



Spectroscopic and microscopic characteristics of natural aquatic nanoscale particles from riverine waters



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ABSTRACT

The physicochemical characterization of colloids in waters is vital for the understanding of their crucial role in transportation of pollutants and biogeochemical processes of trace elements in aquatic systems. However, there are still lack of knowledge about quantitative properties of natural aquatic nanoscale particles owing to their small size and matrix complexity. In the present work, the complementary spectroscopic and microscopic methods were applied to characterize the fluorescent properties of organic colloids, morphology of complex nanoparticles and colloidal speciation of Fe and Mn in rivers, namely Pu River (PR), Xi River (XR) and Haicheng River (HCR), located in northeast of China. Parallel factor analysis (PARAFAC) of excitation-emission matrix (EEM) spectra reveals ten fluorescent components occurring in colloidal organic matter fractionated by ultrafiltration process with cut off 1 kDa or 100 kDa membrane: five humic-like fluorophores (C1, C2, C3, C6 and C8) and five protein-like components (C4, C5, C7, C9 and C10). The majority of humic-like substances is present in small size colloids (1–100 kDa) in these waters and the protein-like materials are, not truly dissolved or “free”, but associated with colloidal materials. Atomic force microscopy (AFM) measurement indicates that small near-spherical particles with height dimensions up to 6 nm are main form in the three rivers and occasionally fibrillary material. The significant shift in the size distribution of natural colloids occurs across three rivers with average particle size of 1.43 ± 1.01 nm in the XR, 1.53 ± 1.22 nm in the PR and 2.22 ± 1.31 nm in the HCR. Analysis by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) combined with ultrafiltration shows that over 73% of total dissolved Fe and <45% of total dissolved Mn are present in the colloidal phase despite diverse distribution of colloidal Fe and Mn in small size (1–100 kDa) or large size (>100 kDa) fractions across selected rivers.

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1. Introduction

Natural aquatic environment is complex system. Based upon component size, it consists of truly dissolved fraction, nano-colloidal and particulate matters. These materials are composed of organic and inorganic components, as well as microorganisms. Natural aquatic nano-colloids are usually defined as naturally occurring nano-particles with one dimension in the size range of 1 nm and 1 μ m (Buffle, 2006; Lead and Wilkinson, 2006). It is becoming increasingly apparent that natural colloidal materials play a crucial role as an intermediary in environmental and biogeochemical processes, such as C, N and P cycling, aggregation and sedimentation, as well as pollutant fate and ecotoxicology because these colloids have a large surface area, a high concentration and dense surface binding sites capable of strong interactions with

trace pollutants (Vignati and Dominik, 2003; Utsunomiya et al., 2009; Liu et al., 2013). Despite the obvious importance of aquatic colloids there is still a lack of quantitative understanding for them. Thus, to understand the role of colloids in the aquatic systems better, it is essential to characterize the size distribution, organic or inorganic components of colloids from different origins.

The natural aquatic colloidal materials are made of inorganic colloids e.g. Fe, Al, Mn oxides, organic materials with low polydispersity, but chemically heterogeneous (e.g. humic substances), and large biopolymers (Wells and Goldberg, 1991; Buffle, 2006; Lead and Wilkinson, 2006). Due to small size and matrix complexity of natural aquatic nanoparticles, the proper characterization of these materials is extremely challenging. Great developments in analytical methods have enabled the detailed characterization of these complex materials, where a combination of different analytical methods gives greater confidence in results and provides a comprehensive insight into the properties of natural nanoparticles. These techniques include separation methods, e.g. flow field flow fractionation (FIFFF) (Baalousha and R., 2007; Lapworth et al., 2013; Neubauer et al., 2013), cross flow filtration

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(CFF) (Liu and Lead, 2006), ultrafiltration (UF) (Pokrovsky and Shirokova, 2013; Shirokova et al., 2013; Majumder et al., 2014) and split-flow lateral transport thin-cell (SPLIT) (Lead et al., 2006), microscopic approaches, such as atomic force microscopy (AFM) (Liu and Lead, 2006; Baalousha and R., 2007), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Baalousha and R., 2007; Hennebert et al., 2013; Lapworth et al., 2013), as well as spectroscopic methods (Liu et al., 2007; Liu et al., 2013; Neubauer et al., 2013), for instance, inductively coupled plasma-mass spectrometry (ICP-MS), UV and fluorescence spectrometry.

Since the 3-D fluorescence excitation-emission matrix (EEM) spectrophotometric technique has been developed, the extensive efforts have been made to the investigation of dissolved organic matter (DOM) from freshwater, coastal waters and wastewaters (Baker and Spencer, 2004; Hudson et al., 2007; Liu et al., 2007). For further interpreting EEMs of complex mixture, Parallel Factor Analysis (PARAFAC) as a multivariate statistical means has been successfully combined with EEMs for the determination of chemically independent but spectral overlapping fluorescence components of DOM (Stedmon et al., 2003; Osburn et al., 2012; Yu et al., 2013; Rutledge et al., 2015). This method separates the fluorescence signal of DOM into individual fluorescent components whose fluorescence intensity can be related to the concentration of DOM precursor materials. Nevertheless, fluorescent DOM in most of these studies is totally based on single filtration through a membrane of 0.45 or 1.0 μm . There has been little study through a combination of ultrafiltration with EEMs-PARAFAC to characterize fluorescent properties of nanoscale colloidal organic materials (COM) in aquatic systems even though our previous studies showed that a large proportion of fluorescent materials were present in COM (Liu et al., 2007; Liu et al., 2013).

