Size partitioning and mixing behavior of trace metals and dissolved organic matter in a South China estuary

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HIGHLIGHTS

- Colloidal size distribution of metals was quantified using asymmetric flow field-flow fractionation and ICP-MS.
- Dominance of dissolved metals in the 1–10 kDa fraction of estuarine waters mixed with industrial effluents
- Small sized colloidal organic complexes were responsible for binding and stabilizing trace metals.
- Both natural and anthropogenic processes affected the transformation of metals among phases in the estuary system.

GRAPHICAL ABSTRACT
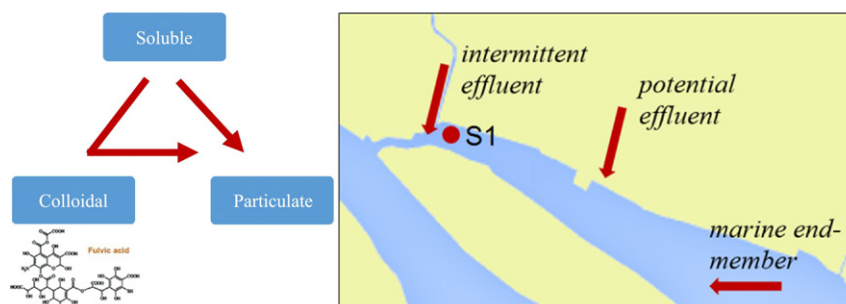
ABSTRACT

The Jiulong River estuary, located in the southeastern China, suffered from metal pollution due to industrial effluent releases. Mixing of effluent and estuarine water may have significantly affected the size distribution of trace metals and their environmental fate. In the present study, colloidal size distribution of organic matter and selected metals were quantified using asymmetric flow field-flow fractionation (AF4) and ICP-MS. We demonstrated a dominance of dissolved metals in the 1–10 kDa fraction, and metals such as Cu, Zn, Ni, Co, Pb, Cd and Mn were mostly regulated by terrestrial fulvic acid. The larger inorganic colloids played a limited role, although Fe reduction was likely to affect the size partitioning of colloidal Mn. The holding pond represented a source of trace metals and chromophoric and humic-like dissolved organic matter to the estuary. Scavenging or removal behavior became evident following the intermittent mixing, and the small sized colloidal organic complexes were responsible for binding and stabilizing trace metals. Variations in particle size distributions indicated different sources, fates and geochemical controls of the metals. Our results highlighted the impacts of both natural and anthropogenic processes on the transformation of trace metals among phases in this dynamic estuary system.

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1. Introduction

Trace metals are of great concerns because of their potentials for substantial and long-term accumulation in sediments and organisms. The partitioning of trace metals in dissolved, colloidal and particulate phases and their interactions and transformation will influence the metal bioavailability and the hazard posed (Simpson et al., 2014).

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Colloids, operationally defined as having a size of 1 nm–0.2 μm, are abundant and play intermediating roles in regulating the speciation, transformation and ultimate fate of trace metals and other chemical species (Guo and Santschi, 2007). There are close linkages between the cycling of trace metals and organic ligands, and a large fraction of many metals (e.g. Cu, Zn, Hg, Ag) has been found to be associated with colloidal organic matter, controlled by the abundance of corresponding functional groups (Santschi et al., 1999). On the other hand, metals such as Pb and Zn may have high affinities for the inorganic iron-rich colloids (Luan and Vadas, 2015), while the residual phase was likely for Cr and Ni.

Different sampling techniques, especially ultrafiltration, have been used to separate the colloidally complexed metals from the dissolved phase (Guo and Santschi, 2007). However, given the heterogeneity of environmental colloids, conventional ultrafiltration can only provide limited information. Asymmetric flow field flow fractionation (AF4), a technique capable of simultaneously separating and characterizing aquatic colloids, can be coupled to different detectors such as UV-absorbance, fluorescence and ICP-MS, depending on the research focus (Baalousha et al., 2011; Zhou and Guo, 2015). Thus, the AF4 technique can provide information on colloidal size and composition at the same time in a continuous mode, and has recently been applied to river systems, estuaries, seawater, and other aquatic environments (Stolpe et al., 2013; Andersson et al., 2006; Stolpe et al., 2010; Saito et al., 2015; Luan and Vadas, 2015; Lin et al., 2016).

Recent studies have shown that colloidal size distribution in estuarine waters are highly heterogeneous and different sized colloids could have different sources, composition and estuarine mixing behaviors (Stolpe et al., 2014; Zhou et al., 2016). The dynamic changes in colloidal size and composition should have a significant influence on the fate and transport of trace metals and other contaminants in estuarine environments. However, variations in size and composition of colloidal trace metals during estuarine mixing remain poorly understood.

