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# Stability of engineered nanomaterials in complex aqueous matrices: Settling behaviour of CeO<sub>2</sub> nanoparticles in natural surface waters



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## ABSTRACT

The stability of engineered nanoparticles (ENPs) in complex aqueous matrices is a key determinant of their fate and potential toxicity towards the aquatic environment and human health. Metal oxide nanoparticles, such as CeO<sub>2</sub> ENPs, are increasingly being incorporated into a wide range of industrial and commercial applications, which will undoubtedly result in their (unintentional) release into the environment. Hereby, the behaviour and fate of CeO<sub>2</sub> ENPs could potentially serve as model for other nanoparticles that possess similar characteristics. The present study examined the stability and settling of CeO<sub>2</sub> ENPs (7.3 ± 1.4 nm) as well as Ce<sup>3+</sup> ions in 10 distinct natural surface waters during 7 d, under stagnant and isothermal experimental conditions. Natural water samples were collected throughout Flanders (Belgium) and were thoroughly characterized. For the majority of the surface waters, a substantial depletion (> 95%) of the initially added CeO<sub>2</sub> ENPs was observed just below the liquid surface of the water samples after 7 d. In all cases, the reduction was considerably higher for CeO<sub>2</sub> ENPs than for Ce<sup>3+</sup> ions (< 68%). A first-order kinetics model was able to describe the observed time-dependant removal of both CeO<sub>2</sub> ENPs ( $R^2 \geq 0.998$ ) and Ce<sup>3+</sup> ions ( $R^2 \geq 0.812$ ) from the water column, at least in case notable sedimentation occurred over time. Solution-pH appeared to be a prime parameter governing nanoparticle colloidal stability. Moreover, the suspended solids (TSS) content also seemed to be an important factor affecting the settling rate and residual fraction of CeO<sub>2</sub> ENPs as well as Ce<sup>3+</sup> ions in natural surface waters. Correlation results also suggest potential association and co-precipitation of CeO<sub>2</sub> ENPs with aluminium- and iron-containing natural colloidal material. The CeO<sub>2</sub> ENPs remained stable in dispersion in surface water characterized by a low pH, ionic strength (IS), and TSS content, indicating the eventual stability and settling behaviour of the nanoparticles was likely determined by a combination of physicochemical parameters. Finally, ionic release from the nanoparticle surface was also examined and appeared to be negligible in all of the tested natural waters.

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## 1. Introduction

Over the past decade, the production and use of engineered nanoparticles (ENPs) have increased exponentially, which will inherently lead to their emission into the environment (e.g., surface water or groundwater), where their often unique and size-related properties could pose a threat to the ecosystem and public health (Klaine et al., 2012; Liu et al., 2013; The Project of Emerging Nanotechnologies, 2014). Particularly metal oxide nanoparticles, including CeO<sub>2</sub> ENPs, are increasingly being incorporated into a

wide range of industrial and commercial products (Keller et al., 2010). CeO<sub>2</sub> ENPs have for instance been used as polishing agents, as fuel additives, as automotive exhaust catalysts, and as electrolytes in solid oxide fuel cells, and have recently also gained interest for biomedical applications (e.g., in radio therapy and cancer treatment) due to their antioxidant properties (Karakoti et al., 2012; Shah et al., 2012). However, evidence of their toxicity to (aquatic) organisms and even human cells is also emerging, making a thorough understanding of their environmental behaviour and fate imperative in order to examine potential exposure routes and further improve risk assessment (Fang et al., 2009; Keller et al., 2010; Tso et al., 2010; Karakoti et al., 2012; Shah et al., 2012).

