



## Behavior and fate of industrial zinc oxide nanoparticles in a carbonate-rich river water



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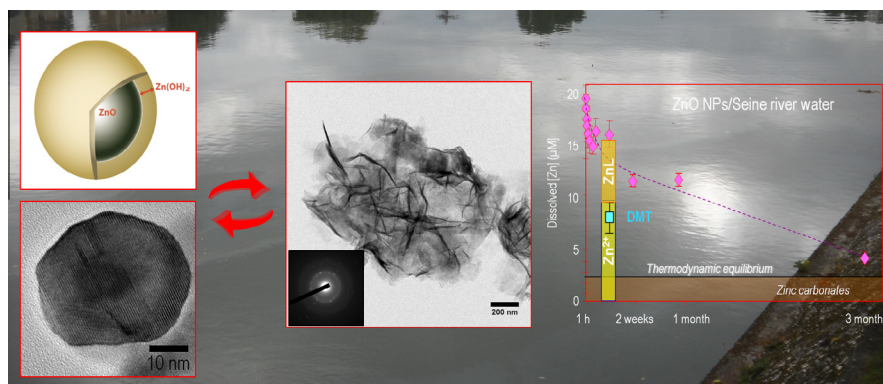
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### HIGHLIGHTS

- The fate of coated and uncoated commercial ZnO NPs was studied in natural water.
- A multi-approach combining DMT, UF and modeling was used for NPs solubility study.
- XPS evidenced the presence of a Zn(OH)<sub>2</sub> layer controlling NPs early dissolution steps.
- Organic coating on NPs was proved to increase both velocity and rate of dissolution.
- NPs dissolution is controlled over the long term by neoformation of carbonate phases.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The present study precisely describes the solubility patterns of commercial uncoated and organic coated ZnO NPs (nc-NPs and c-NPs, respectively) in a natural carbonate-rich water and the physicochemical processes involved. NPs transformation rates were determined with the Donnan Membrane approach (DMT, to obtain Zn<sup>2+</sup> concentration) and ultrafiltration (i.e. Zn<sup>2+</sup> and Zn bound to small organic ligands) and modeled with VMinteq. XPS measurements evidenced the presence on native nc-NPs of a Zn(OH)<sub>2</sub> layer which accounts for almost 22% of total Zn. This Zn(OH)<sub>2</sub> phase is more soluble than ZnO, and could control the early dissolution steps of the nc-NPs in our system. Indeed, nc-NPs display a fast (<1 h) dissolution step reaching 19 µM Zn in solution (<1% of the total initial zinc concentration). Comparatively, c-NPs progressively release zinc during the first 48 h, to finally reach a maximum of 197 µM (10% of total Zn), which is 10 times the maximum value measured for nc-NPs. Over the long term, dissolved Zn concentrations decrease in both systems, corresponding to the neoformation of carbonate phases observed by TEM imaging. The kinetic modeling allows highlighting two different ranges of time, corresponding to (i) first 10 h with a fast precipitation ( $k_p = -182 \cdot 10^{-4}$ ) related to a highly oversaturated solution with respect to carbonate zinc mineral and (ii) a second slower precipitation step ( $k_p = -8 \cdot 10^{-4}$ ), related to the embedding of NPs in the precipitated carbonate matrix. The steady state is reached after 3 months of interaction.

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### 1. Introduction

Recent and rapid progresses in nanotechnology have led to the development of nanoparticles (NPs), generally exhibiting

exceptional physico-chemical properties. These latter have led to their incorporation in an increasing number of common products: as contrasting agents for medical imaging (magnetite NPs), as high-efficiency semiconductor in electronics (metallic nanotubes), as structure reinforcement in wheel polymers (SiO<sub>2</sub> NPs), or even as UV shield in sunscreens (TiO<sub>2</sub> and ZnO NPs). However, this recent increase has simultaneously raised concerns relative to their

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release into natural environments and exposure to living organisms. With estimates for the production of engineered nanomaterials expected to increase to 58 000 tons per year between 2011 and 2020 (UNEP, 2007), it is inevitable that engineered NPs will be released into soils, sediments and aquatic ecosystems. Exposure modeling approaches have been developed to estimate the fluxes of manufactured NPs into the environment (Mueller and Nowack, 2008; Gottschalk et al., 2009; Nowack, 2009). These studies highlighted potentially problematic concentrations for some NPs (e.g. from 10 ng L<sup>-1</sup> to 500 ng L<sup>-1</sup> in surface waters and sewage sludge, respectively, for ZnO). As an important conclusion to those studies, it is postulated that surface waters act principally as dispersive agents while soils and sediments are able to accumulate high amounts of NPs (Gottschalk et al., 2009). Once released into natural waters, NPs can potentially be harmful to most living organisms (Peralta-Videoa et al., 2011, and references therein), but the detailed mechanisms by which NPs develop toxicity on living cells is still a matter of debate and the critical role of the NPs physico-chemical properties for the overall NPs reactivity is not well established yet (Oberdorster et al., 2005). This underlines the interpretation difficulties met by a significant number of authors, highlighting the need of investigating processes at work at the molecular scale in relation with the NPs physico-chemical surface properties determining their stability (Thill et al., 2006), their solubility (Franklin et al., 2007; Afsset, 2010; Reed et al., 2012) and their aggregation state (Slaveykova et al., 2009). In addition, some recent studies even suggest that NPs may undergo major transformations in natural systems by interaction with biota, resulting ultimately in important NPs stability unbalance (Metz et al., 2009; Slaveykova and Startchev, 2009). As such, the NPs behavior in aquatic systems needs to be assessed accurately to provide critical information regarding their general fate in natural systems, and ultimately evaluate the corresponding environmental risks linked to this new class of material.

