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Carbon and nitrogen tracers of land use effects on net ecosystem metabolism in mangrove estuaries, southwest Florida

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Four estuaries in southwest Florida with different land-use characteristics in their watersheds were chosen to investigate the effects of anthropogenic land use on estuarine biogeochemical cycling. We compared C:N ratios, concentrations of dissolved inorganic carbon (DIC), chlorophyll-a (chl-a) and particulate organic carbon (POC), stable isotope ratios of DIC ($\delta^{13}C_{DIC}$) and POC ($\delta^{13}C_{POC}$), and nitrogen isotope ratios of particulate organic nitrogen ($\delta^{15}N_{PON}$) among these estuaries. Values of $\delta^{13}C_{DIC}$ ranged from −14.1 to +0.9‰. The more negative values occurred upstream, resulting from DIC inputs derived from both the degradation of organic carbon and dissolution of carbonates. Upstream DIC concentrations were as high as 8066 μmol L^{-1}, suggesting high respiration rates. Further, a comparison of DIC values to a conservative mixing model indicates net heterotrophic metabolic state in all four estuaries. Supporting this interpretation, low $\delta^{13}C_{POC}$ values suggest that terrestrial plants were the main source of POC in the upstream sampling points. However, C:N ratios ranged from 7.2 to 13.4, and were consistent with the decomposition of both terrestrial and aquatic sources. Chl-a concentrations were variable and typically below 20 μg L^{-1}, indicating moderate to low levels of autotrophy in all estuaries. Elevated chl-a concentrations indicative of increased primary productivity occurred at intermediate salinities, and were possibly caused by the mixing front at mid-estuary locations. There were no apparent differences in $\delta^{15}N_{PON}$ among estuaries, suggesting that the N sources to these estuaries are comparable. The combined results show no differences between near-natural and anthropogenically influenced estuaries, indicating a minimal effect of anthropogenic activities on the parameters measured, possibly as a result of the filtering capacity of the extensive surrounding mangrove vegetation.

1. Introduction

Human activities affect the physical, biological, and chemical characteristics of estuarine surface waters through stream alteration and draining wetlands (e.g., Hopkinson and Vallino, 1995; Sklar and Browder, 1998; Kennish, 2002; Holland et al., 2004; Boëchat et al., 2013), or by degrading the water quality and ecosystem structure of estuaries through pollution (e.g., Zhang, 1996; Carpenter et al., 1998; Howarth et al., 2002; Kennish, 2002; Paerl et al., 2004). In the latter case, the influx of anthropogenic nutrients (typically N and P) promotes eutrophic conditions and increases respiration (e.g., Pelley, 1998; Smith et al., 1999; Kennish, 2002; Jennerjahn et al., 2008; Boëchat et al., 2013), which often results in hypoxic or anoxic conditions (Kennish, 1997). This episodic eutrophication and hypoxia disrupts estuarine ecology. For instance, low oxygen levels typically correlate with lower species diversity (Dauer et al., 1992; Howell and Simpson, 1994) and with increased frequency of red tide blooms, leading to fundamental shifts in estuarine ecology.

Human-induced eutrophication can occur in estuaries that naturally show high nutrient levels, such as those dominated by mangrove forests, which are common in southern Florida. However, the most palpable effects of human activities have been on the hydrology and salinity of these particular estuaries (e.g., Surge and Lohmann, 2002). Estuaries in south Florida have been altered by land-use change involving the development of extensive agricultural and urban areas (e.g., Bricker et al., 1999; Browder et al., 2005; Rudnick et al., 2005). Documenting the effects of human activities

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on estuarine nutrient levels has been problematic due to the influence of natural nutrients released by the surrounding mangrove forests (Valiela et al., 2014). The ability to identify the influence of anthropogenic nutrients on estuarine watersheds is important because of the potentially adverse effects of increased nutrient load on water quality and ecosystem functioning and structure in estuaries.

One way to evaluate the effects of excess anthropogenic nutrient inputs in estuaries involves comparing minimally impacted sites with human-impacted sites (e.g., Campbell et al., 1991; Cifuentes et al., 1996; White et al., 2004), and we employed this approach to compare four estuaries with different land-use characteristics in southwest Florida. Other studies have used similar techniques to successfully track the effects of land use and population density on river biogeochemistry (e.g., Jennerjahn et al., 2008; Boëchat et al., 2013). Three of these estuaries are impacted (Henderson, Blackwater, Faka-Union) and experience different levels and types of land use. One estuary, Fakahatchee, experiences minimal anthropogenic influence, thus serving as a control site. Three methods were used in each estuary to evaluate estuarine metabolism, nutrients, and productivity: (1) determination of estuarine metabolic state (net autotrophic or heterotrophic conditions) through the study of dissolved inorganic carbon (DIC) concentrations and the carbon isotope ratios of DIC ($\delta^{13}C_{DIC}$); (2) assessment of nitrogen sources through the study of the nitrogen isotope ratios of particulate organic matter ($\delta^{15}N_{PON}$); and (3) evaluation of estuarine productivity by measuring chlorophyll-a (chl-a) abundances and the carbon isotope ratios of particulate organic carbon ($\delta^{13}C_{POC}$). To capture estuarine down-gradient variability, samples were collected along the estuary including upstream and downstream end-members to evaluate estuarine mixing. Seasonal effects were taken into account by sampling during both wet and dry seasons.

