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Evaluating the distribution of terrestrial dissolved organic matter in a complex coastal ecosystem using fluorescence spectroscopy

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ABSTRACT

The coastal zone of the Florida Keys features the only living coral reef in the continental United States and as such represents a unique regional environmental resource. Anthropogenic pressures combined with climate disturbances such as hurricanes can affect the biogeochemistry of the region and threaten the health of this unique ecosystem. As such, water quality monitoring has historically been implemented in the Florida Keys, and six spatially distinct zones have been identified. In these studies however, dissolved organic matter (DOM) has only been studied as a quantitative parameter, and DOM composition can be a valuable biogeochemical parameter in assessing environmental change in coastal regions. Here we report the first data of its kind on the application of optical properties of DOM, in particular excitation emission matrix fluorescence with parallel factor analysis (EEM-PARAFAC), throughout these six Florida Keys regions in an attempt to assess spatial differences in DOM sources. Our data suggests that while DOM in the Florida Keys can be influenced by distant terrestrial environments such as the Everglades, spatial differences in DOM distribution were also controlled in part by local surface runoff/fringe mangroves, contributions from seasgrass communities, as well as the reefs and waters from the Florida Current. Application of principal component analysis (PCA) of the relative abundance of EEM-PARAFAC components allowed for a clear distinction between the sources of DOM (allochthonous vs. autochthonous), between different autochthonous sources and/or the diagenetic status of DOM, and further clarified contribution of terrestrial DOM in zones where levels of DOM were low in abundance. The combination between EEM-PARAFAC and PCA proved to be ideally suited to discern DOM composition and source differences in coastal zones with complex hydrology and multiple DOM sources.

1. Introduction

In coastal environments, a significant fraction of dissolved organic matter (DOM) is of terrestrial origin. The importance of terrestrial DOM on the coastal ecosystem function has been widely recognized. For example, colored fraction of DOM namely chromophoric DOM (CDOM) absorbs and controls the penetration of UV light into the water column (Nelson and Siegel, 2013), protecting aquatic organisms (e.g. corals) from photo-inhibition (Baker et al., 2008). Also, terrestrial DOM may affect phytoplankton dynamics (Glibert et al., 2004; Maie et al., 2012) by providing limiting nutrients in the form of dissolved organic nitrogen (DON) or phosphorus (DOP). As such, variations in DOM dynamics in coastal areas, in particular coral reefs, may have an important impact on these light sensitive, oligotrophic ecosystems. Since coral reefs have been identified as ecosystems particularly sensitive to climate change (Baker et al., 2008) and DOM export from terrestrial environments is expected to respond environmental changes (Monteith et al., 2007; Moore et al., 2013), detailed studies for evaluating spatial and temporal variations of terrestrial DOM in such coastal environments is important.

While riverine influences to the nearshore zone can be monitored by the distribution of salinity, DOC concentrations have been shown to negatively relate to salinity (Cauwet, 2002), indicating that combination of salinity and DOC can be useful to monitor the transport and fate of terrestrial DOM in estuaries. However, DOC in coastal environments is a mixture of allochthonous and autochthonous components (Cauwet, 2002; Yamashita et al., 2008), and thus, the terrestrial DOM component cannot easily be separated from in situ produced DOM based only on DOC–salinity relationships. In addition, sometimes salinity cannot be used alone as a simple freshwater tracer in complex coastal systems, where evaporation

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may be important in controlling salinity, or where long residence times obscure the salinity effect (Milbrandt et al., 2010; Maie et al., 2012; Cawley et al., 2012). Therefore, other monitoring techniques are needed for evaluating the distribution of terrestrial DOM in such coastal environments.

Excitation emission matrix fluorescence coupled with parallel factor analysis (EEM-PARAFAC) has been applied to evaluating the dynamics of fluorescent groups of DOM (FDOM) in coastal environments (Stedmon and Markager, 2005; Yamashita et al., 2008; Fellman et al., 2010). The advantage of this technique is its high sensitivity and power to successfully differentiate between autochthonous and allochthonous fluorescent components of DOM. In addition, efforts to develop in-situ fluorescence sensors based on EEM-PARAFAC data have shown much promise thus far (Guéguen et al., 2012). Thus, EEM-PARAFAC seems ideally suited for monitoring the distribution of autochthonous as well as allochthonous DOM in coastal environments. Most of the coastal zone EEM-PARAFAC applications have focused on evaluating the sources and environmental dynamics of individual fluorescent groups in river-dominated estuaries based on their distribution patterns and relationship with salinity (e.g. Yamashita et al., 2008; Kowalczuk et al., 2009; Fellman et al., 2010; Osburn et al., 2012). However, applications in coastal areas where DOM dynamics are not dominated by river discharge have been scarce (Maie et al., 2012; Cawley et al., 2012).

In the present study, we report the first EEM-PARAFAC data to assess the distribution of FDOM in the Florida Keys where salinity cannot be used as a freshwater tracer and multiple sources of DOM prevail. We hypothesized that EEM-PARAFAC can aid in the assessment of DOM sources, and thus, can be used as a monitoring tool for terrestrial DOM at complex coastal environments where salinity cannot be used as a freshwater tracer. Long-term water quality monitoring programs (including total organic carbon; TOC) have been conducted continuously throughout the Florida Keys and Florida Bay for many years, and successfully classified the Florida Keys coastal zone into 6 areas in terms of differences in water quality (Boyer et al., 1997; Boyer and Briceño, 2010). Thus, the Florida Keys, home of the only coral reef track in the continental US, is an area ideally suited to test this approach.

