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## Addressing the complexity of water chemistry in environmental fate modeling for engineered nanoparticles

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### HIGHLIGHTS

- New method to analyze spatial variability in engineered nanoparticle fate models
- Application to titanium dioxide nanoparticles (NPs) in the Rhône River, France
- Heteroaggregation of NPs with suspended particles reflects water chemistry
- Complexity of a wide range of water chemistries reduced by cluster analysis
- The fate of NPs can be predicted when aggregation is strong near the emission source.

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### ABSTRACT

Engineered nanoparticle (ENP) fate models developed to date – aimed at predicting ENP concentration in the aqueous environment – have limited applicability because they employ constant environmental conditions along the modeled system or a highly specific environmental representation; both approaches do not show the effects of spatial and/or temporal variability. To address this conceptual gap, we developed a novel modeling strategy that: 1) incorporates spatial variability in environmental conditions in an existing ENP fate model; and 2) analyzes the effect of a wide range of randomly sampled environmental conditions (representing variations in water chemistry). This approach was employed to investigate the transport of nano-TiO<sub>2</sub> in the Lower Rhône River (France) under numerous sets of environmental conditions. The predicted spatial concentration profiles of nano-TiO<sub>2</sub> were then grouped according to their similarity by using cluster analysis. The analysis resulted in a small number of clusters representing groups of spatial concentration profiles. All clusters show nano-TiO<sub>2</sub> accumulation in the sediment layer, supporting results from previous studies. Analysis of the characteristic features of each cluster demonstrated a strong association between the water conditions in regions close to the ENP emission source and the cluster membership of the corresponding spatial concentration profiles. In particular, water compositions favoring heteroaggregation between the ENPs and suspended particulate matter resulted in clusters of low variability. These conditions are, therefore, reliable predictors of the eventual fate of the modeled ENPs. The conclusions from this study are also valid for ENP fate in other large river systems. Our results, therefore, shift the focus of future modeling and experimental research of ENP environmental fate to the water characteristic in regions near the expected ENP emission sources. Under conditions favoring heteroaggregation in these regions, the fate of the ENPs can be readily predicted.

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### 1. Introduction

The increasing production and use of engineered nanoparticles (ENPs) in consumer products inevitably lead to ENP emissions into the environment (Colvin, 2003; Money et al., 2012; Sun et al., 2014). The potential risks to humans and ecosystems associated with increased ENP emissions depend on the transport and transformation pathways of the ENPs in

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natural systems and ultimately on the ENP concentration in different environmental compartments. Additionally, the magnitude of the risk may depend on whether the emitted ENPs are aggregated or freely dispersed. Risk assessment of ENPs needs to be supported by predictive fate models since measurements of ENP concentrations in the environment are still scarce (Gondikas et al., 2014; von der Kammer et al., 2012).

A new framework of multimedia environmental fate models was developed recently to investigate the transport and fate of ENPs in surface waters including nano-specific process descriptions (Praetorius et al., 2012). This model framework was applied to a case study of nano-TiO<sub>2</sub> in the Rhine River and demonstrated the importance of heteroaggregation between the modeled ENPs and naturally occurring suspended particulate matter (SPM) on the overall fate of ENPs in large rivers. In this framework, the heteroaggregation rate constant,  $k_{\text{heteroaggregation}}$ , is described as a pseudo first-order rate constant because it can be assumed that the SPM concentration is much higher than the expected ENP concentration. The heteroaggregation rate constant is described by:

$$k_{\text{heteroaggregation}} = \alpha_{\text{hetero}} \cdot k_{\text{collision}} \cdot [\text{SPM}] \quad (1)$$

where  $k_{\text{collision}}$  is the collision frequency representing collisions due to perikinetic and orthokinetic motion and differential settling;  $\alpha_{\text{hetero}}$  (heteroaggregation attachment efficiency) is the fraction of collisions between the ENPs and the SPM resulting in attachment (Elimelech et al., 1995); and [SPM] is the SPM concentration. The characteristics of the aggregating particles (diameter and density) and the properties of the surrounding medium strongly affect  $k_{\text{heteroaggregation}}$ . The parameter  $\alpha_{\text{hetero}}$  is influenced by both medium properties and the surface properties of the involved particles; following the principles of colloid science, ionic strength, pH and medium chemical composition will determine the surface charge of both ENPs and SPM, subsequently affecting their attachment efficiency (Chen et al., 2007; Dunphy Guzman et al., 2006; Petosa et al., 2010).

The insights from the earlier study (Praetorius et al., 2012) are valuable, but they were derived from a model that employs a constant environmental composition (represented as constant [SPM]) and a single heteroaggregation rate constant between the modeled ENPs and the SPM) from headwaters to downstream waters. Therefore, the earlier model does not show the possible effects of spatial and temporal variability in environmental conditions on the fate of ENPs. Also other ENP fate models recently developed have been used to study the distribution of ENPs in environmental systems, see Scheringer et al. (2014) and Meesters et al. (2014) for an overview of different modeling approaches.

