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Modeling aggregation and sedimentation of nanoparticles in the aquatic environment



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HIGHLIGHTS

- The aggregation of nanoparticles is modeled based on the experimental results.
- Hetero- and homo-aggregations as well as sedimentation are incorporated in the model.
- The parameterized model reliably reproduces the experimental results.
- It is suitable for the application to field situations.

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ABSTRACT

With nanoparticles being used more and more in consumer and industrial products it is almost inevitable that they will be released into the aquatic environment. In order to understand the possible environmental risks it is important to understand their behavior in the aquatic environment.

From laboratory studies it is known that nanoparticles in the aquatic environment are subjected to a variety of processes: homoaggregation, heteroaggregation to suspended particulate matter and subsequent sedimentation, dissolution and chemical transformation. This article presents a mathematical model that describes these processes and their relative contribution to the behavior of nanoparticles in the aquatic environment. After calibrating the model with existing data, it is able to adequately describe the published experimental data with a single set of parameters, covering a wide range of initial concentrations. The model shows that at the concentrations used in the laboratory, homoaggregation and sedimentation of the aggregates are the most important processes. As for the natural environment much lower concentrations are expected, heteroaggregation will play the most important role instead.

More experimental datasets are required to determine if the process parameters that were found here are generally applicable. Nonetheless it is a promising tool for modeling the transport and fate of nanoparticles in watersheds and other natural water bodies.

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1. Introduction

The development of nanotechnology in recent decades and the subsequent use of engineered nanoparticles in a range of consumer and industrial products have raised concern about the possible consequences for the environment and for human health (Aschberger et al., 2011). Given the wide range of applications, it is almost inevitable that nanoparticles will be released into the aquatic environment (Aschberger et al., 2011; Nowack et al., 2012).

Mathematical models that are able to describe the transport and the processes of nanoparticles can help assess the risks to the environment,

by providing estimates of the concentrations, in what compartments they are present and which sources contribute most.

For such models knowledge of the various sources and emissions of nanoparticles to the environment is required, as well as of the processes that act on the nanoparticles in the environment together with the physicochemical characteristics of the particles.

While the sources and emissions determine to a large extent how much nanomaterial is present in the environment, the processes determine in what form it is present and in what compartment of the water system – in the water phase or in the sediment. It is important to know the form, be it single nanoparticles, coated or not, clusters of nanoparticles or nanoparticles adsorbed to particulate matter, because it determines their bioavailability and toxicity (Clément et al., 2013). If the nanoparticles settle to the sediment, then they may be present

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there for a long time, whereas suspended in the water they will be transported and eventually diluted.

From the available publications a fairly consistent picture can be constructed with respect to the processes that play a role when nanoparticles enter the aquatic environment. Some types of engineered nanoparticles dissolve within a relatively short timescale, for instance silver and zinc oxide nanoparticles (David et al., 2012; Liu et al., 2011; Lowry et al., 2012). Aggregation, the forming of clusters with other engineered nanoparticles or with natural colloidal particles or suspended particulate organic or inorganic matter, is relevant for all types of nanoparticles (Huynh and Chen, 2011; Li and Chen, 2012; Thio et al., 2011). Sedimentation causes a flux of nanoparticles to the sediment where they may accumulate. Furthermore chemical and biochemical transformations may affect the chemical make-up of the nanoparticles, such as the transformation of silver to silver sulfide, which is almost insoluble and therefore has a much lower bioavailability than metallic silver (Lowry et al., 2012). Fig. 1 presents a schematic overview of these processes.

In this paper a process-based mathematical model for metallic and metal oxide nanoparticles is developed, that is, the processes as identified in the literature have been put into a mathematical form (Fig. 1). Within the model the nanoparticles are viewed as a particulate constituent, not as a collection of individual particles. Several fractions of nanoparticles are distinguished to describe the phenomena. The resulting mathematical model was then applied to describe the results of several published laboratory experiments (Brunelli et al., 2013; Quik et al., 2012). The model parameters were tuned so as to approximate the observed concentration timeseries as closely as possible. For this procedure the results for several initial concentrations were used together, rather than the results of individual timeseries. The procedure used here yields parameter sets that are expected to be generally applicable.

2. Materials and methods

2.1. Published data

From the available literature on the behavior of nanoparticles in aquatic environments the two following publications are especially of interest for the purposes of this article, because they provide information on the kinetics of the processes described above. Other publications concerning these processes mostly focus on the influence of such environmental parameters as the pH and the ionic strength and present the equilibrium results only, not the development over time.

Quik et al. (2012) performed laboratory experiments with river water and different initial concentrations of cerium dioxide nanoparticles. They measured the development of the concentration of nanoparticles over a period of 12 days to gain insight in the sedimentation behavior. With a height of 6 cm for the bottles the actual sedimentation velocity can be estimated.

Brunelli et al. (2013) studied the aggregation and sedimentation of titanium dioxide nanoparticles in various types of water. In this study the concentration of the nanoparticles as function of time was measured at intervals of 15 min. There is, however, no explicit information on the dimensions of the cuvettes that were used in the sedimentation experiments. On the assumption that the cuvette was of typical height, that is 3 cm, an absolute sedimentation velocity was estimated. As the sedimentation velocity only occurs in the model equations divided by the height of the cuvette, only this ratio has an influence on the results, not the two separate parameters.

