispersing agent, contaminants, proteins attached to the surface by covalent bonds or by adsorption. Hence, the physicochemical properties of NMs, such as charge and hydrophobicity, can be altered by attaching these molecules to the surface, and then the adsorption behavior can affect stability and mobilization of NMs in environmental media (Table 1). The interaction of NMs with naturally occurring organic matter such as humic substances or polysaccharides results in the formation of nanoscale surface coating on the NMs (Baalousha *et al.*, 2008) and/or the replacement of existing surface coatings (Diegoli *et al.*, 2008). The formation of an organic surface coating on NMs alters NM surface charge (Zhang *et al.*, 2009), aggregation (Illes *et al.*, 2006), disaggregation (Baalousha, 2009), and sedimentation rate (Quik *et al.*, 2010; Petosa *et al.*, 2010). The thickness/load of the organic surface depends on particle properties such as surface charge and physicochemical properties of the media (e.g., pH, ionic strength and ionic valency; Yang *et al.*, 2009). The process of formation of an organic surface coating on NMs is similar to the process reported above of coating of NM by biomolecules such as proteins in biological environments (for a review, see Nel *et al.*, 2009).

Aggregation and disaggregation are two of the key processes in aquatic systems, particularly affecting mobility, size and bioavailability of the NMs.

**TABLE 1.** Overview of selected studies on sorption of nanomaterials to various binding agents

Nanoparticles	Adsorbent	Main conclusions	References
SWCNTs	Suwannee River humic acid	<b>Dissolved organic matter</b> Humic acid significantly retarded the SWCNT aggregation rate, which can be attributed to steric repulsion originating from the adsorbed macromolecular layer	Saleh et al., 2010
nanoFe <sup>0</sup> AuNMs	Natural organic matter Suwannee River humic acid	NOM prevents adhesion of nFe <sup>0</sup> Five mg C.L <sup>-1</sup> humic acid provided a stabilizing effect at low ionic strength and in the presence of monovalent ions only, while elevated concentrations of divalent cations led to enhanced aggregation	Li et al., 2010 Stankus et al., 2010
MWCNTs	Humic acids from a peat soil	The suspension enhancement was attributed to humic acid sorption, which increased electrostatic repulsion and steric hindrance between individual MWCNTs	Zhou et al., 2012
SWCNTs	Sodium dodecylsulfate	<b>Surface active agents</b> Low levels of surfactant are effective in stabilizing and mobilizing SWCNTs in environmental media	Bouchard et al., 2012
C <sub>60</sub>	Atrazine	<b>Organic pollutants</b> Adsorption of atrazine by aqueous dispersions of C <sub>60</sub> increased with a decrease in the pH of the solution. Introduction of humic acid significantly reduced the size of the C <sub>60</sub> particles, and resulted in the increase of the amount adsorbed	Gai et al., 2011
Graphene (GNS) - Graphene oxide (GO)	Polycyclic Aromatic Hydrocarbons	The conformation and aggregation of GNS and GO nanosheets dramatically changed after loading with PAH	Wang et al., 2014
SWCNTs	Polysaccharide and protein	<b>Biological macromolecules</b> The presence of biomacromolecules significantly retarded the SWCNT aggregation rate, which can be attributed to steric repulsion originating from the adsorbed macromolecular layer	Saleh et al., 2010

Aggregation occurs because of the deficiency of stabilizing mechanisms (stability/energy barrier) preventing the natural tendency of NMs to stick together due to van der Waals forces. The stabilizing mechanisms can be either an electrostatic (charge-based) repulsion or a steric repulsion by surface coating (engineered or incidental), or a combination of both in which case an additional surface coating can further stabilize by charge on top of steric stabilization by the coating. Engineered coatings such as citrate, PVP, and others (Römer *et al.*, 2011; Tejamaya *et al.*, 2012) are widely used and may be replaced in environmental or biological compartments by natural organic macromolecules (Cedervall *et al.*, 2007; Baalousha *et al.*, 2008; Domingos *et al.*, 2009; Lowry *et al.*, 2012; Caracciolo *et al.*, 2010; Chen *et al.*, 2012; Pallem *et al.*, 2014). The aggregation of NMs has been shown to depend on particle properties (e.g., size, shape, surface roughness, surface charge, and concentration) and the physicochemical properties of the media (e.g., pH, ionic strength, counterion valency, and presence of organic macromolecules; Bhattacharjee *et al.*, 1998; Chen *et al.*, 2006; Chen and Elimelech, 2006; Chen *et al.*, 2007; Baalousha *et al.*, 2008; Saleh *et al.*, 2008; Baalousha *et al.*, 2013). In the absence of surface coating (engineered or incidental), aggregation/disaggregation is mainly governed by particle intrinsic properties such as size,  $\xi$  potential, and solution ionic strength as described by DLVO theory proposed by Derjaguin, Landau (1941) and Verwey and Overbeek (1948). The DLVO theory takes into account two forces acting on the particles; the attractive van der Waals force which counteracts the repulsive double layer forces. Some of the key equations to evaluate particle-particle and particle-surface interactions are given by Petosa *et al.* (2010). The strength of the electrostatic repulsion between identical NMs can be altered by (a) changing their surface charge density by modifying either the pH of the suspension or the surface chemistry of the particles and/or (b) by changing the ionic strength by modifying the ion concentration or valency in order to alter the charge screening and therefore the range of electrostatic repulsion (Cerbelaud *et al.*, 2008). The DLVO theory assumes that the NMs are spherical particles of a given size and with a given charge density or surface potential (all particles are assumed to be equal in size and charge density) and the counter ions that screen the interactions are point charges following the Boltzmann distribution around the NMs. Although the DLVO theory does not provide precise information regarding the particle arrangement, it usually provides qualitative (or: semi-quantitative) information about the tendency of suspensions to undergo aggregation and the influence of various parameters (e.g., size, zeta potential, and ionic strength) on NM aggregation. Figure 3 exemplifies the variation of interaction energy between NMs as the result of attractive and repulsive forces of particles separated at varying distances. The net energy is given by the sum of the double layer repulsive and the van der Waals attractive forces that the particles experience as they approach one another. As a rule of thumb, a large energy barrier compared to the thermal



**FIGURE 3.** Schematic diagram of the change of free energy with increasing particle distance according to DLVO theory.

energy of the particles (e.g., an energy barrier of *ca.*  $15 k_B T$ , where  $k_B$  is Boltzmann constant and  $T$  is suspension temperature) is generally sufficient to maintain the stability most NM dispersions.

There are still many un-answered questions regarding the applicability and accuracy of DLVO to NMs, including questions related to particle size, shape, structure, composition, roughness, polydispersity, and surface coating. The effect of these parameters on aggregation behavior of NMs has been described elsewhere (Akbulut et al., 2007; Hotze et al., 2010). However, due to the unique shape and composition of NMs as well as the other forces that act on the particles, expanded theoretical approaches may be needed (Gatica et al., 2004). On the other hand it is also of importance to find a balance between the needing to know more and the pragmatic view of the needing to know less. What is needed, are informed simplifications that allow operationalization of theoretical concepts in the heterogeneous (place and time) environment. This in analogy to the current practice in metal risk assessment in which instead of advanced speciation and fate models, conventional and relatively easily deducible partitioning coefficients ( $K_d$ -concept) are used to quantify the fate of metals (Radovanovic and Koelmans, 1998). However, these simplifications can only be made following in depth understanding of NM fate and effects to avoid any unanticipated scenarios. For instance, Baalousha et al. (2013) presented a simplified model to describe the aggregation attachment efficiency of Ag NMs in the presence of SRFA by taking into account the relative contribution of both monovalent and divalent electrolytes. However, this study has been performed in simple suspensions and requires further validation in natural field-collected samples.

Furthermore, the DLVO theory fails to describe the interaction forces (energy) at very short distances (Cerbelaud *et al.*, 2008). Direct-interaction force measurement by atomic force microscopy revealed the existence of other forces such as (a) hydration forces at very short distance (<2 nm; Ducker *et al.*, 1991; Ducker *et al.*, 1992; Butt *et al.*, 1995); (b) steric repulsion forces resulting from adsorbed polymers, polyelectrolyte coating, or natural organic matter (NOM; Sander *et al.*, 2004); (c) hydrophobic forces (Christenson and Claesson, 2001; Hoek and Agarwal, 2006); (d) bridging (Chen and Elimelech, 2007); (e) osmotic (Fritz *et al.*, 2002; Phenrat *et al.*, 2008); and (f) magnetic (Phenrat *et al.*, 2007). These additional forces are collectively known as non-DLVO forces. Mathematical expressions of these forces are provided elsewhere (Janssen *et al.*, 1997; Hotze *et al.*, 2010).

