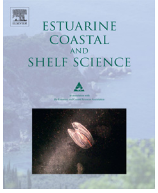
Estuarine, Coastal and Shelf Science 133 (2013) 285–292

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

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



Non-conservative behaviors of chromophoric dissolved organic matter in a turbid estuary: Roles of multiple biogeochemical processes

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ARTICLE INFO

Article history:
Received 18 March 2013
Accepted 11 September 2013
Available online 25 September 2013

Keywords:
dissolved organic carbon
dissolved organic matter
absorption spectroscopy
fluorescence spectroscopy
estuaries
Jiulong Estuary

ABSTRACT

Chromophoric dissolved organic matter (CDOM) may show notable non-conservative behaviors in many estuaries due to a variety of biogeochemical processes. The partition between CDOM and chromophoric particulate organic matter (CPOM) was examined in the Jiulong Estuary (China) using absorption and fluorescence spectroscopy, which was also compared with microbial and photochemical degradations. The absorption coefficient of water-soluble CPOM ($a_{CPOM}(280)$) at ambient Milli-Q water pH (6.1) ranged from 0.11 to 7.94 m^{-1} in the estuary and was equivalent to 5–101% of CDOM absorption coefficient. The $a_{CPOM}(280)$ correlated significantly with the concentration of suspended particulate matter and was highest in the bottom water of turbidity maximum zone. Absorption spectral slope ($S_{275-295}$) and slope ratio (S_R) correlated positively with salinity for both CPOM and CDOM, suggesting decreases in the average molecular weight with increasing salinity. The adsorption of CDOM to re-suspended sediments (at 500 mg L^{-1}) within 2 h was equivalent to 4–26% of the initial $a_{CDOM}(280)$. The adsorption of CDOM to particles was less selective with respect to various CDOM constituents, while the microbial degradation resulted decreases in $S_{275-295}$ and S_R of CDOM and preferential removal of protein-like components. The partition between CPOM and CDOM represented a rapid and important process for the non-conservative behavior of CDOM in turbid estuaries.

1. Introduction

Dissolved organic matter (DOM) is the largest pool of reduced carbon and plays important roles in many biogeochemical processes in aquatic environments (Benner, 2003; Battin et al., 2008; Jiao et al., 2010). The land–ocean flux of DOM is an important linkage between terrestrial and marine ecosystems. Elements of C, N and P bounded in terrestrial DOM can be released during both photochemical and microbial degradation processes, hence affecting the air-sea CO_2 flux, bioavailable inorganic nutrient levels and aquatic production in coastal oceans (e.g., Moran and Zepp, 1997; White et al., 2010; Bauer and Bianchi, 2011). Fluvial discharge is also a major source of chromophoric DOM (CDOM) in many estuaries and coastal oceans, a fraction of DOM which affects both primary production and the habitat for organisms through absorbing both UV and photosynthetically active radiations (Coble, 2007).

Estuary is a dynamic land–ocean interface with large physical, chemical, and biological gradients (Bauer and Bianchi, 2011). Many biogeochemical processes in the estuary may alter the fluvial DOM (including CDOM) that finally reaches the ocean (e.g., Shank et al., 2010; Fellman et al., 2010; Guo et al., 2011; Osburn et al., 2012; Yang et al., 2013a). Detailed studies on those processes are important for assessing their effects on the concentration, chemical composition, and biogeochemical reactivity of DOM in the estuary and for tracing terrestrial DOM in marine environments. In particular, adsorption-desorption of organic matter between particulate and dissolved phases may play important roles in turbid estuaries (Uher et al., 2001; Shank et al., 2005, 2011; Pisani et al., 2011). However, few studies examine the dissolution of water-soluble chromophoric particulate organic matter (CPOM) throughout an estuary from the freshwater end to the marine end, although such studies would provide significant insights into the factors influencing the level and chemical composition of CPOM and the interaction between CDOM and CPOM (Osburn et al., 2012). The turbidity maximum zone (TMZ) is widely present in global

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http://dx.doi.org/10.1016/j.ecss.2013.09.007

estuaries and the adsorption-desorption process may be active in TMZ, which is to be studied to better understand the cycling of CDOM and DOM in estuaries (Xie et al., 2012).

The Jiulong Estuary is a shallow subtropical estuary in southeast China, with a TMZ developed in the upper estuary. There are active addition and removal of CDOM in the river-estuary interface (Guo et al., 2007, 2011), but the mechanism has not yet been well studied. This study aimed to: (1) examine dynamics of CPOM in the Jiulong Estuary; (2) compare the concentration and chemical composition of CPOM with those of CDOM and water-soluble chromophoric sediment organic matter (CSOM); and (3) assess the importance of desorption–adsorption in the non-conservative behavior of CDOM in the estuary, in comparison with other biogeochemical processes. These results also have implications for understanding the biogeochemistry of the bulk DOM in estuaries.

2. Materials and methods

2.1. Field sampling and laboratory incubations

Surface water samples were collected from the Jiulong Estuary using Niskin bottles during three cruises in April, August and November 2011 (Fig. 1). Bottom waters were only sampled at few stations in April and August, since the behavior of CDOM in the bottom water was similar to that in the surface water in this shallow estuary (Guo et al., 2011). Samples from stations S1 and S2 were collected in August to examine the inputs from a small stream flowing through Haicheng Town and the South Jiulong River, respectively (Fig. 1). Salinity was measured using a SBE917 Plus self-contained CTD (conductivity–temperature–depth) profiling system (Sea-Bird Electronics Inc., USA). Suspended particulate matter (SPM) was collected on pre-weighted 47-mm-diamter GF/F filter (pore size of 0.7 μm) and measured by weighting method in August and November.