2. Methodology

2.1. Site description

The estuaries selected for this study are part of the Rookery Bay National Estuarine Research Reserve (RBNERR), which consists of approximately 5245 km^2 of mangrove forests and estuaries located south of Naples, Florida and west of the Everglades (Fig. 1). The local climate is subtropical with an average annual temperature of 24 °C and rainfall ranging from 127 to 140 cm yr^{-1} (Shirley et al., 2004). The climate in this area has a distinct rainfall seasonality with the wet season occurring from June through September (rainfall ranges from 20 to 23 cm per month), and the dry season occurring from November through March (rainfall ranging from 2 to 5 cm per month) (Shirley et al., 2004).

The estuaries in this region are shallow, well mixed, and tidally dominated. Mangrove forests dominate the watersheds and include three main species: white (*Laguncularia racemosa*), black (*Avicennia germinans*), and red (*Rhizophora mangle*) mangroves (Shirley, 2002). In RBNERR and other areas in Florida, the mangrove zonation relates to topography, with the white mangroves dominating high points in wetlands, black mangroves dominating low points in wetlands, and red mangroves dominating the estuarine environments. Four estuaries (Henderson, Faka-Union, Blackwater, and Fakahatchee) were chosen on the basis of the different land-use characteristics in their watersheds (Table 1).

Henderson Creek (HC) - The Henderson Creek watershed is the smallest watershed in this study (14,385 ha; Shirley et al., 2004) draining agricultural areas, golf courses, residential areas, and trailer parks (Rousu, 2000). Although the majority of the residential areas have a reliable sewer system (Delate and Haner, 1994), local developments close to the mouth of the river use septic systems, leaching nutrients and bacteria into Henderson Creek (Rousu, 2000; Shirley, 2002). About 50% of the watershed area is considered developed (Shirley et al., 2004). Belle Meade drains into Henderson Creek and is primarily characterized by highly productive agriculture and low-density development (Delate and Haner, 1994). The Henderson estuary also receives runoff from Water Management District VI, which drains into the northern portion of Rookery Bay. This is the most developed watershed in this study. This watershed is densely populated and receives effluent from two sewage treatment plants, six golf courses, fertilizer runoff, and other urban runoff including road and parking lot runoff and lawn treatment runoff (Delate and Haner, 1994).

Faka-Union Canal (FU) – This watershed (57,800 ha; Shirley et al., 2004) is characterized by high freshwater inputs from the Faka-Union Canal (Surge et al., 2003). The Faka-Union Canal is part

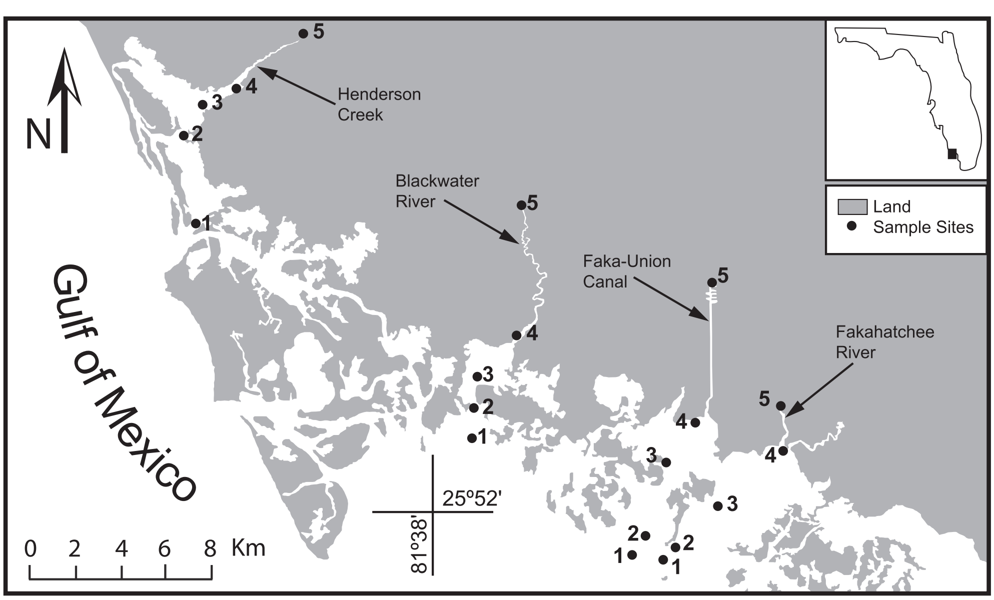

Fig. 1. Area map illustrating relative locations of Henderson, Blackwater, Faka-Union, and Fakahatchee estuaries. Sample locations are labeled 1 (lower estuary) to 5 (upper estuary), and will be used for reference in later figures.