Bare NMs occur only in well-controlled laboratory experiments and rarely occur in natural environmental systems. In the natural environment, the situation is complicated by the presence of different types of cations and NOM, which vary spatially and temporally. In these systems, aggregation of colloids is governed by both DLVO and non-DLVO interactions in complex ways. In addition to charge neutralization by counter ionics, other mechanisms such as steric stabilization, charge enhancement by NOM and bridging by fibrils and by aggregated NOM play important roles in NM aggregation. Natural organic macromolecules such as fulvic and humic acids can enhance NM stability (Wilkinson *et al.*, 1997) by steric stabilization in addition to enhancing colloid surface charge (Sander *et al.*, 2004). However, in the presence of high concentration of divalent cations such as  $\text{Ca}^{2+}$ , humic substances may enhance aggregation via bridging mechanisms (Chen and Elimelech, 2007). The net effect depends largely on surface coverage and the degree of charge alteration. For instance, the adsorption of negatively charged humic substances to positively charged iron oxide has been shown to result in destabilization of NMs only for low/partial surface coverage (Stumm, 1992; Ferretti *et al.*, 1997; Baalousha *et al.*, 2008). Other NOM molecules such as polysaccharides fibrils can induce aggregation of stable suspensions of NMs in the absence of the fibrils by a bridging mechanism due to the low surface charge density of the polysaccharides fibrils, where the NMs may interact with different segments of the polysaccharides fibrils (Filella *et al.*, 1993; Wilkinson *et al.*, 1997). The adsorption of small quantities of the polymer leads to colloidal aggregation by charge neutralization or bridging mechanism, whereas the adsorption of larger quantities is thought to stabilize the colloidal suspension via steric stabilization mechanism.

Several mechanisms may take place together resulting in enhanced aggregation. For instance, alginate-coated hematite NMs aggregate through electrostatic destabilization in the presence of monovalent cations ( $\text{Na}^+$ ) according to DLVO theory. However, in the presence of  $\text{CaCl}_2$ , aggregation increased more than that can be explained by the DLVO theory and was explained by the formation of an alginate coated hematite gel network and



the cross linking between unadsorbed alginate via  $\text{Ca}^{2+}$  bridging, that might form bridges between hematite-alginate gel structures (Chen et al., 2006). Interaction of NMs with biopolymers is likely due to the minimal electrostatic repulsion because of low surface charge density of biopolymers. In such a situation, highly stable NM suspension might produce large aggregates in the presence of biopolymers. Because biopolymers are very long in comparison with the NM diameter, they can serve as long bridges between NMs. The attached NMs may interact with another polymer, leading to the formation of loose aggregate networks extending to large dimension (several  $\mu\text{m}$  in size).

Although the concentration of NMs does not influence the sticking efficiency (slow/fast aggregation rates), the decrease in NM concentration results in lower collision frequency, and the formation of smaller NM aggregates (Baalousha, 2009). Additionally, at lower concentrations, NMs (e.g., Ag NMs) are more susceptible to dissolution (Baalousha et al., 2015). The concentration-dependent behaviors (e.g., aggregation and dissolution) of NMs are crucially important as they are likely to determine the fate and effects of NMs. For instance, small aggregates are known to remain in suspension, travel for long distances. Increased dissolution of NMs will complicate the assessment of NM-specific toxicity and may result in a wide spread of NM by product (e.g., dissolved ions). Studies investigating NM behavior, fate and effects at environmentally relevant concentration are largely absent in the literature as, and further research is immanently required.

Disaggregation (i.e., breakage of NM aggregates) is as important as aggregation in determining the fate and behavior of NMs in the natural environment, but few studies are available on the disaggregation of NMs. Most disaggregation studies have concentrated on the effect of shear force (Newman and Stolzenbach, 1996; Bergendahl and Grasso, 1998) in laboratory systems. However, the effect of solution conditions on disaggregation has rarely been considered. Altering solution conditions by dilution, changing pH, ionic strength, and altering surface charge and chemical composition may induce particle disaggregation or alter their aggregate structure (fractal dimension). For instance, synthetic polymers have been shown to be able to separate aggregated NMs (Ouali and Pefferkorn, 1994). Disaggregation of NOM (peat humic acid) was observed after dilution of a peat concentrate and disaggregation rate increased with pH (Avena and Wilkinson, 2002). NOM (Suwannee River humic acid [SRHA]) has been shown to induce the disaggregation of iron oxide aggregates of NMs, likely due to formation of surface coating of NOM on the surface and pore surfaces of aggregates and thus the enhancement of surface charge within the aggregates (Baalousha, 2008). A similar disaggregation behavior has been observed for ZnO NMs at increased SRHA concentrations (Mohd Omar et al., 2014) and for  $\text{TiO}_2$  NMs at increased concentrations of alginate and SRHA (Loosli et al., 2013). Adsorption of NOM induces an increase of the degree of repulsion

within the aggregate matrix and results in aggregate rupture. Additionally, UV and sunlight radiation have been shown to induce disaggregation of fullerenes (C<sub>60</sub>) and the formation of soluble product (60 carbon cages containing various oxygen functional groups; Hou and Jafvert, 2008; Lee *et al.*, 2009).

Aggregation can be either between the same NMs (homoaggregation) or different NMs such as natural colloids (heteroaggregation). Homoaggregation is likely to be more frequently encountered in laboratory based studies, whereas the more complex heteroaggregation occurs widely in natural systems where NMs encounter different forms of naturally occurring particles including NOM, clays and biocolloids, present in numbers far greater than the number of NMs (Klaine *et al.*, 2008; Hotze *et al.*, 2010). The most obvious and widely studied examples in the literature on heteroaggregation are the aggregation of NMs in the presence of NOM (humic substances and organic biopolymers; Chen *et al.*, 2006; Chen and Elimelech, 2006; Chen *et al.*, 2007; Chen and Elimelech, 2007; Baalousha *et al.*, 2008; Baalousha, 2009; Quik *et al.*, 2010). However, there are very few studies (reviewed below) on the heteroaggregation of NMs with naturally occurring inorganic colloids and suspended particulate matter (Praetorius *et al.*, 2012), and currently there are no studies quantifying the heteroaggregation attachment efficiencies. The studies on the interaction of NOM with NMs provide the basic knowledge required to understand the interaction of NMs with inorganic NMs and suspended particulate matter. For instance, the interaction of Silica NMs ( $d_{50} = 25$  nm, IEP <2.0) with aluminum oxide particles ( $d_{50} = 400$  nm, IEP < 9.0) results in a shift of the isoelectric point (IEP) of aluminum oxide particles to acidic pH (Garcia-Perez *et al.*, 2006) in the same way that humic substances shift the IEP of iron oxide NMs (Baalousha *et al.*, 2008). The heteroaggregation between silica NMs and aluminum oxide particles leads initially to counterbalance the surface charge of aluminum particles (causes rapid sedimentation) and then to its reversal. This process has been successfully simulated applying DLVO theory (Cerbelaud *et al.*, 2008; Cerbelaud *et al.*, 2010). The structure and shape of the aggregates has been shown to depend on the NM concentration (Cerbelaud *et al.*, 2010).

Huynh *et al.* (2012) investigated the heteroaggregation of MWCNTs and hematite NMs. They have shown that the increase in the CNT concentration, while keeping the hematite NM concentration constant, resulted in a corresponding increase in the rate of heteroaggregation up to 3.3 times (at CNT/Hematite mass ratio of 0.0316) the homoaggregation rate of hematite NMs in a diffusion limited aggregation regime (*i.e.*, highest rate). They have also demonstrated that the aggregation occurs through a bridging mechanism of hematite NMs by CNT strands (Huynh *et al.*, 2012), similar to the aggregation of hematite NMs in the presence of alginate macromolecules (Chen *et al.*, 2006). The maximum aggregation rate decreased with the increase of the humic acid (natural organic material surrogate) concentration due to

formation of HS surface coating on both types of NMs and the increase in electrostatic repulsion. Quik et al. (2012) investigated the aggregation and sedimentation behavior of CeO<sub>2</sub> NMs in water samples from two rivers in Europe (the Rhine and the Meuse) and concluded that heteroaggregation of CeO<sub>2</sub> NMs with natural NMs is the dominant factor in the sedimentation of NMs (Quik et al., 2012). However, this study was performed at high (higher than the expected NM concentration in the environment) and environmentally irrelevant CeO<sub>2</sub> concentrations (1–100 mg·l<sup>-1</sup>) and conclusions should be considered carefully. It should be noted in this respect that the study of Quik et al. (2012) suggested that heteroaggregation is even more important at lower NM concentrations that are relevant in the environment. Praetorius et al. (2012), in their model computer simulation to understand the fate of NMs, illustrated the importance of suspended particulate matter (SPM) and its characteristics (e.g., concentration, size, and density) and the affinity of TiO<sub>2</sub> to SPM on the fate of TiO<sub>2</sub> in the environment. However, there is a need for more experimental analysis to understand and quantify the effect of NM and SPM properties on the heteroaggregation and therefore the fate and behavior of NMs in the environment. Thus, heteroaggregation, similar to homoaggregation, depends on NM properties (e.g., size, shape, surface charge) and solution chemistry (e.g., pH, ionic strength and counter ions valency; Garcia-Perez et al., 2006) and can lead to either stabilizing or destabilizing the NM suspension (Buffle et al., 1998; Kong et al., 2004).

