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a review

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Modelling the Release, Transport and Fate of Engineered Nanoparticles in the Aquatic Environment – A Review

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Contents

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1 Introduction

Nanoparticles are a product of nanotechnology. In a broad sense, nanotechnology is the science and technology of manipulating matter at very small scales, down to a few nanometers or even smaller. This leads to nanomaterials, where structures of a few hundred nanometers or less are used for the actual functionality and more specifically to nanoparticles, roughly particles up to 100 nm in size in at least one dimension [see (European Commission 2011) for a refined definition]. Their small size causes them to have specific properties that are useful for widely varying purposes, such as antimicrobial and semiconductor properties or a colour that depends on the particle size. Not only the size and composition characterise nanoparticles, but also the crystalline structure, the form and the coating that is applied for functionalisation are important features (Baumann et al. 2014; Jarvie and King 2010).

Many applications of nanotechnology have been suggested, such as smart medicines that deliver the active ingredients at the desired location in the human body. However, to date most actual applications are found in consumer products like cosmetics, food and food packaging, paints and coatings (Hansen et al. 2016).

With the increasing use of nanoparticles in consumer products and industry the need to understand the possible consequences for human and environmental health is also increasing. This is reflected in the number of publications that concern the possible toxicological and ecotoxicological effects of these relatively new materials but also in the number of publications devoted to the release, transport and fate of nanoparticles in especially the aquatic environment (Peralta-Videa et al. 2011; Bour et al. 2015; Doiron et al. 2012; Farmena et al. 2012; Eduok et al. 2013; Fabrega et al. 2011; Gao et al. 2009). Of the many types of nanoparticles that have been studied, a small number is most commonly described in the literature: nanoparticles based on metal oxide, such as titanium dioxide, zinc oxide and cerium oxide, nanoparticles based on metal, for instance silver and iron, and carbon-based

Table 1 Number of publications reported by Google Scholar that mention nanoparticles of a particular material

Material	Total number of publications	Number of publications also mentioning "environment"
Carbon nanotubes	717,000	305,000
Fullerenes	64,900	39,000
Cerium (di)oxide	75,000	54,000
Copper oxide	1,130,000	390,000
Gold	1,280,000	697,000
Iron (zero-valent)	890,000	411,000
Silica	1,130,000	633,000
Silver	856,000	401,000
Titanium dioxide	179,000	103,000
Zinc oxide	436,000	184,000

nanoparticles, fullerenes and their derivatives, as well as carbon nanotubes. They are also the types most commonly applied in consumer products (Hansen et al. 2016). In Table 1 a summary is given of the number of publications that mention nanoparticles of a certain material.

When these nanomaterials enter the environment, they may have adverse effect on organisms through various mechanisms. The significance of these effects will depend on the actual exposure, which in turn depends on concentration and state of the nanomaterials. Understanding these factors is crucial to the assessment of the risks that nanomaterials present.

Some nanomaterials, like zero-valent iron nanoparticles, might be introduced deliberately to remediate soil contamination by a wide variety of substances (Cundy et al. 2008). In that case it will be necessary to understand how the nanoparticles are transported through the soil and subsequently how they get into contact with these contaminants and how they react with them. Similarly, nanomaterials like titanium dioxide are being investigated for the cleansing of wastewater (see for instance (Mohapatra et al. 2014b)).

An important issue that influences any research into the above questions is the fact that there are currently limited measurement techniques to detect and quantify nanoparticles in such complex matrices as natural waters or soils, although new techniques are being developed (Wagner et al. 2014).

Mathematical modelling techniques can be used to accommodate for this situation. In addition they can be used to analyse scenarios about current and future developments, for example when it comes to release into the environment via the waste stream. Modelling techniques can also help to design the use of nanomaterials for soil remediation or treatment of wastewater.

Another aspect of nanoparticles in the environment where modelling techniques can help is that of understanding and describing the various processes nanoparticles are subjected to, for instance aggregation but also dissolution and chemical transformation. These processes have consequences for the transport of nanoparticles but also for the potential ecotoxicological effects.

In this article publications on the various modelling approaches are reviewed. We focus on publications that describe models for the release, transport and fate of nanoparticles in surface water and soil. In particular, no attempt was made to comprehensively review the literature on modelling toxicity or ecotoxicity of this type of contaminants.

For the review the publications have been divided in three groups to clarify the sort of questions the described techniques can be applied to:

– *Small scale:* Several common theories recur, especially within the literature that deals with laboratory experiments. The DLVO theory, developed by Derjaguin, Landau, Verwey and Overbeek, is commonly used to predict or explain the stability of dispersions of nanoparticles by means of the potential energy caused by van der Waals forces and electrostatic repulsion. For transport of nanoparticles in soil almost all articles use the classical colloid filtration theory. To describe the aggregation of nanoparticles to clusters or adsorption to suspended particulate matter, often population balance theories are used. Here size classes of nanoparticles and aggregates of these particles are considered. An alternative approach is to use the advection-diffusion equation with additional terms to represent these and other processes.

  This type of modelling techniques is especially useful for understanding laboratory experiments, but some can also be applied in the studies into the transport and fate in the environment.
– *Intermediate scale:* The environmental compartments most commonly encountered are: soil and fresh water as well as "technical" compartments like waste-water treatment plants and waste incinerator installations. Surprisingly, no articles were found that consider the modelling of (engineered) nanoparticles in marine or estuarine environments.

  For the description of processes like aggregation and dissolution use can be made of the insights from "small-scale" modelling approaches. In addition, however, it is necessary to know or at least to be able to estimate the release of nanomaterials into the system under study. Here techniques that are generally applied with the large scale in mind can be useful.
– *Large scale:* Articles concerned with the large scale, be it the whole world, a country or a river basin, include: estimation of the world-wide production of nanoparticles, life cycle analysis and multimedia models that consider "generic," fully-mixed, environmental compartments (Mackay et al. 2001).

  Since to date we have no adequate data on the release of nanoparticles into the aquatic or terrestrial environment, we need to rely on analyses of their production, use in consumer products and the use of these products.

To some extent the spatial scale is correlated with the level of detail or the complexity of the modelling approach (see Fig. 1): the larger the spatial scale the less details are included in the modelling with respect to the processes that nanoparticles are subject to, and vice versa.
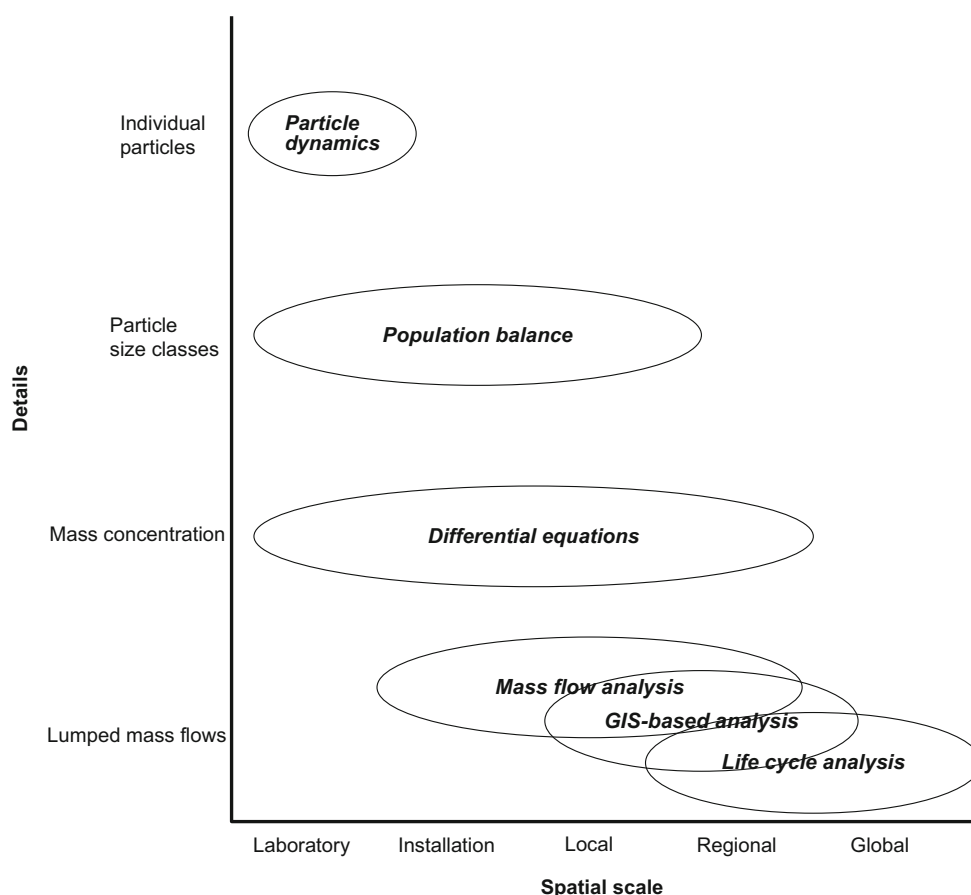
Fig. 1 Schematic classification of the various modelling methods. The vertical axis represents the level of detail these methods provide or require, whereas the horizontal axis represents the spatial scale at which they are typically applied

It is not always possible to strictly distinguish between modelling techniques. Often an actual model will combine several of the techniques described here. For instance, a "global" technique such as life cycle analysis requires some understanding of the behaviour of the contaminants in the environment and a model focusing on the transport of nanoparticles in a river system relies on estimates of emissions obtained perhaps from analyses of production data. The classifications presented here serve as a tool for discussion and interpretation.