In these experiments filtered water was used. For the numerical experiments reported here the concentration of suspended particulate matter (SPM) was therefore assumed to be zero and the processes associated with SPM were excluded.

A few intriguing features can be noted in the original publications:

- Quik et al. (2012) report that the concentration of suspended nanoparticles more or less stabilizes at the end of the experiment. This could mean that the sedimentation of the nanoparticles stops or decreases considerably, possibly because the larger aggregates have already settled and only the very light ones remain. In a more recent publication Velzeboer et al. (2014) conclude that the fraction of nanoparticles that remain in suspension is actually very small (3% or less). In the current mathematical model no such fraction is explicitly distinguished.
- The experiment that Quik et al. (2012) present with the highest initial concentration, 100 mg/L of cerium dioxide nanoparticles, shows a lower end concentration than the experiments with initial concentrations of 1 mg/L and 10 mg/L. In the simulations this phenomenon could only be approximated by an additional homoaggregation process (cf Section 2.2, Eq. (9)).
- Given the relatively high concentrations of nanoparticles in comparison to the concentrations of suspended particulate matter, homoaggregation is likely the dominant process in both sets of experiments.
- The measurements by Brunelli et al. (2013) indicate that even at the lowest concentrations, noticeable sedimentation may occur within a

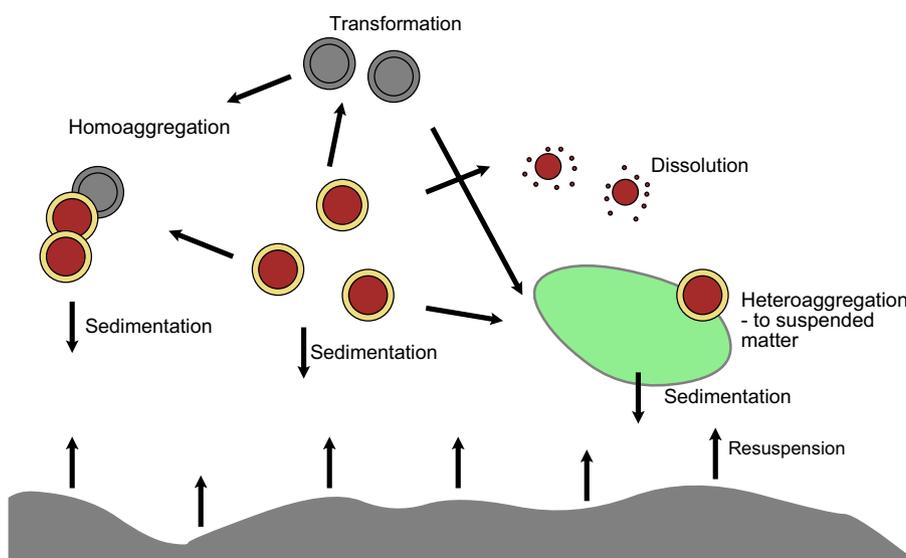


Fig. 1. Schematic representation of the various processes nanoparticles are subject to in the aquatic environment.

time frame of two days. Since the sedimentation velocity of individual nanoparticles is expected to be very low (cf the mathematical description), this may indicate aggregation occurred in early stages of the experiments.

The authors of both articles used regression techniques on the individual experiments to estimate the rates of the sedimentation and aggregation processes. In this work the measured concentrations for all experiments as published in these articles were used to estimate the model parameters instead (see Tables S1 and S2 and the description of the parameter estimation method in the Supporting information).

2.2. Mathematical description of the processes

Each of the processes described in the literature has effect on one or more fractions of nanoparticles (Fig. 1). To describe these processes mathematically, functional expressions were developed, which are presented below. These expressions are formulated in terms of the mass concentration. More fundamental descriptions of the various processes are given by Arvidsson et al. (2011) and Petosa et al. (2010), whereas Hartmann et al. (2014) provide an extensive qualitative overview for metallic and metal oxide nanoparticles as well other types.

2.2.1. Sedimentation and resuspension

Sedimentation is assumed to apply mainly to the nanoparticles adsorbed to the inorganic or organic suspended solids and clusters of nanoparticles. The sedimentation velocity for free nanoparticles is too small to have effect on a timescale of several days. For instance, for spherical particles with a diameter of 100 nm and a density of 5000 kg/m³, Stokes' law predicts a sedimentation velocity of 2 mm/d (Praetorius et al., 2012). It would require such small particles several years to reach the bottom of a lake with a depth of just several meters.

The sedimentation velocity of suspended particulate matter consisting of particles of several μm in diameter is several m/d, which makes it relevant for the typical time scales involved.

The sedimentation process of both adsorbed and aggregated nanoparticles is modeled via the equation below:

$$\frac{dC}{dt} = -\frac{w_s}{H} \cdot C \quad (1)$$

where:

w_s is the sedimentation velocity (m/d)
 H is depth of the water column (m)
 C is the concentration of the nanoparticles adsorbed to the suspended solids (two different fractions actually: organic and inorganic) or the concentration of the clusters of nanoparticles (μg/L).

