



Research papers

Stable isotope characterization of hypoxia-susceptible waters on the Louisiana shelf: Tracing freshwater discharge and benthic respiration

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ABSTRACT

To examine the sources of freshwater and carbon cycling associated with Louisiana shelf hypoxia, we measured $\delta^{18}\text{O}$ and δD of water, $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), salinity and dissolved oxygen (DO) in waters from 37 stations during April and July of 2008. Seafloor $\delta^{18}\text{O}$ values resemble typical Gulf of Mexico seawater ($\approx 1.1\%$) while surface waters values are substantially lower (e.g., $< -2.0\%$) due to mixing with river-sourced freshwater. Salinity- $\delta^{18}\text{O}$ regressions for 2008 surface waters show the $\delta^{18}\text{O}$ of discharge to average -6.8% in April and -5.1% in July. Salinity- δD regressions show the δD of discharge to be -38% in April and -28% in July. Together these regressions suggest Mississippi discharge was the dominant freshwater source in the study area in April followed by a shift to nearly total Atchafalaya discharge during July, a trend that coincides with summer coastal current reversals. The $\delta^{13}\text{C}_{\text{DIC}}$ of July surface water varies from -5.0 to 1.2% and correlates with salinity indicating mixing of seawater and river water. April surface water shows no relationship with salinity because of the influence of primary productivity, which enriches certain waters in $\delta^{13}\text{C}_{\text{DIC}}$ and DO. The $\delta^{13}\text{C}_{\text{DIC}}$ of sub-pycnocline water ranges from -2.3 to 0.3% , with lower values reflecting increased respiration. The inshore (10 m depth) $\delta^{13}\text{C}_{\text{DIC}}$ -DO relationship yields a lower y-intercept relative to offshore (20 m depth) bottom waters, possibly indicating a terrestrial source of OC being respired. Mass balance estimations of respired OC do not have the accuracy to quantify any difference between nearshore and offshore locations. Regardless, the $\delta^{13}\text{C}_{\text{DIC}}$ -DO relationships suggest that the $\delta^{13}\text{C}$ of biogenic carbonates may provide a valuable tool for paleo-redox studies in this region.

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1. Introduction

Hypoxia, or depletion of dissolved oxygen, is a common feature of bays, estuaries, and river-dominated continental margins. It is defined by dissolved oxygen (DO) concentrations below 1.4 mL L^{-1} (compared with normal concentrations between 4 and 6 mL L^{-1} ; Pavela et al., 1983; Rabalais et al., 2001). Hypoxia generally occurs when the water column becomes stratified from the convergence of water masses of different salinities and/or temperatures, and then sub-pycnocline respiration of organic matter depletes DO.

In the last century, hypoxia has become a major environmental concern. The global number of hypoxic zones has doubled every decade since 1960, with prevalence near large population centers (Diaz and Rosenberg, 2008). Historically, hypoxic zones have been mostly limited to semi-enclosed to enclosed bays or basins,

however more recently they have developed in coastal seas such as the Baltic Sea, East China Sea and Gulf of Mexico. The occurrence of hypoxia is promoted by nutrient-loading (Turner and Rabalais, 1994; Rabalais et al., 2002; Conley et al., 2009). Nutrients from fertilizers are carried by runoff into rivers and fluxed onto the continental shelf, creating or contributing to phytoplankton blooms (Rabalais et al., 1999; Mitsch et al., 2008). As these blooms flourish, they flux organic matter to the seafloor in the form of copepod fecal pellets and dead plankton, which are respired by bacteria, depleting bottom waters of oxygen.