The morphology investigation of natural colloidal particles requires a direct and nonperturbing measurement technique. Atomic force microscopy (AFM) is such a nonperturbing and quantitative technique for imaging nanoparticles in water systems. Because of its greater resolution and the possibility of imaging under ambient conditions, low concentration, high sample polydispersity or high sample complexity, AFM has been increasingly used for the size determination and conformation of natural aquatic nanoparticles including humic substances, inorganic colloids and aquatic complex colloids (Plaschke et al., 2002; Lead et al., 2005; Guo and Ma, 2006; Liu and Lead, 2006; Baalousha and R., 2007; Baalousha and Lead, 2013; Lapworth et al., 2013). Despite these advantages, the technique still remains widely untested for the quantification of size distributions and number concentrations from various natural aquatic systems (Kaegi et al., 2008), due to its time-consuming for the microscopic analysis of individual colloidal particle and sample preparation dependence of results (Baalousha and Lead, 2013).

There is no single technique for determining all natures of nanoscale colloids that are the complex mixture because of the non-specificity of each technique and the low concentrations in natural aquatic systems. To date, very few studies have been performed on the same water sources for their spectroscopic and microscopic properties of colloidal particles using different techniques. Additionally, little study has been carried out by a combination of ultrafiltration with EEMs-PARAFAC to investigate fluorescent properties of nanoscale colloidal organic materials (COM) in aquatic system.

Therefore, in this study, a range of complementary methods were used for the characterization of natural nanoscale colloids from riverine waters in the Daliao River Watersystems (DLRW), located in the northeast of China. The specific objectives were to characterize fluorescent properties of colloidal organic matter through a combination of UF system with EEMs-PARAFAC, to investigate the size distribution and morphology of aquatic complex colloids using AFM technique and to examine colloidal speciation of inorganic Fe and Mn derived from UF coupled with ICP-OES analysis. It is expected that addressing these issues would give a greater confidence in quantitative results for morphology and phase forms of nature complex colloids in the DLRW,

which could provide further insight into natural aquatic nanoscale colloids and a better quantitative understanding of colloidal nature.

2. Experimental methods

2.1. Sampling area and site descriptions

Sampling was conducted in three tributary rivers within the DLRW, namely, Pu River (PR), Xi River (XR) and Haicheng River (HCR) during two sampling periods (wet and dry seasons) for this study. The DLRW is located in the northeast of China. It consists of the mainstream of Hun River (HR) and Daliao River (DLR). The HR rises on the north slope of Gunma mountain in Qingyuan county, then flows through cities of Fushun and Shenyang, joining with the Taizi River (TZR) at Sanchahe Wetland near Haicheng city to form the DLR. The TZR runs from Hongshilizi mountain within Xinbing county in northeast of Benxi city, through the cities of Benxi, Liaoyang and Anshan before joining with the HR at Sanchahe Wetland. The PR, a tributary of the HR and with the 180 km long, is situated in north of Shenyang city, running from the upstream of Qipanshan Reservoir to the village of Heiyougou within Liaozhong county where it meets the HR. The PR is the natural river, in recent years however, it has been seriously influenced by human activities such as urbanization, industrialization and waste discharge from small towns or villages. The XR is a typical urban river and the largest recipient of industrial effluents and domestic wastewater from the city of Shenyang which is an important industrialized city and an economic and cultural center in northeast of China. The XR is 78 km long, across the Tiexi industrial zone of Shenyang, entering the HR in the village of Huanglatuozhi in Liaozhong county. The HCR is a tributary of the TZR, the major recipient of wastewater discharge from printing and dyeing industries located along the river. The HCR is 88 km long, rising in the southeast of Haichen city flowing northwest to join the TZR at Xiaojiemiao near a small town of Niuzhuang.

The sampling locations were shown in Fig. 1. The thirteen, eight and seven sampling sites were respectively located on the PR, XR and HCR, labelled as P1–P13, X1–X8 and HC1–HC7 from the upstream to downstream of the corresponding rivers with special attention to the potential discharge points from sewage treatment plants, inputs from industrial zone and the urban areas.

2.2. Sampling campaigns and measurement

A total of 56 surface water samples were taken in 1-L glass bottles from the fields during dry season (DS) and wet season (WS). Prior to sampling, all sampling bottles were soaked with 5% detergent overnight and rinsed thoroughly with deionised then high pure water ($R = 18.2 \Omega\text{cm}$). Samples were transported to the laboratory and filtered through pre-combusted 0.7 μm glass fiber filters (GF/F, Whatman) within 3 days to remove large particles. A preliminary study was carried out to select water storage conditions (e.g. in the refrigerator at 4 °C in the dark or at –18 °C) for total organic carbon (TOC) and fluorescent measurement. The results showed that water storage at –18 °C with minimum variation in TOC value and fluorescent intensity would be recommended. The filtered waters were placed into pre-cleaned plastic containers and stored in the refrigerator at –18 °C before processing fractionation and fluorescence analysis. Conductivity, pH, temperature and dissolved oxygen were monitored in-situ.

2.3. Size fractionation

The filtered waters (<0.7 μm) were passed through ultrafiltration cell (Model 8400, Millipore) with cut off 1 kDa or 100 kDa regenerated cellulose membrane. The concentration factor (cf) is one of the key parameters for ultrafiltration evaluation, calculated as follows: $cf = (V_p + V_r) / V_i$, where V_p and V_r are the permeate and retentate volumes respectively. High cf. values lead to the breakthrough of high molecular

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