Resuspension of particles that have sedimented on the bottom can occur under the influence of shear forces due to turbulent flow. This process can be described using a classical formulation like that of Partheniades (1962):

$$\frac{dC}{dt} = +M \left(\frac{\tau}{\tau_c} - 1 \right) \quad (2)$$

where:

M is the resuspension rate (g/m²d)
 τ is the shear stress (Pa)
 τ_c is the critical shear stress (Pa).

If the shear stress exceeds this critical value, resuspension occurs.

2.2.2. Dissolution and transformation

Several types of nanoparticles, notably silver and zinc oxide, are subject to dissolution (Liu et al., 2011; Mudunkotuwa et al., 2012). In addition, the formation of silver sulfide, which is almost insoluble, is considered an important process (Lowry et al., 2012; Dale et al., 2013; Kaegi et al., 2013).

On the other hand, nanomaterials such as titanium dioxide and cerium dioxide nanoparticles have very low solubility, so that dissolution can be ignored (Cornelis et al., 2011; Quik et al., 2011), but a different transformation plays a role for titanium dioxide: coated TiO₂ nanoparticles exhibit less photocatalytic activity than bare particles (Labille et al., 2010; Virkutyte et al., 2012).

Dissolution and physical or chemical transformation have in common that one fraction of a nanomaterial is transformed into another. Mathematically, they are described via the relations:

$$\frac{dC_1}{dt} = -(k_{diss} + k_{trans}) \cdot C_1 \quad (3)$$

$$\frac{dC_2}{dt} = +k_{trans} \cdot C_1 \quad (4)$$

$$\frac{dC_{diss}}{dt} = +k_{diss} \cdot C_1 \quad (5)$$

where:

C_1 is the concentration of either “pristine” (Ag) or coated (TiO₂) free nanoparticles (μg/L).
 C_2 is the concentration of free nanoparticles with a shell (of Ag₂S) that makes them insoluble (Ag) or bare free nanoparticles that exhibit photocatalytic activity (TiO₂) (μg/L). Note that the sum of the concentrations C_1 and C_2 is equal to the total concentration of free nanoparticles, C_{free} .
 C_{diss} is the concentration of the dissolved fraction (μg/L).
 k_{diss} is the rate constant for the dissolution of the nanoparticles (d^{-1}).
 k_{trans} is the rate constant for the transformation of the nanoparticles into an insoluble variety because of a shell being formed (d^{-1}).

The transformation of titanium dioxide from coated to uncoated particles, can be modeled by setting the dissolution rate k_{diss} to 0.

For the dissolution of silver nanoparticles the presence of oxygen is required as a catalyst (Liu and Hurt, 2010). In most aquatic systems the concentration of dissolved oxygen is so high that it does not influence the rate of the dissolution process. For that reason, in this article there is no attempt to describe the influence explicitly. Note, that the oxygen concentration may play a role in the sediment, as many such sediments are anoxic or nearly anoxic.

2.2.3. Homoaggregation

Homoaggregation is an important process in laboratory experiments (Brunelli et al., 2013). The mathematical form used here is:

$$\frac{dC_{free}}{dt} = -k_{homoagg} \cdot f(S) \cdot C_{free}^2 \quad (6)$$

$$\frac{dC_{agg}}{dt} = +k_{homoagg} \cdot f(S) \cdot C_{free}^2 \quad (7)$$

$$f(S) = \frac{(S/S_{crit})^2}{1 + (S/S_{crit})^2} \quad (8)$$

where:

C_{free} is the concentration of free, that is non-adsorbed and non-aggregated, nanoparticles (μg/L).

C_{agg} is the concentration of aggregations of nanoparticles ($\mu\text{g/L}$).
 $k_{homoagg}$ is the rate coefficient for the homoaggregation process ($\text{L}/\mu\text{g}\cdot\text{d}$).
 $f(S)$ is the attachment efficiency as function of salinity S (—).

The mathematical form of this function was chosen to capture the qualitative characteristics reported about the effects of salinity or ionic strength (Li and Chen, 2012).

The hypothesis is that free nanoparticles can collide and form a larger cluster (Praetorius et al., 2012). These clusters may in turn collide with other clusters or with nanoparticles, leading to increasingly larger clusters.

When there are already clusters of nanoparticles present, these may in turn capture free nanoparticles, thus augmenting the concentration of aggregated particles. This process of “secondary” aggregation can be approximated by the following equations:

$$\frac{dC_{free}}{dt} = -k_{sec_agg} \cdot f(S) \cdot C_{free} C_{agg} \quad (9)$$

$$\frac{dC_{agg}}{dt} = +k_{sec_agg} \cdot f(S) \cdot C_{free} C_{agg} \quad (10)$$

where:

k_{sec_agg} is the rate coefficient for the aggregation of nanoparticles to existing aggregates of nanoparticles ($\text{L}/\mu\text{g}\cdot\text{d}$).
 $f(S)$ is again a function to capture the effect of salinity on the attachment efficiency.

As these processes are unlikely to be significant with the low concentrations of nanoparticles that are expected for surface waters (Praetorius et al., 2012), they are only considered for simulating the laboratory experiments (cf Section 3.1).