The Jiulong River estuary is a shallow estuarine system on the southeast coast of China, characterized by high fluctuation of hydrological and geochemical conditions under both natural processes and anthropogenic impact. Trace metal cycling and the role of colloids in this estuarine system have rarely being studied. After over 30 years of rapid economic development, increased contamination of metals, nutrients and emerging chemicals has become evident, especially in coastal areas (Wang et al., 2014). For example, intermittent effluent discharges and continuous drainage water releases are common in the Jiulong River estuary (Wang et al., 2014), with inputs of industrial contaminates including metals and organic matter in an unprecedented manner, likely altering the partitioning of metals and their environmental fate (Wang and Wang, 2016). However, the partitioning of metals and organic matter among dissolved, colloidal, and particulate phases and the role of colloids in the transport and transformation of metals have not been systematically studied.

The main purpose of this study was therefore to use this highly contaminated environment as a natural laboratory to reveal the size distribution and mixing behavior of selected metals. Our objectives were to examine 1) size distributions of trace metals in both colloidal and particulate phases; 2) the relative importance of organic and inorganic binding ligands; and 3) the conservative or non-conservative behavior of metals and organic matter in different size fractions during estuarine mixing. Time-series samplings were conducted in the Jiulong River estuary during two seasons. Colloids were fractionated by the AF4 technique, with on-line and off-line measurements for organic matter and metals (Cu, Zn, Ni, Co, Pb, Cd, Mn, Fe, Al), respectively. Particles were size fractionated with filters into three size fractions. Our hypothesis was that dissolved organic matter could stabilize trace metals and plays an important role in regulating metal partitioning and transport in the estuarine environment. Our results should provide insights into understanding of trace metal biogeochemical cycling mechanisms in estuaries under anthropogenic impact.

2. Material and methods

2.1. Study sites and sampling

The Jiulong River, with an annual flow rate of 14 billion m^3, discharges to the coastal sea of Xiamen. The estuary is a typical subtropical macro-tide system (Yan et al., 2012), with a catchment area of 14,741 km^2. This study chose the sampling site (S1, 24°28′43″N, 117°54′35″E) in the north branch of the Jiulong River estuary, close to newly established industrial zones that host a large number of factories (Wang et al., 2011). Untreated industrial effluents are usually stored in holding ponds (mixed with stream water), controlled by a water gate and are discharged irregularly into the estuary when tidal level reached a certain height (Wang et al., 2014). Station S1 was thus directly receiving visible intermittent effluent, which was characterized by high levels of suspended particulate matter, dissolved organic matter and metals.

Two sampling campaigns were carried out in March and May 2016. Water samples were also collected from the holding pond as an end-member station. During March 24, the three sampling points were all influenced by the effluent discharge. During May 25, four time-series sampling points were sampled, with the 3rd and 4th ones without the direct influence of intermittent input. The interval between each sampling points was 1 h. Duplicate samples were collected for backups. All samples were stored in fridge after field sampling, and were processed and analyzed as logistically soon as possible (within 3 days for colloidal size fractionation).

Clean techniques were strictly followed during the whole process to minimize contamination (Allen, 2000). All plastic bottles were pre-cleaned with 5% HNO_3 (trace metal grade). Surface waters were collected by hand-dipping beneath the surface with 0.5 L polyethylene bottles and a pre-cleaned perspex water sampler helped collect estuarine waters from 50 cm above the bottom. Physicochemical parameters including salinity and dissolved oxygen were measured in situ together with water sampling and were recorded with a calibrated multi-probe sensor (YSI Pro Plus).

2.2. Processing of water samples

The water samples were filtered through 0.2 μm polyethersulfone membranes (Stericup-GP, Millipore) in low vacuum to remove large particulate materials immediately after sampling. To facilitate the separation and characterization of colloidal DOM and metals using AF4, the filtered water samples (<0.2 μm, dissolved fraction) were pre-concentrated using a 70 mL stirred cell ultrafiltration unit (Advantec MFS) equipped with 1 kDa regenerated cellulose membrane (PLAC, Millipore). Trace element clean procedures were employed with caution, and the apparatus was previously washed by 5 mmol/L Na_2EDTA solution and Milli-Q water according to Saito et al. (2015). The concentration factors were 4–8 for all the samples. Dissolved, retentate (1 kDa–0.2 μm, colloidal fraction) and permeate (<1 kDa, soluble fraction) samples for metal analysis were preserved in 0.2% HNO_3.

In order to investigate the particle size distribution and to separate sand, silt, and clay fractions (operationally classified by >50 μm, 5–50 μm, 0.2–5 μm, respectively), additional filtrations were carried out. Total water samples of known volume (100 mL) were filtered through 50 μm nylon membranes which had been thoughtfully cleaned by nitric acid and Milli-Q water. Also, onboard filtration was conducted with acid-washed in-line syringe cellulose acetate filters of 5 μm (Sartorius). The samples and filtrates were stored at 4 °C in the dark before further processing.

2.3. Size fractionation using AF4

Characterization of colloidal metal complexes was performed by an asymmetric flow field-flow fractionation system (AF 2000 MT, Postnova) equipped with a polyethersulfone membrane of 1 kDa cut-off and an injection loop of 1.1 mL. The carrier solution used in this study was trace