



Origin, composition and quality of suspended particulate organic matter in relation to freshwater inflow in a South Texas estuary



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ABSTRACT

South Texas has a semi-arid climate with a large interannual variability of freshwater inflows. This study sought to define how changes in freshwater inflow affect the composition, quantity and quality of suspended particulate organic matter (SPOM) in a South Texas estuary: the Mission-Aransas estuary. The study was implemented 1.5 months after a large rain event in September 2010 and continued for 10 months of drought conditions. The composition of SPOM originating from rivers, the Gulf of Mexico and the estuary were determined using stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$). The quantity and quality of SPOM were assessed using organic carbon content, chlorophyll *a* concentrations and C/chl *a* ratios. Our results demonstrated that autochthonous phytoplankton was the dominant component of SPOM in the Mission-Aransas estuary during droughts. Benthic organic matter from local primary producers (i.e., seagrass, salt marsh plants, benthic microalgae) did not influence SPOM composition, either as fresh material or as detritus. A comparison with a positive estuary (i.e., Sabine-Neches estuary, TX) indicates that decreases in freshwater inflow may lead to decreases of terrestrial organic matter inputs and to increase the ratio of autochthonous phytoplanktonic material in SPOM.

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1. Introduction

Estuaries are among the most productive ecosystems on Earth, with production equal to that of tropical rain forests (McLusky, 1989). The quantity and timing of freshwater delivery to the mixing zone is essential to their functioning (Montagna et al., 2002). Freshwater inflows play key roles in carrying continental organic matter from the watershed to the estuary (Hedges et al., 1997), and in balancing effects of tidal inputs of saltwater and of evaporation,

consequently affecting the structure of habitats. As a result, freshwater inflows affect inputs of continental and marine organic matter and autochthonous pelagic and benthic primary production (Longley, 1995). Increasing human populations will result in an increasing demand for freshwater, which will affect freshwater inflow into estuaries and have consequences on the functioning of estuarine ecosystems (Montagna et al., 2002).

One consequence is the potential change of composition of suspended particulate organic matter (SPOM), an integral component of estuarine food webs (Longley, 1994). Organic matter locally produced in estuaries or provided by rivers or the sea varies in terms of quantity and quality depending on its origin and its state of decay (Dunton et al., 2001; Raymond and Bauer, 2001). This diversity of primary productions can be used by many different consumers, making highly complex estuarine food webs. Consequently, estuaries provide many ecological functions, including breeding grounds, nurseries and feeding sites for a large diversity of pelagic and benthic species (Beck et al., 2001). For example, SPOM is generally the main food source of suspension feeders like oysters.

Abbreviation: SPOM, suspended particulate organic matter; Chl *a*, chlorophyll *a*; GoM, Gulf of Mexico; POC, Particulate organic matter.

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As a result, a change of abundance or composition of SPOM may severely affect the oyster diet (Riera and Richard, 1997), and therefore the general functioning of oyster reefs, which provide many ecological functions (Beck et al., 2011; Grabowski et al., 2012).

The origins, quantity, and quality of SPOM can be determined by measuring several variables, including stable isotope ratios, chlorophyll *a* (chl *a*) content and C/chl *a* ratios. Stable isotope ratios of carbon and of sulfur provide information about the origin of organic matter. Stable isotopes of carbon allow for discrimination between the different estuarine primary producers (Fry and Sherr, 1984; Peterson and Fry, 1987) and are often used to determine composition of SPOM in estuaries (Cifuentes et al., 1988; Riera and Richard, 1997; Savoye et al., 2003, 2012; Modéran et al., 2012). Due to potential overlaps of carbon stable isotope composition between different primary producers and the effects of decay processes on isotopic composition (Benner et al., 1987), stable isotopes of sulfur can be used to discriminate between the different food sources. Primary producers from continental areas are generally much more ^{34}S -depleted than primary producers from oceanic environments (Peterson et al., 1985; Peterson and Howarth, 1987; Thode, 1991). Stable isotope composition of nitrogen is generally used to determine the trophic levels of consumers (Minagawa and Wada, 1984; Vander Zanden and Rasmussen, 1999), but can also be an indicator of anthropogenic influence (i.e., release of wastewater from treatment plants) due to increase of $\delta^{15}\text{N}$ values with bacterial activity (McClelland and Valiela, 1998; Mooney and McClelland, 2012). The measurement of these three stable isotopes enables discrimination between the different pools of organic matter in order to determine its origin. The measurement of total organic carbon, chl *a* and C/chl *a* ratios along with these stable isotope ratios help determine the quantity and the quality of SPOM along a salinity gradient. The aim of this study was to determine how the different primary producers and inputs of allochthonous organic matter (i.e., from continental and marine origins) affect the composition, quantity and quality of SPOM, and to determine the evolution of these parameters in relation to changes in freshwater inflows. This study was conducted in the Mission-Aransas estuary, Texas, a semi-arid estuary that is vulnerable to changes in natural and anthropogenic changes in freshwater inflow.

