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Extent of Mississippi River water in the Mississippi Bight and Louisiana Shelf based on water isotopes

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ABSTRACT

The northern Gulf of Mexico is a complex and very productive coastal river-dominated system that receives freshwater from numerous rivers including the Mississippi River. The dynamics of coastal ecosystems in the northern Gulf of Mexico are greatly influenced by the freshwater discharge but also by the high nutrient loads carried by the Mississippi River that lead to the seasonal development of one of the largest coastal hypoxic areas. Constraining the origin and fate of the freshwater inputs in the northern Gulf of Mexico will help increase understanding the physical and biogeochemical processes occurring in this region. Here, we focus on investigating the extent of the Mississippi River plume on both sides of the Mississippi River Delta: to the east in the Mississippi Bight, and to the west over the Louisiana Shelf. We determined the water isotopic signature ($\delta^{18}\text{O}$ and δD) along with salinity of the different river plumes and performed a river mixing model on the coastal waters. Our findings provide useful information to better understand the functioning of the northern Gulf of Mexico ecosystem. In particular, the development of hypoxia is often attributed to the nutrient load of the Mississippi River, yet the Mississippi River seemed to have a limited influence on the Mississippi Bight. That is, the dominant source of freshwater in the Bight was supplied by local Mississippi/Alabama rivers. Furthermore, the water isotope mixing model showed that the source of freshwater to the Louisiana Shelf was dominated by the Atchafalaya River in summer, and by the Mississippi River during non-summer seasons. This pattern is consistent with the general shelf circulation that reverses in summer, but could not have been shown solely by the use of salinity.

1. Introduction

Coastal areas are key regions between the continent and the open ocean where freshwater and land-derived chemical elements supplied by rivers mix with seawater (Martin and Whitfield, 1983). Coastal river-dominated systems are also complex physically and biogeochemically, and are very productive regions (Nixon et al., 1986).

The central northern Gulf of Mexico is a coastal river-dominated system that receives fresh water from the largest river system in North America, the Mississippi/Atchafalaya River system (Fig. 1), with a watershed extending over three million square kilometers in the US Midwest and parts of two Canadian provinces. The contribution of this river system to hypoxia on the Louisiana Shelf, both in terms of nutrient supply and stratification of the water column, is well-established (e.g., Rabalais et al., 2002). However, the fresh water outflow from this system is not entirely homogeneous. The Atchafalaya River, which carries 30% of the combined flow of the Lower Mississippi and Red

Rivers, has some compositional difference from the mainstem of the Mississippi River. This is a result of both the effect of the Atchafalaya Swamp and contributions from the Red River to the Atchafalaya River (e.g., Joung and Shiller, 2014; Shen et al., 2012; Xu, 2006). Moreover, not all of the delta outflow goes to the Louisiana Shelf; some of the delta waters go offshore or to the east, depending on seasonal winds and currents (Cochrane and Kelly, 1986; Dinnel and Wiseman, 1986). Thus, understanding how these freshwater sources are distributed on the shelf is important for elucidating the anthropogenic nutrient sources that are a key component of the development of seasonal hypoxia in this region (e.g., Rabalais et al., 2007).

In addition to the Mississippi/Atchafalaya outflow, numerous regional and local rivers with smaller watersheds relative to the Mississippi/Atchafalaya system also supply significant freshwater to the Gulf of Mexico. For instance, the Mobile Bay system, which has a discharge about 10% that of the Mississippi River, empties onto the shelf region about 170 km northeast of the Mississippi River Delta. Because

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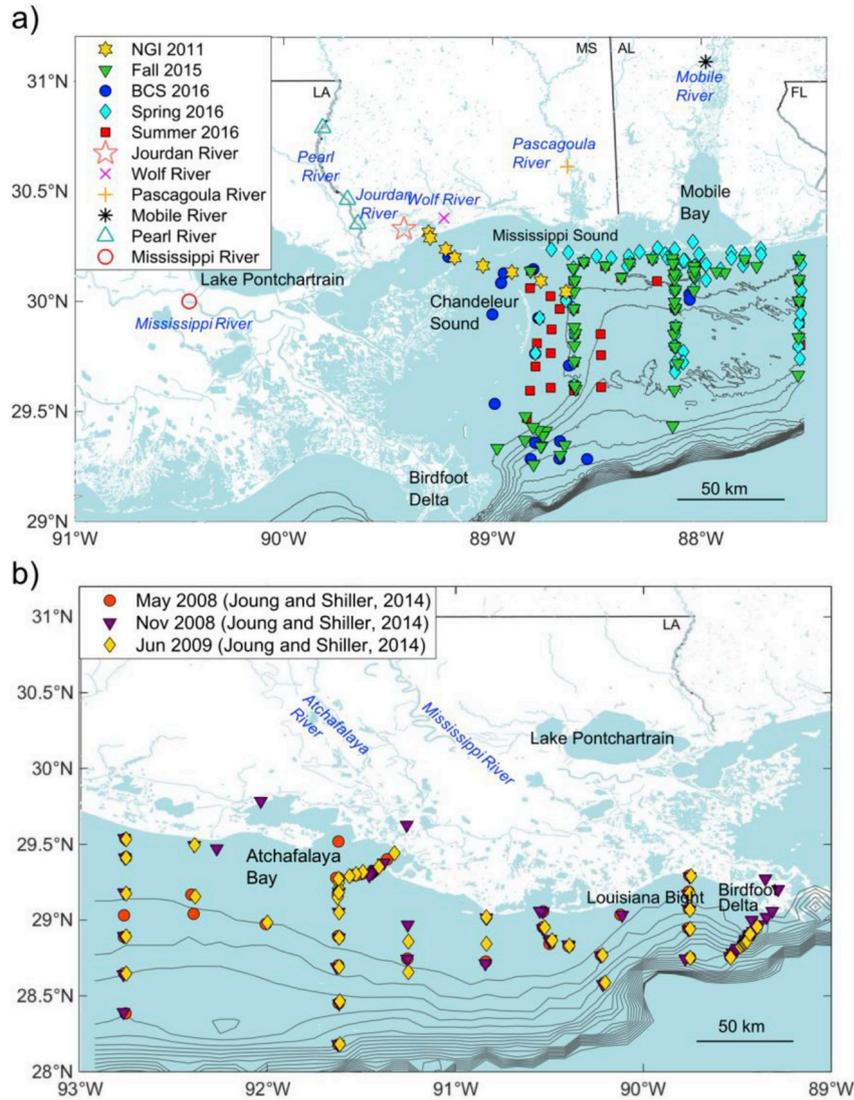


