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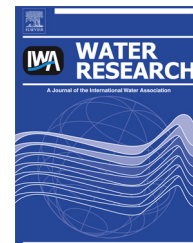
# Heteroaggregation and sedimentation rates for nanomaterials in natural waters

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## ARTICLE INFO

## ABSTRACT

Exposure modeling of engineered nanomaterials requires input parameters such as sedimentation rates and heteroaggregation rates. Here, we estimate these rates using quiescent settling experiments under environmentally relevant conditions. We investigated 4 different nanomaterials ($C_{60}$, $CeO_2$, $SiO_2$–Ag and PVP–Ag) in 6 different water types ranging from a small stream to seawater. In the presence of natural colloids, sedimentation rates ranged from 0.0001 m d$^{-1}$ for $SiO_2$–Ag to 0.14 m d$^{-1}$ for $C_{60}$. The apparent rates of heteroaggregation between nanomaterials and natural colloids were estimated using a novel method that separates heteroaggregation from homoaggregation using a simplified Smoluchowski-based aggregation-settling equation applied to data from unfiltered and filtered waters. The heteroaggregation rates ranged between 0.007 and 0.6 L mg$^{-1}$ day$^{-1}$, with the highest values observed in seawater. We argue that such system specific parameters are key to the development of dedicated water quality models for ENMs.

## 1.    Introduction

The production and use of engineered nanomaterials (ENMs) are growing, which increases their emission to environmental compartments (Nowack and Bucheli, 2007). Consequently, understanding the safety, environmental and human health implications of nanotechnology-based products is of worldwide importance (Klaine et al., 2012; Wiesner et al., 2006).

Although the benefits of ENMs have shown to be manifold, the implication of large quantities of ENMs entering the environment has yet to be understood (Batley et al., 2013; Hendren et al., 2011). There is a growing need for risk assessment of different nanomaterials in order to support their safe production and use (Morris et al., 2011). The environmental risk assessment is based on the determination of adverse effects on organisms and on evaluation of the environmental

concentrations to which biota are exposed (EU, 2008; Quik et al., 2011). Recently, modeling approaches for estimating the environmental exposure concentration of nanomaterials have been suggested (Arvidsson et al., 2011; Gottschalk et al., 2010; Praetorius et al., 2012; Quik et al., 2011). These studies acknowledge the lack of input parameters valid for environmentally relevant conditions, such as sedimentation rates in natural waters (Gottschalk et al., 2010; Quik et al., 2011) and heteroaggregation rates for collisions between natural colloids (NCs) and ENMs (Arvidsson et al., 2011; Praetorius et al., 2012). Since there is no validated framework for calculation of these parameters for ENMs, they need to be estimated experimentally (Hotze et al., 2010; Lin et al., 2010; Petersen et al., 2011; Westerhoff and Nowack, 2013).

The aggregation rate constants for heteroaggregation ($k_{het}$) can be split up in the product of collision frequency ($K$) and the attachment efficiency ($\alpha$), i.e. $k_{het} = K \times \alpha$ (Friedlander, 2000; Petosa et al., 2010). For homoaggregation, several studies use this approach to derive the attachment efficiency $\alpha_{homo}$ as an important parameter driving homoaggregation kinetics for a certain ENM under a range of test conditions, such as ionic strength or DOC concentration (Chen and Elimelech, 2008; Keller et al., 2010). Consequently, such attachment efficiencies are conditional and represent the average behavior of particles present. The uncertain and conditional nature of $K$ and $\alpha$ may be even bigger for heteroaggregation because natural colloids can be assumed to be much more heterogeneous and fundamentally indeterminate. Current methods to estimate attachment efficiencies $\alpha$ from observed aggregation rates rely on the collision frequency $K$ being constant or known among a range of test conditions. However, due to the range of water and NC characteristics present in natural systems, the collision frequency $K$ will not be constant. Furthermore, current theory of colloid behavior is not likely to be sufficient to estimate the collision frequency for natural systems. After all, this theory is based on ideal systems with spherical particles. In practice, fate models or water quality models for nanoparticles do not require separate attachment efficiencies $\alpha$, nor separate collision frequencies $K$. They require the aforementioned product $k_{het} = K \times \alpha$ (Arvidsson et al., 2011; Praetorius et al., 2012). The heteroaggregation rate constant $k_{het}$ is the primary parameter used in current exposure modeling approaches which take heteroaggregation into account (Praetorius et al., 2012). We argue that conditional values of $k_{het}$ are highly needed for the further development of fate models for ENMs.