For DOC and optical measurements, water samples were filtered through pre-combusted (500 °C for 5 h) GF/F filters. One aliquot of the filtrate was acidified with HCl and stored in a freezer for DOC measurements, while the other was stored in the cold (4 °C) and dark without acidification for CDOM optical measurements. Particles on the GF/F filter were stored in a freezer before the extraction of CPOM in August and November.

CPOM was extracted following a procedure for extracting water-soluble organic compounds from soils and aerosols (Mladenov et al., 2009, 2011). Briefly, particles on the GF/F filter were extracted in dark with 100 mL Milli-Q water (pH = 6.1) at 30 °C for 2 h on a constant temperature shaker. The resultant solution was filtered through GF/F filters and the filtrate was used for measuring water-soluble organic carbon (WSOC_P) and optical properties following the procedures for DOC and CDOM optical measurements. The measured WSOC_P and absorption coefficient of CPOM were corrected with the volume of water samples filtered in the field for collecting particles. In August, CPOM at stations A3–A8 were measured in triplicate and the mean analytical precisions were 10.4% and 6.5% for WSOC_P and absorption coefficient. Most CPOM samples were determined for surface waters and only one was for the bottom water of TMZ in August (station A8).

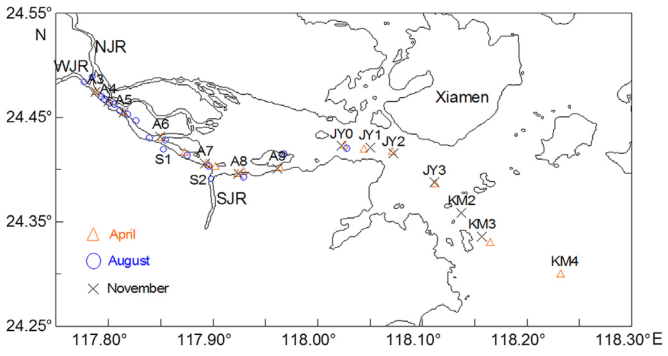

Fig. 1. Sampling stations of the Jiulong Estuary in 2011 (NJR: North Jiulong River; WJR: West Jiulong River; SJR: South Jiulong River).

Surface sediments were grabbed at stations A3–A6 and A8 and stored in a freezer in April. They were freeze dried and homogenized through gentle grinding for the extraction of CSOM and adsorption experiment following the procedure described by Uher et al. (2001) and Shank et al. (2005). CSOM from ~50 mg sediments was extracted, filtered and measured with a procedure similar to that for CPOM. To evaluate the adsorption of CDOM to sediments in the turbid upper estuary, ~50 mg of sediments were added into 100 mL filtrates (through GF/F filters) at stations A3–A6 and A8 and shaken in dark at 30 °C for 2 h. The resultant solution was re-filtered for measuring DOC and optical properties after desorption–adsorption. Adsorptions of DOC and CDOM were calculated as the initial contents in the filtrates plus desorption quantities from sediments (as determined in the CSOM extraction experiment) minus the final contents after desorption–adsorption. All the experiment times for the extractions of CPOM and CSOM and the adsorption were set to 2 h because: (1) the partition of organic matter between solid and liquid phases occurs mainly within 15 min and almost stops after 2 h; and (2) microbial degradation within 2 h can be ignored (Kaiser and Zech, 1998; Zhou and Wong, 2000). Both CPOM and CSOM showed weak fluorescence signals which were not shown.

Microbial degradation of CDOM was examined in April following the procedure described by Fellman et al. (2010). Water samples with salinities of 0 and 10 were initially filtered through pre-combusted GF/F filters to remove the majority of microbial biomass. The freshwater filtrate was added with microbial inocula collected at four salinities (0, 10, 22, and 30) with a volume/volume ratio of 9/1. The filtrate with a salinity of 10 was added with the microbial inoculum collected at the same station. At the start of the experiment and after incubations for 7 and 28 days at 25 °C in the dark, the solution was re-filtered for DOC and optical measurements. All incubations were carried out in triplicate and the mean variation coefficients were 6.4%, 1.1%, and 2.7% for DOC, absorption coefficient and fluorescence intensities. Microbial inocula were prepared by filtering whole waters through pre-combusted GF/D filters (nominal pore size 2.7 μm).

2.2. DOC, absorption, and fluorescence measurements

DOC, absorption, and fluorescence were measured using the methods described previously (Yang et al., 2013b). Briefly, the DOC concentration was measured with high temperature catalytic oxidation after removing dissolved inorganic carbon by oxygen purging, using a Multi N/C 3100 TOC-TN analyzer (Analytik Jena, Germany). Each sample was measured in triplicate with an analytical precision of 2%. Solutions of potassium hydrogen phthalate were used as standards and Low Carbon Water and Deep Sea Water (from Dr. D. A. Hansell, University of Miami) were used to verify the accuracy of the measurement.

Absorbance spectra of CDOM were scanned using a Techcomp 2300 UV–Vis spectrometer at wavelengths of 240–800 nm. The absorption coefficient at 280 nm ($a_{\text{CDOM}}(280)$) was used to indicate the abundance of CDOM in this study. The absorption spectral slope of CDOM over 275–295 nm ($S_{275-295}$) and the slope ratio (S_R: the ratio of the spectral slope over 275–295 nm to that over 350–400 nm) were calculated to trace compositional changes of CDOM (Helms et al., 2008).