Fig. 1. a) Map of the Mississippi Bight showing the locations of the NGI transect where samples were collected monthly between June 2011 and November 2011, as well as the locations of the samples collected during the CONCORDE project in 2015 and 2016. The locations where the freshwater samples were collected from five local rivers (Jourdan, Wolf, Pascagoula, Mobile, and Pearl Rivers) and from the Mississippi River are also shown. The thin gray lines represent the bathymetry from 20 m to 200 m depth with a 10-m interval. b) Map of the Louisiana Shelf showing the locations of the samples from Joung and Shiller (2014).

surface waters in the northern Gulf at least seasonally have a predominant westward flow (e.g., Dzwonkowski et al., 2011; Walker et al., 2005) the Mobile Bay outflow as well as that of other smaller rivers may well dominate the fresh water (and fluvial nutrient) supply to the Mississippi Bight region, east of the Mississippi River delta. Since these more regional rivers tend to have lower nutrient concentrations than the Mississippi River (Dunn, 1996), understanding the origin of the various freshwater sources to the Mississippi Bight is critical to better constrain the development of hypoxia (dissolved oxygen $< 2 \text{ mg L}^{-1}$) in that area. The multiple sources of freshwater flowing into the northern Gulf of Mexico therefore complicate our understanding of the freshwater influence on functioning of this coastal system including the development of seasonal hypoxia. Finding tracers for these freshwater sources is thus a problem of significance.

The stable isotopic composition of freshwater (i.e., $\delta^{18}\text{O}$ and δD) offers a possible tracer for separating at least some of the key fresh water sources in the northern Gulf of Mexico. The oxygen and hydrogen stable isotopic composition of water has been shown to be an effective tool to identify the origin of the freshwater input (Craig and Gordon, 1965). Processes such as evaporation and precipitation fractionate meteoric water resulting in different isotopic signatures of meteoric

precipitation generally as a function of latitude (Bowen and Wilkinson, 2002; Craig, 1961; Craig and Gordon, 1965; Dansgaard, 1964). As a result, rivers that originate from different catchments may have different $\delta^{18}\text{O}$ and δD signatures (Kendall and Coplen, 2001). In a sense, water isotopes are the ultimate water tracer because they are part of the water itself. The oxygen and hydrogen isotope data $\delta^{18}\text{O}$ and δD represent the deviation of the $^{18}\text{O}/^{16}\text{O}$ and the $^2\text{H}/^1\text{H}$ isotopic ratios, respectively, from that of the international reference Vienna standard mean ocean water (VSMOW). Delta- ^{18}O and δD (or $\delta^2\text{H}$) values are expressed in per mille (‰) and are defined as follow:

$$\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{Sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} \right] \times 1000 \quad (1)$$

and

$$\delta\text{D} = \left[\frac{(^2\text{H}/^1\text{H})_{\text{Sample}} - (^2\text{H}/^1\text{H})_{\text{VSMOW}}}{(^2\text{H}/^1\text{H})_{\text{VSMOW}}} \right] \times 1000 \quad (2)$$

Fairbanks (1982) and Schlosser et al. (1994) showed the utility of this water isotope tracer in early studies of mixing of waters in the New

York Bight, Gulf of Maine, and Arctic Ocean shelf regions. The methodology has also been applied in several studies of the northern Gulf of Mexico. [Wagner and Slowey \(2011\)](#) first applied this method to waters of the Louisiana Shelf, suggesting that $\delta^{18}\text{O}$ versus salinity plots might distinguish the influence of Mississippi River Delta versus Atchafalaya outflow on shelf waters. [Strauss et al. \(2012\)](#) and [Joung and Shiller \(2014\)](#) likewise used simple extrapolation of water isotope versus salinity plots to distinguish these two freshwater sources to Louisiana Shelf surface waters. Further to the west in the northern Gulf, [DiMarco et al. \(2012\)](#) used $\delta^{18}\text{O}$ versus salinity data to argue that hypoxia in Texas coastal waters in summer 2007 was linked to high discharge from the Brazos River rather than to downcoast advection of nutrient-rich Mississippi/Atchafalaya River water. More recently, [Montiel et al. \(2018\)](#) used the stable isotope signature of different water sources (including fluvial, marine, and groundwater) to constrain the water budget of Mobile Bay.

The Mississippi River plays a key role in the quality of the coastal ecosystem of the Northern Gulf of Mexico; therefore, this work focuses on addressing the following question: what is the extent of the Mississippi River plume relative to the numerous other local rivers? To address this question, we conducted a quantitative study to determine the fraction of freshwater associated with the Mississippi River on both sides of the Mississippi River Delta: in the Mississippi Bight to the east and over the Louisiana Shelf to the west. The sole use of salinity is very limited for this purpose because of the multiple sources of freshwater. Thus, we combined measurements of salinity and water isotopic composition of coastal waters and of the different sources of freshwater to perform a mixing model.

2. Materials and methods

2.1. Study area

The main channel of the Mississippi River flows through the bird-foot delta, dividing the continental shelf region in the northern Gulf of Mexico. The Louisiana Shelf is the narrow and shallow shelf that extends westward from the birdfoot delta ([Fig. 1](#)). The Atchafalaya River is formed from approximately 30% of the combined flow of the Mississippi and Red Rivers, and discharges onto the Louisiana Shelf, 175 km west of the Delta. While the Mississippi River is highly channelized, the Atchafalaya River flows through an extensive wetland. The annual average fluxes from the Mississippi and Atchafalaya Rivers are approximately $7.0 \times 10^{11} \text{ m}^3\text{y}^{-1}$ and $3.4 \times 10^{11} \text{ m}^3\text{y}^{-1}$, respectively ([Wagner and Slowey, 2011](#)).