In the present article we provide an overview of the modelling approaches that have been published to date. These modelling approaches all have their pros and cons, while none is suitable to answer all questions. Which one to choose depends on the particular questions that need to be answered. Spatial scale and level of detail as well as the environmental compartment of interest determine to a large extent which approach is suitable. Therefore the article concludes with some suggestions as to how to choose the most appropriate model.

2   Previous Overviews and Critical Publications

The literature on nanoparticles has been summarized in many reviews, concentrating on specific aspects. The subject of modelling the release, transport and fate of nanoparticles is no exception. Each group of authors of course has their own emphasis and goal with these reviews. For instance, Hendren et al. (2013a) have reviewed the various approaches to modelling environmental exposure with specific emphasis on the use for risk-based decision making. A particular point of attention is whether the approaches allow for handling uncertainty: the scarcity of experimental and environmental data regarding the fate of nanoparticles make it necessary to explicitly deal with this issue. They plea for the use of methods such as probabilistic modelling and sensitivity analysis and for a closer cooperation between modellers and experimentalists.

The overview by Wagner et al. (2014) is meant to highlight the differences and the similarities between engineered and natural nanoparticles. They describe the range of environmental processes that nanoparticles are subject to and use generally encountered modelling concepts to illustrate these processes.

In a more or less similar way, but with emphasis on the modelling techniques, Dale et al. (2015a) present an introduction to the current state of fate models for nanoparticles. Their message is that while much progress has been made over the past years, existing fate models concentrate on processes such as heteroaggregation, dissolution and sedimentation (see Fig. 2). However, current models cannot account for the influence of coatings or the various environmental conditions, such as pH, temperature and the presence of oxygen and sulfide.
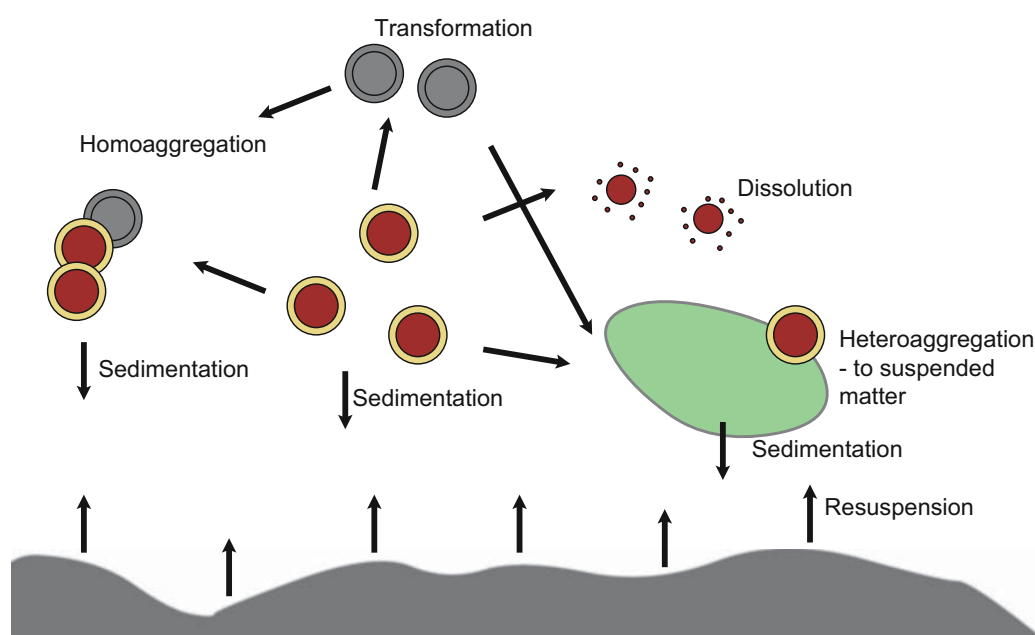
Fig. 2   Sketch of the most important processes that nanoparticles are subject to. [Reproduced from (Markus et al. 2015)]

Praetorius et al. (2014) argue about a particularly common approach to deal with one aspect of the fate of nanoparticles, i.e. the adsorption of nanoparticles to suspended particulate matter (SPM), and the misuse of the concept of partition coefficients in models to describe this phenomenon. They observe that, unlike ordinary, dissolved, contaminants, nanoparticles form an unstable suspension, where there is no thermodynamic equilibrium. The absence of such an equilibrium is the reason partition coefficients cannot be used for describing the adsorption of nanoparticles.

Other aspects of the fate of nanoparticles in the environment have been the subject of critical examination too. Goldberg et al. (2014) conclude after examining the performance of various models for the transport of nanoparticles in saturated soil, that none of the existing models is really satisfactory. Instead of abandoning these models, however, they suggest to investigate the performance of the models separately for retention profiles and breakthrough curves. Furthermore they suggest to critically examine the available data and to make sure that the data are sufficient for calibrating the models.

General guidelines with respect to the use of multimedia models can be found in a publication by Buser et al. (2012). While they do not consider nanoparticles, their advices should hold for any model that employs the multimedia idea (see also Sect. 5.1). The gist of these guidelines is:

– The purpose of the modelling should be clear, that is: what decision-related questions are considered, what substances are relevant in what environmental setting and what are the technical requirements for the modelling.
– The modelling should be reproducible by independent researchers, so that it is necessary to describe what model is used and what input is used, for example, besides emission data also the model parameters. Also document the origin of these data.
– Describe the output of the model and show via a sensitivity analysis what input data have the largest influence on the output. Furthermore the limitations of the model and the limits of the applicability of the results should be clarified. This will help researchers and decision makers to interpret the results.

A comprehensive comparison between experimental studies and modelling studies has been made by Gottschalk et al. (2013), with the conclusion that the two types of research are in fact largely in agreement as to the expected concentrations of engineered nanoparticles in the environment (see also Table 2). They refer to knowledge gaps and scarcity of data with respect to production, application and release, but also to the problem that model results and measurements do not always allow for a comparison due to the differences in particle size and form that are studied.

Table 2 Concentrations of engineered nanoparticles in surface water and soils (treated with sewage sludge and untreated)—results of modelling studies and direct measurements. Adapted from (Gottschalk et al. 2013)

Type of nanoparticle	Water (µg/l)	Soil (µg/kg)
nano-TiO$_2$ (modelled)	$2 \times 10^{-2} - 10^1$	$7 \times 10^{-5} - 2 \times 10^3$
nano-TiO$_2$ (measured)	$3 \times 10^{-1} - 10^1$	–
nano-Ag (modelled)	$10^{-5} - 4 \times 10^{-1}$	$8 \times 10^{-5} - 4 \times 10^{-1}$
nano-Ag (measured)	$7 \times 10^{-3} - 3 \times 10^{-3}$	–
nano-ZnO (modelled)	$2 \times 10^{-4} - 10^{-1}$	$4 \times 10^{-1} - 3 \times 10^2$
carbon nanotubes (CNT; modelled)	$10^{-5} - 10^{-3}$	$10^{-2} - 2 \times 10^0$
fullerenes (modelled)	$2 \times 10^{-5} - 10^{-4}$	$7 \times 10^{-4} - 2 \times 10^{-1}$
CeO$_2$ (modelled)	$7 \times 10^{-3} - 7 \times 10^{-1}$	–

3 Small-Scale Modelling

Crucial to most if not all modelling techniques is the idea that some form of conservation law applies. Often it is the mass of a substance that must conform to a balance equation. If a substance leaves one compartment due to transport, then the mass that is removed from that compartment must be added to that in the receiving compartment, unless some chemical process transforms the substance into a different substance. Population balance models, however, deal with the number of particles (the population) of similar size and composition instead of the mass. With this type of models the number of particles evolves according to a conservation law. Particles can aggregate into larger particles, thereby changing to a different size—the number of small particles is reduced and the number of large particles is increased.

Both the number of particles and the mass of the particles are useful measures, but they require different modelling approaches. As discussed in Sect. 6.3, which measure is the most appropriate for quantifying the exposure is a matter of debate (see also (Grieger et al. 2010)), but both model types can be used in combination with a hydrological model to predict the transport of nanoparticles.

The strong point of this type of modelling is that it can help us better understand the processes that are involved. Some of the modelling techniques are directly applicable in larger-scale models, but some like the particle tracking require too much resources and instead the insight they provide has to be translated for the larger scale.

3.1 Population Balance Models

One of the processes that determine the fate of the nanoparticles in the environment, is the clustering of these particles, either forming homogeneous clusters, so-called

homoaggregation, or clusters with clay and organic particles in the micrometer range, so-called heteroaggregation (see Fig. 2). Many authors seek to describe these processes in terms of the number of particles and clusters of a particular size, e.g. Degueldre et al. (2009).

The "free" nanoparticles and the nanoparticles in clusters are divided into size classes and equations are developed to describe the evolution of the number of particles and clusters in each size class [see Appendix A for details; (Quik et al. 2014)].

