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# Effects of molecular weight-dependent physicochemical heterogeneity of natural organic matter on the aggregation of fullerene nanoparticles in mono- and di-valent electrolyte solutions

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## ABSTRACT

Given the wide presence of heterogeneous natural organic matter (NOM) and metal ions (Na<sup>+</sup>/Ca<sup>2+</sup>/Mg<sup>2+</sup>), as well as their significant role in governing nanoparticle stability in aqueous environments, it is of great importance to understand how the molecular weight (MW)-dependent physicochemical properties of NOM impact fundamental transportation processes like the aggregation of engineered nanoparticles (ENPs) in the presence of Na<sup>+</sup>/Ca<sup>2+</sup>/Mg<sup>2+</sup>. Here, we report on the aggregation behavior of a model ENP, fullerene nanoparticles (nC<sub>60</sub>) in the presence of five MW fractions of Suwannee River NOM (M<sub>F</sub>-SRNOMs, separated by ultrafiltration techniques) and three electrolytes (NaCl, CaCl<sub>2</sub> and MgCl<sub>2</sub>). We found that in all NaCl treatments and low concentration CaCl<sub>2</sub>/MgCl<sub>2</sub> treatments, the enhancement of nC<sub>60</sub> stability positively correlated with the MW of M<sub>F</sub>-SRNOMs. Whereas, the stability efficiency of identical M<sub>F</sub>-SRNOM in different electrolytes followed an order of NaCl > MgCl<sub>2</sub> > CaCl<sub>2</sub>, and the enhanced attachment of nC<sub>60</sub>-SRNOM associations was observed in high MW M<sub>F</sub>-SRNOM (SRNOM > 100 kD and SRNOM 30–100 kD) at high concentration CaCl<sub>2</sub>/MgCl<sub>2</sub>. Our results indicate that although the high MW NOM with large humic-like material is the key component for stabilizing nC<sub>60</sub> in monovalent electrolyte, it could play a reversed role in promoting the attachment of nC<sub>60</sub>, especially in long term aggregations and at high concentrations of divalent cations. Therefore, a detailed understanding of the effects of heterogeneous NOM on the aggregation of ENPs should be highly valued, and properly assessed against different cation species and concentrations.

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## 1. Introduction

NOM is a poorly defined, complex mixture of molecules with different physical structures, chemical compositions and properties (Chen et al., 2002; Peuravuori and Pihlaja, 1997), and can be regarded as a heterogeneous structure consisting of hydrophobic backbones and hydrophilic side chains (Qu et al., 2010). In aqueous environments, the structure of NOM is closely related to its chemical composition and functional groups, with molecular size, shape and aggregation state considered as key factors influencing physicochemical reactions (Piccolo, 2001; Baalousha et al., 2006). Electrolytes and pH can govern the surface charge and spectroscopic/photochemical properties of NOM in solutions (Her et al., 2003; Christl and Kretzschmar 2001). Furthermore, for di- and multivalent cations, in addition to the electrostatic interaction, interactions such as complexation/cation-bridging effects between functional groups in/among NOM and them, could result in significantly changes of NOM structures as well (Baalousha et al., 2006; Wang et al., 2013; Kloster et al., 2013). It is therefore of environmental significance to understand how the heterogeneous properties of NOM in environmental relevant conditions impact their physicochemical interactions with exogenous substances, especially the engineered nanoparticles (ENPs).

Fullerenes ( $C_{60}$ ) are among the most widely used ENPs in industry and consumer products (Mauter and Elimelech, 2008). In addition, naturally occurring  $C_{60}$  is also widely observed in natural carbonaceous materials (Jehlicka et al., 2005) and combustion process (Murr and Soto, 2005). However, even water treatment plants could not remove all  $C_{60}$ . It has been reported that  $C_{60}$  in  $\mu\text{g L}^{-1}$  range was detected in the effluents of water treatment plants (Farre et al., 2010). Thus, it is predictable that the environmental exposure of  $C_{60}$  would be inevitably promoted. Although it has an extremely low water solubility (Jafvert and Kulkarni, 2008), molecular  $C_{60}$  can form stable nanoscale aggregates ( $nC_{60}$ ) in water through solvent-exchange and extended stirring (Brant et al., 2006; Ma and Bouchard, 2009). Despite the low toxicity of  $nC_{60}$  to aquatic organisms (Henry et al., 2011) and limited hazard through human exposure (Aschberger et al., 2010), an emerging environmental issue is the role of  $nC_{60}$  as a contaminant carrier, which influences the transport, fate and bioavailability of  $nC_{60}$ -adsorbed contaminants in aqueous environments (Baun et al., 2008). Elucidating the toxicity and risks of  $nC_{60}$  requires more detailed studies on its environmental fate and behavior (Lowry et al., 2012; Petosa et al., 2010). This is highly dependent on the size heterogeneity of  $nC_{60}$  aggregates in the aqueous environment (Chae et al., 2010), which thus highlights the importance of understanding the aggregation process of  $nC_{60}$ .