2. Site description

The Florida Keys region is an archipelago of sub-tropical islands of Pleistocene origin, which extend in a northeast to southwest direction from Miami to Key West and out to the Dry Tortugas (Fig. 1). The waters of the Florida Keys are characterized by complex water circulation patterns and are directly influenced by the Florida Current, the Gulf of Mexico Loop Current, inshore

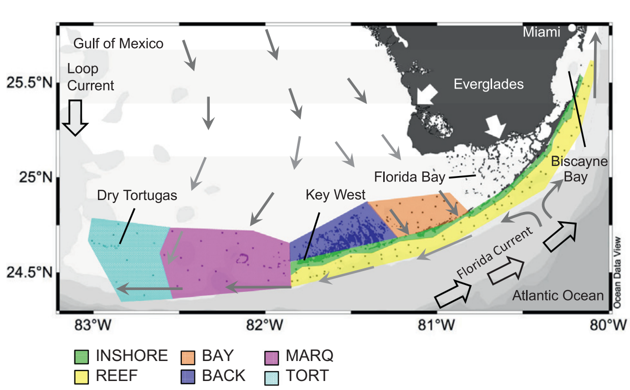

Fig. 1. Map of sampling locations and six zones of the Florida Keys determined by water quality parameters (Boyer and Briceño, 2010). Schematic representations of the average flow patterns are modified from Hunt and Nuttle (2007).

currents of the southwest Florida Shelf, freshwater discharge from mangrove rivers from the south western and southern areas of the Everglades, and by tidal exchange with both Florida Bay and Biscayne Bay (Lee et al., 1994, 2002).

Seagrass communities are common throughout Florida Bay and along the Florida Keys, while coral reef development occurs mostly offshore on the Atlantic side of the Florida Keys archipelago (Porter and Porter, 2002). Thus, water quality of the Florida Keys may be directly affected both by external nutrient and DOM transport and internal loadings through natural runoff and anthropogenic activities (Gibson et al., 2008). Previous reports using satellite imagery suggest that terrestrial CDOM exported through river drainage of the southwest region of the Everglades (Jaffé et al., 2004; Bergamaschi et al., 2012) can reach the Florida Keys (Hu et al., 2003, 2004). On the other hand, seagrasses, mangrove patches surrounding the Keys and scattered throughout Florida Bay, and photo-dissolution of re-suspended sediments were suggested to be other contributors to the CDOM pool in this region (Stabenau et al., 2004; Zepp et al., 2008; Shank et al., 2010a, 2011; Maie et al., 2012).

Based on water quality parameters collected over 15 years (http://serc.fiu.edu/wqmnetwork/), the Florida Keys coastal environment was statistically divided into six zones (Fig. 1; Boyer and Briceño, 2010). The BACK zone was composed primarily of stations located inside and north of the Lower Keys (Fig. 1). This zone was characterized by the highest nutrient and TOC levels among the six zones. The BACK zone is believed to be influenced by solutes transported from the southwest Florida Shelf and/or derived from benthic sources. The BAY zone included sites most influenced by Florida Bay and waters moving in a southerly direction from the southwest Florida Shelf. This zone is characterized by highest in SiO_2 and elevated TOC levels, but was relatively low in inorganic nutrients and chlorophyll *a* (Boyer and Briceño, 2010). The water quality of the INSHORE, MARQ, REEF, and TORT zones was most similar to each other but statistically distinct. The INSHORE included the innermost sites of the Keys, which are shallow, and closest to any possible anthropogenic sources. The REEF was made up of all Hawk Channel and reef tract sites off the mainland Keys. The INSHORE was slightly elevated in inorganic nitrogen and TOC relative to the REEF. The MARQ is a zone of relatively shallow water which separates the southwest Florida Shelf from the Atlantic Ocean. The MARQ had higher total phosphorus (TP) and chlorophyll *a* (Chl*a*) than TORT and REEF but was comparable in nitrogen. The TORT was composed of sites located western part of the study region, including those in Dry Tortugas National Park. The distinction between the REEF and TORT was driven by the slightly higher TOC concentrations and lower TP found in the REEF zone (Boyer and Briceño, 2010).

Here we report EEM-PARAFAC data on FDOM from the six abovementioned water quality zones, based on one intensive sampling exercise, in an attempt to assess spatial DOM source distributions and to test the applicability of this technique to spatial monitoring in complex coastal regions.

3. Materials and methods

Surface water samples were collected from 155 sites located in the Florida Keys during 8 January–15 February 2008 (Fig. 1). These stations represented the same sampling sites originally established for the long-term water quality monitoring program in the Florida Keys (Boyer and Briceño, 2010). Samples for optical characterization of DOM were collected in pre-washed (soaked in 0.1 M HCl and 0.1 M NaOH for 24 h each), brown polyethylene bottles and were stored on ice, returned to the laboratory, and filtered through pre-combusted (450 °C, 3 h) GF/F filters prior to analysis. The sample collection, field measurements and analytical methods for water