The stability of ENPs in complex aquatic media such as natural surface waters, is a key parameter governing their fate and

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potential toxicological risks, as well-dispersed nanoparticles could persist longer in the environment, be transported over larger distances, or could also potentially be involved in particle-facilitated contaminant transport, thus increasing their possible bioavailability or influence the bio-accessibility of other toxic pollutants (Gimbert et al., 2007; Fang et al., 2009; Quik et al., 2010; Liu et al., 2013). Aggregation, sedimentation, and dissolution are some of the main physicochemical processes affecting the stability and ultimate fate of ENPs in natural waters, and are highly influenced by both nanoparticle properties as well as the characteristics of the receiving medium (Boxall et al., 2007; Batley and McLaughlin, 2010; Velzeboer et al., 2014). Numerous studies have already addressed the effects of individual aqueous parameters such as pH, ionic strength (IS), cation valence, or the type and amount of natural organic matter (NOM) on these processes (Domingos et al., 2009; French et al., 2009; El Badawy et al., 2010; Quik et al., 2010; Liu et al., 2013). However, the vast majority of these studies have done so using simplified artificial solutions, where the full complexity and heterogeneity of real environmental systems is lacking (i.e., the combined effect of pH, IS, NOM, suspended solids, and other properties of the aqueous media) (Keller et al., 2010; Tso et al., 2010; Quik et al., 2012; Velzeboer et al., 2014). Therefore, there is still a need to study and elucidate the physicochemical behaviour and fate of ENPs in complex natural aquatic samples.

This study aimed to contribute to the general knowledge on the fate of nanoparticles in aquatic environments, by assessing the stability and sedimentation kinetics of CeO<sub>2</sub> ENPs in natural aqueous media, and identifying potential physicochemical factors affecting their behaviour in such complex environmental matrices. Therefore, CeO<sub>2</sub> ENPs (5 mg L<sup>-1</sup>) were dispersed in 10 distinct natural surface waters, and the evolution of their mass concentration over time (7 d), under stagnant and isothermal conditions (4–6 °C), was measured and evaluated by means of a first-order settling rate model proposed by Quik et al. (2012). Additionally, Ce<sup>3+</sup> ions were treated in the same way for comparison purposes.

## 2. Materials and methods

### 2.1. Surface water sampling and characterization

Surface water samples ( $\pm 20$  L) were collected from 10 different locations in the Flanders region (Belgium) (Table 1 and

**Table 1**  
Detailed overview of the different sampled surface waters.

Sample ID	Surface water	Type	Location	Coordinates	
				Latitude	Longitude
PUM	Putse Moer	Fen	Kalmthout	51° 22' 49"N	04° 26' 09"E
SC1	Scheldt	River	Doel	51° 17' 47"N	04° 16' 56"E
SC2	Scheldt	River	Linkeroever (Antwerp)	51° 12' 21"N	04° 22' 02"E
GAL	Galgenweel	Lake	Linkeroever (Antwerp)	51° 12' 47"N	04° 22' 43"E
RUP	Rupel	River	Niel	51° 05' 53"N	04° 20' 09"E
NIK	Nielse Kleiputten	Lake	Niel	51° 06' 28"N	04° 20' 25"E
OLS	Old Scheldt	Stream	Weert	51° 06' 20"N	04° 12' 06"E
DEN	Dender	River	Oudegem	51° 00' 41"N	04° 04' 16"E
GTC	Ghent–Terneuzen Canal	Canal	Zelzate	51° 11' 50"N	03° 48' 03"E
COC	Coupure Canal	Canal	Ekkerghem (Ghent)	51° 03' 11"N	03° 42' 35"E