2.2.4. Heteroaggregation

The adsorption of nanoparticles to organic or inorganic particulate matter, also known as heteroaggregation, depends on a number of factors, notably the pH and the ionic strength or the salinity (Chowdhury et al., 2012; Huynh and Chen, 2011; Li and Chen, 2012). Not all encounters between particles lead to the formation of a persistent aggregate as a consequence for instance of steric or electrostatic hindering. This effect is usually expressed via the attachment efficiency (Praetorius et al., 2012).

In this article the aggregation process is modeled via these equations:

$$\frac{dC_{free}}{dt} = -k_{agg} \cdot f(S) \cdot C_{sed} \cdot C_{free} \quad (11)$$

$$\frac{dC_{ads}}{dt} = +k_{agg} \cdot f(S) \cdot C_{sed} \cdot C_{free} \quad (12)$$

where:

k_{agg} is the maximum rate of heteroaggregation ($\text{L}/\text{g}\cdot\text{d}$).
 $f(S)$ describes the attachment efficiency as function of salinity S (—). This need not be the same function as in the case of homoaggregation, as two different types of particles are involved.
 C_{free} is the concentration of free nanoparticles ($\mu\text{g/L}$).
 C_{ads} is the concentration of adsorbed nanoparticles (either adsorbed to inorganic or organic) ($\mu\text{g/L}$).
 C_{sed} is the concentration of suspended particulate matter (either inorganic or organic; mg/L).

S is the salinity (g/L).
 S_{crit} is the salinity above which aggregation is no longer hindered by electrostatic forces (g/L).

A distinction is made between nanoparticles adsorbed to organic matter and those adsorbed to inorganic matter, as organic matter can be mineralized (see the next process).

While this aggregation process resembles the adsorption of dissolved substances like organic micropollutants or metal ions to suspended particulate matter, an important difference is that nanoparticles are not likely to achieve a *thermodynamic* equilibrium, so that a concept like partition coefficients is not applicable (Praetorius et al., 2012). Instead of equilibrium partitioning the ongoing adsorption should be treated as a dynamic process.

2.2.5. Mineralization

If nanoparticles are adsorbed or aggregated to organic material, they can be released as a consequence of the mineralization of the organic material. In mathematical form, assuming a first-order process:

$$\frac{dC_{ads}}{dt} = -k_{min} \cdot C_{ads} \quad (13)$$

$$\frac{dC_{free}}{dt} = +k_{min} \cdot C_{ads} \quad (14)$$

where:

k_{min} is the rate of mineralization (d^{-1}).
 C_{ads} is the concentration of the nanoparticles adsorbed to the organic matter
 C_{free} is the concentration of free, non-adsorbed, nanoparticles ($\mu\text{g/L}$).

This process does not play a role in the laboratory experiments, but it does in the aquatic environment.

3. Results

3.1. Simulation of the laboratory experiments

In the two laboratory experiments that are considered here (Brunelli et al., 2013; Quik et al., 2012), not all processes described in the previous section are of interest. Both experiments involved insoluble nanomaterials and the organic matter in the media consisted of humic and fulvic acids. For this reason no distinction is made in this mathematical model between the various possible organic fractions. The published experiments also do not allow the influence of salinity to be examined in a systematic way. Even though Brunelli et al. (2013) use different types of artificial or natural seawater, there are only a few values for the salinity and other differences in the water types may obscure the effect of salinity on the attachment efficiency.

3.2. Simulation of experiments with cerium dioxide

The first experiment that was simulated by this model was that of the sedimentation of cerium dioxide nanoparticles in Rhine and Meuse water (see Table S1; (Quik et al., 2012)). The differences between these two water types are limited to the concentration of suspended solids, as far as the modeling is concerned, 12 mg/L for the Rhine and 5 mg/L for the Meuse. Other differences in the chemical composition are not taken into account.

As there are no separate measurements for aggregated and non-aggregated nanoparticles, only the total concentration of nanoparticles in the water as predicted by the model can be compared to these measurements (see Figs. 2 and 3).

The model parameters were determined via an automatic optimization method (Powell, 2009). For this method to work a suitable cost function, had to be defined that measures the discrepancy between the model results and the measurements. The chosen function has the property that the relative errors are weighed, resulting in a more even weighting for the whole range of observed concentrations. The details can be found in the Supporting information. The parameter values are listed in Table 1. Error estimates regarding these parameters are presented in the Supporting information.

As can be seen in the figures, the model is able to describe the observed concentration as function of time quite reasonably for most cases. Only for the case with the highest initial concentration, 100 mg/L, in Meuse water (Fig. 3), does the model result show significant deviations from the measurements. For this case the model shows much lower concentrations after 2 days than were measured. A speculative explanation for this is that in the laboratory experiment the nanoparticles were partly aggregated from the start. That would result in a relatively large mass quickly sinking to the bottom of the vessel, leaving only the individual nanoparticles and small aggregates. Such a situation could be simulated in the model by assuming a non-zero initial concentration for the aggregates as well as for the free nanoparticles.

To quantify the relative importance of the various processes, the mass balance has been examined (see Fig. 4). The figure shows the relative contribution of each process over the simulation period. For the two highest initial concentrations, 10 mg/L and 100 mg/L, only homoaggregation and sedimentation of the aggregates play any role. For the lowest initial concentration, however, adsorption to suspended particulate matter and sedimentation of that matter with the adsorbed nanoparticles has some impact. At lower concentrations heteroaggregation would become more important (see the Supporting information).

