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Size and composition of colloidal organic matter and trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as characterized by flow field-flow fractionation

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ABSTRACT

The continuous colloidal size spectra (0.5–40 nm) of chromophoric and fluorescent organic matter, Fe, P, Mn, Cu, Zn, Pb, and U, were determined by on-line coupling of flow field-flow fractionation (FFF) to detectors including UV-absorbance, fluorescence, and ICP-MS, in samples from the lower Mississippi River, the Atchafalaya River, the Pearl River, and from marine stations in the northern Gulf of Mexico. The colloidal size spectra showed the presence of 3–4 colloid populations; 0.5–4 nm CDOM-colloids, binding most elements, 3–8 nm protein-like colloids, binding P in seawater, and 5–40 nm Fe-rich colloids, binding P, Mn, Zn, and Pb. Moreover, protein-like colloidal matter, Fe, P, Mn and Pb were largely found in the >40 nm fraction. We hypothesize that the CDOM-colloids represent terrestrial fulvic acid, and that the protein-like colloids are mostly derived from in situ biological production, while the iron-rich colloids are largely inorganic and contain Fe(III)-hydroxide/oxyhydroxide. The colloidal concentrations, determined by both FFF and ultrafiltration, were generally much higher in the Pearl River than in the other rivers, and decreased seaward in the Gulf of Mexico. The colloidal size distribution of protein-like organic matter, Fe-rich colloids and associated elements were shifted to larger sizes in the Mississippi and Atchafalaya Rivers compared with the Pearl River.

1. Introduction

Rivers contribute considerable amounts of dissolved organic carbon (DOC), trace elements, and nutrients to the sea (Meybeck, 2003), affecting water quality and primary production on continental shelves (Boesch et al., 2009). However, the reactivity, bioavailability, and transport of elements from rivers to the sea are poorly understood, and may largely depend on their partitioning between dissolved, colloidal and particulate phases. Aquatic colloids, defined as having a size of 1–1000 nm, are highly dynamic intermediaries between dissolved species and particles, and include a variety of organic and inorganic compounds (Guo and Santschi, 1997; Wilkinson et al., 1997).

Ultrafiltration has been widely used to isolate and quantify colloidal organic carbon (COC) and trace elements in natural waters (Guo et al., 1995; Wen et al., 1999). However, aquatic colloids are heterogeneous in composition and size, and ultrafiltration methods provide limited information about the colloidal size spectrum. Flow field-flow fractionation (FFF) is a chromatography-like elution technique in which the retention times of colloids are proportional to their hydrodynamic diameters (Giddings, 1993). On-line coupling of FFF to different detectors such as UV-absorbance (Wells, 2004), fluorescence (Zanardi-Lamardo et al., 2002), and inductively coupled plasma mass spectrometry (ICP-MS) (Baalousha et al., 2006; Hassellöv et al., 1999; Stolpe et al., 2005) provides continuous colloidal size spectra, allowing size and compositional determination of distinct types of colloids.

The Mississippi River is the largest river in the North America, and discharges around 5×10^{11} m³ of water annually, with significant amounts of nutrients, organic matter and trace elements (Shiller and Boyle, 1991; Turner et al., 2007), causing eutrophication, hypoxia and other environmental concerns in the northern Gulf of Mexico (Boesch et al., 2009). The size distribution and chemical composition of colloids in the Mississippi River and the northern Gulf of Mexico have rarely been studied. Available reports on the application of FFF in this

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important region are restricted to UV-absorbing organic matter (Chen et al., 2004; Wells, 2004), while colloidal trace element characterization by FFF-ICP-MS has mostly been reported for boreal rivers with much higher concentrations of terrestrial organic matter (Andersson et al., 2006; Baalousha et al., 2006; Dahlqvist et al., 2007, 2004; Stolpe et al., 2005). In this study, we have used FFF coupled on-line to UV absorbance and fluorescence detectors and ICP-MS, to examine the continuous colloidal size spectra of chromophoric dissolved organic matter (CDOM), humic-type and protein-type fluorescent organic matter, and selected trace elements in three rivers with different water chemistries; the lower Mississippi River, the Atchafalaya River and the Pearl River. In addition, surface seawater samples from the outflow region of these rivers in the northern Gulf of Mexico, were studied.

2. Experimental

2.1. Study sites and sampling

The lower Mississippi River (MR) and the Atchafalaya River (AR) are the two major distributaries of the Mississippi River system, which drains an area of 3×10^6 km^2 (Duan et al., 2007b). Both rivers are naturally high in alkalinity and suspended particles (Alexander et al., 2001; Turner et al., 2007). In addition, human activities such as extensive agriculture in the drainage basin, nutrient input, and building of dams and levees have largely influenced the suspended load and the concentrations and character of the organic matter in the river system (Bianchi et al., 2004; Duan et al., 2007b; Opsahl and Benner, 1998). However, the AR is less surrounded by man-made levees than the MR, and can therefore be expected to receive a larger input of organic matter from local forest and swamps (Wang et al., 2004). The PR is a comparatively small black-water river, with a 2×10^3 km^3 drainage basin, largely covered by forest (Duan et al., 2007b). The PR has a higher DOC concentration (Duan et al., 2007b) and a considerably lower alkalinity than the MR and AR (Alexander et al., 2001).

