Marine Chemistry 162 (2014) 96–113

Contents lists available at ScienceDirect

Marine Chemistry

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

Optical and chemical characterization of base-extracted particulate organic matter in coastal marine environments

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ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form 1 February 2014
Accepted 20 March 2014
Available online 28 March 2014

Keywords:
POM
Absorption
Fluorescence
PARAFAC
Carbon stable isotopes

ABSTRACT

Absorbance and fluorescence measurements were measured on base-extracted particulate organic matter (BEPOM) to examine POM biogeochemistry in coastal marine environments. BEPOM trends from August 2011–September 2012 in the Neuse River Estuary (NRE) were compared against single sampling events in Charleston Harbor (CHS) and the inner Louisiana–Texas Shelf of the Gulf of Mexico (GOM) in July 2011 and July 2012, respectively. Spectral slope values, $S_{275–295}$, and the ratio of spectral slopes, S_R values, were mainly influenced by distinct structure in the UV-B region of BEPOM absorption spectra, which was similar to prior laboratory work on autochthonous, planktonic sources of chromophoric dissolved organic matter (CDOM). A PARAFAC model with five components was fit to BEPOM excitation–emission matrix (EEM) fluorescence data. Excitation and emission spectra of the five components were similar to those found for dissolved organic matter (DOM) in other coastal environments, with two components attributed to planktonic sources and two components attributed to terrestrial (humic) sources. A fifth component was attributed to microbial humic substances. Principle components analysis of PARAFAC results separated autochthonous, planktonic components from allochthonous, terrestrial components and explained >70% of the variance in the data. Surface water stable carbon isotope ($\delta^{13}C$) values of BEPOM from the NRE and CHS ranged from −29 to −23‰, with most enriched values occurring synchronous with high Chl-a concentrations, and indicating that enriched $\delta^{13}C$ values in BEPOM reflected a planktonic source. Notably, $\delta^{13}C$-BEPOM values for the GOM shelf below 50 m water depth were depleted (<−30‰), and a mixing model indicated that 30–40% of the POM could originate from methanic carbon. BEPOM absorption and fluorescence results suggested a planktonic POM as a source of CDOM in coastal marine environments.

1. Introduction

The chemical composition of organic matter (OM) in coastal environments is complex, being comprised of allochthonous and autochthonous sources. Allochthonous compounds are delivered to coastal environments (e.g., through estuaries) from their catchments, whereas autochthonous sources are formed within coastal environments (predominantly from primary and secondary production). Allochthonous OM is dominated by humic substances, which are poorly characterized aggregates of individual compounds, high in molecular weight and generally existing as polymeric units (Sleighter and Hatcher, 2007). In contrast, autochthonous compounds generally are non-humic in that they tend to retain their chemical identity within a mixture. OM transformations may occur within coastal environments, which may alter its chemical identity. Important processes are photochemical bleaching, bacterial degradation, and autochthonous production by phytoplankton and microbes (Rochelle-Newall and Fisher, 2002; Romera-Castillo et al., 2011).

Optical properties of organic matter (OM) play an important role in understanding OM sources and chemistry (Del Vecchio and Blough, 2004). In coastal environments (estuaries to the inner shelf of the coastal ocean), the optical properties of dissolved organic matter (DOM) that absorb light and the corresponding fraction that fluoresces light, which are known as CDOM and FDOM, respectively, have been extensively studied (Coble, 2007). While rapid and informational, absorption and fluorescence historically have only been applied to dissolved organics.

Particulate organic matter (POM) often is operationally defined as organic matter greater than 0.7 μm and represents a pool of potential chromophoric and fluorophoric organic material in coastal environments. While POM absorption has been measured (e.g., Vernet and

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http://dx.doi.org/10.1016/j.marchem.2014.03.006
0304-4203/

Whitehead, 1996), limited success has been achieved by measuring organic matter fluorescence in the solid phase (Chen et al., 2000). A recent method involving base extraction of particulate organic matter (BEPOM) has raised the opportunity of conducting fluorescence spectroscopy on these extracts and comparing BEPOM to CDOM (Osburn et al., 2012). The method has its origins in studies of alkaline extracts of soils and sediments (e.g., Santín et al., 2009). As this is a new technique, BEPOM fluorescence patterns are unknown in coastal environments, let alone the open ocean where autochthonous processes apparently contribute to oceanic CDOM (Nelson and Siegel, 2013). It is hypothesized that BEPOM fluorescence and absorbance have similar properties to CDOM in coastal systems.

Use of multivariate statistical tools, such as parallel factor analysis (PARAFAC) to statistically decompose individual fluorescing excitation and emission matrices (EEMs) of samples and model prevalent fluorescence spectra, has dominated recent literature (Stedmon et al., 2003; Kowalczuk et al., 2009; Fellman et al., 2011). This technique is an inexpensive and efficient means of providing insights into organic matter sources and cycling. FDOM studies have ranged from using mesocosms to understand the influence of microbes and phytoplankton, tracing various allochthonous sources in coastal waters, to modeling its global distribution (Steinberg et al., 2004; Osburn and Stedmon, 2011; Jørgensen et al., 2011). In addition, several works have used principle components analysis (PCA) to model relatedness of samples modeled by PARAFAC and relatedness of model components to other ecosystem properties such as salinity and dissolved organic carbon (DOC) concentration (Santín et al., 2009; Chen et al., 2010; Cawley et al., 2013).