Dissolution and sulfidation of NMs are also influenced by solution chemistry as well as NM properties (e.g., size, shape, surface coating). For instance, the dissolution of AgNMs has been shown to depend on the surface functionalization and the storage temperature, with higher rate and degree of dissolution of polyvinylpyrrolidone (PVP) coated AgNMs than citrate-coated AgNMs and increased dissolution at higher temperatures (Kittler et al., 2010). The dissolution of Tween coated Ag NMs has also been shown to increase following dilution in deionized water (Baalousha et al., 2015). The dissolution of organic (including PVP and gum arabic) coated AgNMs has been shown to increase with the decrease in particle size (Ma et al., 2011). Halogens including iodide, bromide, and chloride have been shown to promote the oxidative dissolution of 40 nm PVP coated Ag NMs (Li et al., 2010; Li et al., 2012). Although ligands can accelerate AgNM dissolution, they will not necessarily promote the release of Ag<sup>+</sup> into aqueous environment. In fact, the opposite has been observed in several cases, where a precipitation of AgCl, Ag<sub>2</sub>S or complexation with NOM reduces the concentration of free Ag<sup>+</sup> ions (Jacobson et al., 2005; Liu et al., 2010; Levard et al., 2011). The precipitate can also form a surface coating layer on the original NMs, resulting in surface passivation and prevent further dissolution (Ho et al., 2010; Li et al., 2010; Liu et al., 2010; Levard et al., 2011). More details on the parameters controlling the dissolution of AgNMs are presented in the case study on AgNMs (see the following).

Sulfidation of AgNMs is of great current interest. The extent of sulfidation of AgNMs ( $39 \pm 9$  nm, PVP coated) has been shown to increase with the increase of S/Ag ratio (1% and 100% Ag<sub>2</sub>S at S/Ag ratio of 0.055 and 1.079), to decrease degree of dissolution with the increase of S/Ag ratio, to result in the loss of carbon surface coating, to influence their surface charge (shift the point of zero charge to higher pH values with the increase of S/Ag ratio), and to enhance the aggregation of AgNMs (Levard et al., 2011). Other types of NMs such as (ZnO, CuO, iron oxides, manganese oxides, cobalt oxides) are also susceptible to sulfidation process (Chen and Chiang, 2011; Babé et al., 2012; Neveux et al., 2012; Urbanová et al., 2012). The vacancy defects in these metal oxides NMs clearly promote complete oxide-sulfide conversion, where the conversion products were hollow metal sulfide NMs. These conversions by sulfidation proceed rapidly. The sulfidation intermediates, when the supply of sulfur was insufficient, had interesting structures, in which the metal oxide cores were surrounded by metal sulfide shells or had surfaces that were decorated with metal sulfide islands. The mechanism of surface nucleation, shell formation, and void formation by diffusion processes was proposed (Chen and Chiang, 2011). For Ag NM, it was recently demonstrated that sulfidation occurs does not occur homogeneously throughout the particle surface, but rather heterogeneous Ag NM sulfidation, where subgrains of Ag NM retain their Ag<sup>0</sup> nature and continue to dissolve over extended period of time (Kaegi et al., 2013; Thalmann et al., 2014; Baalousha et al., 2015).

Electromagnetic radiation can also influence the environmental fate and behavior of NMs. For instance, sunlight can catalyze some redox reactions (photooxidation and photoreduction) of photoactive NMs (e.g., TiO<sub>2</sub>, CNTs, fullerenes) and produces reactive oxygen species when exposed to sunlight (Chen and Jafvert, 2011). Others may be oxidized or reduced by sunlight, changing their redox state, charge, and therefore aggregation state and toxicity (Hou and Jafvert, 2008; Lee et al., 2009). Sunlight has been shown to cause the degradation of gum arabic coating on AgNMs and result in enhanced aggregation and removal (sedimentation) of NMs from solution (Cheng et al., 2011). Additionally, ozone react with C<sub>60</sub>, breaking the carbon cage structure and increasing the stability of NMs against aggregation (Cho et al., 2009; Fortner et al., 2007).

Redox active NMs (e.g., Ce<sub>2</sub>O, zero valent iron, AgNMs) can undergo changes in their surface speciation as a result of interaction with the component of the aquatic media. For instance, the interaction of these NMs with ligands alters their speciation. The interaction of Ce<sub>2</sub>O with NOM and biological media results in their oxidation; that is an increase in the fraction of Ce<sup>4+</sup> ions on the NM surface (Baalousha et al., 2010), which is likely to have implication for the surface charge and thus the environmental behavior of the particles.

Biodegradation is another important factor that can influence the fate, behavior and impact of NMs and has to be considered. Adverse effects may

occur when particles are not biodegraded or readily eliminated (excreted) from the body. Biodegradation can occur at the level of surface coating or the NM itself. For instance, the biodegradation of the capping agent (polyethylene oxide) has shown to induce NM aggregation (Kirschling et al., 2011). SWCNTs can be biodegraded through enzymatic catalysis (Allen et al., 2008; Allen et al., 2009; Kagan et al., 2010), which suggests an interesting means of regulating the fate of CN in biological systems, provided that the process can be controlled. Human neutrophil myeloperoxidase has been shown to efficiently degrade SWCNT, which reduced the pulmonary inflammation by the SWCNTs (Kagan et al., 2010). Superparamagnetic iron oxide NMs (SPIOIN) are biodegradable and the NMs can be processed by the cells as part of the physiological iron metabolism, evidenced by the increase in iron values in the serum after administration (Weissleder et al., 1989). Although biodegradation of NM is an important process determining their fate, behavior and impact, currently there is little information available on the extent and rates of NM biodegradation in environmental and biological systems, and clearly more work is needed in this area.

## CASE STUDIES ON THE NM PROPERTIES AFFECTING FATE AND BEHAVIOR IN THE AQUATIC ENVIRONMENT OF GROUPS OF NANOMATERIALS

In this section, a number of case studies on well-defined groups of NMs are presented. Each of the case studies provides an overview of the main characteristics of the NMs considered in terms of specific properties affecting their life cycle and their fate and behavior, thus integrating the current knowledge on the underlying processes.

### MNMs – AgNMs and AuNMs Emission

There is no clear total production estimate of silver or gold NMs, but it is well known that AgNMs are more commonly used, and by far most information on the environmental fate and behavior of MENMs is available for AgNMs. Emission to the environment may occur during all life-cycle steps. For consumers the use of the product may result in both dermal and inhalation exposure to AgNMs, and release to the aquatic and terrestrial environment. In most parts of the world, wastewaters are collected and treated before channeling back to the aquatic environments (e.g., rivers and oceans). As a result, most NMs emitted to wastewaters will also undergo the water treatment processes that are generally considered to have a high efficiency (up to 99.9% depending on the type of the treatment process/plant) for removal of particulate materials. During water treatment, the addition of chemical coagulants further promotes the agglomeration of particulate materials, which

also increases their sedimentation. The processes of coagulation, sedimentation, and filtration during water treatment are therefore likely to remove a large proportion of the NMs before the (treated) water enters other water bodies.