The collision rates that determine the formation and destruction of clusters of particles can be related to the properties of the particles and the surrounding water (Praetorius et al. 2012; Arvidsson et al. 2011). The equations can be extended to include such processes as sedimentation to or resuspension from the water bottom, as these processes also influence the number of particles in surface water systems.

In principle one needs to distinguish size classes of all sizes, but in practice a reasonable limit is chosen, based on the idea that ever larger clusters are very rare. The introduction of SPM like clay or organic particles to describe heteroaggregation makes the population balance equation more complicated and some simplifications must be made. Quik et al. (2014) for instance analysed the equations for possible simplifications and on this basis applied the assumption that only clusters of nanoparticles exceeding a critical size and nanoparticles attached to SPM, are subject to sedimentation. This simplifies the mathematical model, as now essentially only two classes have to be distinguished. In a follow-up study, using a numerical model which could deal with the extra complexity, Quik et al. did distinguish several size classes (Quik et al. 2015).

Atmuri et al. (2013) combined the population balance approach with the DLVO theory (see Sect. 3.5), to predict different regimes of aggregation, at varying salt concentrations. Some tuning of the various model parameters was required and the aggregation rates they predicted were much faster than those observed.

3.2 Mass Concentrations

A drawback of population balance models is that they involve a large number of parameters (the collision rate coefficients for the various interacting classes), even if simplifying assumptions like one value for all collision rate coefficients k_{ij} can be made, but also require arbitrary choices, such as the number of size classes to distinguish. A further drawback is that the number concentration is much less intuitive than the mass concentration. In some areas of environmental science the number concentration is widely used, for instance in atmospheric pollution studies, but it is not often used in connection with the aquatic environment.

The classical representation of concentrations as mass concentrations can, however, be used for nanoparticles just as it is used for dissolved substances. For instance, Brunelli et al. (2013) used a first-order differential equation, $dC/dt = -kC$, to find the sedimentation rate coefficient k of titanium dioxide

nanoparticles in the diverse natural and synthetic waters in their study. The coefficient thus obtained is specific for each experiment. The results can not readily be applied to other experiments or natural systems.

Markus et al. (2015) used a set of differential equations linking the mass concentrations of various fractions of nanoparticles to develop a more extensive model of the sedimentation and aggregation processes. They applied it to published laboratory experiments and derived a more or less universal set of process parameters, so that application to other systems is possible.

3.3 Dissolution

An important property of nanoparticles is the solubility of the material, as it determines the rate at which ions are released and therefore determines at least part of the toxicity (Beer et al. 2012). The solubility depends on the material the nanoparticles are made of, including the coating, and can be influenced by other chemical transformations, such as the formation of sulfides in the case of silver (Dale et al. 2013; Levard et al. 2012). Both silver and zinc oxide nanoparticles are known to dissolve to some degree. Other commonly used inorganic nanoparticles, such as cerium dioxide and titanium dioxide, are much less subjected to chemical transformations or dissolution.

Dissolution of silver nanoparticles turns out to be a complex process, which involves the oxidation of silver to silver ions and may lead to the formation of silver sulfide (Levard et al. 2012; Liu et al. 2011a). In general the rate at which nanoparticles dissolve depends on the size, as shown experimentally by David et al. (2012), as well as Zhang et al. (2011). The use of the Oswald-Freundlich equation, which relates the solubility to the curvature of the particles' surface, to explain the size-dependence was criticised by Kaptay (2012). The thermodynamic exposé he presents shows that the effect is caused by the specific surface area instead. Mihranyan and Strømme nevertheless invoked this same equation to study the solubility of nanoparticles with a rough surface, instead of the often assumed ideal spherical shape (Mihranyan and Strømme 2007). They found that the solubility is significantly enhanced with respect to the classical theory.

Zhang et al. (2010) studied the effect of size on the dissolution of zinc sulfide nanoparticles, but they also included the effects of pH. The net effect is rather complicated, as it is influenced by the chemistry of the nanoparticles and the coatings that are applied. What is clear, however, is that both particle size and pH strongly influence the dissolution. To explain the effects, Zhang et al. used a thermodynamic analysis.

David et al. (2012), Zhang et al. (2011), (2010) have presented data on the dissolution kinetics of zinc oxide, silver and zinc sulfide, respectively, that show a timescale of one to several hours before the equilibrium concentration is reached. This means that dissolution is a fast process, at least in the circumstances they studied.

In contrast to these findings, Lowry et al. (2012) mention that in their constructed wetland not all silver is transformed into silver sulfide, even after 18 months. Some 30 % is still bio-available. Thus the time scale for these processes can vary widely and there is little understanding what causes the difference.

## 3.4 Chemical and Physical Reactivity

As already mentioned in the introduction, to date few, if any, models are capable of handling the various environmental factors that influence the fate of nanoparticles (Dale et al. 2015a). This includes the pH and the ionic strength of the water. Work by Kaegi et al. (2011), Brunetti et al. (2015) and Dale et al. (2013) has shown the importance of sulfidation for silver nanoparticles. As silver sulfide is virtually insoluble in water, whereas silver is soluble, this has consequences for the fate of silver nanoparticles. Due to sulfidation a shell is formed around silver nanoparticles and the nanoparticles persist as particles, whereas zinc oxide nanoparticles may completely dissolve.

Other aspects of the interactions between nanoparticles and their surroundings, such as the photocatalytic properties, receive only little attention in the context of modelling. As an exception, Hotze et al. (2010) developed a framework for predicting the reactivity of aggregates of nanoparticles, for instance the generation of reactive oxygen species (ROS) by fullerenes and their derivatives. According to their theory aggregates of nanoparticles may be much more reactive than one would expect from measurements of the ROS generation by separate nanoparticles. As nanoparticles mostly exist as aggregates, this means that for the proper modelling of ROS generation aggregates will have to be treated separately.

3.5 DLVO Theory

The most commonly used theory to explain the aggregation behaviour of nanoparticles is the classical DLVO theory developed by Derjaguin and Landau and independently by Verwey and Overbeek, in the 1940s, with or without extensions specific to nanoparticles (Wikipedia 2015). Petosa et al. (2010) provide an overview of the different approaches to describe aggregation and deposition of nanoparticles, including the various phenomena that are not considered in the classical theory. In their publication deposition is to be understood as the deposition of nanoparticles on macroscopic surfaces or the surfaces of particles in the micro- and millimeter range.

In its simplest form the DLVO theory predicts the potential energy between a colloidal particle and a (macroscopic) surface or between two colloidal particles as the sum of electrostatic and van der Waals forces. The two parameters in this theory, the Debye-Hückel length and the Hamaker constant, both depend on the
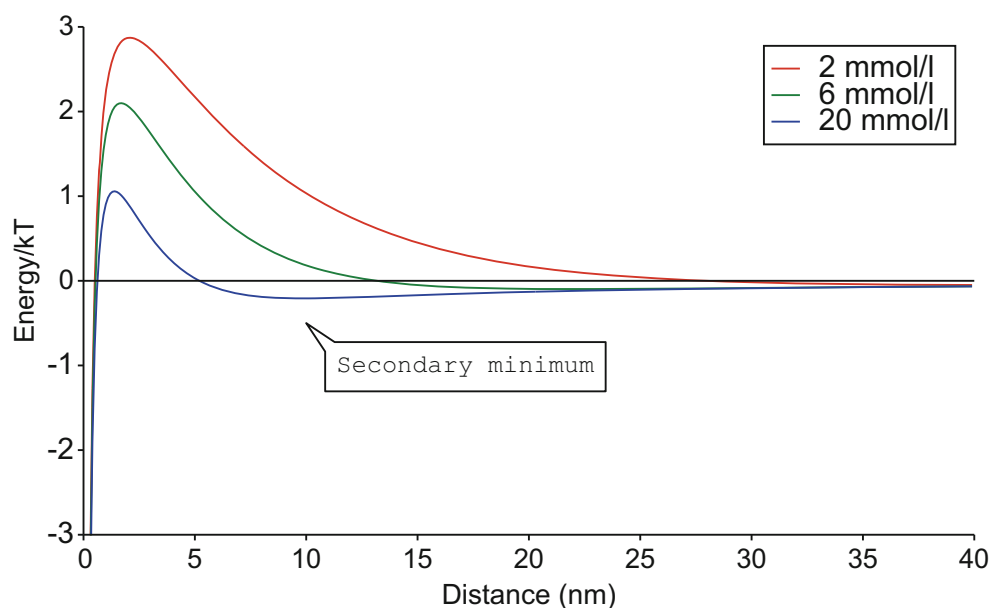
Fig. 3 Illustration of the interaction energy according to the DLVO theory, with different ionic strengths. The secondary minimum, visible in one curve, can cause the particles to form loose aggregates. The inverse Debye-Hückel length was set to $\sqrt{(I)}/0.3$ nm, I being the ionic strength in mol/l.

ionic strength of the medium. The Hamaker constant also depends on the characteristics of the colloidal particles and the surfaces in question. The theory is used to examine if there is a minimum in the potential energy, which indicates whether the colloidal particles remain separated or instead aggregate in this minimum (see Fig. 3).