The inevitable encounter of NOM upon the released  $nC_{60}$  and other ENPs in the environment has increased the interest in their active interactions (Lowry et al., 2012; Zhang et al., 2009; Xie et al., 2008). Previous studies have attempted to extend our understanding of ENP interactions with bulk (Zhang et al., 2009) or specific components (Xie et al., 2008; Zhang et al., 2013; Lin and Xing, 2008) of NOM, such as humic acid (HA), fulvic acid (FA) and low-molecular-weight

organic acids. It was observed that  $nC_{60}$  could be stabilized in the presence of bulk or specific components of NOM by invoking steric repulsion (Qu et al., 2010; Chen and Elimelech, 2007) resulting from adsorbed NOM layers on  $nC_{60}$ . Moreover, FA was found to be less effective than HA as FA has a lower affinity with  $nC_{60}$  due to its higher charge density and smaller aromatic backbone (Terashima and Nagao, 2007). In addition, the occurrence of NOM- $nC_{60}$  aggregation may lead to the enhanced aggregation of  $nC_{60}$  in solutions with high concentrations of divalent cations (Chen and Elimelech, 2007). It is therefore of significant interest to systematically study how the molecular weight (MW)-dependent physicochemical properties of NOM impact fundamental processes such as the aggregation of  $nC_{60}$ , both in the presence and absence of divalent electrolytes. However, to date, only a single study has been reported regarding the influence of simply fractionated NOM (molecular weight  $>100$  kD and  $<100$  kD) on the aggregation behavior of gold nanoparticles in NaCl solutions (Louie et al., 2013). Moreover, to the best of our knowledge, no studies have considered the MW-dependent effects of NOM on the stability of ENPs against different electrolyte species.

The primary objective of this work is to study the effects of MW-dependent physicochemical heterogeneity of NOM on the aggregation kinetics of  $nC_{60}$ . To this end, pristine Suwannee River natural organic matter (SRNOM) and isolated MW fractions of SRNOM ( $M_f$ -SRNOMs) were comprehensively characterized, and their impacts on  $nC_{60}$  aggregation were investigated in monovalent and divalent electrolyte solutions at varying concentrations. Additionally, the adsorption of  $M_f$ -SRNOMs onto  $nC_{60}$ , surface charge change of  $nC_{60}$ , and long term aggregation were fully investigated to assist the discussion. To our knowledge, this is the first study on the impacts of MW distribution and chemical properties' heterogeneity of NOM on the aggregation behavior of  $nC_{60}$  in both monovalent and divalent electrolytes.

## 2. Materials and methods

### 2.1. Materials

Suwannee River NOM (SRNOM, 1R101N) was obtained from the International Humic Substances Society (St. Paul, MN).  $C_{60}$  powder (purity greater than 95%) was obtained from Sigma–Aldrich (St. Louis, MO). All solutions and suspensions were prepared using 18 M $\Omega$  cm water produced with a Millipore Milli-Q Gradient system (Billerica, MA). Toluene was obtained from Fisher Scientific (Fair Lawn, NJ). Other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China).

### 2.2. Preparation of pristine and molecular weight fractions of SRNOM

A 500 mg sample of SRNOM was dispersed in 500 mL of deionized water and stirred for 12 h in dark. The solution was then filtered through a 0.45  $\mu\text{m}$  pore-size hybrid fiber membrane to remove any undissolved SRNOM. This filtered solution was referred to as pristine-SRNOM. A molecular weight-based fractionation of pristine-SRNOM was performed using

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