Science of the Total Environment 554–555 (2016) 228–236

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Application of a multi-method approach in characterization of natural aquatic colloids from different sources along Huangpu River in Shanghai, China

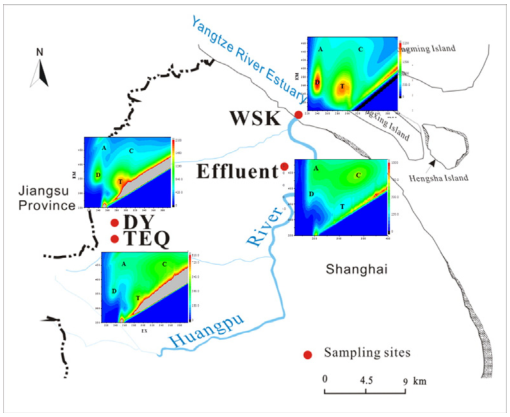
Caixia Yan [a,b,c], Minghua Nie [a], Jamie R. Lead [b], Yi Yang [c,d], Junliang Zhou [c], Ruth Merrifield [b], Mohammed Baalousha [b,*]

[a] School of Geography and Environment, Key Laboratory of Poyang Lake Wetland and Watershed Research, Ministry of Education, Jiangxi Normal University, 99 Ziyang Road, Nanchang 330022, China
[b] Center for Environmental Nanoscience and Risk, Arnold School of Public Health, University of South Carolina, 921 Assembly Street, Columbia 29208, USA
[c] State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, China
[d] Key Laboratory of Geographic Information Science of the Ministry of Education, Department of Geosciences, East China Normal University, 3663 North Zhongshan Road, Shanghai, 200062, China

HIGHLIGHTS

- Natural aquatic colloids from different sources were isolated using cross flow ultrafiltration.
- Multi-method approach is applied for colloidal characterization.
- Colloids in pristine natural river water showed higher aromaticity, humification, fluorescent intensity, and smaller sizes.
- Optical properties of colloids are size-dependent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 January 2016
Received in revised form 27 February 2016
Accepted 28 February 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
Colloids
Absorbance
Fluorescence

ABSTRACT

Natural colloid properties and the impact of human activities on these properties are important considerations for studies seeking to understand the fate and transport of pollutants. In this study, the relationship between size and fluorescence properties of natural colloids from 4 different sources were quantified using a multi-method analytical approach including UV–visible and fluorescence spectroscopy, flow field flow fractionation (FlFFF) coupled online to fluorescence spectrometer, and atomic force microscopy (AFM). Results indicate that colloids from pristine natural river water have higher aromaticity and humification, higher fluorescent intensity, and smaller size compared to those from the rivers impacted by livestock. The majority of colloids are smaller than 10 nm in size as measured by AFM and FlFFF. Colloid size measured by FlFFF coupled to fluorescence spectroscopy increases in the order peak C (Ex/Em at 300–340/400–460 nm) < peak D (Ex/Em at 210–230/340–360 nm) < peak T (Ex/Em at 270–280/330–370 nm) < peak A (Ex/Em at 210–250/400–460 nm), revealing that optical properties such as fluorescence are correlated with size. This trend is confirmed by the principal compo-

---

* Corresponding author.
E-mail address: MBAALOUS@mailbox.sc.edu (M. Baalousha).

http://dx.doi.org/10.1016/j.scitotenv.2016.02.198

Size distribution
Principle component analysis (PCA)

nent analysis, which demonstrates that the first principal component (PC1) reflecting colloid optical properties decrease with the increase in PC3 which is correlated to the colloid size.

1. Introduction

Aquatic colloids are heterogeneous mixtures of particles with different sizes, shapes, coatings, surface chemistry and chemical composition, and are defined as solid materials with at least one dimension between 1 nm and 1 μm (Lead and Wilkinson, 2006; Wilkinson and Lead, 2007). Colloids in natural systems are generally derived from natural processes, such as volcanic eruptions and bacterial activity, or anthropogenic activities such as wastewater treatment plants (WWTPs) effluent, livestock wastewater, or their distribution systems (Buzea et al., 2007). Colloid properties play important roles in regulating the fate and behavior of contaminants in the aquatic environment (Kalmykova et al., 2013; Nie et al., 2014a; b). It has been established that small size, high organic carbon content and high humic-like fluorescence intensity of natural aquatic colloids are among the main factors controlling pollutant–colloid interactions such as sorption behavior (e.g. pesticide, estrogens and pharmaceuticals) (Ngueleu et al., 2013; Nie et al., 2014a; b; Yan et al., 2015).