While DLVO theory generally includes these two forces to describe the stability of a suspension of nanoparticles, one frequently needs to deal with magnetic forces, e.g. when iron nanoparticles are involved, steric interactions as well as hydration forces. These effects lead to extra terms in the expression for the potential energy.

Magnetic forces in particular have been studied by Phenrat et al. (2007). Their experimental evidence confirms that the magnetic attractive forces of iron nanoparticles cause an enhanced aggregration compared to non-magnetic nanoparticles. This has consequences for the application of such particles in soil remediation projects. They recommend to use the aggregation size rather the size of individual particles to characterize the nanoparticles in analyses.

Li and Chen (2012) applied an extended form of the DLVO theory to their experiments with the aggregation of cerium dioxide nanoparticles in aqueous solutions with varying ionic strengths and concentrations of humic acids. They concluded that this extended theory fits the experimental results well. Of particular interest is that humic acids in some circumstances appear to hinder aggregation but in other circumstances promote aggregation. The latter occurs when a sufficiently high concentration of a divalent electrolyte is present.

Besides postulating the form that the potential energy expression should have, given the various forces acting on the nanoparticles and determining from that the

behaviour of a suspension, one can also simulate the behaviour of collections of nanoparticles (see also Sect. 3.6). Two publications relating the DLVO theory to such simulations are: Macpherson et al. (Macpherson et al. 2012) who investigate the effect of the Hamaker constant and the particle concentration on the aggregates that are formed and Dahirel and Jardat (2010) whose review describes under which circumstances DLVO theory is not an adequate approach. The particle tracking techniques on which these articles rely may in principle allow us a better understanding of the aggregation behaviour, but they also show that the details of the process depend on many aspects of the medium and of the nanoparticles in question. At present particle tracking is not suitable for studying practical questions.

3.6 Particle Dynamics

Several publications have been dedicated to the structure of the aggregates that are formed during the aggregation process with the intention of better understanding the properties of these aggregates and how they are related to the properties of the nanoparticles. Two modelling approaches are described:

– Model the motion of individual nanoparticles as a consequence of Brownian motion and the forces between the nanoparticles, for which the DLVO theory with or without extensions is commonly used. An example of this approach is given by Peng et al. (2010) and to a lesser extent, as it focuses on particles of micrometer scale, by Satoh and Taneko (2009). In both cases simulation of the motion of individual particles and the subsequent formation of aggregates is used to determine how fast the aggregates are formed and what the size and other characteristics are.

   Tracking individual particles is a computationally intense method, since large numbers of particles are involved with interactions between pairs of particles or aggregates. Liu et al. (2011b) mention that for their simulations concerning a population of 10,000 particles, where new particles were inserted into simulation after an aggregate was formed to keep the population at the same number, the computer required 15 days to complete the task.

   An alternative mathematical approach, used by Lattuada et al. (2006), seeks to describe the dynamics not in terms of individual particles, but rather as size populations. While this approach is closely related to the population balance models (Sect. 3.1), they emphasize the process of aggregation as influenced by the forces between the particles, not the effects on the size distribution.

– Use the concept of fractals to characterize the geometry of the aggregates—a large fractal dimension means that the aggregates are compact, whereas a small fractal dimension indicates a loose structure. This has consequences for the reactivity of the aggregates, as the available surface area depends on the geometry. Zhou and Keller (2010) used this concept to determine the character of

aggregates that result in the so-called reaction-limited regime of aggregation (RLCA) and the diffusion-limited regime (DLCA), where they used both spherical and irregularly shaped nanoparticles.

Furthermore, the concept of a fractal dimension was used by Di et al. to describe the effect of aggregation on the dissolution of silver nanoparticles (He et al. 2013). This resulted in a model to predict the release of silver ions under different environmental circumstances, which is important for the prediction of the toxicity of this type of nanoparticles to organisms.

4 Intermediate Scale: Environmental and Technical Compartments

The second category of models holds the middle ground between small-scale modelling techniques, concerned with the details of the physico-chemical processes, and large-scale techniques where these processes are described mostly with semi-empirical relations. The approach of this category of models is to consider the processes to which the nanomaterials are subject, using the insights obtained from small-scale modelling, as described in the previous section, in conjunction with the detailed hydrology or hydrodynamics of the system in question.

4.1 Groundwater and Soil

Various authors, for instance Müller et al. (2013) and Gottschalk et al. (2013), have concluded that most nanoparticles end up in landfills, because the ash left after sewage has been incinerated will be stored there, or in soil, when sewage sludge is used as fertilizer. Thus, understanding the fate of nanoparticles in these environmental compartments is of paramount importance. Quite a few publications have been devoted to this problem, but the majority focuses on the behaviour in idealized soils, for instance glass beads or clean sand (Ben-Moshe et al. 2010; Li et al. 2011). While such artificial soils are much easier to define and characterise, the question is whether they can indeed be representative for what happens in real soils. Also the preparation of the columns in which the experiments are performed may influence the results: columns made out of glass beads will not have the sort of inhomogeneities that real soils have, such as cracks, inclusions of other material and so on (Fang et al. 2009).

When it comes to modelling the transport of nanoparticles in soils, be they real or idealized, most authors use classical filtration theory to explain the form of the breakthrough curves and retention profiles—properties like the time the contaminants appear in the water that has passed through the column and the total amount of

contaminants that actually leave the column versus the amount that was injected (Liang et al. 2013). The classical filtration theory is summarised in Appendix A.

The retention of nanoparticles, that is, either adsorption to the soil particles or blocking because the nanoparticles are too large for the canals between the soil particles, is most often described via an exchange between a mobile fraction and an adsorbed fraction. It is then assumed that the exchange is governed by first-order processes (adsorption or, as it is often also called, deposition to the soil particles and release into the water phase), whose rate coefficients have to be determined empirically (Li et al. 2011).

Little is known about the adsorption and desorption rate coefficients, but Tufenkji and Elimelech (2004) have developed a semi-empirical formula for the collision rates of colloidal and nano-sized particles with the soil as a consequence of various transport mechanisms. Unfortunately, to calculate the net attachment rate, one also needs to know the efficiency by which such collisions lead to a permanent attachment. Badawy et al. (2013) actually used the theoretical relations presented by Tufenkji and Elimelech to estimate the adsorption efficiency (see Appendix A).

Goldberg et al. (2014) published a critical overview of the various model formulations that have been used to explain the observed retention profiles and breakthrough curves. Their conclusion was that complicated models do not necessarily explain the laboratory experiments better than simpler models. A crucial point of concern is that the data obtained in the experiments must enable the determination of the various parameters in the model. Alternatively, the model formulation should allow experimental determination.

Besides column experiments several authors present studies of the transport in two or three dimensions. Bai and Li (2012) for instance studied the distribution of fullerenes (nC_{60}) using a groundwater model extended with the relevant attachment processes (MT3DMS) and Cullen et al. (2010) modelled the mobility of carbon-based nanoparticles (fullerenes and various types of carbon nanotubes) in a field with heterogeneous permeability to mimic the environmental conditions. The basic description of the processes involved is in both cases very similar to what is described above.

Areepitak and Ren (2011) and Boncagni et al. (2009) also used colloid filtration theory to describe the exchange of nanoparticles between a stream and its streambed. In this situation an additional complication exists, however, namely that water is exchanged between the stream and the bed under wave action. Just as in the column experiments discussed above the adsorption efficiency is an important parameter.

The NanoRem project takes a markedly different approach (NanoRem 2015). The purpose of this project is to further develop methods for soil remediation using nanoparticles like nano zero-valent iron. Besides experiments to elucidate the behaviour of nanoparticles in the soil and the ecotoxicological aspects the project involves modelling the behaviour of nanoparticles at pore level. The advantage of this scale is that fundamental physical laws can be applied to describe the behaviour of the particles. The phenomena that are observed on this microscopic scale are then to be translated to a macroscopic scale, so that they can be applied in a groundwater like MODFLOW (USGS 2015). This is work in progress.

4.2   Surface Waters

The current literature contains a small number of publications that focus on the modelling of the transport of nanoparticles in freshwater bodies. No publications were found that consider marine or estuarine water systems.

Praetorius et al. (2012) developed a model for titanium dioxide in the river Rhine, based on earlier work by Blaser et al. (2008). The hydrodynamics of the Rhine was modelled schematically, using a series of boxes, in which river flow, bed load transport and interaction with the sediment are distinguished. The processes nanoparticles are subject to, sedimentation, homoaggregation and hetero-aggregation, were modelled using a population balance approach (see Sect. 3.1 for some details and Fig. 2). Crucial in this model is the efficiency of the heteroaggregation process. To gain insight in its effect on the distribution of the titanium dioxide nanoparticles, they used a range of values, 0.001–1, for the aggregation efficiency in their model simulations. Other influences on the aggregation process, were modelled explicitly: Brownian motion, fluid motion and differential settling (Elimelich et al. 1998).

The same modelling technique was applied to the lower Rhône river in France by Sani-Kast et al. (2015). Their purpose was to overcome some limitations of the models to date, namely the lack of spatial and temporal variability and to analyse the effect of widely varying environmental conditions, that is, variations in the water chemistry. To this end the model was run with a wide range of conditions and the results were analysed using cluster analysis. Heteroaggregation was found to be a significant factor: if the circumstances favour the attachment of nanoparticles to SPM, then other factors like the water chemistry had little influence on the transport and fate.