Among other NPs, ZnO constitutes a potentially important diffuse source of NP contamination (Ju-Nam and Lead, 2008) because of its incorporation into sunscreens and cosmetics, and subsequent wash-off from individuals into the environment. ZnO NPs were already identified in 31 nanoparticles containing products (<http://nanotechproject.org/44>), whereas recent studies on ZnO NPs have shown some toxicological activity on algae (Adams et al., 2006), bacteria (Brayner et al., 2006; Franklin et al., 2007), and tests organisms (Wang et al., 2010). Furthermore, NPs in general and more particularly ZnO NPs are often commercialized and used with an organic coating which aims to better control their surface properties. Hence, when industrial NPs will be released in environment, their core structure will rarely be in direct contact with the natural media, and the impact of these organic coatings on ZnO NPs behavior is totally unknown.

Based on these facts, the overarching goal of the present study is to gather significant information relative to the fate of ZnO NPs in a representative natural water and concentrations relevant for both toxicological studies and natural systems like sediment interstitial pore water or groundwater. Specific focus will be held on: (i) the methodological approach used to study NPs solubility; (ii) the stability, solubility and transformation characteristics of ZnO NPs in the Seine river water and (iii) the impact of industrial organic coating on ZnO NPs transformation in these natural medias.

## 2. Experimental section

### 2.1. Choice of NPs

The most relevant choice is to work with industrial NPs, which are produced in significant amounts and may potentially be

released in the environment. The studied zinc oxide NPs (ZnO-NPs) were kindly provided by Kobo Products®, an industrial manufacturer major purveyor of the cosmetic industry. Both uncoated ZnO-NPs (nc-NPs) and organic coated ZnO-NPs (c-NPs) were studied, in order to determine the role of coating on NPs behavior in environment. Information provided by manufacturer on c-NPs and nc-NPs are displayed in Table S1 (Appendix A).

### 2.2. Choice of natural media

Surface waters were shown to be one of the major vectors of NPs dispersion in environment (Gottschalk et al., 2009). Hence, a sample of the Seine river water was used as it is highly representative of a natural carbonate-rich system and of a highly anthropized watershed. The Seine river sample was collected in front of the University Paris Diderot (Quai Panhard et Levassor, Paris, France, 48°50'01.20"N, 2°22'43.40"E). The river sample was collected and filtered through a 0.2 µm cellulose acetate membrane, stored in pre-cleaned, acid-washed polyethylene bottles and divided in two subsamples: one half used for NPs solubility experiments and the other one for elemental analyses. Sampling and analytical procedures were described by Benedetti et al. (2003). The Seine river water pH was 8.05 and DOC was 2.445 mg L<sup>-1</sup>. Chemical composition is displayed in Table S2 (Appendix A).

### 2.3. Characterization studies

All solid phases (native NPs and secondary phases) were characterized with microphysical techniques. The native size of NPs was determined by three different techniques (i.e. XRD, TEM and DLS), following recommendations from (Domingos et al., 2009). The crystalline structures were determined by X-ray diffraction (XRD) using a Panalytical X'pert Pro diffractometer equipped with a multichannel X'celerator detector, and using a Co K $\alpha$  radiation ( $\lambda = 1.7889 \text{ \AA}$ ) in the  $2\theta$  range of 20–100°. Diluted suspensions of the solid phases were deposited on copper grid to observe their sizes and shapes by Transmission Electron Microscopy (TEM), using a JEOL 2100F electron microscope operating at 200 kV and equipped with a field emission gun, a high-resolution UHR pole piece and a Gatan GIF 200 L imaging filter. To perform chemical analysis, this microscope was coupled with electron-dispersive X-ray spectroscopy (EDXS) using a JEOL detector with an ultrathin window allowing detection of low atomic mass elements. TEM pictures were treated with the software ImageJ 1.43u. The hydrodynamic size of the native NPs was measured by Dynamic Light Scattering (DLS) using Malvern Zetasizer HS 3000 (Malvern Instruments) at a concentration of 2.5 mM of Zn introduced as ZnO and dispersed at 22 °C. Specific surfaces were determined by the Brunauer, Emmett and Teller method (BET) with N<sub>2</sub> as inert gas. For X-ray Photoelectron Spectrometry (XPS), samples were settled on a carbon adhesive tape and degassed one night long to remove atmospheric carbon and water. Analyses were performed using an ESCALAB 250 (ThermoElectron, ENSCP, Paris, France). ICP-OES and HR-ICP-MS analyses (ThermoScientific iCAP 6200 and Element II, resp.) were performed to determine the elemental concentrations in aqueous solutions (samples and blanks).

### 2.4. NPs solubility studies

ZnO c-NPs and nc-NPs was assessed using both ultrafiltration (UF, 1 kDa) and Donnan Membrane Technique (DMT). The latter method was developed by Fitch and Helmke (1989) and modified by (Temminghoff et al., 2000) to allow a direct measurement of the free metal ion concentration (here Zn<sup>2+</sup>) in soil suspensions (Cances et al., 2003) or laboratory experiments with rare earth elements (Marang et al., 2006), while the UF membrane small

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