In the Gulf of Mexico (GoM), hypoxia is prevalent along the Louisiana and eastern Texas shelf at depths not usually exceeding 30 m (Rabalais et al., 2001; Bianchi et al., 2010). Hypoxia extends westward of the Mississippi Delta along Louisiana coastal waters, occasionally encroaching upon the middle Texas shelf (Harper et al., 1981). This is the largest coastal hypoxic zone on the western Atlantic, measuring upto $20,000 \text{ km}^2$ (Rabalais et al., 2001). The hypoxia is caused by the annual influx of nearly 600 km^3 of nutrient-rich waters from the Mississippi and Atchafalaya Rivers. It occurs seasonally from late spring to early fall during

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a confluence of peak river discharge from spring rains, weakening of wind-driven coastal currents, limited wave activity, and increased solar intensity, creating conditions favorable for phytoplankton blooms and water column stability (Wiseman et al., 1997; Rabalais et al., 2001; Bianchi et al., 2010).

Better understanding of the relative influences of the sources of freshwater (i.e. Atchafalaya vs. Mississippi) and organic carbon (OC) (i.e. terrestrial vs. marine) on the formation of Louisiana shelf hypoxia can improve its predictability (Justić et al., 2007). Discharge from the Mississippi and Atchafalaya Rivers, the primary sources of freshwater on the Louisiana continental shelf (Dinnel and Wiseman, 1986), is the principal driver of water column stratification and nutrient input. The Atchafalaya River diverges from the Mississippi River at the Old River Control Structure, where it receives 30% of the Mississippi River flow as well as flow from the Red River. Because Mississippi River water accounts for the majority of Atchafalaya River flow, the discharge of both Mississippi and Atchafalaya rivers are frequently considered a single freshwater influence (Rabalais et al., 2002). Furthermore, prediction models have only considered the rivers as point sources of nutrient export (Scavia et al., 2003; Turner et al., 2006; Scavia and Donnelly, 2007), omitting direct OC fluxes. More recently, a hydrodynamic circulation numerical model has shown spatially separated hypoxia regions east and west of Terrebonne Bay, with stratification in the eastern zone associated with the Mississippi River discharge, and stratification in the western zone influenced by discharge of the Atchafalaya River and runoff from its associated wetlands (Hetland and DiMarco, 2008).

In addition to freshwater export, large deltaic regions near continental margins account for the majority of organic carbon deposition in marine sediments (Bernier, 1982). This organic carbon deposition contains a significant component of terrestrial material (Hedges et al., 1988), the importance of which has not been thoroughly evaluated with regard to hypoxia formation within and especially outside the Mississippi or Atchafalaya River plumes (Bianchi et al., 2011 and references therein).

Here we use oxygen and hydrogen stable isotopes ($^{18}\text{O}/^{16}\text{O}$, D/H) of Louisiana shelf waters during a period of hypoxia and peak

spring discharge to examine the relative influence of the Mississippi and Atchafalaya Rivers on freshwater spatial distribution and hypoxia formation. While salinity has traditionally been used to trace freshwater masses, O and H isotopes improve on the measure by providing a tracer for freshwaters from different drainage basins, and have been extensively utilized to trace freshwater sources in coastal seas (Redfield and Friedman, 1969; Frank, 1972; Torgersen, 1979; Wagner and Slowey, 2011). The method relies on the fact that the oxygen and hydrogen isotope compositions of river waters are dependent upon drainage basin geography and evaporative flux of river water. Due to Rayleigh distillation, drainage basins of lower latitudes typically exhibit higher $\delta^{18}\text{O}$ values than the more isotopically “rained out” high latitude drainage basins (Kendall and Coplen, 2001). Oxygen and hydrogen isotopes of Atchafalaya River water are consistently high relative to Mississippi River water due to the incorporation of Red River drainage (Coplen and Kendall, 2000; Lee and Veizer, 2003).