A different approach was taken by Dale et al. (2013) in their study of the fate of silver nanoparticles in freshwater sediments. The objective was to develop a model that can predict the distribution of these nanoparticles in the sediment and the speciation of the silver. Chemical transformation of silver into silver sulfide is a relevant environmental process, because it influences the toxicity of the silver: silver sulfide is almost insoluble and therefore not biologically available, whereas metallic silver and especially silver ions are. The model they developed predicts that the resulting coating of the nanoparticles with silver sulfide reduces the release of silver ions. In a later publication (Dale et al. 2015b) they elaborated on this work for other types of nanoparticles, such as the chemical transformations that zinc oxide nanoparticles are subjected to.

Quik et al. (2015) used a population balance model with five size classes of both engineered nanoparticles and natural suspended solids to describe the transport of nanoparticles in rivers, using a Dutch river for a case study (see also Sect. 3.1). Their main conclusion is that both spatial heterogeneity and particle size distribution should be explicitly modelled. They found that ignoring this factor could lead to an underestimate of the concentrations in the sediment by a factor 20.

In a follow-up study from (Markus et al. 2015, 2016) describe the application of their model for the aggregation and sedimentation processes to the transport and fate of metallic nanoparticles (zinc oxide, titanium dioxide and silver) in the river Rhine (Markus et al. 2015). The basis for this work was a hydraulic model of the Rhine from Basel in Switzerland up to the central parts of the Netherlands. They studied several scenarios regarding the release of nanoparticles through wastewater: one assuming only release via the wastewater treatment plants and others assuming an additional diffuse emission due to leaching of nanoparticles from land-applied sewage sludge. The model calculations showed that the contribution of zinc oxide nanoparticles in terms of mass is likely in the order of 5–10 % of the observed zinc concentrations.

4.3 Wastewater Treatment Plants and Other Technical Compartments

The so-called technical compartments, wastewater treatment plants (WWTP), waste incineration plants (WIP) and others, are a subject of study for several reasons. First of all, they form a buffer between the waste stream from households and industry on the one hand and the environment on the other. The most important aspects are then: can they filter out the engineered nanoparticles and to what extent does the passage alter the character of these materials? Secondly, one can actively use nanoparticles to clean the wastewater, for instance using the photocatalytic properties of titanium dioxide nanoparticles to reduce organic micropollutants (Mohapatra et al. 2014b).

Benn and Westerhoff (2008) investigated the release of silver from commercial textiles and the fate of this silver in a WWTP. They used a straightforward mass-balance model with non-linear sorption to predict the distribution of the silver over effluent and sewage. The conclusion was that much of the silver will be retained in the sewage sludge, which as a consequence may no longer be suitable as a fertilizer. Note, however, the critique by Praetorius et al. (2014) as this model assumed a thermodynamic equilibrium (see Sect. 2).

A comparable approach was taken by Yang et al. (2015) to analyse the experimental results they obtained with a sequential batch reactor (SBR) to simultaneously remove nanosilver and fullerenes from wastewaster. In the experiments 95 % of the fullerenes and 90 % of the silver was removed. The authors claimed that the distribution coefficients they found can be used to predict the removal of nanoparticles in such installations.

Mahmoodi et al. (2008) used titanium dioxide nanoparticles, fixed to polymer membranes, to degrade an organic pollutant of agricultural origin, fenitrothion, via the photocatalytic action of these nanoparticles. The degradation process was modelled using first-order decay. Their full model was one-dimensional, in order

to describe the complete experimental set-up, but they made no effort to model the photocatalysis explicitly.

The role of waste incineration in the fate of nanoparticles has been discussed above (see Sect. 5.2). Roes et al. (2012) indicates that not all nanoparticles will actually be caught in the residue but will instead escape via the off-gas. This holds especially for particles smaller than 100 nm. The authors use a conceptual model of WIPs and results from previous studies, combined with technical details of the various types of WIPs in use to arrive at their conclusions.

4.4   Probabilistic Methods

In general the fate of nanoparticles in natural waters or in technical installations, like wastewater treatment plants is poorly understood, as a consequence of the difficulty of measuring the concentrations and the wide variety of circumstances that influence the processes. In order to deal with these uncertainties probabilistic methods are often used, where inputs into the system and process coefficients are varied, to gain insight in the range of emissions and concentrations.

In the literature one can find at least two categories of probabilistic modelling approaches that are of interest here: Monte Carlo simulations (MC) and "direct" probabilistic modelling. MC simulations are often used to quantify the distribution of the output parameters the authors are interested in. For instance Barton et al. (2015) used the technique to estimate the removal of three types of metal and metal oxide nanoparticles in wastewater treatment. The reason for using an MC technique is that the parameters involved are not known with any precision. They applied a large number of random values for these parameters and then determined a probability distribution of the emission of nanoparticles (see also Sect. 5.2).

Hendren et al. (2013b) also used this technique for modelling the fate of silver nanoparticles in wastewater treatment. One characteristic of this approach is that one needs to assume a reasonable distribution for the various parameters, so that the output is more or less realistic. Choosing such a distribution may not be trivial (see also Section and the analysis by Ferson et al. (2001).

Probabilistic modelling can take a different form as well, as illustrated by Jacobs et al. (2015). They used the results of a previous deterministic study regarding the use of silica nanoparticles in food to quantify the various sources of uncertainty. The most important were the uncertainty in the dose causing effects (the benchmark dose), variation among individuals and the extrapolation from subchronic to chronic effects. All parameters do not have an equal contribution to the total uncertainty and by focussing on the most important parameters efforts to reduce the uncertainty become more efficient.

5 Large-Scale Modelling

As stated in the introduction, several techniques are used for answering or analysing regional or even global issues. They have in common that the transport of contaminants between the various parts of the system under study is described via general concepts such as transfer coefficients instead of via hydrodynamic or hydrological models (Mackay et al. 2001). Geographical details are often "lumped," which leads to the representation of the system via a number of interacting "boxes," all with their own characteristics. The exception to this is the use of GIS as a modelling tool.

5.1 Multimedia Models

The purpose of multimedia models is to determine the distribution of a contaminant, in this case of nanoparticles, over various environmental compartments but often also over so-called technical compartments. The latter type is used to be able to deal with relevant industrial processes, such as the production of nanoparticles or the effects of wastewater treatment on the release into the environment. In the context of this review environmental compartments include: surface water (mostly inland waters), effluent, sludge, air and soil (see Fig. 4).

The interaction of one compartment with another is often very complex. For instance incineration of sewage sludge may bring nanoparticles into the atmosphere (Buha et al. 2014), so that they are spread via the wind but later they are deposited on the soil due to rainfall or sedimentation of the particles. Taking all details into account is an almost impossible task and therefore multimedia models often
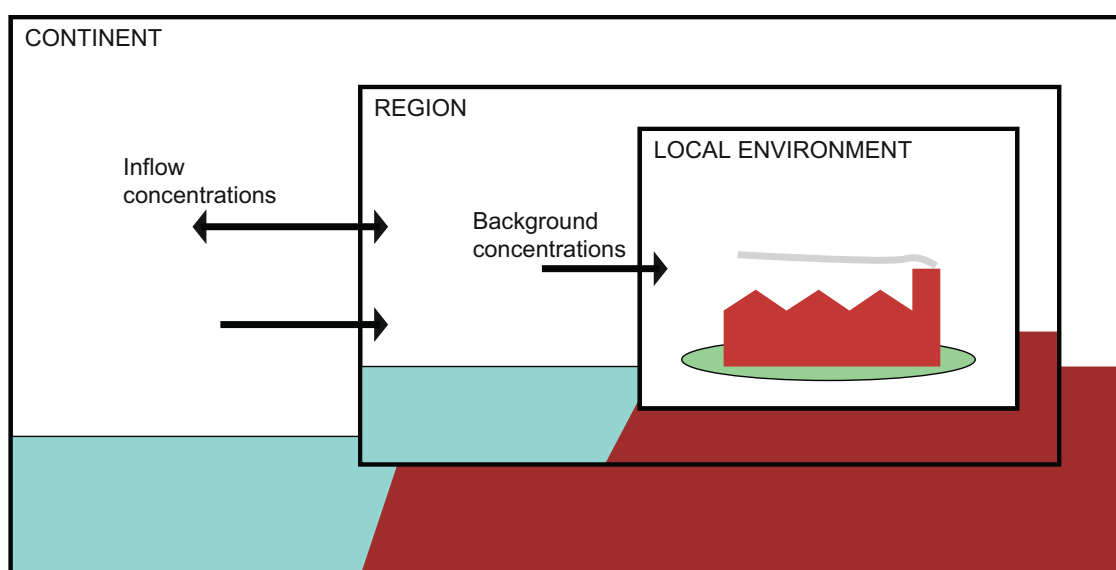
Fig. 4 Example of the set-up used in multimedia modelling. The area of interest is conceptually divided into "boxes," called "unit worlds" in Mackay et al. (2001), between which matter is exchanged. Adapted from (Mackay et al. 2001)

aggregate the details into a small set of exchange processes that work on "generic" compartments. Instead of describing every single river or agricultural area, a generic river and a typical piece of arable land are considered. A mass balance calculation is then used to calculate the final (average) concentrations that occur in each compartment as a function of the inputs into the whole system.