Fig. A.1), and were characterized thoroughly within 48 h upon arrival at the lab. All samples were stored at 4–6 °C under dark conditions and settling experiments were initiated 48 h after sample collection. Electrical conductivity (EC) was measured using a type LF537 conductivity probe (WTW, Weilheim, Germany). A model 520A pH electrode (Orion Research Inc., Boston, MA, USA) was used to acquire the solution-pH. Total organic carbon (TOC) and inorganic carbon (IC) content were determined by means of a TOC analyser (TOC-V<sub>CPN</sub>, Shimadzu, Kyoto, Japan). Dry residue (DR) was obtained by evaporating 100 mL of surface water sample in a pre-weighed beaker at 105 °C, and recording the mass difference. The total suspended solids (TSS) content was obtained after (vacuum) filtration of 100 mL of water sample over pre-dried and pre-weighed 0.45 µm filters (Porafil RC, Macherey-Nagel GmbH & Co. KG, Düren, Germany), and determining the mass difference. Ion exchange chromatography (IEC) (761 Compact IC, Metrohm AG, Herisau, Switzerland) was applied to quantify anionic species (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>) present in the water samples. Colorimetric determination of nitrite (NO<sub>2</sub><sup>-</sup>) was carried out by first adding 1 mL sulfanilic acid solution (i.e., 1.5 g sulfanilic acid and 50 mL 37% HCl in 200 mL H<sub>2</sub>O), 1 mL  $\alpha$ -naphthylamine hydrochloride solution (i.e., a filtered solution of 1.2 g  $\alpha$ -naphthylamine in 2 mL 37% HCl added to 200 mL H<sub>2</sub>O), and 1 mL sodium acetate solution (i.e., 135 mg sodium acetate trihydrate in 500 mL H<sub>2</sub>O) to 20 mL of surface water sample. Then, this solution was shaken and allowed to fully react for 15 min prior to analysis using a Jenway 6400 Spectrophotometer (Bibby Scientific Ltd., Staffordshire, UK) at 520 nm. Concentrations of main elements (Na, K, Ca, and Mg), trace elements (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), and cerium in the surface waters were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Vista-MPX CCD Simultaneous ICP-OES, Agilent Technologies, Santa Clara, CA, USA) after being properly digested (i.e., 50 mL of surface water sample was boiled for 2 h on a hotplate at 150 °C under reflux using a beaker and a watch glass, after 5 mL 65% HNO<sub>3</sub> and 2 mL 30% H<sub>2</sub>O<sub>2</sub> had been added, and was quantitatively transferred to 100 mL volumetric flasks).

### 2.2. Nanoparticles

The CeO<sub>2</sub> ENPs (average particle size:  $4 \pm 2$  nm,  $\zeta$ -potential:  $+40 \pm 5$  mV, concentration: 50,000 mg L<sup>-1</sup>) were obtained from PlasmaChem GmbH (Berlin, Germany) in the form of an aqueous dispersion. Additional particle size analysis was performed by means of photon correlation spectroscopy (PCS) (Malvern PCS-100, Malvern Instruments Ltd., Worcestershire, UK). PCS measurements were performed in quadruplicate, at 25 °C using a HeNe laser (633 nm) positioned at a scattering angle of 150°. The so-called Z-average hydrodynamic particle size was obtained through cumulant analysis, while particle size distributions (PSDs) were obtained via multi modal analysis. Furthermore, the nanoparticles were visualized via transmission electron microscopy (TEM) (JEM-2200FS, Jeol Ltd., Tokyo, Japan) equipped with energy dispersive X-ray spectrometry (EDS), subjected to UV–vis spectroscopy (6400 Spectrophotometer, Jenway, Bibby Scientific Ltd., Staffordshire, UK), and to zeta ( $\zeta$ ) potential measurements (Zetasizer 3000 HSA, Malvern Instruments Ltd., Worcestershire, UK) to assess the nanoparticles surface charge. Ionic cerium (as Ce(NO<sub>3</sub>)<sub>3</sub>) (Plasma HIQU, 10 000  $\pm$  20 µg Ce<sup>3+</sup> mL<sup>-1</sup> in 2–5% HNO<sub>3</sub>) reference standard solution was purchased from ChemLab NV (Zedelgem, Belgium). All chemicals used were of analytical grade.

### 2.3. Settling experiments

Firstly, a screening experiment was conducted to examine the suitability of two potential settling recipients (i.e., conical-

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