## TRANSFORMATION

Dissolution is a critical environmental transformation process that determines the effects of silver NMs in the environment and within organisms. Liu *et al.* (2010a) concluded that silver ion ( $\text{Ag}^+$ ) release from AgNMs is a cooperative oxidation process requiring both protons and dissolved  $\text{O}_2$ . The dissolution of AgNMs was found to be controlled by their primary particle size, shape, surface coating and concentration (Liu *et al.*, 2010b; Zhang *et al.*, 2011; Ma *et al.*, 2012; Peretyazhko *et al.*, 2014). Moreover, the effects of environmental parameters (e.g., dissolved oxygen, pH, ionic strength, chloride and ammonia content, temperature, salinity, and dissolved organic carbon) on the dissolution of AgNMs potentially were interpreted as well (Li *et al.*, 2010; Liu *et al.*, 2010; Kent and Vikesland, 2011; Zhang *et al.*, 2011; Li and Lenhart, 2012; Chambers *et al.*, 2013; Kostigen Mumper *et al.*, 2013; Peretyazhko *et al.*, 2014). Additionally, physical processes such as aggregation were found to become the most important factor controlling silver release in the natural surface water (Li and Lenhart, 2012).

Unlike AgNMs, gold NMs are resistant to oxidative dissolution and release of dissolved Au ions, whereas another characteristic is that they are present at low natural background concentrations (Judy *et al.*, 2011, 2012a, 2012b; Merchant, 1998). At the same time, the pathway and mechanism for transformation of metal ions into metal NMs were also discovered in recent studies (Akaighe *et al.*, 2011; Yin *et al.*, 2012). For example, Yin *et al.* (2012) found that dissolved organic matter (DOM) in environmental waters can mediate the reduction of ionic Ag and Au to their metallic NMs under natural sunlight, implying that this process may be general for metals with high reduction potential. It was also found that the thermal or photochemical reduction process is another possible source of naturally occurring AuNMs in natural environments, which possibly has critical impacts on the transport and transformation of Au and engineered AuNMs (Yin *et al.*, 2014). Contemporary studies suggest that reactive oxygen species (ROS) such as superoxide dominate the toxicity mechanism of AgNMs, while ROS is also able to reduce silver (I) ions with resultant production of AgNMs (Jones *et al.*, 2011). This means that the ability for AgNMs to undergo catalytic cycling provides a pathway for the continual generation of ROS and the regeneration of AgNMs following oxidation (Jones *et al.*, 2011).

In addition, the sulfidation process of AgNMs is one of the most likely corrosion phenomena that may happen in the aquatic environment (Liu *et al.*, 2011). Sulfidation can strongly affect surface properties of AgNMs in terms

of surface charge and dissolution rate, which will affect the reactivity, transport, and toxicity of AgNMs in soils (Levard et al., 2011). The sulfidation of AgNMs followed pseudo first-order kinetics, with rate coefficients increasing with decreasing AgNMs diameter and increasing metal sulfide concentration and depending on the type and crystallinity of the reacting metal sulfide (e.g., CuS and ZnS; Thalmann et al., 2014). Moreover, PVP-coated AgNMs in terrestrial soils could be transformed to Ag<sub>2</sub>S, whereas AgNMs in the sub-aquatic sediment could be present as Ag<sub>2</sub>S and Ag-sulfhydryl compounds (Lowry et al., 2012a). It was also found that AgNMs may undergo a rich set of biochemical transformations, including accelerated oxidative dissolution in gastric acid, thiol binding and exchange, photoreduction of thiol- or protein-bound silver to secondary zero-valent AgNMs, and rapid reactions between silver surfaces and reduced selenium species (Liu et al., 2012).

#### AGGREGATION AND SEDIMENTATION

The behavior and fate of MNMs in the environment are influenced by many physical processes (e.g., aggregation and sedimentation; Petosa et al., 2010). Physical transformation thus becomes one of the most representative behaviors of MNMs such as AgNMs in the environment (Levard et al., 2012; Lowry et al., 2012b). These physical transformations will be complex processes with many environmental variables such as solution chemistry and DOM affecting the processes (El Badawy et al., 2010; Jin et al., 2010; Stankus et al., 2010; McLaughlin et al., 2012). In addition, the suspension stabilization through the use of capping agents can also dramatically influence the surface changing behavior and aggregated particle size of AgNMs (El Badawy et al., 2010). El Badawy et al. (2010) addressed that the type of stabilizing mechanism had a profound effect on the aggregation potential of AgNMs. Thus, the potential fate and transport of AgNMs are more closely associated with the chemistry of the capping agent. Contemporary studies also indicate that changes in aggregation occur as a function of AgNMs surface coating, media composition, pH, and ionic strength, potentially resulting in substantial changes during NMs (eco)-toxicological exposures (Stebounova et al., 2011; Tejamaya et al., 2011; Baalousha et al., 2013). Similar to AgNMs, the aggregation behavior of AuNMs is controlled by environmental factors such as DOM. Adsorption of DOM on AuNMs was found to provide decreased particle aggregation, depending on capping agent, pH, ionic strength, and electrolyte valence (Pallem et al., 2009; Stankus et al., 2010). A recent study also indicates that the aggregation of AuNMs was affected by the molecular weight distribution and the chemical properties of DOM (Louie et al., 2013). However, Hitchman et al. (2013) found that sterically stabilized PVP AuNMs do not aggregate under relevant environmental conditions and do not interact significantly with natural organic macromolecules, unlike most types of nanoparticles studied to date.

## Stable Oxides: TiO<sub>2</sub> and CeO<sub>2</sub> NMs

### EMISSION AND TRANSPORT

*Release During the Product Life Cycle.* There is no clear total production estimate of TiO<sub>2</sub> or CeO<sub>2</sub>. The most current estimate lies between 7800 and 38000 tons/year for TiO<sub>2</sub> and 35 and 700 tons/year for CeO<sub>2</sub> NMs in the United States alone (Hendren et al., 2011). In a recent review by Nowack et al. (2012), two case studies of TiO<sub>2</sub> NMs as sunscreen and paint were discussed. They show the direct release of TiO<sub>2</sub> NMs from these two usage scenarios (Kaegi et al., 2008). TiO<sub>2</sub> are present in dispersed form in cosmetics such as sunscreen, which is washed off and released directly to surface waters or wastewaters (Nowack et al., 2012). TiO<sub>2</sub> in paint is mainly released by abrasion of the solid matrix in which it is encapsulated, thus this is a slower release compared to sunscreen (Kaegi et al., 2008; Nowack et al., 2012). Corresponding to these findings of direct release of TiO<sub>2</sub> to surface waters or wastewaters, measurements of colloidal or dissolved Ti (<0.45 μm) indicated a higher concentration in urban or industrial waters compared to rural upstream areas (Neal et al., 2011). TiO<sub>2</sub> NMs will undergo several transformations immediately after release that will influence their further fate in the aquatic environment. In addition to paint and sunscreen, TiO<sub>2</sub>, not necessarily in the nano form, is also used in foods as a pigment (E171), other metal oxides such as MgO (E530) and SiO<sub>2</sub> (E551; Chaudhry et al., 2008; Dekkers et al., 2011). For CeO<sub>2</sub> the main use is as an additive to fuel and thus the release would be due to combustion of the fuel (Cassee et al., 2011). However little is known about the release or transformation of CeO<sub>2</sub> NMs during combustion (Nowack et al., 2012). Other uses of CeO<sub>2</sub> are in cosmetics (Masui et al., 2000) and as a polishing agent (Sabia and Stevens, 2000).

### TRANSFORMATION

The main transformation processes for TiO<sub>2</sub> and CeO<sub>2</sub> NMs in the aquatic environment are changes to the coating due to adsorption or desorption processes, biotransformation, degradation and photochemical transformation (Nowack et al., 2012). TiO<sub>2</sub> NMs used in sunscreens have two coatings, first a Al(OH)<sub>3</sub> coating to reduce ROS production and then a hydrophobic coating against dispersion in water (Nowack et al., 2012). This hydrophobic coating can desorb and oxidize on contact with water (Auffan et al., 2010; Labille et al., 2010). Photochemical transformation can occur when the TiO<sub>2</sub> itself is subject to UV radiation and can generate free radicals (Brunet et al., 2009) or can change the interaction with adsorbed compounds (i.e., self-cleaning capacity; Carp et al., 2004). This self-cleaning capacity of TiO<sub>2</sub> NMs was also shown for the removal of penicillin antibiotic from water due to absorption and increased degradation (Peterson et al., 2012).



As the main application of CeO<sub>2</sub> is thought to be as additive to fuel, a rapid transformation is expected during the combustion process (Nowack et al., 2012).