Within the literature specifically concerned with nanoparticles two articles in particular apply this type of modelling: Meesters et al. (2014) and Liu and Cohen (2014). The models differ in the emphasis on particular processes: Meesters et al. use a mechanistic approach, so that aggregation in surface water and deposition through rain on soil are explicitly described, while Liu and Cohen rely exclusively on exchange coefficients.

Some authors argue that the processes that need to be taken into account can be described via simple first-order expressions (Quik et al. 2011). The main argument for this approach is that to date there is too little quantitative information to justify a more complicated description.

Multimedia models are particularly suited for screening purposes: to identify where contaminants will end up and to estimate at least the order of magnitude of the concentration in the entire environment. If one seeks a more or less global approach, then multimedia models are certainly a good candidate (Westerhoff and Nowack 2013).

5.2 Material Flow Analysis and Exposure Modelling

The goals of material flow analysis (MFA) are less all-embracing than those of multimedia models in the sense that the focus is on tracing mass flows for instance from wastewater produced by households to receiving surface waters, instead of considering all environmental compartments. But in common with multimedia models MFA uses transfer coefficients to describe the flow of contaminants from one compartment to the next. More emphasis is put on dealing with the uncertainties in the transfer coefficients and emission estimates by using probabilistic techniques (Sun et al. 2014; Gottschalk et al. 2010a, b).

Basically, for each transfer coefficient a likely probability distribution is estimated, which can be as straightforward as a uniform distribution, defined by a minimum and a maximum value or which can have a more complicated form. The model is then run for a large number of values for the transfer coefficients drawn from the probability distributions and from these runs one can determine the shape of the distribution of emissions to or the concentrations in the environment.

Figure 5 shows possible sources and pathways of contaminants in waste (Dutch National Government 2015). Each source may contribute to the total emission via the given pathways. Such a schematisation may be used as the basis of a deterministic calculation, if sufficient knowledge is available for estimates, but also a probabilistic calculation (see also the discussion in Sect. 6.1). In essence the various sources of nanoparticles or other contaminants are traced via recognised pathways
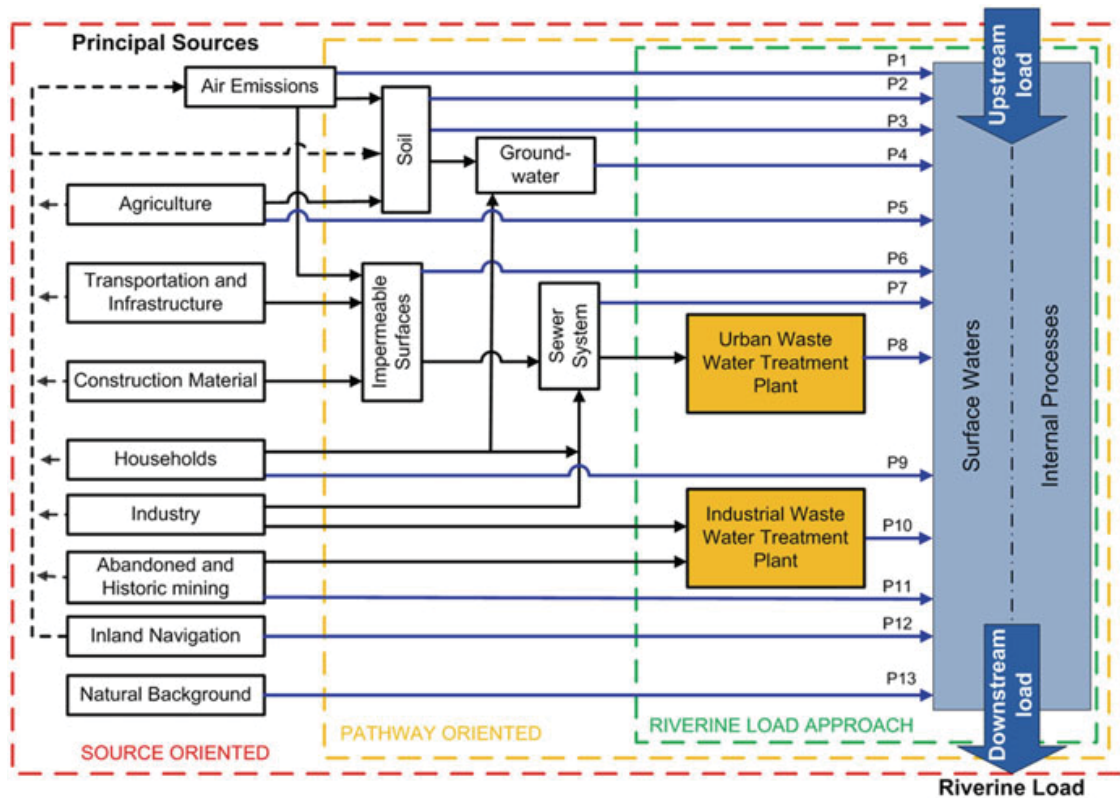
Fig. 5 Sketch of the contributions and pathways of wastewater containing nanoparticles (Dutch National Government 2015)

to the receiving aquatic environment, making the estimation of the total emission possible.

Müller et al. (2013) used such a probabilistic technique to gain insight in the fate of various types of engineered nanoparticles during waste handling processes such as the incineration of sewage sludge. Buha et al. (2014) compared their model results based on probabilistic MFA with their measurements of particle sizes in fly ash. Their study demonstrated that nanoparticles may survive the incineration process and even that new nano-sized particles may be formed.

Koehler et al. (2011) considered the incineration process in greater detail, showing that these models are not limited to global set-ups but can be used for detailed analyses. That does not mean, however, that such models are applicable everywhere: the transfer coefficients the model relies on have to be measured or estimated in some way and often the lack of detailed information will hinder such estimation. If the transfer of material from one compartment to another cannot be described as a linear process, the modelling needs to be adjusted to accommodate an alternative mathematical description or a different approach needs to be taken.

Müller et al. (2013) included both waste incineration plants and landfills in their study. While some aspects are specific to the situation in Switzerland, notably the fact that almost all sewage sludge is incinerated, their analysis predicted that most engineered nanomaterial will end up in the slag resulting from the incineration process and therefore eventually in landfills. Other mass flows were smaller by at

least an order of magnitude. Of the nanoparticles they examined, titanium dioxide is the most important one—the mass flows of zinc oxide, silver and carbon nanotubes are smaller by at least one or two orders of magnitude.

Furthermore, they concluded that most data in the literature relate to *mass* as the determining quantity, whereas sometimes the *number of particles* is preferred, especially in the context of ecotoxicology. This point was also addressed by Arvidsson et al. (2012), who used a variant of MFA to directly predict the number concentrations of titanium dioxide nanoparticles [see also (Arvidsson 2012) and Sect. 6.3].

A necessary input for material flow analysis to provide an estimate of the emissions of nanoparticles to any environmental compartment is that we have estimates or, preferably, tangible data about the number or concentration of nanoparticles or any other contaminant that is being put into the waste. To this end several authors have attempted to make an inventory of the use of nanoparticles in consumer products and industrial processes at various scales: local, regional and global (Keller and Lazareva 2014; Robichaud et al. 2009; Lorenz et al. 2011; Piccinno et al. 2012). Some of these efforts consider only a single type of nanoparticle, like Robichaud et al. (2009), who focussed on titanium dioxide nanoparticles, while others consider a very broad spectrum, like Lorenz et al. (2011), who identified the possible exposure of consumers in Germany to engineered nanoparticles in general.

The problem is that no reliable sources of information on the actual use of nanoparticles in consumer products exist. Even a much quoted database as the one from the Woodrow Wilson Institute is inaccurate and incomplete (Berube et al. 2010). This is partly due to the listed products having a short life time—quite often one cannot find a particular product anymore—and partly due to the manufacturers not providing information. Boxall et al. (2007) provided some of the more comprehensive estimates published to date, but this remains a significant problem.

Publications such as by Boxall et al. (2007) but also by Lorenz et al. (2011) enabled Markus et al. to predict the relative contribution of engineered nanoparticles to the total metal load of the Rhine and Meuse rivers (Markus et al. 2013). Their conclusion was that based on the available information engineered nanoparticles released within the Netherlands might contribute 5–10 % to the total load of these metals, in terms of mass.

5.3 GIS Approaches

Geographical information systems (GIS) are frequently used for analysing environmental problems, for instance Hüffmeyer et al. (2009) and Comber et al. (2013), but they do not seem very popular in relation to nanoparticles. In the European project NanoFATE water bodies have been classified by their hydrochemical characteristics (Hammes et al. 2013). First the water bodies were examined for similarities between pH, alkalinity, electric conductivity and other parameters,

using principle components analysis. The analysis led to the definition of six classes of water bodies, which especially differ in ionic strength and organic content. All water bodies were assigned to one of these classes. The classification was then used to predict the fate of nanoparticles, that is, predict the tendency of colloidal and nano-scale particles to aggregate. Generally speaking, a high ionic strength means the particles are likely to aggregate and a low ionic strength means that the suspension is more stable. The authors used a georeferenced database containing chemical information about 800 European rivers for their analysis.