Freshwater discharge onto continental shelves also causes variations in the carbon isotope composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$; Pierre et al., 1991; Kendall and McDonnell, 1998; Mackensen, 2001). However, the $\delta^{13}\text{C}_{\text{DIC}}$ will also vary in response to photosynthesis, respiration, upwelling, and exchange with atmospheric CO_2 (Quay et al., 2003), and thus can serve as a tracer for carbon cycling. On the Louisiana shelf bottom, the dominant process controlling carbon cycling in bottom waters is respiration (Dortch et al., 1994). The influence of bottom water respiration on $\delta^{13}\text{C}_{\text{DIC}}$ depends on the $\delta^{13}\text{C}$ of the organic carbon respired (e.g., terrestrial vs. marine). We explore the potential of $\delta^{13}\text{C}_{\text{DIC}}$ to trace organic carbon sources onto the Louisiana shelf, an important factor in the development of hypoxic waters (Dagg et al., 2004; Green et al., 2006; Bianchi et al., 2009, 2010).

2. Methods

Water was collected on two cruises to the Louisiana shelf during April and July of 2008 on the *R/V Pelican* operated by the Louisiana Universities Marine Consortium (LUMCON). Sampling

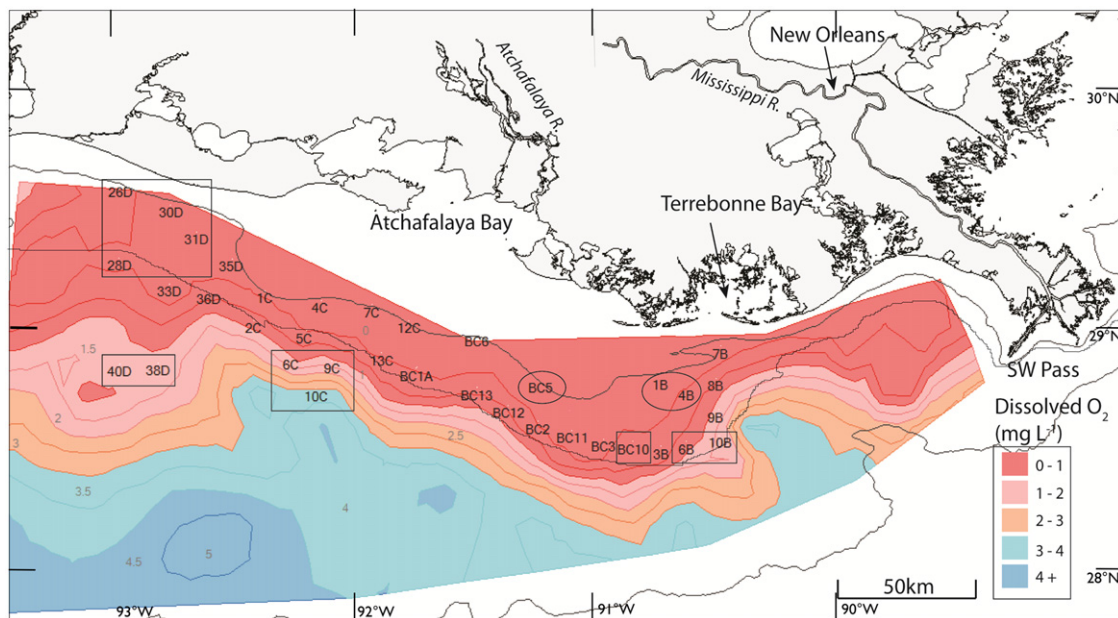


Fig. 1. Map of April and July 2008 sampling stations and bottom water dissolved O_2 concentration on the Louisiana shelf. Stations enclosed in boxes were only sampled in July; stations encircled were only sampled in April. Dashed yellow and dotted blue rectangles and ovals reflect stations where April surface waters yield distinct S- $\delta^{13}\text{C}_{\text{DIC}}$ relationships (see Fig. 4). Contours of DO (interval = 0.5 mg L^{-1}) represent observations during July NOAA SEAMAP cruises aboard *R/V Oregon II* (data available at <http://ecowatch.ncddc.noaa.gov/hypoxia>). Bathymetric contours of 10 m and 200 m are illustrated. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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