The Mississippi Bight is a wide and shallow shelf area to the east of the birdfoot delta. The Mississippi Bight extends from Mobile Bay to the Chandeleur Islands and has a northern boundary delimited by the barrier islands of the Mississippi Sound ([Fig. 1](#)). The numerous smaller rivers that discharge into the Mississippi Sound include the Jourdan River, the Wolf River, the Pascagoula River, and the Pearl River. Five rivers (Mobile River, Spanish River, Tensaw River, Apalachee River, and Blakeley River) flow through the Tensaw-Mobile River Delta into the Mobile Bay and constitute its primary freshwater source with a total typical average flow of $5.5 \times 10^{10} \text{ m}^3\text{y}^{-1}$ ([Montiel et al., 2018](#)). About 64% of the Mobile Bay outflow discharges directly into the Mississippi Bight while the other third flows into the Mississippi Sound ([Kim and Park, 2012](#)). The river flow displays a seasonal variability with a peak in late winter/early spring and a minimum discharge observed in late summer/early fall ([Fig. 2](#)). The exchange of water between the Mississippi Sound and the Mississippi Bight is tide-dominated and occurs frequently through several barrier island inlets ([Cambazoglu et al., 2017](#)). The total freshwater discharge from all the local rivers is approximately one order of magnitude lower than the Mississippi River (i.e., $\sim 7 \times 10^{10} \text{ m}^3\text{y}^{-1}$; Water data USGS). A flood structure operated by the US Army Corps of Engineers, the Bonnet Carré Spillway (BCS), is installed in the lower Mississippi River to relieve the pressure

downstream generally caused by heavy rainfall in the Midwest, allowing freshwater to discharge through Lake Pontchartrain into the western Mississippi Sound and Bight.

The northern Gulf of Mexico receives large amount of nutrients from numerous rivers, and in particular from the Mississippi River. The mean annual total nitrogen and phosphorus loads introduced by the Mississippi River are 1.3×10^6 and 1.1×10^5 tons, respectively, while the Atchafalaya River discharges 4.7×10^5 tons of total nitrogen and 4.8×10^4 tons of total phosphorus ([Dunn, 1996](#)). Even though the annual mean load of the Atchafalaya River is significantly lower than the Mississippi River, the nutrient concentrations are similar between the two rivers ([Dunn, 1996](#)). The annual nutrient loads from the smaller, local rivers east of the delta are significantly lower than those from the Mississippi River, e.g., the Pearl River carries annually in average 1.3×10^4 tons of nitrogen and 1.5×10^3 tons of phosphorus ([Dunn, 1996](#)). In addition to smaller water discharge, the lower annual nutrient input from local rivers results from lower nutrient concentrations ([Cochrane and Kelly, 1986](#); [Dinnel and Wiseman, 1986](#); [Dunn, 1996](#)). The dissolved inorganic nitrogen (DIN) concentrations in the local rivers (Jourdan, Wolf, Pearl, Pascagoula, and Mobile Rivers) are similar and around 0.3 mg L^{-1} , while the DIN concentration in the Mississippi River is approximately 1.50 mg L^{-1} ([Dortch et al., 2007](#)).

Wind forcing plays a critical role in the structure of the river plumes and their transport over the coastal region of the Mississippi Bight and the Louisiana Shelf. The direction of the Mississippi River plume therefore varies throughout the year depending on the wind regime. The general freshwater transport in the Mississippi Bight and the Louisiana Shelf extends eastward in spring and summer, and westward in fall and winter ([Dzwonkowski and Park, 2010](#); [Morey et al., 2003](#); [Nowlin et al., 2005](#)). However, some smaller scale variations can also be observed. For example, the salinity at the mouth of the Mobile Bay varies on timescales of a few days between relatively fresh and saline water from the Bight, suggesting some frequent intrusion of Mississippi Bight waters towards the Bay depending on the wind direction ([Cambazoglu et al., 2017](#)). Eddies can also be formed due to the interaction of the Loop Current with the Louisiana Shelf break ([Oey, 1995](#)).

2.2. Sample collection

The data discussed here are mainly from sampling efforts conducted in 2011 (“NGI transect”) and between 2015 and 2016 (CONCORDE project; [Greer et al., 2018](#)). The NGI transect extended from the mouth of St. Louis Bay (located in between the Wolf and Jourdan rivers) through the western end of the Mississippi Sound into the Mississippi Bight. Eight locations were visited along this transect every month between June and November 2011 providing insights on the variations of the freshwater extent across the Mississippi Sound ([Fig. 1a](#)). Four campaigns were conducted in the framework of the CONCORDE project in the Mississippi Bight: in fall 2015 (Oct 29 – Nov 5), winter 2016 (Feb 10–12), spring 2016 (March 30 – Apr 10), and summer 2016 (July 23–30).

Seawater samples were collected at the surface by means of a trace metal clean bottle attached to a PVC pole and deployed over board. Additional seawater samples were collected at mid- and bottom-water column depths using trace metal clean GoFlo bottles mounted on a rosette system.

Freshwater samples were collected in the main rivers discharging into the Mississippi Bight during five field trips conducted between October 2015 and June 2016. The rivers that were sampled are: Jourdan River, Wolf River, Pearl River, Mississippi River, Pascagoula River, and Mobile River. The river samples were collected in Oct 2015, and in January, February, March, and June 2016. The locations of the seawater and river water samples collected are shown in [Fig. 1](#).