In the present study we provide estimates of sedimentation rates and heteroaggregation rate constants, based on sedimentation data for 4 different ENMs in the presence and absence of NCs in 6 different natural water types. Heteroaggregation rates are usually measured by directly measuring the increase in particle size in time (Afrooz et al., 2013; Huynh et al., 2012). For natural waters, direct measurement of aggregation rates is problematic due to the limitations of measurement techniques for such complex systems. We therefore propose a novel method to estimate these heteroaggregation rates from sedimentation data. We used fullerene ($C_{60}$) as a carbon based ENM, Cerium dioxide ($CeO_2$) ENM as a metal oxide and Silver (Ag) ENM with two different coatings, polyvinylpyrrolidone (PVP) and silicon dioxide ($SiO_2$). Quiescent settling was measured in water from six different water bodies ranging from a small pond and stream to lake and seawater. These water samples cover a range in water quality characteristics such as salinity, acidity and organic matter content. Earlier work showed that NCs governed the sedimentation of ENMs in river water (Rhine and Meuse) (Quik et al., 2012). Here, this mechanism is studied for a much wider range of water types, including brackish tidal water and marine water. Sedimentation rates and heteroaggregation rates for ENMs and NCs are reported. To our knowledge, this is the first study that reports these parameters on the interaction of ENMs with NCs in surface waters.

## 2. Materials and methods

### 2.1. Engineered nanomaterials

Polyvinylpyrrolidone coated silver (PVP–Ag) nanoparticles (hydrodynamic diameter ($d_h$): 90.5 nm) and $SiO_2$ coated silver ($SiO_2$–Ag) nanoparticles ($d_h$: 124 nm) were purchased from nanoComposix (San Diego, CA). Ceriumdioxide ($CeO_2$) nanoparticles ($d_h$: 175 nm) were kindly supplied by Umicore Ltd. (Brussels), as part of the EU NanoInteract project. $CeO_2$ nanoparticles from the same batch have previously been used in several fate and effect studies (Quik et al., 2010, 2012; Van Hoecke et al., 2011; Van Hoecke et al., 2009). Fullerene ($C_{60}$, $d_h$: 217 nm), 99 wt% purity was obtained as powder from Cheaptubes (Brattleboro, VT). A $C_{60}$ nanoparticles stock suspension was prepared by dispersing 1 g L$^{-1}$ $C_{60}$ in deionized water by shaking (150 rpm) for 4 weeks in a glass bottle screened from sunlight. Other properties and electron microscopy images of the ENMs are provided as Supporting Information (Table A1, Figure A1, Figure A2).

Particle size distribution and particle number concentration were measured using nanoparticle tracking analysis (NTA). This was done using the NanoSight LM 20 (NanoSight Ltd., Salisbury, UK) using a previously described method (Quik et al., 2010) and NTA software version 2.2. It should be noted that the NTA method is not very sensitive to particles <50 nm with a low refractive index and particles >1500 nm. This implies that the NTA based characteristics are operationally defined. Electrophoretic mobility was measured with a Zeta-Sizer instrument (nano series, Malvern Instruments Ltd., Worcestershire, UK). Throughout this paper, the term 'concentration' refers to mass concentration unless indicated otherwise.

### 2.2. Water sampling

Six different natural waters were sampled using polyethylene containers. Samples were taken from the North Sea (NZ, coastal sea), Rhine (RL, river), Brabantse Aa (AA, small stream), IJsselmeer (IJ, freshwater lake), Nieuwe Waterweg (MS, tidal water), and Karregata (KG, small acid pond), all located in the Netherlands. Details on sampling and exact locations are provided as Supporting Information (Table A2). Sedimentation experiments were started on the same day of sampling. To remove NCs, part of the water was filtered with 0.2 μm membrane filters (Nuclepore filters, PALL), following earlier