2. Material and methods

2.1. Study area

The Mission-Aransas estuary is one of seven major estuarine systems located along the Texas coast (Fig. 1). It is a shallow, bar-built estuary composed of Aransas bay, the primary bay located closest to the Gulf of Mexico inlet, and Copano Bay, the secondary bay located closest to the two main rivers: the Mission and Aransas rivers. The Mission-Aransas estuary is 2 m deep on average, its surface is 463 km² and its volume is 0.93 km³ (Armstrong, 1987). The Copano bay watershed is 4851 km² (Borel et al., 2015); 49% of the freshwater comes from the Mission river and 15% from the Aransas river (Orlando et al., 1993).

The Mission-Aransas estuary is located in a sub-tropical humid climate. Rainfalls generally occur as brief and intense rain showers and as a result, freshwater inflows occur as episodic pulses. Rainfall, and consequently freshwater inflows, varies from year to year with alternating dry and wet periods (Evans and Morehead Palmer, 2012). From 2001 to 2010, freshwater inflows from both rivers ranged from 17 to 430 million m³ y⁻¹ (U.S. Geological Survey, 2012). On an annual basis, Mission-Aransas estuary is losing water due to higher evaporation (1513 mm y⁻¹) than precipitation (886 mm y⁻¹) (Armstrong, 1987). The estuary has low mixing efficiency (<0.05) and long residence times (~360 days, Solis and Powell, 1999). The

salinity structure is driven by episodic freshwater pulses that depress salinities and then maintain low salinities for a prolonged period (Orlando et al., 1993).

The Mission-Aransas estuary hosts diverse primary producers and is fueled by different allochthonous sources i.e., continental organic matter from Mission and Aransas rivers in Copano bay, pelagic organic matter from the Gulf of Mexico in Aransas bay, organic matter from San Antonio bay transported southward across the Mesquite bay via the Intracoastal Waterway (Solis and Powell, 1999).

2.2. Sampling stations

Five stations were sampled along a salinity gradient in the Mission-Aransas estuary, with station 1 (St. 1) the closest to the Aransas river mouth and station 5 (St. 5) the closest to the Gulf of Mexico (Fig. 1). Three other stations were sampled to collect freshwater from the two main rivers: Mission river (MIS) and Aransas river (ARA), and sea water from the Gulf of Mexico (GoM). Freshwater inputs into Copano bay were determined by summing flows of Mission and Aransas rivers using data from USGS gauge stations (Fig. 1) located at Refugio (Mission river, Site ID: 08189500) and Skidmore (Aransas river, Site ID: 08189700) (U.S. Geological Survey, 2012).

2.3. Collection of water samples and sample processing

At each station, three samples of surface water were collected on a monthly basis, from November 2010 (relatively high freshwater inflow) to August 2011 (relatively low freshwater inflow). All water samples were collected far enough from the shore to be representative of the river or bay water mass. Due to restricted access, it was impossible to sample water at the mouth of the Mission river.

Salinity was measured with an YSI 6920 multiprobe sonde, using practical salinity scale. Water samples were pre-filtered on a 250- μm sieve to eliminate large zooplankton and detritus. For each water sample, SPOM was collected on four different filters (pre-combusted Whatman GF/F glass fiber filters, 0.7 μm porosity) in order to measure stable isotope composition ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$) and chl *a* concentration. A volume ranging from 5 to 325 ml was filtered under moderate vacuum; filters were then frozen at $-20\text{ }^{\circ}\text{C}$ and freeze-dried. Carbonates were removed from filters for $\delta^{13}\text{C}$ and $\% \text{C}$ analyses by contact with HCl fumes in a vacuum-enclosed system.

2.4. Collection of primary producers for stable isotope analyses

To determine the composition of SPOM, the main primary producers (C_3 and C_4 salt marsh plants, seagrass, benthic microalgae) were sampled at different locations along the salinity gradient and during different seasons to examine possible spatio-temporal changes in isotopic composition. Vascular plants (leaves) and seagrass (leaves and roots) were collected, placed in plastic bags and stored in ice until return at the lab. They were then rinsed with tap water to remove detritus and sediment, frozen at $-20\text{ }^{\circ}\text{C}$, freeze-dried and ground to a fine and homogeneous powder using a ball mill.

Benthic microalgae were collected by scraping surface sediments in the field and then by extracting the microalgae in the laboratory following the method of Riera and Richard (1996), slightly modified by Herlory et al. (2007). Extracted samples were checked under a microscope for purity, then benthic microalgae were collected on three different filters (pre-combusted Whatman GF/F glass fiber filters) in order to measure stable isotope composition ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$). Samples were frozen at $-20\text{ }^{\circ}\text{C}$ then freeze-dried.

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