Additionally, we reexamined data from the Louisiana Shelf, which were previously published by [Joung and Shiller \(2014\)](#). Those

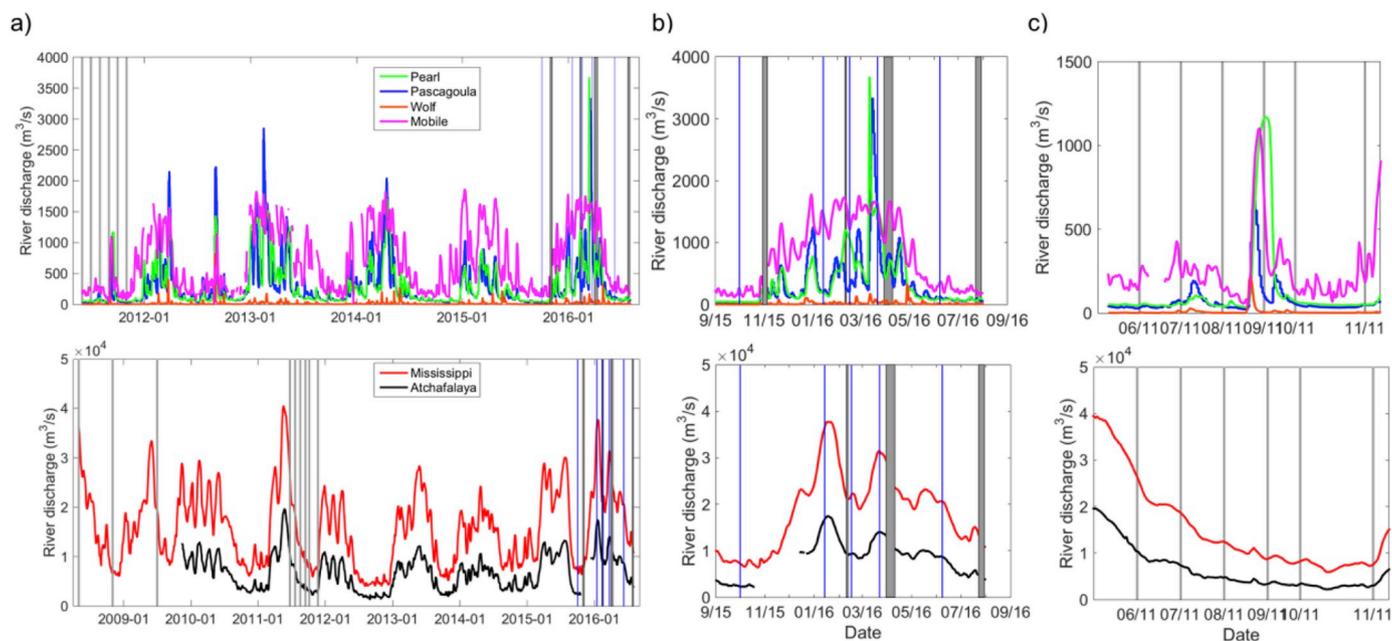


Fig. 2. Panel a shows the river discharge ($\text{m}^3 \text{s}^{-1}$) of the local rivers (top) that discharge into the Mississippi Bight and of the main rivers that discharge onto the Louisiana Shelf (bottom). The river discharge data were downloaded from USGS National Water Information System (<https://waterdata.usgs.gov/nwis/sw>; Mississippi River at Baton Rouge, Atchafalaya River at Simmesport, Pearl River at Bogalusa, Pascagoula River at Merrill, Wolf River at Landon, Mobile River at river mile 31.0 Bucks). Note that no data of the Atchafalaya River discharge was available prior 2010, however, the proportion of Atchafalaya vs Mississippi River is known and fixed at 30% by the Army Corps of Engineers. The periods associated to the cruises conducted over the Louisiana Shelf (May 2008, Nov 2008, and June/July 2009), the NGI cruises (2011) and the CONCORDE cruises (Fall in Oct 2015, and BCS in Feb, Spring in Apr, and Summer in July of 2016) conducted on the Mississippi Bight are highlighted in gray. The blue vertical lines show the time of river sampling (Oct 2015, and Jan, Feb, March, June 2016). Panels b and c show a zoom of the river discharge data for the CONCORDE and NGI cruise periods, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

campaigns were conducted over the Louisiana Shelf in May 2008, November 2008, and June/July 2009 (Fig. 1b). Details regarding this Louisiana Shelf sampling and analysis can be found in [Joung and Shiller \(2014\)](#).

2.3. Sample analysis

Salinity data were obtained from a CTD deployed on the rosette. However, for the February and April 2016 cruises, due to the large salinity gradient at the surface in this river-dominated region as well as the placement of the sensor near the bottom of the rosette, the surface salinity data were often biased high. Thus, for those surface waters we estimated the salinity by determination of the dissolved molybdenum (Mo) concentrations in the actual water samples. Molybdenum behaves generally conservatively in seawater, including in the northern Gulf of Mexico region ([Collier, 1985](#); [Joung and Shiller, 2016](#)). Freshwater and seawater samples for Mo analysis were filtered soon after collection through acid-cleaned $0.45 \mu\text{m}$ pore size polyethylene syringe filters. The water samples were acidified to $\text{pH} < 2$ with 6 M ultrapure hydrochloric acid and stored in acid-cleaned bottles. The Mo concentrations were measured on a high resolution inductively coupled plasma-mass spectrometer (ThermoFisher Element XR) using an isotope dilution method ([Ho et al., 2018](#)). Briefly, $50 \mu\text{L}$ of sample was spiked with a known quantity of isotopically-enriched ^{95}Mo (96.45%; Oak Ridge National Laboratory) and diluted 30-fold with ultrapure water prior to measuring the $^{95}/^{98}\text{Mo}$ ratio. The Mo concentrations ranged from 20.6 nM to 122.7 nM in seawater, and from below detection to 17.2 nM in rivers, which is consistent with previous Mo values reported in the area ([Joung and Shiller, 2016](#)). The maximum salinity measured (35.67) was taken as the seawater end-member and had a Mo concentration of 116.1 nM, which is relatively close to the mean oceanic Mo concentration ([Collier, 1985](#)). The average Mo concentration (2.8 nM) and salinity (0.07) in river samples were taken as the river

end-member. The surface salinity was then determined by simple conservative mixing based on the Mo concentrations. The uncertainty in the Mo-derived salinity data is estimated to be 2.3% based on the uncertainty of repeated analysis of Mo in seawater samples ([Ho et al., 2018](#)).