#### SEDIMENTATION

Many studies have shown the stabilizing effect of NOM against homoaggregation of TiO<sub>2</sub> and CeO<sub>2</sub> NMs in suspensions containing relatively simple salt solutions with added NOM (Yang et al., 2009; Zhang et al., 2009; Domingos et al., 2009; Keller et al., 2010; Quik et al., 2010; Li and Sun, 2011; Ottofuelling et al., 2011). In addition to stabilization against homoaggregation, NOM can also stabilize against heteroaggregation (Chen et al., 2012; Chowdhury et al., 2012; Thio et al., 2011). This was shown for interaction of TiO<sub>2</sub> with sand columns (Chen et al., 2012), bacteria (Chowdhury et al., 2012), and silica surfaces (Thio et al., 2011). Although NOM generally stabilizes against aggregation, it can also enhance it by bridging flocculation, which occurs when there are free sites for interaction on the particle surface. This generally occurs at low NOM concentrations (Domingos et al., 2010). This indicates that depending on adsorption of any stabilizing agent to TiO<sub>2</sub> or CeO<sub>2</sub> (NOM or manmade) prior to release to the aquatic environment, the NOM present there can also stabilize against heteroaggregation.

The studies for TiO<sub>2</sub> that are done with water or particulate matter from a purely natural origin are scarce. Keller et al. (2010) showed the differences in stability in several natural water types, calculating sedimentation rates and attachment efficiencies. The adsorption of TiO<sub>2</sub> NMs to *E. coli* bacteria in river water from the Seine was reported (Planchon et al., 2013). The heteroaggregation of CeO<sub>2</sub> NMs with natural colloids present in surface water was shown by comparing NM sedimentation in filtered and unfiltered surface waters by calculating sedimentation rates and attachment efficiencies (Quik et al., 2012; Quik et al., 2013).

Although current exposure assessment modeling lacks many of the NM relevant processes as reported here, several studies have calculated exposure concentrations as reported in a recent review by Batley et al. (2012). For TiO<sub>2</sub> NMs predicted exposure concentrations below 16  $\mu\text{g}\cdot\text{l}^{-1}$  are reported (Mueller and Nowack, 2008; Kiser et al., 2009; Gottschalk et al., 2011) and below 1  $\mu\text{g}\cdot\text{l}^{-1}$  for CeO<sub>2</sub> NMs (O'Brien and Cummins, 2010). However, in a recent study by Praetorius et al. (2012), concentrations of TiO<sub>2</sub> NMs for the Rhine were calculated to be in the ng/l range in the water phase and in the mg/kg range in the sediment.

All of the studies reported here on the aggregation and sedimentation of TiO<sub>2</sub> and CeO<sub>2</sub> particles use relatively high NM concentrations ranging from 1 to 100  $\text{mg}\cdot\text{l}^{-1}$ , which is about 100–10,000 times higher than the currently predicted exposure concentrations expected in the aquatic environment (Batley et al., 2012). Attachment efficiencies and other quantitative parameters are important for fate modeling of NMs (Praetorius et al., 2012). However,

due to the sometimes high and environmentally irrelevant NM concentrations, these quantitative results should be considered carefully before using them in modeling.

## Iron Oxides

Iron oxide NMs (IONM) subsume a group of nanoparticulate iron oxide and iron oxide-hydroxide minerals with different composition and mineralogy (Cornell and Schwertmann, 2003). Major examples are hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), Goethite ( $\alpha$ -FeO(OH)), and magnetite (Fe(II)Fe(III)<sub>2</sub>O<sub>4</sub>).

### EMISSIONS AND MAIN CHARACTERISTICS

While investigated and produced for a wide variety of current and future applications, they are ubiquitous in the environment and applied in industry and technology for centuries (Zhang et al., 2010). IONMs are found as pigments in paints and cosmetics, where their nanocharacteristics may be unintentional but evolves from the manufacturing process. Applications where the nanocharacteristics are essential part of the working principle of the products are super-paramagnetic IONMs which are developed to serve as drug delivery vehicles, contrast agents in nuclear magnetic resonance imaging or in hyperthermia cancer treatment (Brunner et al., 2006). It has been shown that IONMs cause cytotoxic effects and that these effects are attenuated by coating the particle surface. The mechanism of cytotoxicity is thought to be the production of radicals on the particles' surface (Brunner et al., 2006; Soenen and De Cuyper, 2010). IONMs are discussed and tested for the remediation of contaminated groundwater (Cundy et al., 2008) and in wastewater treatment (Xu et al., 2012). As microscale iron oxide particles are known for their adsorption capacity for metal ions (Bailey et al., 1992; Martin et al., 2000; Gupta et al., 2005; Guo et al., 2007; Kundu and Gupta, 2007), increased specific surface area and higher as well as more selective reactivity can be reached by producing the particles in the nanoscale (Madden et al., 2006; Cundy et al., 2008). Those IONMs may even be even generated by anaerobic bacteria (e.g., bio-magnetite; Lloyd, 2003). Bio-magnetite NMs are active against a broad range of redox active toxic metals or metalloids, such as Cr(VI), As(V), and radionuclides (Cundy et al., 2008; Lloyd, 2003).

IONMs will be emitted from general use (via wastewater treatment plants), from hospitals (pharmaceutical use), and use directly in the groundwater (remediation). In the latter case they will be applied to reduce the pollution and its associated toxicity, to manage potential risks their mobility in the subsurface should be low or well controlled. From consumer products (e.g., pigments) and pharmaceutical use we can expect to see much more complex structures emerging (and being emitted) compared to the natural

or synthetic IONMs that have been extensively studied. Hence, although being quite natural and relatively well understood, manufactured IONMs need to be further investigated for unexpected behavior arising from coatings, structures helping drug delivery or hybrid structures (e.g., core-shell types).

IONMs are one of the major groups of environmental NMs and colloids beside silicates and organic matter. Because of their importance for environmental processes, natural iron oxide colloids and IONM have been investigated intensively (Banfield and Zhang, 2001). Due to their relatively straightforward synthesis (although receiving a certain property in a reproducible way can become an art) and widely available synthesis protocols (Schwertman and Cornell, 2000) they have been used as model colloids/NMs to understand aggregation processes (Hunter et al., 1997; Mylon et al., 2004; Chen et al., 2006; Baalousha et al., 2008) and colloidal/nanoparticulate transport (Kretzschmar and Sticher, 1997; Grolimund et al., 1998; Kretzschmar et al., 1997; Kuhnen et al., 2000) and contaminant cotransport in freshwaters, soil porewaters (Von der Kammer et al., 2004), and groundwaters (Forstner et al., 2001).

Hence, there is a rich literature base on the reactions and behavior of IONM available in the environmental sciences, geosciences, marine sciences, and the colloid chemistry.

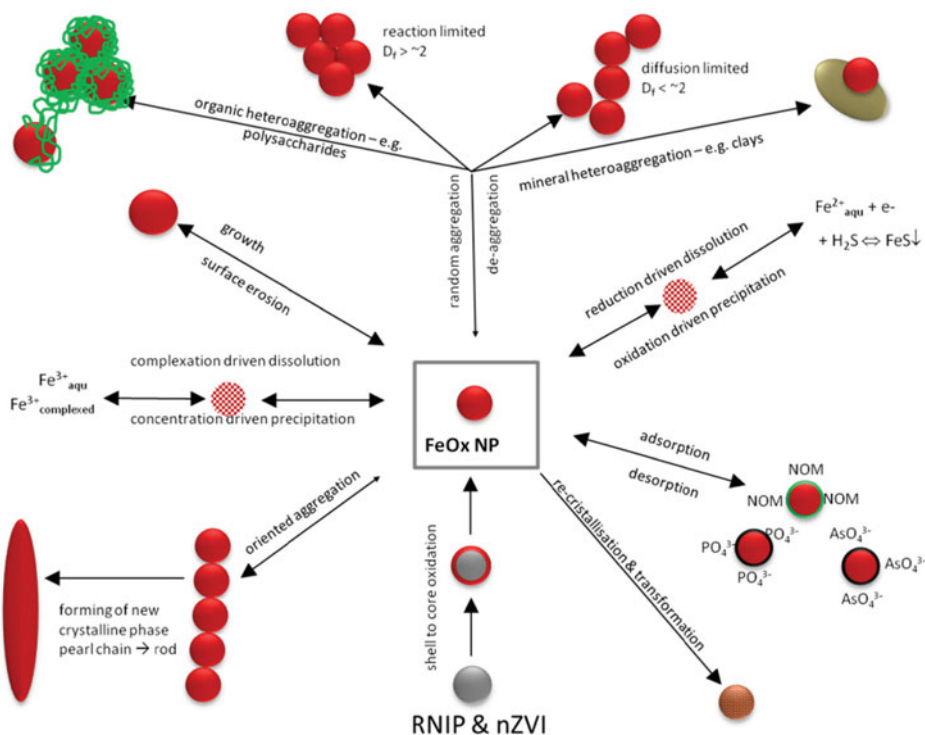
Not directly related but including interesting mechanistic studies in respect to mobility in groundwaters is the work on reactive nano-zero-valent iron particles (RNIP and nZVI) used for remediation of groundwaters (Cundy et al., 2008; Müller and Nowach, 2010; Noubactep et al., 2012). Although not essentially IONM they become partially or even completely oxidized after deployment in the groundwater and later behave similar to IONM.