3.3. Simulation of experiments with titanium dioxide

The results from one set of experiments by Brunelli et al. (2013), namely the experiments where Adriatic seawater was used, have been simulated in a similar way. The results for the different types of water are similar, so we deemed that a single set would suffice.

As mentioned before, they did not document the dimension of the cuvette used for these experiments, so that only the combination of sedimentation velocity divided by depth can be determined. The result is shown in Fig. 5, which uses the same logarithmic transformation for the concentration as in their article (see Table S2).

In these experiments the concentration decreases, presumably as a consequence of sedimentation, even for the lowest initial concentration

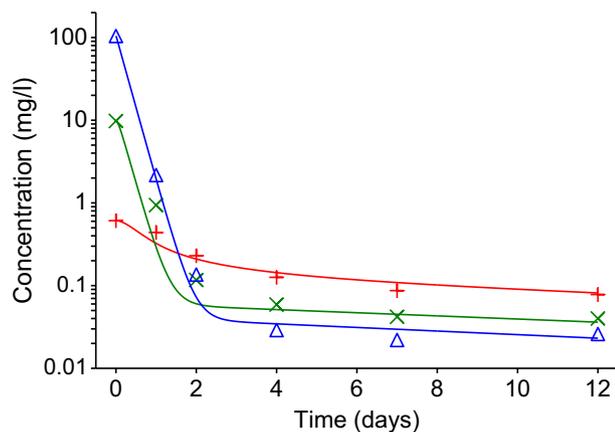


Fig. 2. Concentration of cerium dioxide nanoparticles as simulated for Rhine water compared to the measurements by Quik et al. (2012). The symbols represent the measurements, and the lines represent the model results. +: initial concentration of 1 mg/L, x: 10 mg/L, Δ: 100 mg/L.

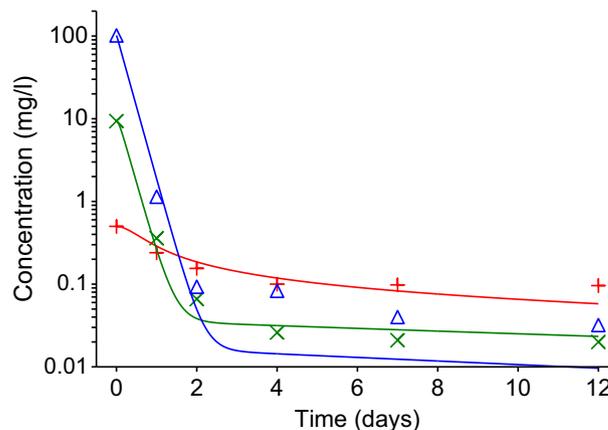


Fig. 3. Concentration of cerium dioxide nanoparticles as simulated for Meuse water compared to the measurements by Quik et al. (2012). The symbols represent the measurements, and the lines represent the model results. +: initial concentration of 1 mg/L, x: 10 mg/L, Δ: 100 mg/L.

(0.01 mg/L). The calibration procedure results in a sedimentation velocity of 0.034 m/d, assuming that the cuvette was 3 cm, as is typical for such equipment. This is an order of magnitude larger than predicted by Stokes' law (cf Section 2.2).

A possible explanation for this is that the nanoparticles as used in the experiments by Brunelli et al. were initially aggregated to a certain extent, thereby forming larger particles that can settle with a velocity that is noticeable within the time frame of the experiments. While they were unable to measure the sizes of the particles and aggregates at the lowest initial concentration, it seems likely that some initial aggregation occurred for all dispersions (Brunelli et al., 2013, Table 2 therein). The consequences of a zero settling velocity for free nanoparticles are examined more closely in the Supporting information.

4. Discussion

When using regression techniques, it is common to look at each timeseries separately (Brunelli et al., 2013). This leads to parameter values that are specific to that series. With the mathematical model and the estimation method presented here “generic” parameter values are obtained. The individual experiments are unified in a single set of equations and parameters with terms that have a physical–chemical meaning. This allows one to make predictions about the behavior in other circumstances, for instance, when there is more or less suspended particulate matter present.

The parameters found for the cerium dioxide and titanium dioxide experiments show some common features (see Table 1 and the section on error estimates in the Supporting information). First of all the values are more or less in the same order of magnitude, indicating that these processes have the same timescale: homoaggregation occurs in a

Table 1
Parameters fitted for the sedimentation experiments with cerium dioxide by Quik et al. (2012) and those with titanium dioxide by Brunelli et al. (2013).

Parameter	Cerium dioxide (Meuse and Rhine)	Titanium dioxide (Seawater)
Transformation rate k_{trans} ; d^{-1}	–	–
Homoaggregation $k_{homoagg}$; $L/mg \cdot d$	1.77	0.618
Secondary aggregation k_{sec_agg} ; $L/mg \cdot d$	2.28	2.254
Aggregation to SPM k_{agg} ; $L/mg \cdot d$	0.0073	–
Sedimentation aggregates w_{sed_agg} ; m/d	0.24	0.111
Sedimentation SPM w_{sed_spm} ; m/d	0.003	–
Sedimentation free NPs w_{sed_free} ; m/d	0.002	0.034

Notes: Process parameters that were set to zero to exclude the associated processes are indicated by “–”. As there is no information on the dimensions of the cuvettes for the titanium dioxide experiment, a height of 3 cm was assumed.