Water samples for oxygen and hydrogen stable isotopes ($\text{O}^{18}/\text{O}^{16}$ and D/H) were filtered with $0.45 \mu\text{m}$ pore size polyethylene syringe filters and stored in glass bottles that were tightly sealed until measurement to prevent evaporation. The $\delta^{18}\text{O}$ and δD analysis was performed using isotope ratio infrared spectroscopy (L2120-i cavity ring-down spectrometer, Picarro Inc.), which required 0.8 mL of solution per sample. The data were calibrated using in-house reference waters that had been standardized to the VSMOW reference material and drift corrected following [van Geldern and Barth \(2012\)](#). The analytical uncertainties associated to the $\delta^{18}\text{O}$ and δD were 0.07‰ and 0.5‰ (1 sigma), respectively. We also calculated the deuterium excess ($d\text{-excess}$) according to [Dansgaard \(1964\)](#). The $d\text{-excess}$ is the deviation of the isotopic composition from the Global Meteoric Water Line (GMWL): $d\text{-excess} = \delta\text{D} - 8 \times \delta^{18}\text{O}$. The $d\text{-excess}$ is primarily sensitive to evaporative processes, which result in a more negative deviation of the residual water as compared with the evaporated vapor (e.g., [Frohlich et al., 2001](#)). Based on the uncertainties of the individual isotopic measurements, we estimated the uncertainty of $d\text{-excess}$ as 0.8‰.

2.4. River fraction analysis

A mixing analysis was performed to determine the relative contributions of fresh water sources to seawater in the continental shelf of the northern Gulf of Mexico. The river mixing analysis was adapted from the standard ocean water mass analysis ([Peters et al., 2018](#); [Tomczak, 1999, 1981](#)) and was based on the principle of conservative mixing of $\delta^{18}\text{O}$ and salinity. For the Louisiana Shelf, there are only two significant sources of fresh water, the Mississippi and Atchafalaya

Rivers, and they are isotopically distinct from each other (Joung and Shiller, 2014; Wagner and Slowey, 2011). For the Mississippi/Alabama coastal waters, there are a number of local rivers which, while not isotopically distinct from each other (see below as well as Kendall and Coplen, 2001), are isotopically distinct from the Mississippi River. Additionally, previous work has shown little variability in the isotopic composition of high salinity open Gulf of Mexico seawater (Frank, 1973; Wagner and Slowey, 2011). Thus, for both coastal regions, we modeled the mixing based on three components: open Gulf of Mexico seawater, Mississippi River water, and either local river water (Mississippi/Alabama) or Atchafalaya River water (Louisiana). In the equations below, we use the abbreviation “LR” to indicate that third (local or Atchafalaya) source.

A set of two linear mixing equations describing the mixing between seawater (SW), the Mississippi River (MR), and the local rivers (LR) can be written as follows, and was solved for each sample collected in the surface coastal waters (depth < 2 m) of the Mississippi Bight:

$$\delta^{18}\text{O}_{\text{sample}} = f_{\text{MR}} \delta^{18}\text{O}_{\text{MR}} + f_{\text{LR}} \delta^{18}\text{O}_{\text{LR}} + f_{\text{SW}} \delta^{18}\text{O}_{\text{SW}} + \varepsilon_1 \quad (3)$$

$$\delta\text{Sal}_{\text{sample}} = f_{\text{MR}} \text{Sal}_{\text{MR}} + f_{\text{LR}} \text{Sal}_{\text{LR}} + f_{\text{SW}} \text{Sal}_{\text{SW}} + \varepsilon_2 \quad (4)$$

where $\delta^{18}\text{O}_{\text{sample}}$ and $\text{Sal}_{\text{sample}}$ are the water isotopic composition and salinity of the given sample; $\varepsilon_{1,2}$ (and ε_3 , cf eq. (5)) are the residuals, $f_{\text{MR,LR,SW}}$ are the fractions of the Mississippi River, the local rivers, and the seawater; and $\delta^{18}\text{O}_{\text{MR,LR,SW}}$ and $\text{Sal}_{\text{MR,LR,SW}}$ are the isotopic composition and the salinity of the three end-members: seawater, the Mississippi River, and the local rivers. An additional constraint is that the sum of the water source fractions ($f_{\text{MR}}, f_{\text{LR}}, f_{\text{SW}}$) should be equal to one, which is described by the following equation:

$$f_{\text{MR}} + f_{\text{LR}} + f_{\text{SW}} = 1 + \varepsilon_3 \quad (5)$$

These three equations are independent and have only three unknowns, and thus can be solved uniquely for the water source fractions (f s). We used a non-negative least squares optimization (function “lsqnonneg” in MATLAB) in order to constrain the solution to positive river fractions. In essence, if the exact solution resulted in a negative fraction of one of the fresh water sources, the method sets that fraction to zero. The Mississippi River influence is discussed below based on the ratio $f_{\text{MR}}/(f_{\text{MR}} + f_{\text{LR}})$ determined in our coastal seawater samples, with values above 0.5 indicating that the major source of freshwater in a sample originated from the Mississippi River.

The water isotope data and the salinity from Joung and Shiller (2014) were also used to investigate the relative influence of the Mississippi River and the Atchafalaya River over the Louisiana Shelf. In this case, the river fraction analysis was performed using the same equation (3)–(5), but considering the Mississippi River (MR), the seawater (SW), and the Atchafalaya River (AR) as end-members.

3. Results and discussion

3.1. $\delta^{18}\text{O}$ and δD relationship

The $\delta^{18}\text{O}$ and δD in the river samples followed a straight line ($\delta\text{D} = 7.8 \times \delta^{18}\text{O} + 11.2$, $r^2 = 0.97$; Fig. 3) that corresponds to the GMWL prediction for precipitation within the 95% confidence interval (Craig and Gordon, 1965; Rozanski et al., 1993). The Mississippi River had a distinct signature with an isotopically light $\delta^{18}\text{O}_{\text{MR}}$ and $\delta\text{D}_{\text{MR}}$ of $-6.6 \pm 0.3\text{‰}$ and $-41.9 \pm 2.9\text{‰}$ (standard error), respectively (Fig. 3), in agreement with previous studies (Joung and Shiller, 2014; Wagner and Slowey, 2011). Strauss et al. (2012) found some seasonal variability in the water isotope composition of the lower Mississippi River that they attributed at least partly to seasonally changing snowmelt contributions. Likewise, we observed a correlation between the dissolved Mo concentration of the lower Mississippi River and its water isotope composition (Fig. 4), which is similarly suggestive of changing proportions of different freshwater sources within the river basin (e.g.,