In this study, BEPOM absorbing and fluorescing properties were compared for three coastal environments. The main focus of this study was the Neuse River Estuary (NRE) in eastern North Carolina. NRE was compared to Charleston Harbor (CHS) in South Carolina and the inner Louisiana–Texas Shelf, east of the Mississippi River plume, in the northern Gulf of Mexico (GOM). PARAFAC was used to model and validate six components. These results were examined against absorption spectral slope and chemical measurements of base-extracted particulate organic carbon (BEPOC) concentrations and corresponding stable carbon isotope values (δ^{13}C-BEPOM). Using BEPOM optical and chemical measurements to evaluate POM quality in coastal ecosystems improved our understanding of organic matter cycling and potential planktonic sources of CDOM.

2. Methods

2.1. Study sites

Location information, basic water quality measurements, and key absorption and fluorescence results for all stations in this study are presented in Table 1. Station locations of each coastal environment are shown in Fig. 1. Surface samples (n = 168) were collected on a monthly basis from August 2011 to September 2012 from the Neuse River Estuary (NRE) and Trent River (TR), a tributary located near the estuary's headwaters, in Eastern North Carolina (Table 1). NRE is a shallow, river and wind-dominated micro-tidal estuary that discharges into Pamlico Sound, the second largest estuarine complex in the United States. Neuse River watershed covers an area of approximately 16,000 km^2, flowing through wetlands, forests, and heavy agriculture. Over the past 4 decades, the NRE has suffered declining water quality and habitat conditions due to nutrient over-enrichment. The system is also strongly impacted by a recent rise in tropical cyclones and more extreme wet–drought cycles (Paerl et al., 1998, 2006; Burkholder et al., 2006).

Samples from thirteen stations were collected over the 70 km transect along the estuary's main axis as part of the Neuse River Estuary Modeling and Monitoring Program (ModMon). Station names increase from NR000 to NR180 with increasing salinity downstream. Samples were collected twice each month during August 2011, September 2011, and March 2012. NRE samples were collected in clean polyethylene bottles and shipped on ice to the laboratory at North Carolina State University. Estuarine particles were collected onto a 0.7 μm GF/F filter and stored frozen until further analysis.

Charleston Harbor estuary (CHS) is a harbor shelf environment dominated by marine processes, yet having three small riverine inputs (Table 1). CHS lies in the extensive southeastern coastal plain of the United States and its catchment is dominated by substantial *Spartina* marshes and tidal creeks (Wiegert and Freeman, 1990). Depth profiles were taken from seven stations in summer 2011. Sample sites included three rivers, Ashley, Cooper, and Wando, inside the harbor, and approximately 11 km off shore in the South Atlantic Bight (SAB).

The inner continental shelf of the northern Gulf of Mexico (GOM), the third site for this study, is strongly influenced by Mississippi River outflow, primarily through Southwest Pass (Table 1). Globally, the Mississippi River has the third largest drainage basin area in the world and sixth largest freshwater discharge accounting for around 60% of total suspended matter transported from the continental United States (Milliman, 1991; Presley et al., 1980). Sampling sites were located south and west of the main discharge through Southwest Pass, and were influenced both by the Mississippi River plume and by marine processes. Sta. 3 was located near a sunken oil rig. The GOM sampling occurred in summer 2012 and also included depth profiles.

Samples collected from CHS and GOM each occurred during one time sampling events and were compared to the synoptic study of the NRE. CHS and GOM samples were filtered on site and frozen GF/F filters for particulate and chlorophyll a (CHS only) analysis were transported to North Carolina State University. In CHS, samples of the benthic bottom boundary layer (nepheloid) were pumped into collection vessels through an intake funnel affixed to a metal frame ca. 15 cm above the sediment (Pohlman et al., 2002). Silicone tubing and a Teflon pneumatic pump were used in this apparatus.

2.2. Base extraction of POM (BEPOM)

Base-soluble POM was extracted from each GF/F filter into 0.1 *N* sodium hydroxide (NaOH) for 24 h at 4 °C. The basic solution was neutralized with concentrated hydrochloric acid (HCl) and filtered (0.2 μm PES filter) to remove filter particles prior to absorbance and fluorescence measurement on Varian Cary 300 and Eclipse instruments, respectively. Details of the BEPOM extraction procedures are in Osburn et al. (2012).

BEPOM absorbance spectra were measured from 220 to 800 nm. Samples with raw absorbance greater than 0.4 at 240 nm were diluted. All samples were blank-corrected against a neutralized NaOH control. Absorbance measurements were converted into Napierian absorption coefficients (m^{-1}):

$$a(\lambda) = a(\lambda_0)e^{S(\lambda_0-\lambda)} \quad (1)$$

where a is the absorption coefficient at reference wavelength, λ_0, and S is the slope of the exponential fit to data over a given range (Bricaud et al., 1981). Absorption coefficients were back-corrected for any dilution. Two spectral slopes were calculated on linear fits to natural log-transformed BEPOM absorption data for this study over ranges between 275 and 295 nm ($S_{275–295}$) and between 350 and 400 nm ($S_{350–400}$). Slope ratios (S_R) of $S_{275–295}$ to $S_{350–400}$ were also calculated (Helms et al., 2008).

Fluorescence of BEPOM samples was measured at excitation wavelengths 220–500 nm at 5 nm intervals, with 5 nm excitation slits. Emission was measured between 240 and 600 nm at 2 nm intervals with 5 nm emission slits. Fluorometer voltage measurements ranged from 800 to 950 nm (depending on sample response) at a scan rate of 4800 nm min^{-1}. Integration time was 0.025 s. Fluorescence measurements were corrected for inner-filter effects, calibrated against