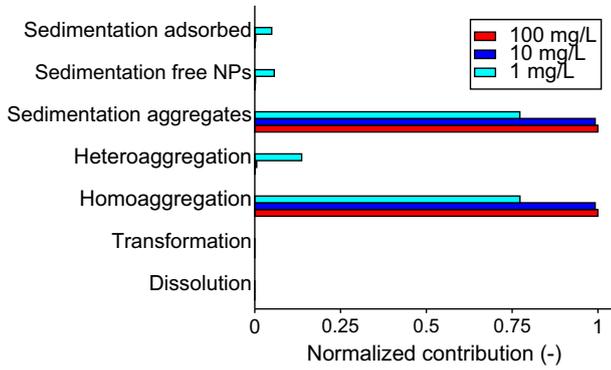


Fig. 4. Normalized contributions of the various processes, contributing to the fate of cerium dioxide nanoparticles in Rhine water at three different initial concentrations.

timescale of 0.5 to 2 days, whereas the sedimentation velocity of the aggregates is in the order of 10 to 20 cm per day. It remains to be seen if that is the case with other nanoparticles and environmental matrices as well. Yet another feature is that the model parameters seem to be fairly robust with relatively narrow ranges with the exception of the rate coefficient for secondary aggregation. This gives confidence in the model, in that the parameters found in this work can be used as a first estimate in applications.

Compared to the current model, the model described by Quik et al. (2014) is somewhat simpler and it has a structure that allows for an analytical solution. In the equation below the two fractions that are distinguished in the original article are combined to get the total concentration:

$$C = (C_0 - C_{ns})e^{-At+B(e^{-Dt}-1)} + C_{ns} \quad (15)$$

where C_0 is the initial concentration, C_{ns} is the concentration of nanoparticles that do not settle to the bottom and A , B , and D are the coefficients related to the physical parameters (see Table 2 for the fitted parameter values):

$$A = K_{homoagg} \quad (16)$$

$$B = \frac{k_{agg} C_{sed,0} H}{w_s} \quad (17)$$

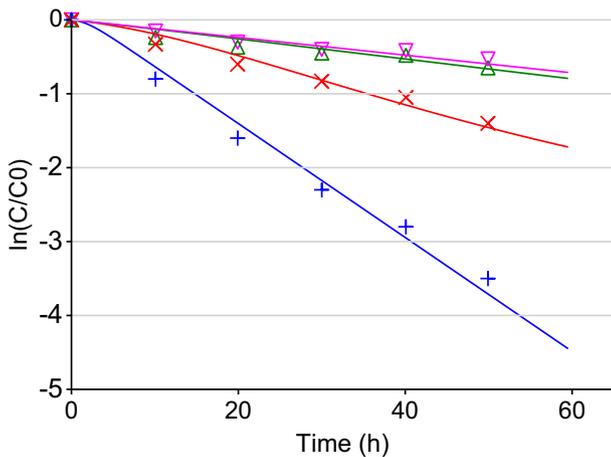


Fig. 5. Natural logarithm of the concentration of titanium dioxide nanoparticles as simulated, divided by the initial concentration, using the “best” parameter set for this experiment (see Table 1). +: initial concentration 100 mg/L, x: 10 mg/L, Δ: 0.1 mg/L, ∇: 0.01 mg/L.

Table 2

Parameter values determined for Eq. (15). The values were found using the same optimization procedure as in the section on the simulation of the laboratory experiments.

Parameter	Value	Unit
C_{ns}	0.035	mg/L
$K_{homoagg}$	3.13	d^{-1}
k_{agg}	4.19	L/mg·d
v_{sed}	5.06	m/d

$$D = \frac{w_s}{H} \quad (18)$$

where:

$K_{homoagg}$ is the homoaggregation rate constant (d^{-1}).

k_{agg} is the heteroaggregation rate constant (L/mg·d).

$C_{sed,0}$ is the initial concentration of suspended particulate matter (mg/L).

H is the height of the water column (m).

w_s is the sedimentation velocity (m/d).

Here the homoaggregation is assumed to depend linearly on the concentration of nanoparticles, unlike in the current model (cf. Section 2.2). Analysis of simulations of the Von Smoluchowski equation showed this approximately linear behavior (Quik et al., 2014). The concentration of suspended particulate matter decreases exponentially with time as a consequence of sedimentation.

The solutions tend to follow the two cases with high initial concentrations (10 and 100 mg/L) more closely than the third case with the low initial concentration (1 mg/L), as can be seen in Fig. 6. The consequence is that the concentrations for this third case are underestimated considerably.

A closer examination of the coefficients reveals that the one parameter responsible for the sedimentation of suspended particulate matter, D in Eq. (15), is very large in comparison to the time scale – $D = w_s / H = \text{circa } 5.06/0.06 = 84 d^{-1}$ – so that the concentration of suspended particulate matter will be almost zero according to the model and after a short while an exponential solution is left with an offset equal to the concentration of non-settling nanoparticles:

$$C = (C_0 - C_{ns})e^{-At-B} + C_{ns}. \quad (19)$$

In Fig. 6 this can be seen as the initial very rapid decrease of the concentration.