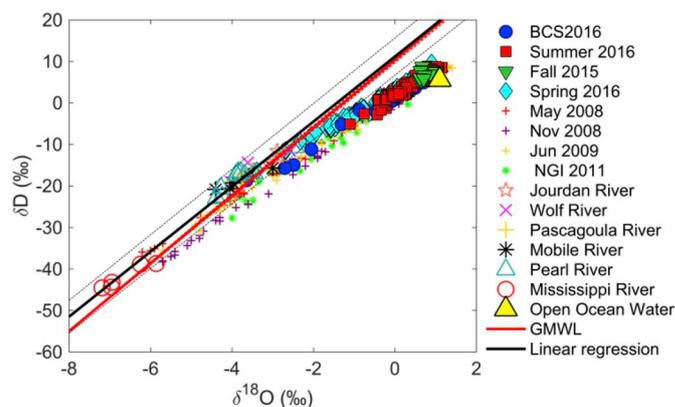


Fig. 3. Oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) isotopic composition of coastal waters of the Mississippi Bight, Louisiana Shelf, and of the different rivers. The isotopic signature of open ocean water for the Gulf of Mexico is from Frank (1973) and Wagner and Slowey (2011). The red line represents the Global Meteoric Water Line (GMWL, $\delta\text{D} = 8.17 \times \delta^{18}\text{O} + 10.35$; Craig and Gordon, 1965; Rozanski et al., 1993). The black continuous line represents the linear regression on the river samples ($\delta\text{D} = 7.8 \times \delta^{18}\text{O} + 11.2$, $r^2 = 0.97$) and the black dashed lines delimit the 95% confidence level. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

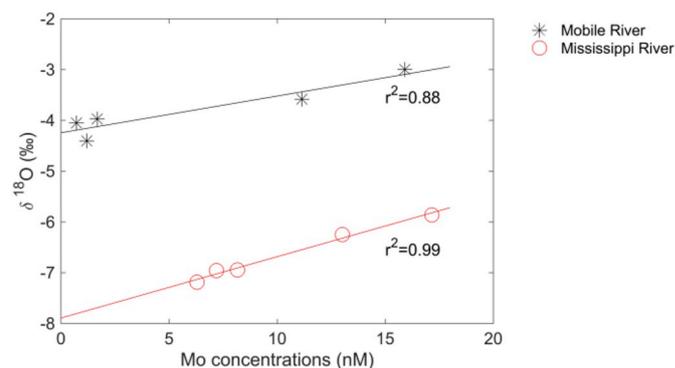


Fig. 4. Variations of molybdenum (Mo) concentrations and water isotope composition ($\delta^{18}\text{O}$) in the Mobile and Mississippi River during the five field trips.

Shiller, 1997). A correlation between the Mo concentrations and $\delta^{18}\text{O}$ values is also observed in the Mobile River water (Fig. 4). The highest Mo concentrations were associated with the heaviest $\delta^{18}\text{O}$ values and were observed in samples collected in October and June collected during the minimum river discharge (Fig. 2). The other local rivers displayed very similar water isotopic compositions (and Mo concentrations) between them with no significant temporal variations. The local rivers were characterized by a $\delta^{18}\text{O}_{\text{LR}}$ of $-3.6 \pm 0.2\text{‰}$ and $\delta\text{D}_{\text{LR}}$ of $-17.2 \pm 4.5\text{‰}$ (standard error), which is significantly more positive than the Mississippi River signature. These values are slightly more positive, though within the range of variability, of the isotopic composition of rainfall reported for Tuscaloosa, Alabama (Lambert and Aharon, 2010). These results are consistent with the inverse relationship between latitude, and both $\delta^{18}\text{O}$ and δD of meteoric precipitation (Bowen and Wilkinson, 2002; Dansgaard, 1964; Killops and Killops, 2013), and the more northerly origin of waters of the Mississippi River basin versus the local rivers. Finally, $\delta^{18}\text{O}_{\text{LR}}$ and $\delta\text{D}_{\text{LR}}$ are in agreement with recently published stable isotope signature of freshwater source to Mobile Bay (Montiel et al., 2018).

Evaporation (E) and precipitation (P) also need to be considered as potential contributors to the isotopic signals discussed here. Although this aspect of the freshwater balance on the Mississippi Bight has not been previously considered, Etter et al. (2004) and Dinnel and Wiseman

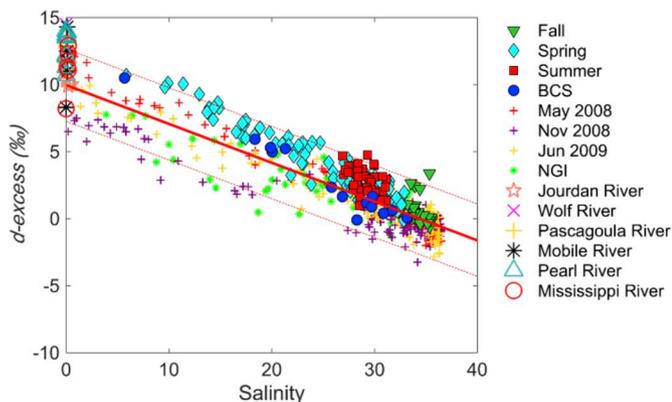


Fig. 5. Deviation of the isotopic composition from the Global Meteoric Water Line ($d\text{-excess} = \delta D - 8 \times \delta^{18}O$) as a function of salinity. The samples collected in May 2008, Nov 2008, and June 2009 are from the Louisiana Shelf (Joung and Shiller, 2014). The red line is the linear regression on all the coastal seawater samples ($r^2 = 0.8$). The red dashed lines define the 2-sigma confidence limits. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(1986) examined E and P for the Louisiana Shelf and showed that they are generally minor compared to river inflow, with E generally being more important than P. Because rainfall in this region (Lambert and Aharon, 2010) is isotopically similar to the local rivers, any contribution of rainfall would be indistinguishable from a local river signal. Regarding E, we note that Strauss et al. (2012) estimated the evaporative flux from Atchafalaya Bay would have only a minor effect on the isotopic composition. However, Etter et al. (2004) did note a potential significant effect of evaporation during the fall.