The ubiquity of natural IONMs and their chemical and structural similarity to manufactured IONMs will make a differentiation in environmental media virtually impossible, as long as the manufactured particles do not carry a specific label.

## TRANSFORMATIONS

IONMs undergo various reactions and transformations in the environment, which are schematically shown in Figure 4. The most important for their behavior and fate in the environment are the following:

1. Aggregation and surface deposition
2. Reductive dissolution
3. Interaction with natural organic matter (coating, influence of surface charge) or solutes (adsorption/surface complexation)
4. Transformation to other mineral phases (e.g., FeS, FeCO<sub>3</sub>) via recrystallization or dissolution and precipitation

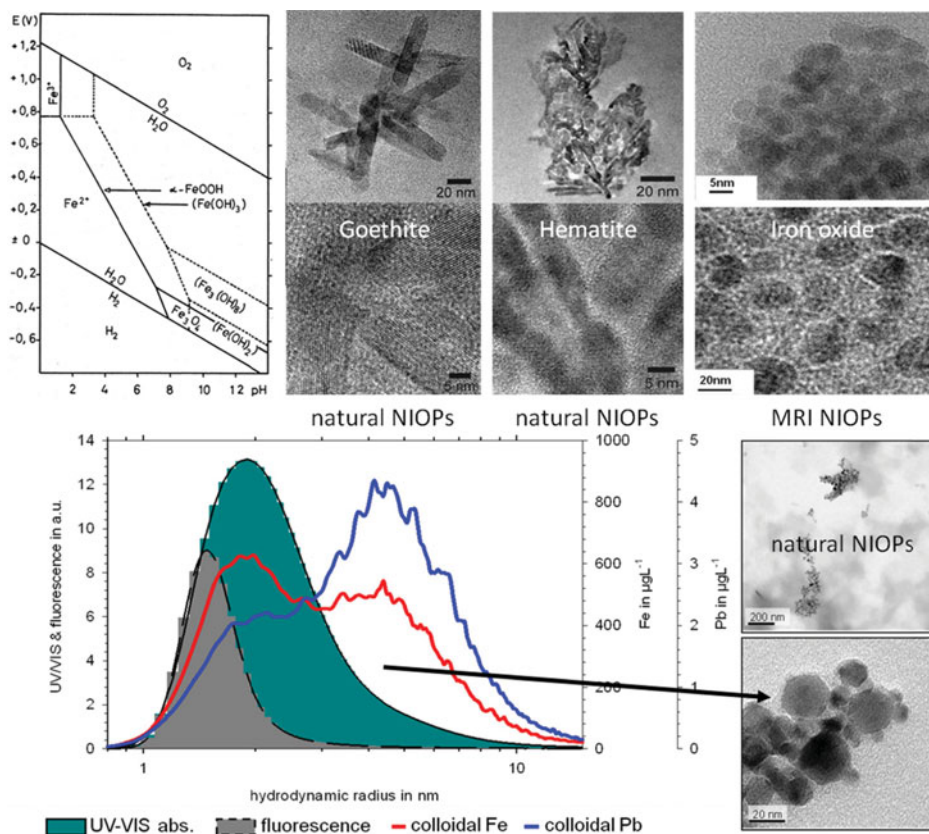


**FIGURE 4.** Reactions and transformations typical for iron oxide particles (including nanomaterials) in the environment.  $D_f$  = fractal dimension. Pathways are explained in the text.

Although highly stable at pH values above 3 and in the presence of oxygen (Figure 5), IONMs must be regarded as only partially persistent in the aquatic environment, especially when anoxic (micro-) environments are considered (Cornell and Schwertmann, 2003). Dissolved and reprecipitated IONM should not be considered manufactured NMs. Even if the atoms constituting them were derived from manufactured IONM, they will have been produced by an entirely normal environmental process and will not be distinguishable from their natural counterparts unless they were isotopically labeled.

#### AGGREGATION AND STABILIZATION

In the absence of  $\text{CO}_2$ , bare IONMs dispersed in water show an isoelectric point/point of zero charge (IEP/PZC) at pH between 7 and 9 (Kosmulski, 2006, 2009a, and 2009b). IONMs belong to the phases that potentially appear with positive surface charge in the environment, making them prone to attach to other natural surfaces, which are typically negatively charged. However, presence of  $\text{CO}_2$  results in adsorption of carbonate ions to the IONM surface that can lower the IEP by about one pH unit. Adsorption of natural organic matter can shift the IEP to pH values as low as 2–3 and cause a charge



**FIGURE 5.** The stability diagram of iron in the Eh and pH domain (Scheffer and Schachtschabel, 1970) and TEM micrographs of (left to right) natural hematite and goethite IONMs found in the floodplain soils of Clark fork River, Montana (US) (modified from Plathe et al. (2013)) and bare uncoated IONMs produced for magnetic resonance imaging (from Yu et al., 2012). Bottom: elemental and particle size distribution showing complexed Fe(III) with natural organic matter (left peak) and spherical shaped natural IONM in the size range of 5–25 nm (modified from Hassellöv and Von der Kammer, 2008).

reversal of the IONMs. The extent of this effect is of course dependent on the ratio of NOM concentration and charge density to the IONMs surface area concentration.

IONMs have been used extensively to study aggregation processes (Bushell et al., 2002; Chen et al., 2005; Baalousha, 2009) and colloidal transport in soils (Kretzschmar and Sticher, 1997; Kretzschmar et al., 1997). Their stabilization against aggregation by adsorption of NOM is well studied (Kretzschmar and Sticher, 1997; Forstner et al., 2001). However, the interaction with polysaccharides (e.g., in waste water treatment plants) will lead to immediate aggregation and removal (Chen et al., 2005).

IONMs are unstable under anoxic conditions and dissolve, forming ferrous iron ions. There are some Fe(II) compounds known, which can form nanoparticulate and colloidal phases under anoxic conditions, such as Fe(II)CO<sub>3</sub> (Jimenez-Lopez and Romanek, 2004) and Fe(II)S. Anoxic conditions are frequently encountered in the aquatic environment, especially when bioavailable organic matter is microbially decomposed in situations of limited oxygen supply. This situation is present in lower layers of surface water sediments, heavy wetted soils and groundwater influenced by elevated NOM concentrations. Subsequent oxidation of iron-rich anoxic waters results in precipitation of iron oxide phases, which can lead to the formation of new IONM phases (Wolthoorn *et al.*, 2004). However, often the formed NMs grow or aggregate to larger structures, are the sedimented or filtered out (Wolthoorn *et al.*, 2004).

IONMs are strongly adsorbing phosphate or arsenic ions as well as many trace metals. They may therefore act as scavengers (if immobile) or transporters (if mobile) of these compounds. Although the abundant natural IONMs can influence transport of low soluble main and trace elements (Hasselov and Von der Kammer, 2008; Neubauer *et al.*, 2013), the transport capacity of manufactured IONMs is however limited by their small concentrations. For this reason manufactured IONMs (as all other MNMs) will only act as transporters of pollutants in very special cases (Hofmann and Von der Kammer, 2009).

### Carbon Nanotubes: SWCNTs MWCNTs

Carbon nanotubes are long, thin, hollow cylinders composed of one (SWCNTs) or many (MWCNTs) concentric layers of graphenic carbon (Chen *et al.*, 2010). CNTs show unique properties and are used in different consumer products like paints, composite materials and sporting or technical equipment. CNTs can be released over their whole life cycle and different abiotic and biotic parameters will affect and change the fate and behavior of the CNTs. Here, we review the influence of interactions of natural organic matter (NOM) with CNT influencing the stability of pristine CNTs in aquatic environments.