Sampling locations, dates and the hydrographic parameters on the time of sampling are listed in Table 1 and depicted in Fig. 1. All three rivers were sampled during high discharge, close in time to the date of the maximum annual discharge (http://waterdata.usgs.gov/nwis/rt). Surface water (40 L) was pumped directly from the river (3 m from the bank), through an in-line filtration system, equipped with a 0.45 μm polycarbonate filter cartridge (Memtrex, Osmonics, USA), into acid cleaned 20 L polyethylene containers. Surface seawater samples were taken from the Mississippi Sound (MS) and the Mississippi Bight (MB), by the University of Southern Mississippi research vessel Lemoyne, using the same procedures as in the river sampling. Before the sampling, both seawater stations had received extensive freshwater inputs from the MR through Lake Pontchartrain, due to the opening of the Bonnet Carré spillway, resulting in comparatively low salinities (Table 1). The colloidal fractions of the samples were pre-concentrated over a pre-calibrated 1 kDa ultrafiltration membrane (Amicon S10Y1, Millipore), using trace-element clean procedures that have been described previously (Guo et al., 2000). The concentration factors were 16–19 for the river samples and 26 for both seawater samples.

Table 1
Sampling locations and their hydrographic parameters.

Sample ID	Location	Sampling date	Discharge (m^3/s)	Salinity
Mississippi River (at Baton Rouge)	30.43°N; 91.19°W	Mar 25, 2008	26,000	0.2
Atchafalaya River	30.39°N; 91.67°W	Mar 25, 2008	5400	0.3
Pearl River (at Bogalusa)	30.79°N; 89.82°W	Mar 14, 2008	500	0.1
Mississippi Sound	30.14°N; 89.13°W	Apr 22, 2008	–	8.7
Mississippi Bight	30.02°N; 88.89°W	Apr 22, 2008	–	23.5

2.2. Instrumentation

The on-line coupling of the FFF system (F-1000, Postnova) to a UV-absorbance detector (Model 228, ISCO) and a high resolution ICP-MS (ELEMENT 2, Thermo Scientific), has been described previously (Stolpe et al., 2005). Only modifications of that method will be presented here. FFF and ICP-MS instrument parameters are shown in Table 2. The ultrafiltration retentate from each sample was further concentrated inside the FFF system by on-channel preconcentration (Lyvén et al., 1997). Since previous studies have shown the presence of multiple populations of colloids in the <50 nm size range (Stolpe and Hassellöv, 2007; Stolpe et al., 2005), the FFF conditions were chosen to give a high resolution in the 0.5–40 nm size range, corresponding to a separation time of 120 min per sample. After 120 min, the cross flow was turned off, and the sample remaining in the channel (>40 nm components) was rapidly eluted by the channel flow. This method thus allowed the characterization of both the high resolution 0.5–40 nm colloidal size spectrum, and the bulk concentrations associated to colloids in the >40 nm size range. Even though the 0.5–40 nm size range is only a small fraction of what is usually referred to as 'colloidal', for simplicity we have denoted this size range as the 'colloidal size spectrum'. Quality of dissolved metal results was assured by use of an internal standard (2 ppb In), external standardization by serial dilution of NIST-traceable commercial single element solutions (High Purity Standards), and an accuracy check by determination of certified reference waters. Relative precision for total element concentrations for samples well above the detection limit is estimated to be ±5% (1 σ) and accuracy is within 10%. Detection limits for total element concentrations were based on replicate determinations of blanks and low concentration standards, and were determined to be (concentrations in nmol L^{-1}): U≤0.005; Pb≤0.01; Cr, Cu and Ni≤0.1; Mn≤1; Fe and P≤3; and Ca≤100. Detection limits for colloidal concentrations by FFF were determined to be (concentrations in nmol L^{-1}): Fe≤0.5; P≤6; Mn≤0.07; Cu≤0.08; Zn≤0.5; Pb≤0.003; and U≤0.0002 (Stolpe et al., 2005). In separate FFF runs, the ICP-MS was replaced by a fluorescence detector (Acufluor, LabAlliance). Since most UV-absorbing and fluorescent colloidal matter was very small in size, the measurements with these detectors were only extended to 60 min, corresponding to the 0.5–20 nm size range. UV-absorbance measured at 254 nm (UV_{254}) was taken as an indicator of CDOM (Chen et al., 2004). Fluorescence was measured at three different sets of excitation/emission wavelengths; 350/480 nm ($Fluo_{350/480}$), 310/420 nm ($Fluo_{310/420}$) and 275/340 nm ($Fluo_{275/340}$). These wavelengths are often referred to as 'humic-type' ($Fluo_{350/480}$), 'marine humic-type' ($Fluo_{310/420}$) and 'protein-type' or 'tryptophan-type' ($Fluo_{275/340}$) fluorescence, due to their sensitivities for specific fluorophores (Coble, 1996). DOC and COC were measured by high-temperature combustion Shimadzu TOC-V Analyzer (Guo et al., 1995). The element concentrations in the batch 0.45 μm filtrate and in the 1 kDa–0.45 μm size fraction are called 'dissolved concentrations' and 'colloidal concentrations', and are denoted either as $C_{<0.45\mu m}$ and $C_{1kDa-0.45\mu m}$ or as $[Fe]_{<0.45\mu m}$ and $[Fe]_{1\ kDa-0.45\mu m}$ (examples given for Fe). The ratio between the colloidal concentration and the dissolved concentration is called the 'colloidal fraction'.

2.3. FFF calibration and data handling

The relation between FFF retention time (t_R) and diffusion coefficient (D) was graphically determined after calibration with proteins with known D. The proteins ovalbumin ($D=7.76\times10^{-11}$m^2 s^{-1}), bovine serum albumin ($D=6.15\times10^{-11}$ m^2 s^{-1}), β-amylase ($D=4.42\times10^{-11}$ m^2 s^{-1}), ferritin ($D=3.61\times10^{-11}$ m^2 s^{-1}) and