We can take the investigation of E a step further by examining the $d\text{-excess}$ (Dansgaard, 1964) of our samples. A plot of $d\text{-excess}$ versus salinity for our CONCORDE samples shows they fall on a mixing line between the higher $d\text{-excess}$ of the rainfall-dominated river waters and the lower $d\text{-excess}$ of the more evaporation-influenced surface seawater endmember, with only 5% falling outside of the 2-sigma confidence limits (Fig. 5). Thus, evaporative effects do not appear to be a significant component of those data. Note that the $d\text{-excess}$ of Mississippi River water was not significantly different from the $d\text{-excess}$ of the local rivers. Interestingly, the $d\text{-excess}$ for many of the low-salinity NGI samples do fall significantly below the trend of the CONCORDE data (Fig. 5). We note first that the samples with the lowest $d\text{-excess}$ (relative to the overall trend) are from the September and October 2011 NGI transects and the November 2008 Louisiana Shelf survey. Etter et al. (2004) indicate that evaporation is seasonally highest in the fall and, on the Louisiana Shelf, can even be a dominant aspect of the freshwater balance at that time, which is consistent with the low $d\text{-excess}$ from the November 2008 cruise. Furthermore, although most of the $d\text{-excess}$ values in our river samples were close to the average of 12‰, the two lowest $d\text{-excess}$ values were both around 8.5‰ in fall 2015, close to the extrapolated zero-salinity endmember of the fall 2011 NGI $d\text{-excess}$ vs salinity plot. Thus, the low Sept./Oct. 2011 NGI $d\text{-excess}$ values may reflect both seasonal changes in the contribution of evaporation to the shelf water balance as well as seasonal changes in the $d\text{-excess}$ of river water. Our fall 2015 CONCORDE data do not show this effect possibly because of the remnants of Hurricane Patricia that passed through the area shortly before that cruise, which flushed and mixed the waters of the Mississippi Sound and Bight (Dzwonkowski et al., 2017).

The $\delta^{18}O_{SW}$ and δD_{SW} isotopic signature of coastal waters in the Mississippi Bight and Sound spanned a large range of values between the negative signature of rivers and the positive signature of the surface open ocean water of the Gulf of Mexico (Fig. 3). Gulf of Mexico seawater was previously characterized by a mean $\delta^{18}O$ of $1.1 \pm 0.05\text{‰}$ and mean δD of 5.6‰ (Frank, 1973; Wagner and Slowey, 2011). The

$\delta^{18}O_{SW}$ and δD_{SW} follow a straight line between the river signature and the open ocean signature suggesting that the $\delta^{18}O_{SW}$ and δD_{SW} of the coastal waters results from the mixing between river water and open ocean water. The $\delta^{18}O_{SW}$ and δD_{SW} measured in fall 2015 were relatively homogeneous ($\delta^{18}O_{SW}$: from $+0.6\text{‰}$ to $+1.0\text{‰}$, δD_{SW} : from $+5.5\text{‰}$ to $+8.7\text{‰}$) over the whole Mississippi Bight and tended toward the open ocean water signature. This could be the result of limited river discharge (Fig. 2) consistent with the high salinity, and a well-mixed water column that could be explained by the passage of Hurricane Patricia over the northern Gulf of Mexico few days before the fall 2015 cruise (Cambazoglu et al., 2017; Rogers et al., 2017). In summer 2016, the $\delta^{18}O_{SW}$ and δD_{SW} were slightly more negative and covered a wider range ($\delta^{18}O_{SW}$ from -1.1‰ to $+1.2\text{‰}$, δD_{SW} : 5.1‰ to $+10.4\text{‰}$) consistent with relatively larger freshwater river inputs than in fall (Fig. 2). The range of the water isotopic values in coastal seawaters increased again in spring 2016 with $\delta^{18}O_{SW}$ ranging from -3.4‰ to $+1.1\text{‰}$, and δD_{SW} ranging from -16.4‰ to 9.7‰ . The most negative $\delta^{18}O_{SW}$ and δD_{SW} values were observed during the cruise conducted after the opening of the Bonnet Carré Spillway (BCS 2016). During the BCS 2016 cruise, the $\delta^{18}O_{SW}$ ranged from -3.6‰ to 1.0‰ , and the δD_{SW} ranged from -18.7‰ to $+7.9\text{‰}$. Note that the maximum δD_{SW} data reported here exceeds the range of values (5.5–6.3‰) previously published for central Gulf of Mexico waters by Frank (1973), though some of his data from the Bay of Campeche do approach our maximum value. For $\delta^{18}O_{SW}$, our maximum value was in agreement with Wagner and Slowey (2011). The water isotope data along the NGI transect across the western end of the Mississippi Sound were similar to those observed in the Mississippi Bight. In June and September 2011, some of the water isotope data were especially negative (Fig. 3), which was likely due to the proximity of those samples to the Mississippi River plume.

3.2. Salinity - $\delta^{18}O$ relationship in the Mississippi Sound and Bight

The signatures of the three end-members (local rivers, Mississippi River, and open ocean waters) are very distinct on a salinity- $\delta^{18}O$ diagram (Fig. 6). A large variability of salinity was observed in the Mississippi Bight between the different sampling periods. For example, salinity was high and fairly homogeneous during November 2015, which is consistent with low river discharge in fall (Fig. 2), and thus a $\delta^{18}O$ of the coastal waters similar to the open ocean water value. Both datasets from the cruises conducted in spring and after the opening of the BCS showed the lowest $\delta^{18}O$, consistent with low salinity. The monthly repeated NGI transect across the Mississippi Sound also showed some variability in salinity and $\delta^{18}O$, with the lowest salinities observed in June, July and September 2011.

The $\delta^{18}O_{SW}$ in the coastal waters of the Mississippi Bight and Sound varied linearly along the gradient of salinity due to the conservative mixing of the water isotopes between the negative $\delta^{18}O$ values from rivers and the positive $\delta^{18}O$ value from open ocean seawater. The intercept of the regression line at zero salinity therefore provides information on the dominant source of freshwater. The $\delta^{18}O$ -salinity regression lines for most of the cruises were all relatively similar and displayed a zero-salinity intercept close to the local river $\delta^{18}O$ signature, suggesting a dominant influence from local freshwater inputs. However, some data points fell below these regression lines, suggesting an occasional significant freshwater contribution from the isotopically light Mississippi River to the low salinity coastal surface waters in the Mississippi Bight and Sound. This was especially the case in February 2016 and September 2011 when these data points formed regression lines with an intercept close to the Mississippi River end-member. For the majority of our samples, however, even though the Mississippi River is the largest river in the vicinity of the Mississippi Bight and Sound, the coastal waters appeared to be mainly under the influence of freshwater originating from the local rivers regardless of the season.