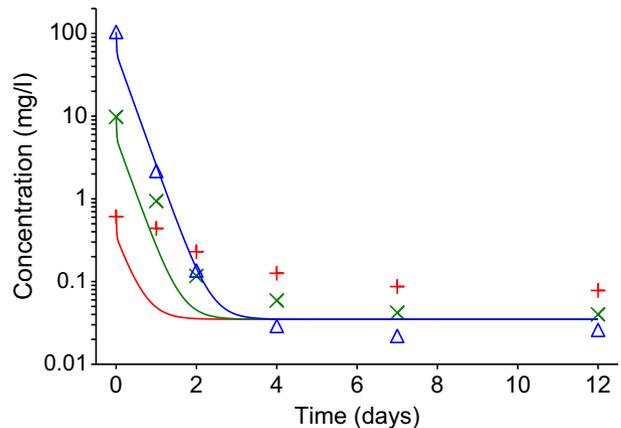


Fig. 6. Concentration of cerium dioxide nanoparticles as simulated for Rhine water using the model described by Quik et al. (2014). +: initial concentration 100 mg/L, x: 10 mg/L, Δ: 1 mg/L.

It should be noted that this method of determining coefficients forces a single value for the concentration of non-settling nanoparticles. Instead, Quik et al. (2014) estimated this concentration as the concentration after 15 days (the end of the experiment time) for each series individually.

Descriptive models, such as Eq. (15) and the one presented in Section 2.2, can be applied in new situations, if the parameter values and the process descriptions are “generic” enough. Also the individual contributions of the various processes can be determined, giving insight in which process requires most attention. As a next step the model is currently used to examine the transport and fate of nanoparticles in a large European river.

The model presented here (cf Section 2.2) can be also applied in combination with models for other constituents, for instance, an algal growth model, so that attachment to living or dead organic material can be taken into account. When this set-up is extended even further it may be possible to model the uptake of nanoparticles by organisms, although the specific mathematical modeling of such processes is certainly not included in the current model.

Some caution is, however, warranted, as is illustrated extensively by Beven and Freer (2001). In many cases models of sufficient complexity cannot be uniquely distinguished one from the other. The data that are available for such distinction allow different parameter sets or even a different model structure that all give good enough fits to these data, the so-called equifinality concept (see also the Supporting information).

With this caution in mind, the model adequately describes the experimental results which cover a large range of initial concentrations and thus is a promising tool for application to more natural water bodies. As the number of state variables and process parameters is limited, it should be easy to apply the model, even though data on nanomaterial in the environment is very scarce.

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Appendix A. Supplementary data

The supporting information contains tables documenting the laboratory data that were used (Tables S1 and S2), as well as details concerning the optimization method and an alternative fit for the data from Brunelli et al. (2013). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2014.11.056>.