In the environment, water composition and SPM concentration and composition change spatially and temporally as a result of natural and anthropogenic processes. From the source to the mouth of the river, the chemical and physical composition of water and SPM is affected by the bedrock composition and water–rock interaction. Inflows from large tributaries, which carry SPM in various concentrations and compositions, e.g., mineralogy and grain size, may also differ in their water chemistry, and therefore can strongly contribute to the spatial variability along the river.

According to the River Continuum Concept, geomorphological changes in large rivers are an additional cause of spatial variation; creating spatial variation in ecological processes and nutrient availability, these processes give rise to spatial variation in natural organic matter (NOM) composition (Vannote et al., 1980). Furthermore, in large rivers, anthropogenic impacts such as sewage emission, presence of dams and urban and agriculture runoff contribute to spatial and temporal variation in water composition (i.e. pH, major and trace elements) and SPM content (Alberto et al., 2001; Jarvie et al., 2006; Ollivier et al., 2010, 2011).

Unlike the effect of pH and ionic strength, the complex effect of NOM on ENP behavior is less predictable, as it is governed by numerous

factors. Previous studies have demonstrated that NOM can stabilize or destabilize ENPs depending on the intricate relationship between the water composition, the NOM molecular composition and the ENP surface properties (Chen et al., 2007, 2012; Deonaraine et al., 2011; Labille et al., 2010; Loosli et al., 2013; Louie et al., 2013).

The combined effect of all mentioned parameters determines the fate of ENPs in natural waters (Christian et al., 2008; Keller et al., 2010). However, the effects of numerous variations in these parameters are laborious and time-consuming to evaluate, by means of solely an experimental approach, as an attempt to study the natural environment; it would require an extensive sampling of the modeled system to determine water properties at different points in time and space and an experimental determination of  $\alpha_{\text{hetero}}$  between the ENP and SPM in the different water samples. In this situation, numerical methods come in useful because they can be used to investigate the influence of various parameter combinations on the fate of ENPs in a given system.

For this purpose we developed a model capable of incorporating numerous combinations of diverse environmental conditions along a river system and applied a cluster analysis to identify the key features affecting the overall ENP fate. We report our findings using a case study of nano-TiO<sub>2</sub> in the Lower Rhône River, France.

## 2. Methods

### 2.1. General approach

To address the objectives of this study, we further developed an existing ENP river fate model (Praetorius et al., 2012) to incorporate spatial variability in water composition. Measured data on water composition (mainly SPM concentration and size distribution), obtained from a recent sampling campaign of the Lower Rhône River (Slomberg et al., in preparation), were incorporated in the model. The positions of the eight sampling locations (see Fig. 1) were used to divide the river into sections. The sampling locations were chosen to represent water inflowing from the main tributaries of the Lower Rhône River, since it is assumed that inflow from tributaries is a key factor determining the spatial variability in SPM composition and water chemistry. In addition, the sampling locations were chosen to be far from dams and branched sections of the river. To each river section represented in the model, the SPM composition and concentration were assigned that were measured at the sampling location at the upstream end of the section. In this study, we consider nano-TiO<sub>2</sub> emissions from a single point source at Lyon. In reality, effluents from every sewage treatment plant and different non-point sources contribute to the ENP load to surface waters. However, multiple ENP emission sources would mask the effect of spatial variation in water composition on the fate of the ENPs. Therefore, we only include emissions from the single source at Lyon and, accordingly, our study provides insights into the effect of spatial heterogeneity in water composition on the fate of ENPs in the river, but not a realistic estimation of nano-TiO<sub>2</sub> concentrations in the Lower Rhône River.

To account for the effect of spatial variability in water composition (pH value, ionic strength, NOM concentration, etc.) on the aggregation rate between SPM and the modeled nano-TiO<sub>2</sub>, each river section was assigned a distinct  $\alpha_{\text{hetero}}$  value. To consider changes in water composition, for example due to seasonal variations, many sets of  $\alpha_{\text{hetero}}$  values (one value for each river section) were randomly sampled, where each set represents a specific combination of environmental conditions in the different sections. The parameter  $\alpha_{\text{hetero}}$  is used as a placeholder that implicitly reflects the effects of variable water chemistry (pH value, salinity, type of SPM, type and concentration of NOM). In order to reduce the computational effort, the water chemistry and SPM composition within each river section were assumed to be constant. Therefore, the position and length of each section define the resolution of the model with respect to variability in environmental conditions (water chemistry and SPM composition). Spatial nano-TiO<sub>2</sub> concentration profiles

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