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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.

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

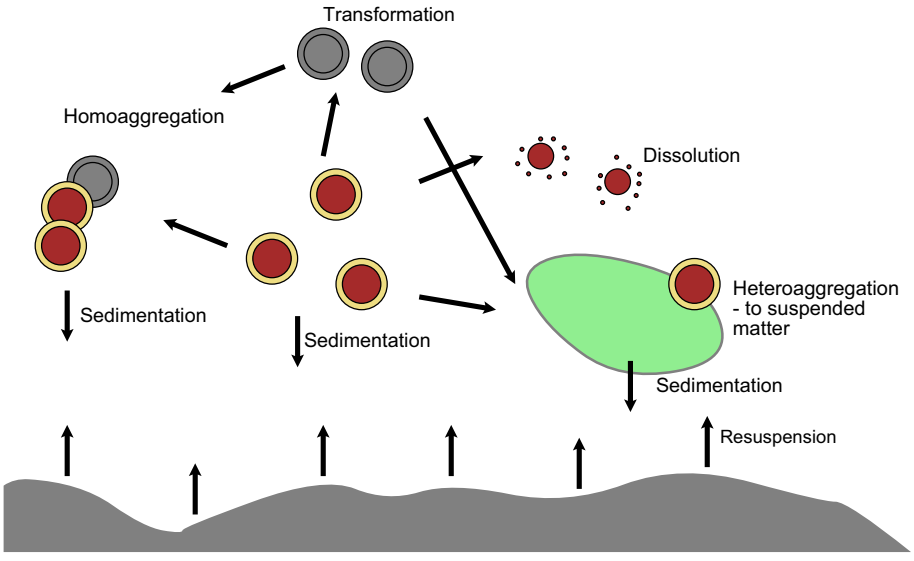

Fig. 1. Schematic representation of the various processes nanoparticles are subject to in the aquatic environment.