A different approach was taken by Dumont et al. (2015), who used a combination of a GIS and a hydrological model, called GWAVA, with a water quality component. The latter was used to calculate the concentrations of silver and zinc oxide nanoparticles from the emission of nanoparticles as a function of the population density. Akin to this is the use of the GREAT-ER model by Kehrein et al. (2015), although they focussed on micropollutants, rather than nanoparticles.

The combination of GIS systems with associated databases regarding population, land use and such, is a powerful one, especially if the relevant hydrological information is available, for instance via the development of models for nutrients or other contaminants.

6   Conclusions and Summary

The collection of articles on the modelling of nanoparticles in the environment, as presented here, shows that many different approaches are used to answer the question of how to predict the release, transport and fate of engineered nanoparticles in the environment (Table 3). An important motivation for these modelling efforts is that we lack actual empirical data on the occurrence and fate of these contaminants, except under controlled circumstances.

Each of the modelling approaches described in the literature has its pros and cons. For instance, if the problem is to determine the distribution of nanoparticles produced by traffic over air and soil, then—due to the spatial scale—it is not feasible, given current computational resources, to use a model that tracks the position of individual nanoparticles as a consequence of air flow and Brownian motion. That would require tracing the position of billions of particles over a considerable period. Instead a multimedia model would be a more suitable choice. However, such a model is not suitable for answering questions about the size distribution of aggregates of nanoparticles. That is a question that might arise when considering the potential consequences of nanoparticles for bottom-dwelling organisms (Schaumann et al. 2015). Large aggregates will quickly sink to the bottom of a lake whereas small aggregates and individual nanoparticles are likely to stay in suspension for a long time.

Table 3 Overview of the modelling techniques and their predictive capabilities

Modelling technique	Predictions, remarks
Small-scale	Describe processes (fate) in models for transport
Population balance	Number concentration and size distribution. Chemical transformation processes and dissolution require special attention
Mass concentrations	Mass concentration, processes like dissolution easily modelled (mass conservation)
DLVO theory	Useful for understanding aggregation. Complications arise for particular types of nanoparticles, reducing practical usefulness
Particle dynamics	Useful for understanding aggregation Computationally intensive
Intermediate-scale	Models for transport based on hydrodynamics or hydrology, mostly limited to one medium, but especially suitable for specific geographical areas Chemical and physical processes based on small-scale techniques
Groundwater models	Spreading of nanoparticles in groundwater, released from sewage sludge or used for remediation
Surface water models	Spreading of nanoparticles in surface water Consequences of release into the environment
Technical compartments	Estimation of distribution over sludge and effluent Fate in waste incineration plants—distribution over ash and out-gas (atmospheric pollution)
Large-scale	Models for transport based on "lumped" transfer processes Chemical and physical processes based on
Multimedia models	Designed for predicting the fate of contaminants in several media Especially useful for screening/regulatory purposes Limited attention for transport details Chemical and physical processes based on small-scale techniques
Material flow analysis	Easily combined with probabilistic techniques, providing insight in consequences of uncertainty
GIS modelling	Process large amounts of data, mapping the results No or very limited interaction between geographical elements

6.1 Data on Use, Production and Emission

We do not have reliable data on the production volumes, the application in consumer products or the subsequent release into the various environmental compartments. All we have are estimates of production and use and, based on experiments on laboratory and pilot scale, insights in transport of nanoparticles through wastewater treatment plants and waste incineration plants.

The method of material flow analysis is often used to examine the mass flows through a natural or technical compartment, like waste incineration plants or landfills (Sect. 5.2). This presumes at least some knowledge of the amounts of nanoparticles involved, however. Multimedia models encompass more than one such compartment and again rely on some knowledge of emissions (Sect. 5.1).

As mentioned in Sect. 5.2, material flow analysis is often combined with probabilistic techniques. To illustrate that, a simplified schematisation, based on Fig. 5 has been used, together with some fairly arbitrary numbers:

– Only sources and pathways via the sewer system or the surface water are considered.
– All sources are assumed to be known exactly, but the percentage of wastewater that is being treated, $f_{treated}$ is assumed to be between 70 and 90 %.
– Similarly, the wastewater treatment plant retains a large fraction of the nanoparticles in the sewage sludge, thereby reducing the emission to the surface water. This fraction is assumed to be between 85 and 95 % ($f_{treated}$)
– A fraction of the sewage sludge, between 15 and 25 % is assumed to be used as fertilizer (f_{fert}) and 15–25 % of the nanoparticles contained in the sludge is assumed to eventually leach into the surface water (f_{leach}).

The total fraction $f_{release}$ of the nanoparticles in the original wastewater that enters the aquatic environment is:

$$f_{release} = f_{treated} \times (1 - f_{retained}) + (1 - f_{treated}) + f_{retained} \times f_{fert} \times f_{leach} \qquad (1)$$

If for each of the fraction a uniform distribution is used, this leads to a probability density like the one given in Fig. 6. The assumption of a uniform distribution may be replaced of course by any other suitable distribution, but the very use of (continuous) distributions gives a distinctly shaped graph that suggests more insight than is actually warranted.

While the uniform distribution is often regarded as the simplest possible, Ferson et al. (2001) argue that even with this distribution implicit assumptions are made that have to be justified with actual data or theoretical analyses. The alternative they propose is to analyse the *bounds* on the various output parameters that result from the bounds of the input parameters. This way implicit assumptions about statistical distributions can be avoided, while retaining all the information that is actually available. In the above example the result would be a range of 0.17–0.46 instead of the skewed graph.

What these methods have in common is that they take a "generic" approach: not a particular production line or a specific incineration plant, but an average production system or an average incineration plant. This leads to generally applicable results and insights, but for a given natural system or installation, things may turn out quite differently. Note that this "generic" approach is of a practical nature, rather than a fundamental limitation.

Modelling efforts using GIS systems have the advantage that they can provide regional and even local details about population density or land use to estimate the emission to a river system in detail, for instance. Such estimates can be used to feed a hydrological model for the river system at hand.
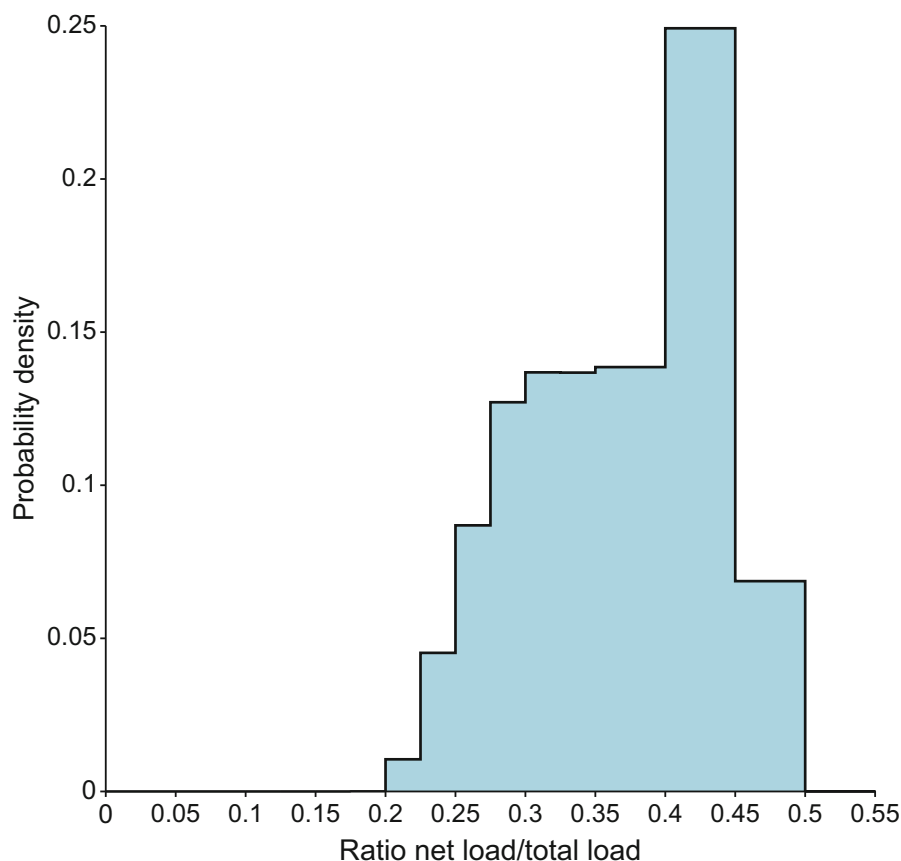
Fig. 6 Probability distribution of the fraction of the total emitted to the aquatic environment, calculated based on Eq. (1)

6.2 Modelling Processes in the Environment

Once the nanoparticles—of widely different shapes, sizes and materials—enter the environment, they are subject to a whole range of processes. Some are important only for certain types of nanoparticles, such as dissolution and chemical transformations, others are quite general—aggregation to SPM for instance. One can study these processes in laboratory settings and derive a mathematical model, but actual field data are required to verify that such a model is indeed adequate. A related problem is that coatings that have been applied for the proper functionalisation, and environmental factors like pH, the presence of oxygen, sulfide and natural organic matter as well as ionic strength all have influence on the fate of nanoparticles, but quantifying these influences turns out to be beyond our present capabilities.