There are strong indications that the geochemical composition and properties of colloids vary with size (Khalaf et al., 2003). Understanding the relationship between colloidal composition and size distribution requires improvement in colloid separation and analysis using a hyphenated multi-method approach. Several analytical techniques such as cross-flow ultrafiltration (CFUF), flow field flow fractionation (FlFFF) (Laborda et al., 2011; Batchelli et al., 2009), atomic force microscopy (AFM)(Baalousha and Lead, 2007a; Wilkinson et al., 1999), and inductively coupled plasma mass spectrometry (ICP-MS) (Stolpe et al., 2005) have been applied for the characterization of colloids. However, due to the profound complexity, heterogeneity and polydispersity of colloids, there is a need for in-depth characterization of colloids using a multi-method approach to quantify their properties (Lapworth et al., 2013; Yang et al., 2015), in particular applying high resolution size separation techniques such as FlFFF, prior to further characterization using other analytical techniques to reduce colloid polydispersity and thus improve detection of subtle differences in colloid properties (Weishaar et al., 2003). As an important portion of colloid, properties of the chromophoric dissolved organic matter (CDOM) have been shown to be size-dependent (Guéguen and Cuss, 2011). For instance, in samples from an urban lake and a rural river, tryptophan-like fluorescence and a small fraction of fulvic-like fluorophores occurred mainly in the dissolved phase (permeates), while humic/fulvic-like materials primarily occurred in the concentrated colloidal phase (retentates) (Liu et al., 2007). However, there is little information on the relationship between fluorescence and size of colloids and the results are contradictory. For example, the humic-like fluorescent fraction of DOM is usually found in the range 0.5–5 kDa in pristine natural waters (Thurman, 1985; Huguet et al., 2010), but in the Damariscotta River estuary, Boehme and Wells (2006) detected fluorescence in larger sized fraction 13–150 kDa. These differences can be attributed to the different techniques and methodologies applied in the different studies, sample origin, and colloid polydispersity.

Therefore, to overcome these challenges, a range of complementary methods were selected in this study to characterize the colloids, including UV–visible and fluorescence spectroscopy, FlFFF coupled online to fluorescence spectroscopy, and AFM. Absorption and fluorescence spectroscopy are powerful tools to identify the colloidal component and assess the sources and dynamics of natural colloids (Persson and Wedborg, 2001; Hong et al., 2012). FlFFF measures colloids diffusion coefficient, which can be converted to colloid hydrodynamic diameter using Stocks Einstein equation, with the inherent assumption that these colloids are hard-spheres, although comparison of data from the two methods can yield information on colloidal softness (permeability)(Baalousha and Lead, 2007a). FlFFF has been coupled with several detectors such as fluorescence, light scattering, AFM, and ICP-MS (Wyatt et al., 1998; Baalousha and Lead, 2007a; Bouby et al., 2008) to characterize the continuous molecular size information of colloids and their interaction with pollutants (Guéguen and Cuss, 2011; Cuss and Guéguen, 2015). AFM measures colloidal height above a substrate, which are typically used to construct colloid size distribution assuming spherical shape. Crucially, FlFFF and AFM operate at the same nanoscale size, but are based on different basic principles as discussed above, and are thus highly complementary for colloid characterization. Coupling of both methods enables the validation of the Stokes Einstein assumption (Baalousha and Lead, 2007a,b; Lapworth et al., 2013).

For FlFFF analysis, both UV and fluorescence detector have been coupled to FlFFF in previous studies (Moon et al., 2006; Baalousha and Lead, 2007a; Guéguen and Cuss, 2011; Lapworth et al., 2013). However, measured size distributions were different between absorbance and fluorescence, because chromophores did not have the same size distribution as the fluorophores, especially for the larger sized colloids in rivers and coastal waters (Zanardi-Lamardo et al., 2004; Guéguen and Cuss, 2011). Furthermore, the results from fluorescence are sampled dependent. No significant variation in colloid size distribution was observed in the analysis of protein-like materials (Moon et al., 2006), while significant variation in colloidal size distribution were identified when using the fluorescence signal for humic material (Hassellöv, 2005). These findings illustrate that fluorescence signatures might be size-dependent. Thus to rationalize the variability in the colloid size-dependent optical properties (fluorescence), it is necessary to couple FlFFF to a fluorescence detector with various wavelengths. Therefore, according to the fluorophores measured in the batch fluorescence analysis (see details in the following discussions), four Ex-Em pairs representing fulvic-like, protein-like, tryptophan-like and humic-like materials were selected in this study to monitor colloidal size distribution following fractionation by FlFFF. This is one of the very few studies that demonstrate the difference in colloidal size distribution by FlFFF at different fluorescence wavelengths.

In this study, colloids were collected from different sources including the confluence of rivers, effluent of WWTP, and rivers impacted by livestock in Shanghai, China (Fig. 1). The objectives of this paper are to optimally couple multiple techniques, and to systematically assess the relationships of properties (e.g. fluorescence vs. size) of aquatic colloids, and the impact of human activities on colloid properties. To achieve this goal, we (1) determine the absorbance, fluorescence and size distribution of colloids from different sources; (2) investigate the relationship between fluorescence and size distribution using FlFFF analysis; and (3) extract the latent variables from several parameters of colloids using principal component analysis (PCA). Latent variables were in turn used to predict size distribution using only the fluorescence properties thereof.

2. Materials and methods

2.1. Sample collection

Four water samples were collected from different sources along the Huangpu River in Shanghai, China (Fig. 1). Of these sampling sites, Wusongkou (WSK) is the confluence of the Huangpu River and the Yangtze River, representing the overall effect of the human activity and the pristine natural process; “Effluent” is the final effluent of an