#### STABILIZATION OF CNTs IN SUSPENSION BY NOM

CNTs are mainly removed from the water phase via agglomeration and subsequent sedimentation (Schwyzer *et al.*, 2012). On the other hand several mechanisms such as electrostatic and steric repulsion are known to hinder agglomeration and thus stabilize CNTs in suspensions (Chen *et al.*, 2010). NOM, which consists of substances such as humic and fulvic acids, is ubiquitous in aquatic environments and interacts with NMs hence codetermining CNT fate and behavior (Saleh *et al.*, 2008; Gigault *et al.*, 2012). CNT surfaces are modified by adsorption of organic substances once released into

the aquatic environment (Gigault et al., 2012), which has been shown to stabilize CNTs in suspensions even facilitating individually dispersed CNTs in suspension (Hyung et al., 2007; Hyung and Kim, 2008; Saleh et al., 2008, 2010; Gigault et al., 2012; Schwyzer et al., 2012).

The interaction between CNTs and NOM depends not only on the NOM properties (e.g., aromaticity, charge density) but also on the properties of the CNTs (e.g., functionalization, diameter, length; Hyung et al., 2007; Chappell et al., 2009; Hyung and Kim, 2009; O'Driscoll et al., 2010; Schwyzer et al., 2012). NOM adsorption mainly occurs by hydrophobic  $\pi$ - $\pi$  interactions and is therefore dominated by humic substances with high aromatic carbon content but also hydrophilic interactions between adsorbed functional groups can be important (Hyung et al., 2007; Hyung and Kim 2008; Chen et al., 2010).

As a considerable increase in suspension stability is accompanied by only a small change in electrophoretic mobility, it is proposed that the adsorbed NOM cause steric repulsion rather than electrostatic repulsion (Chen et al., 2010; Saleh et al., 2008, 2010). However, in other studies an increase in the negative surface potential after NOM adsorption was observed, leading to the conclusion that the suspensions are stabilized by electrostatic interaction (Schwyzer et al., 2012). Further research on the mechanisms of CNT stabilization by NOM is needed to understand and predict the effects.

#### DESTABILIZATION OF CNTs IN SUSPENSION BY NOM

Beside the stabilization effect different circumstances may also lead to a destabilization of CNTs in suspension. The ionic strength of the media is another important parameter affecting the stability of CNTs in suspension. With increasing ionic strength the stabilization effect of adsorbed NOM can be reduced or even neutralized (Hyung and Kim, 2008; Yang and Xing, 2009, Schwyzer et al., 2012) thus leading to higher agglomeration and consequently deposition of the CNTs. This effect is more pronounced by the presence of divalent cations (Schwyzer et al., 2012). The destabilization is caused by reduced electrostatic repulsion, and bridging flocculation of the adsorbed NOM with cations such as  $\text{Ca}^{2+}$  or by the neutralization of the negative charges on the CNT surface. In cases where CNTs are only partially coated with NOM, bridging flocculation between different CNTs or CNTs and other surfaces may also occur (Domingos et al., 2009; Chen et al., 2012).

The stabilization of the CNTs after NOM adsorption increased with increasing NOM concentration and higher adsorbed NOM density (Gigault et al., 2012; Hyung et al., 2007). However, the NOM adsorption is affected by the pH of the media, with lower adsorption at higher pH values, due to higher electrostatic repulsion and therefore less hydrophobic and hydrogen-bond interactions (Hyung and Kim, 2008; Yang and Xing, 2009).

Conceptually, we can gather from the findings that different parameters like the pH, the type or concentration of the NOM as well as the valence and

the concentration of cation in the media can either stabilize or destabilize CNTs in the aquatic media. However, detailed information about critical values of these parameters, which can be used for modeling, is not finally identified and has to be investigated in further studies.

NOM is ubiquitous present in aquatic environments and due to its ability to promote suspension stability under various chemical conditions, NOM plays an important role in determining CNT fate and behavior in aquatic environments. This statement is based on results of several studies, hence suggesting also a significant environmental mobility. However, most of the studies were conducted in simplified model systems, investigating the influence of different individual parameters and processes on the behavior of CNTs in suspensions. These results are not directly transferable to natural systems. The understanding of the influence of different mechanisms and changes in the aquatic condition on the stability and mobility of CNTs in the aquatic environment increased during the last years. Anyhow some determining factors and especially the interplay between the difference factors are still not understood so that no scientifically sound prediction on the stability of CNTs in the aquatic environment can be made.

## MWCNTs

### EMISSION AND TRANSPORT

*Release From the Product During the Product Life Cycle.* Emission, fate and risks of MWCNTs were recently reviewed by Petersen et al. (2011). The total CNT production has been estimated as 350–500 tons·year<sup>-1</sup> (Mueller and Nowack, 2008) and more recently as 55–1100 tons·year<sup>-1</sup> in the US alone (Hendren et al., 2011). Two main categories of emission to the environment may be distinguished: MWCNT release during the life cycle of polymer nanocomposites, and release due to burning of polymer nanocomposites. After release from the product, various transport pathways may bring MWCNTs to aquatic systems (Nowack et al., 2012). MWCNT may be released from nanocomposites as used in tennis rackets, bicycle frames, and automobile bumpers, due to processes such as abrasion, scratching, sanding, washing, diffusion, and matrix degradation (Petersen et al., 2011; Nowack et al., 2012). Among these speculated mechanisms, especially the pathway through matrix degradation has been relatively well documented. Similar to all polymers, polymers containing MWCNTs lose their structural integrity and become brittle due to exposure to UV light (photo-oxidation) or increased temperature (Kamal et al., 1992). Nguyen et al. (2009a; 2009b; 2011) reported such degradation of nanocomposites and resultant accumulation of a dense entangled CNT layer on the composite surface. Similar entanglement networks have been reported for burned residues of nanocomposites (Kashiwagi et al., 2008) or natural soot particles (Murr, 2004, 2005), and seem to protect the underlying polymer layer from further degradation. None of these studies



reported release of MWCNTs during the experiments, which typically lasted <1 year. It is unknown what the release rates from these surface-entangled composite fragments are under environmental conditions.

*Release From the Product by Incineration, Burning, and Combustion.* Burning of nanocomposites during the process of incineration or in accidental fires may also form a release pathway for MWCNTs, but information is scarce. Typically, CNTs or carbon nanofibers (CNFs) are identified in the residual chars, but not in the emitted particles (Davis and Kim, 2010; Nyden et al., 2010). Petersen et al. (2011) conclude that either CNTs are trapped in the network that comprises the char, or are destroyed in the flame. During incineration, airborne release of CNT may occur, but theoretically all particles should be mineralized during incineration, because of the high temperature and presence of oxygen during incineration (Petersen et al., 2011; Nowack et al., 2012). However, MWCNT release was observed through emitted aerosols after combustion in an oven (Bouillard et al., 2010). Furthermore, mechanical stress on such char particles has been observed to increase emission of submicron particles, including CNT particles. More work has to show to what extent MWCNTs can be released through similar mechanism and at which rate.

*Transport Pathways From the Product to the Aquatic Systems.* The previous information suggests that mobility and release are limited, and that if there is release, it probably is very slow (Nowack et al., 2012). Once released from the product, MWCNTs may reach aquatic systems through run off or subsurface transport (i.e., seepage) from the terrestrial environment (i.e., from a landfill; Cornelis et al., 2013; Kasel et al., 2013), upstream inputs or through domestic or industrial waste streams that pass through waste water treatment plants (WWTP), or direct atmospheric deposition of MWCNT containing aerosols. For terrestrial environments, subsurface and run-off transport rates are highly variable, dependent on the functionalization of the MWCNTs and local conditions (Petersen et al., 2011; Cornelis et al., 2013). For wastewater treatment plants, MWCNT removal efficiencies are found to be high (He et al., 2012), and values >95% retention were used in the mass balance studies by Gottschalk et al. (2009; 2010), further limiting the input to aquatic systems. The transport through these pathways would also contribute to the aggregation and encapsulation of primary particles due to interaction with DOM and extracellular polymeric substances (EPS). Atmospheric deposition of aerosols containing MWCNT is expected to form a relatively direct pathway for primary particles. In aerosols, however, MWCNTs are present in heterogeneous mixtures with similarly structured entangled CNTs from natural origin, probably present at much higher quantities (Murr, 2004, 2005; Koelmans et al., 2009).