That does not mean that nothing is possible. On the contrary, the various publications referred to in this paper show that we know a lot about the fate of nanoparticles. The models that are currently available, however, do not handle several important details, as indicated above. Approaches based on differential equations for the concentration and approaches based on particle population dynamics are both suitable as an add-on to surface and groundwater models.

Choosing the right parameters to describe the processes may be a challenge, given the variety of environmental factors, but general techniques like probabilistic modelling and sensitivity analysis will help.

6.3 Open Questions and Guidelines

Notwithstanding the variety of modelling studies and their findings as well as the available experimental studies, several important questions remain to be answered.

While some researchers prefer to use number concentrations, others work with mass concentrations. There is currently no clarity about which is to be preferred. It is not even clear if another measure should be used, such as the total surface area (Grieger et al. 2010):

- For silver nanoparticles consensus is that silver ions are the cause of the toxicity. Therefore a suitable measure would be the mass concentration.
- On the other hand, if the toxic effect of nanoparticles is due to disruption of the cell wall, as is reportedly the case of such materials as carbon nanotubes, then the number concentration seems more appropriate. This is also the measure that is used most often in the context of atmospheric pollution.
- But if the toxic effect is caused by the formation of reactive oxygen species at the surface of the particles, the total surface area might serve a better role.
- Some measurement techniques, such as single-particle ICP-MS or electron microscopy, are more naturally related to number concentrations than to mass concentrations. It might therefore be advantageous to further explore modelling techniques that connect to such measurements.

Currently there is a bias towards mass as the relevant measure, as noted by Müller et al. (2013). This is true for modelling as well as for measurements and published data. A conversion between the three measures is possible if the size distribution is known. To illustrate this, consider a set of nanoparticles ranging from almost zero to 200 nm. The number distribution is assumed to be uniform over this range. Then:

- Half of the particles will be below 100 nm in size.
- The mass of these smaller particles represent is 1/64 of the total mass.
- The surface area of these smaller particles is 1/24 of the total surface area.

These fractions will differ for different size distributions, but the example gives some insight in the order of magnitude small particles will contribute to the various measures.

The fact that we have too little concrete data and therefore rely on a large number of assumptions, albeit reasonable ones, leads to the realisation that the consequent uncertainty will influence the predictions of our models and that we need to explicitly deal with it.

Fortunately the variety of model approaches makes it possible to study the subject from different perspectives, thus providing a multitude of insights. In a nutshell:

- For a "quick" scan of possible issues, use methods like multimedia models or material flow analysis, as in general they do not require detailed data about a particular area. They do require proper insight in the phenomena at play, such as how much material is typically exchanged between compartments.
- For a more specific study of the transport and fate, use modelling techniques based on differential equations for the mass concentration or population balances for the number concentration. The model set-up includes a schematic representation of the area under study as well as a comprehensive mathematical description of the processes that play a role.
- The choice between a representation via "particle populations" or via "mass concentrations" is, perhaps, a matter of convenience. Some processes are easier to represent mathematically via a population balance, such as aggregation, others via mass concentrations, e.g. dissolution. Guaranteeing conservation of mass is definitely easier via mass concentrations.
- Consider the use of GIS systems to provide the regional information needed. The underlying databases will need to provide the correct level of detail, of course, but the data are already organised with respect to the geography and that is what is needed for a schematisation.
- Besides the choice of modelling approach, three additional aspects of nanoparticles in the environment ought to be taken into consideration:

  - All data we have available on the release of nanoparticles into the environment and their behaviour exhibit substantial uncertainties, as discussed by Hendren et al. (2013a). These have to be accounted for somehow, for instance via probabilistic modelling techniques.
  - As argued by Wagner et al. (2014), it is far from trivial to distinguish between natural and engineered nanoparticles. Still this needs to be done, even if mathematical models are well suited to make the distinction in principle—it is in the input data that this difference must be made.
  - The ultimate goal of these models must be to answer the question whether the spreading of (engineered) nanoparticles into the environment is harmful or not. That means that we need to know more about their ecotoxicology and how to relate that to the concentrations that we find via modelling. This also means that we need to better understand the possible (chemical) transformations as well as the reactivity, e.g. the production of ROS under influence of UV irradiation.

The most important consideration is that the model approach matches the questions that need to be answered. As there is a multitude of techniques to chose from, it should well be possible to find one that indeed matches. It should also be clear that besides the obvious questions additional aspects need to be addressed: uncertainties in the releases to be used, uncertainties in the processes (both the

process parameters and which processes actually play a role) and what quantity (number or mass concentration) is suitable for expressing the amount and the ecotoxicological effect of nanoparticles in the aquatic environment.

A Mathematical Details

A.1 Population Balance Theory

The "free" nanoparticles and the nanoparticles in clusters are divided into size classes and equations are developed to describe the evolution of the number of particles and clusters in each size class (Quik et al. 2014):

$$\frac{dN_j}{dt} = \frac{1}{2} \sum_{i=1}^{i=j-1} k_{i,j-i} N_i N_j - N_j \sum_{i=1}^{i=\infty} k_{i,j} N_i \tag{2}$$

where:

$k_{i,j}$ rate coefficient for the (successful) collision of particles in size classes i and j

N_i concentration of particles in the size class i

The first term in this equation represents the formation of larger clusters from individual particles or smaller clusters. The second term represents the reduction in number of the particles and clusters due to the formation of these larger clusters. No provision is made here for the disintegration of these clusters.

A.2 DLVO Theory

In its simplest form the DLVO theory predicts the potential energy between a colloidal particle and a (macroscopic) surface or between two colloidal particles as the sum of electrostatic and van der Waals forces. If furthermore the particles are assumed to be identical and therefore have the same surface potential and radius, then the interaction energy can be expressed as (Wikipedia 2015; Macpherson et al. 2012):

$$W(h) = W_{vdW}(h) + W_{dl}(h) = -\frac{AR^*}{6\pi h} + 2\epsilon\epsilon_0 R\psi_0^2 e^{-\kappa h} \tag{3}$$

$$R^* = \frac{R_1 R_2}{R_1 + R_2} = \frac{1}{2}R \tag{4}$$

where:

A   the Hamaker constant
h   distance between the particles' surfaces
R   radius of the particles
ε_0 the electric permittivity of vacuum
ε the dielectric constant of water
κ the inverse Debye-Hückel length
ψ_0 the surface potential of the particles

In this equation the first term is the contribution of the van der Waals forces and the second term is the contribution of the electrostatic forces, as modelled via the double-layer theory (Macpherson et al. 2012). The Debye-Hückel length and the Hamaker constant both depend on the ionic strength of the medium. The Hamaker constant also depends on the characteristics of the colloidal particles and the surfaces in question. The theory is used to examine if there is a minimum in the potential energy, which indicates whether the colloidal particles remain separated or instead aggregate in this minimum (see Fig. 3).

A.3 Transport and Adsorption in Groundwater

The equations that link the concentration of nanoparticles in the porewater (C) to the concentration of nanoparticles retained in the soil (S) are:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{n}\frac{\partial S}{\partial t} - \frac{\partial}{\partial z}D\frac{\partial C}{\partial z} + v\frac{\partial C}{\partial z} = 0 \tag{5}$$

and:

$$\frac{\rho_b}{n}\frac{\partial S}{\partial t} = k_{att}C - k_{det}S \tag{6}$$

where:

ρ_b soil bulk density
n porosity
v velocity of the porewater
C concentration of nanoparticles in the porewater
S concentration of adsorbed nanoparticles

D   diffusion coefficient
k_{att} adsorption (attachment) rate coefficient
k_{det} desorption (detachment) rate coefficient

This model formulation allows an arbitrarily high concentration of adsorbed nanoparticles, whereas in reality the adsorption capacity is finite. To accommodate a limited adsorption capacity, a blocking function may be introduced which effectively reduces the rate of adsorption as a function of the concentration of adsorbed nanoparticles (Liang et al. 2013; Kasel et al. 2013). Experience with such experiments has shown that the adsorption often depends on the distance from the entrance, leading to expressions like:

$$\psi = \left(1 - \frac{S}{S_{max}}\right)\left(\frac{d_{50} + z}{d_{50}}\right)^{-\beta} \tag{7}$$

where:
S_{max} capacity (maximum concentration) for the adsorption (deposition)
d_{50} size of the soil particles
z distance to the entrance
β shape parameter

and k_{att} in Eq. (6) is replaced by $k_{att}\psi$.

Tufenkji and Elimelech developed the following semi-empirical formula for the collision rates of colloidal and nano-sized particles with the soil as a consequence of various transport mchanisms (Tufenkji and Elimelech 2004):

$$k_{att} \sim 10^{-3.25} N_{LO}{}^{0.51} N_{E1}{}^{-0.27} N_{DL}{}^{1.06} \tag{8}$$

where:
N_{LO} the London number, relating the Hamaker constant, the viscosity of the fluid, the flow velocity and the particle diameter
N_{E1} the first electrokinetic parameter, which depends on the surface charge of the particles
N_{DL} the ratio of the particle diameter and the Debye-Hückel length

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