References

- Arvidsson Rickard, Molander Sverker, Sandén Björn A, Hassellöv Martin. Challenges in exposure modeling of nanoparticles in aquatic environments. *Hum. Ecol. Risk Assess.* 2011;17:245–62.
- Aschberger Karin, Micheletti Christian, Sokull-Klöttgen Birgit, Christensen Frans M. Analysis of currently available data for characterising the risk of engineered nanomaterials to the environment and human health – lessons learned from four case studies. *Environ. Int.* 2011;37:1143–56.
- Beven Keith, Freer Jim. Equifinality, data assimilation, and uncertainty estimation in mechanistic modelling of complex environmental systems using the GLUE methodology. *J. Hydrol.* 2001;249:11–29.
- Brunelli Andrea, Pojana Giulio, Callegaro Sarah, Marcomini Antonio. Agglomeration and sedimentation of titanium dioxide nanoparticles (n-TiO₂) in synthetic and real waters. *J. Nanoparticle Res.* 2013;15:1–10.
- Chowdhury Indranil, Cwiertny David M, Walker Sharon L. Combined factors influencing the aggregation and deposition of nano-TiO₂ in the presence of humic acid and bacteria. *Environ. Sci. Technol.* 2012;46:6968–76.
- Clément Laura, Hurel Charlotte, Marmier Nicolas. Toxicity of TiO₂ nanoparticles to cladocerans, algae, rotifers and plants – effects of size and crystalline structure. *Chemosphere* 2013;90:1083–90.
- Cornelis Geert, Ryan Brooke, McLaughlin Mike J, Kirby Jason K, Beak Douglas, Chittleborough David. Solubility and batch retention of CeO₂ nanoparticles in soils. *Environ. Sci. Technol.* 2011;45:2777–82.
- David Calin A, Galceran Josep, Rey-Castro Carlos, Puy Jaume, Companys Encarnació, Salvador José, Monné Josep, Wallace Rachel, Vakourov Alex. Dissolution kinetics and solubility of ZnO nanoparticles followed by AGNES. *J. Phys. Chem. C* 2012;116:11758–67.
- Hartmann Nanna B, Skjolding Lars M, Foss Hansen Steffen, Kjølholt Jesper, Gottschalk Fadri, Baun Anders. Environmental fate and behaviour of nanomaterials, new knowledge on important transformation processes. Technical Report. Danish Environmental Protection Agency; 2014.
- Huynh Khanh An, Chen Kai Loon. Aggregation kinetics of citrate and polyvinylpyrrolidone coated silver nanoparticles in monovalent and divalent electrolyte solutions. *Environ. Sci. Technol.* 2011;45:5564–71.
- Kaegi Ralf, Voegelin Andreas, Ort Christoph, Sinnet Brian, Thalmann Basilius, Krismer Jasmin, Hagendorfer Harald, Elumelu Maline, Mueller Elisabeth. Fate and transformation of silver nanoparticles in urban wastewater systems. *Water Res.* 2013;47:3866–77.
- Labille Jérôme, Feng Jinghuan, Botta Céline, Borschnek Daniel, Sammut Magali, Cabie Martiane, Auffan Mélanie, Rose Jérôme, Bottero Jean-Yves. Aging of TiO₂ nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment. *Environ. Pollut.* 2010;158:3482–9.
- Dale Amy Lauren, Victor Lowry Gregory, Casman Elizabeth A. Modeling nanosilver transformations in freshwater sediments. *Environ. Sci. Technol.* 2013;47:12920–8.
- Li Kungang, Chen Yongsheng. Effect of natural organic matter on the aggregation kinetics of CeO₂ nanoparticles in KCl and CaCl₂ solutions: measurements and modeling. *J. Hazard. Mater.* 2012;209–210:264–70.
- Liu Jingyu, Hurt Robert H. Ion release kinetics and particle persistence in aqueous nanosilver colloids. *Environ. Sci. Technol.* 2010;44:2169–75.
- Liu Jingyu, Pennell Kelly G, Hurt Robert H. Kinetics and mechanisms of nanosilver oxy-sulfidation. *Environ. Sci. Technol.* 2011;45:7345–53.
- Lowry Gregory V, Espinasse Benjamin P, Raju Badireddy Appala, Richardson Curtis J, Reinsch Brian C, Bryant Lee D, Bone Audrey J, Deonarine Amrika, Chae Soryong, Therezien Mathieu, Colman Benjamin P, Hsu-Kim Heileen, Bernhardt Emily S, Matson Cole W, Wiesner Mark R. Long-term transformation and fate of manufactured Ag nanoparticles in a simulated large scale freshwater emergent wetland. *Environ. Sci. Technol.* 2012;46:7027–36.
- Mudunkotuwa Imali A, Rupasinghe Thilini, Wu Chia-Ming, Grassian Vicki H. Dissolution of ZnO nanoparticles at circumneutral pH: a study of size effects in the presence and absence of citric acid. *Langmuir* 2012;28:396–403.
- Nowack Bernd, Ranville James F, Diamond Stephen, Gallego-Urrea Julián A, Metcalfe Chris, Rose Jerome, Horne Nina, Koelmans Albert A, Klaine Stephen J. Potential scenarios for nanomaterial release and subsequent alteration in the environment. *Environ. Toxicol. Chem.* 2012;31:50–9.
- Partheniades E. A Study of Erosion and Deposition of Cohesive Soils in Salt Water (PhD thesis) Berkeley, USA: University of California; 1962.
- Petosa Adamo R, Jaisi Deb P, Quevedo Ivan R, Elimelech Menachem, Tufenkji Nathalie. Aggregation and deposition of engineered nanomaterials in aquatic environments: role of physicochemical interactions. *Environ. Sci. Technol.* 2010;44:6632–49.
- Powell MJD. The BOBYQA Algorithm for Bound Constrained Optimization Without Derivatives; 2009 (August, Internet, DAMTP 2009/NA06).
- Praetorius Antonia, Scheringer Martin, Hungerbühler Konrad. Development of environmental fate models for engineered nanoparticles – a case study of TiO₂ nanoparticles in the Rhine river. *Environ. Sci. Technol.* 2012;46:6705–13.
- Quik Joris TK, Vonk Jan Arie, Hansen Steffen Foss, Baun Anders, Van De Meent Dik. How to assess exposure of aquatic organisms to manufactured nanoparticles? *Environ. Int.* 2011;37:1068–77.
- Quik Joris TK, Stuart Martien Cohen, Wouterse Marja, Peijnenburg Willie, Jan Hendriks A, van de Meent Dik. Natural colloids are the dominant factor in the sedimentation of nanoparticles. *Environ. Toxicol. Chem.* 2012;31:1019–22.
- Quik JT, Velzeboer I, Wouterse M, Koelmans AA, van de Meent D. Heteroaggregation and sedimentation rates for nanomaterials in natural waters. *Water Res.* 2014;48:269–79.
- Thio Beng Joo Reginald, Zhou Dongxu, Keller Arturo A. Influence of natural organic matter on the aggregation and deposition of titanium dioxide nanoparticles. *J. Hazard. Mater.* 2011;189:556–63.
- Velzeboer I, Quik J, van de Meent D, Koelmans AA. Rapid settling of nanoparticles due to hetero-aggregation with suspended matter. *Environ. Toxicol. Chem.* 2014;33:1766–73.
- Virkutyte Jurate, Abed Souhail R, Dionysios Dionysiou. Depletion of the protective aluminum hydroxide coating in TiO₂-based sunscreens by swimming pool water ingredients. *Chem. Eng. J.* 2012;191:95–103.