## TRANSFORMATION

Petersen *et al.* (2011) provided an overview of possible transformation reactions, which, in the absence of environmental MWCNT studies, was mostly based on chemistry and chemical engineering studies. Fullerene-like end caps and defects on MWCNT side walls are supposed to be susceptible for oxidation (Niyogi *et al.*, 2002; Li *et al.*, 2005), where smaller MWCNT diameters are associated with a higher reactivity. Chemical oxidation requires strong oxidative forces, unlikely to occur in the environment, yet photo-oxidation is possible. Oxidation then results in the opening of the end-cap and introduction of oxygen containing groups such as carboxyl, hydroxyl, carbonyl, and ester groups, similar to oxidation of black carbon (Hammes *et al.*, 2008). Biodegradation rates for MWCNTs are not known, but black carbon degradation rates have been proposed as a proxy for MWCNT degradation (Koelmans *et al.*, 2009). In well-aerated environments such as soils, degradation half-lives of 50–500 years have been reported (Hammes *et al.*, 2008). This implies that degradation of MWCNTs is not relevant given the water residence times of freshwater aquatic systems, except for very large lakes. However, in anoxic marine sediments a half-life of 10–20 kyr has been reported (Middelburg *et al.*, 1999), a time scale that may be assumed to be valid for anoxic freshwater sediments as well. Given the much higher burial rates of aquatic sediments, burial rather than degradation would be the primary removal process from sediment top layers. For SWCNTs, enzyme mediated breakdown has been reported. It is unknown, however, whether such enzymes are similarly capable of transforming MWCNTs.

## SEDIMENTATION

The fate and transport of MWCNTs in aquatic systems depends mainly on MWCNT colloid stability and sedimentation behavior. Because naturally occurring NMs and colloids are ubiquitous in natural waters (Koelmans *et al.*, 2009; Chen *et al.*, 2010; Praetorius *et al.*, 2012), heteroaggregation will dominate and determine the onset of sedimentation (Huynh *et al.*, 2012; Quik *et al.*, 2012; Quik *et al.*, 2014; Velzeboer *et al.*, 2014). Clay particles have been found to stimulate aggregation of MWCNTs by binding surfactants that originally stabilized the MWCNTs (Han *et al.*, 2008). MWCNTs were shown to have a factor three higher heteroaggregation rate with hematite NMs, compared to homoaggregation (Huynh *et al.*, 2012). Increase of DOM concentration decreased the aggregate growth rate due to a decrease in the hematite surface available for interaction with the MWCNTs. In many studies DOM has been found to increase the colloid stability of MWCNTs (Hyung *et al.*, 2007; Lin *et al.*, 2010; Petersen *et al.*, 2011; Smith *et al.*, 2012; Zhou *et al.*, 2012), probably by steric repulsion of the macromolecules associated with the MWCNTs.

Homoaggregation may be assumed less relevant, unless natural colloid concentrations are very low. Pristine CNTs are very hydrophobic and will rapidly aggregate by homoaggregation and settle. However, there is a wide variety of functionalizations that bring hydrophilic functional groups on the MWCNT surface, thus increasing the stability in water. Saleh et al. (2008), observed aggregation of MWCNTs to decrease with increasing pH due to dissociation of such functional groups on the MWCNT surface. Smith et al. (2009) observed critical coagulation concentrations to increase with the degree of oxidation of the MWCNT surface.

It must be noted that these aggregation processes are important for primary particles, such as those deposited on the surface of aquatic systems from the atmosphere. MWCNTs entering from upstream, through runoff, or from wastewater treatment plants most likely are already aggregated. For these MWCNT-natural colloid aggregates and agglomerates, the further association with suspended solids is a very important process governing the distribution and scavenging in natural waters. Generally, cations and DOM appear to influence the stability of MWCNTs with respect to association with suspended solids in the water column. Cations may screen the surface charge of MWCNTs and suspended solids, thus increasing their interaction (Zhang et al., 2011). Presence of DOM may yield steric hindering of MWCNTs and natural colloids approaching, thus leading to stabilization in the water column. Therefore, absence of DOM (e.g., hard waters and seawater) leads to aggregation and more association of MWCNTs with suspended sediments, leading to efficient scavenging from the water column and overall faster sedimentation. This implies that aquatic sediments are a major sink for MWCNTs. Recently, Zhang et al. (2011) provided Freundlich-type association parameters for MWCNT association with peat model solids, thus explaining the sedimentation rates for the MWCNTs from the sedimentation characteristics of the peat particles. Given literature data on efficient association with settling solids, Koelmans et al. (2009) predicted steady state MWCNT concentrations in sediments, which were shown to be much lower than those of naturally occurring NMs originating from chars and nanosized soot particles.

## SYNTHESIS – MAJOR ASPECTS RELATED TO MODELING FATE AND BEHAVIOR OF NMS IN AQUATIC MEDIA

Exposure concentrations of dispersed NMs in the environment are related to the chemistry and morphometry of the compartment of interest, rather than to the mass dosed. It is challenging to quantify the fate of NMs in aquatic media: due to their intrinsic reactivity, NMs tend to interact with virtually any surface present in solution, with the kinetics of the interactions depending on the specific physicochemical properties of the NMs and the composition

of the medium. Especially the presence of DOC and the ionic strength are determinative in this respect, the general trend being that NMs tend to be stabilized in media of low ionic strength and high DOC.

When in aquatic environments, NMs are likely to undergo a variety of transformations that may lead to a change in their physicochemical properties, and/or loss of the nanostructure. Depending on various factors, such as pH, ionic concentration, presence of other dissolved substances, and particulate materials, the NMs may undergo agglomeration, aggregation, degradation, solubilization, sorption, and/or sedimentation. In an aquatic environment, NMs may also bind other moieties on their surfaces, and such surface modifications may further influence their physicochemical properties, fate, behavior, and effects. Currently, there are major knowledge gaps in regard to the fate and behavior of most NMs in aquatic environments. Much of the published work so far relates to the agglomeration behavior of NMs, which has been documented for several metal (oxide) and carbon-based NMs in aquatic media. Despite the apparent knowledge gaps, a few key factors are likely to play a major role in determining the overall fate of NMs in an aquatic environment. These include partitioning between sedimented and suspended forms, and degradation by chemical (pH, reaction with other chemical substances), physical (sunlight, oxidation, hydrolysis), and/or biological means (enzymes, aquatic microorganisms, aquatic animal and plant species).

When filling data and knowledge gaps on the essential issues regarding fate modeling of NMs, it is of importance to find a balance between the need to know more and the pragmatic view of the need to know less. What is needed, is informed simplicity that allows to operationalize theoretical concepts in the heterogeneous (place and time) environment. This in analogy to the current practice in metal risk assessment in which instead of advanced speciation and fate models, conventional and relatively easily deducible partitioning coefficients ( $K_d$ -concept) are commonly used as a first tier to quantify the fate of metals. Despite the apparent knowledge gaps regarding fate assessment of NMs, the existing leading (DLVO) theory on the behavior of aquatic colloids may be used as a first approach to at least qualitatively assess the aggregation behavior of NMs. After all, the DLVO theory usually provides qualitative (or semiquantitative) information about the tendency of suspensions to undergo aggregation and the influence of various parameters on NM aggregation. It should be realized in this respect, however, that information on the variation of free energy of the NMs as the result of attractive and repulsive forces of particles separated at varying distances, is lacking. A major research need in this respect is the development of a database of reaction kinetics and thermodynamics that allows quantifying the interactions of NMs in aquatic media of various compositions. The database is to be supplemented with data on the water characteristics that need to be monitored in order to allow for future quantification and

extrapolation of fate and behavior properties of NMs in freshwater compartments of varying composition.

A key question to be answered is whether the current approaches and models used to quantify colloidal interactions and transport are applicable to NMs. It is evident that our current understanding of NM deposition and aggregation precludes a definitive unified answer. Although generalizations on the role of specific particle and environmental properties cannot yet be established, the review reveals that traditional DLVO theory can generally semiquantitatively describe NM aggregation and deposition behavior. However, certain particle properties can lead to non-DLVO behavior; for instance, surface modifications such as polymer or surfactant coatings give rise to steric stabilization resulting in decreased NM deposition or aggregation. Moreover, unusual particle shapes, such as in the case of CNTs, can give rise to additional capture mechanisms (e.g., straining), which result in unpredicted NM transport patterns. Most common experimental and theoretical approaches used for evaluation of NM deposition and aggregation are applicable for spherical particles; however, limitations for nonspherical or very small particles clearly exist.

Overall, a lot of information on fate and behavior of NMs is available as are some leading theories on particle interactions. However, a lot is still uncertain and some of the leading theories are commonly not that useful after all. Yet we do know that for those NMs that simply settle within days regardless of what mechanism causes the initial attachment, we have a strong informed simplification, which in fact is sufficient for the gross time and spatial scales that current exposure and water quality models usually work with.

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