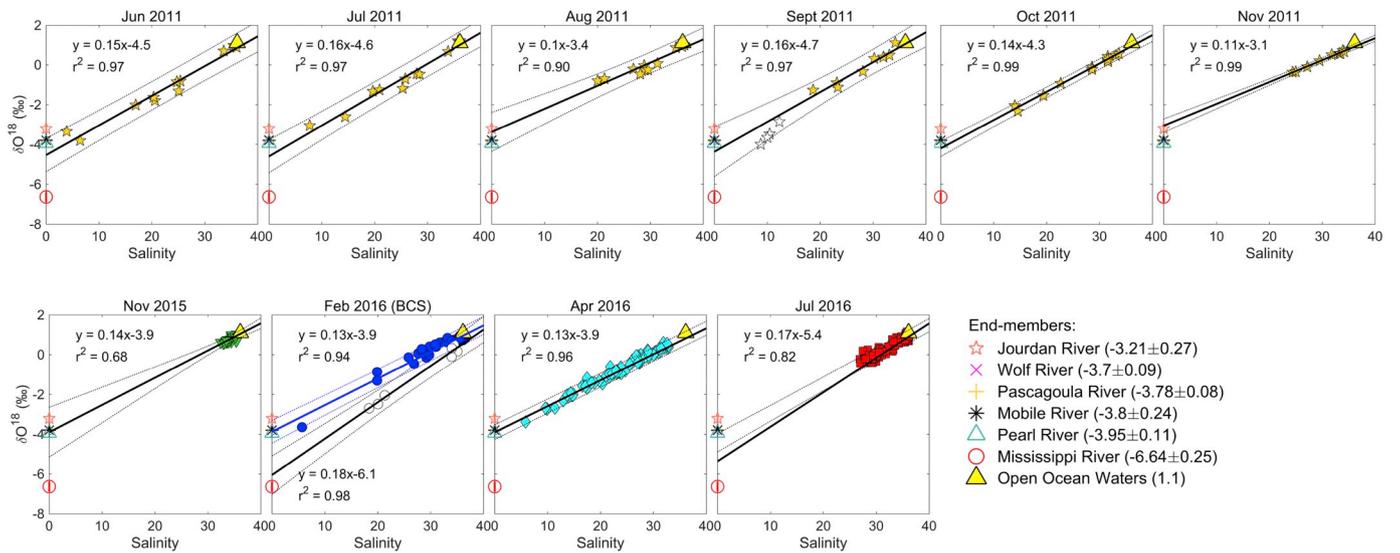


Fig. 6. Oxygen isotopic composition ($\delta^{18}\text{O}$) of coastal waters including surface, subsurface, and bottom samples of the Mississippi Sound (top) and Bight (bottom) as a function of salinity. The regression lines of the coastal seawater samples are plotted for each cruise (the color code matches the location of the samples in Fig. 1). The $\delta^{18}\text{O}$ of the river samples from the different sampling trips were averaged and represented by a single symbol. The averages and standard errors of the $\delta^{18}\text{O}$ for each river are reported in parenthesis in the legend. The linear fit is shown in each plot with a continuous black line, the 95% confidence interval is represented by the dashed black lines. Note that the $\delta^{18}\text{O}$ of the Wolf River, Pascagoula River, and Mobile River are almost identical, thus the symbols overlapped in the different panels. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3. River mixing model

Because the surface samples for fall 2015 as well as the sub-surface (> 5 m) samples from all cruises had high salinities, the fresh water fraction of these samples was too small for reliable application of our mixing model. Therefore, the system of equations (3)–(5) was only solved for surface samples from the BCS (February), spring, and summer 2016 cruises, along with the NGI transects and the Louisiana Shelf samples.

The Mississippi River $\delta^{18}\text{O}_{\text{MR}}$ and Sal_{MR} end-members, were taken as $-6.6 \pm 0.3\text{‰}$ (Std Error) and 0.14 ± 0.02 , respectively (see Sec. 3.1, above). The $\delta^{18}\text{O}_{\text{LR}}$ and Sal_{LR} for the local rivers, were taken as $-3.6 \pm 0.2\text{‰}$ (Std Error) and 0.12 ± 0.02 , respectively. According to Wagner and Slowey (2011), the average $\delta^{18}\text{O}_{\text{SW}}$ for surface water of the Gulf of Mexico is $1.1 \pm 0.05\text{‰}$ and is associated with a salinity of 36.1 ± 0.3 . The highest $\delta^{18}\text{O}_{\text{SW}}$ value that we measured was found in

summer 2016 in the mid water column in the Mississippi Bight and was equal to 1.15‰ and associated to a salinity 35.81, which is very similar to Wagner and Slowey's (2011) value. The Atchafalaya River $\delta^{18}\text{O}_{\text{AR}}$ and Sal_{AR} values that were used to solve the system of equations were based on samples collected in the Atchafalaya River plume (Joung and Shiller, 2014) and were $-4.9 \pm 0.2\text{‰}$ and 0.1 ± 0.02 , respectively. The Atchafalaya River is formed from a fraction of the Mississippi River that is diverted and merged with the Red River. Because the Red River drainage basin does not extend as far north as the Mississippi River basin, it is characterized by more positive water isotope values resulting in the roughly 1.7‰ more positive $\delta^{18}\text{O}_{\text{AR}}$ than $\delta^{18}\text{O}_{\text{MR}}$ (Kendall and Coplen, 2001; Wagner and Slowey, 2011). Our $\delta^{18}\text{O}_{\text{AR}}$ values are more positive than the previously published value of -5.8‰ by Wagner and Slowey (2011) and Strauss et al. (2012). However, given the observed seasonal variability in $\delta^{18}\text{O}_{\text{MR}}$ (Kendall and Coplen, 2001) as well as changes in the relative proportions of Red and Mississippi River waters

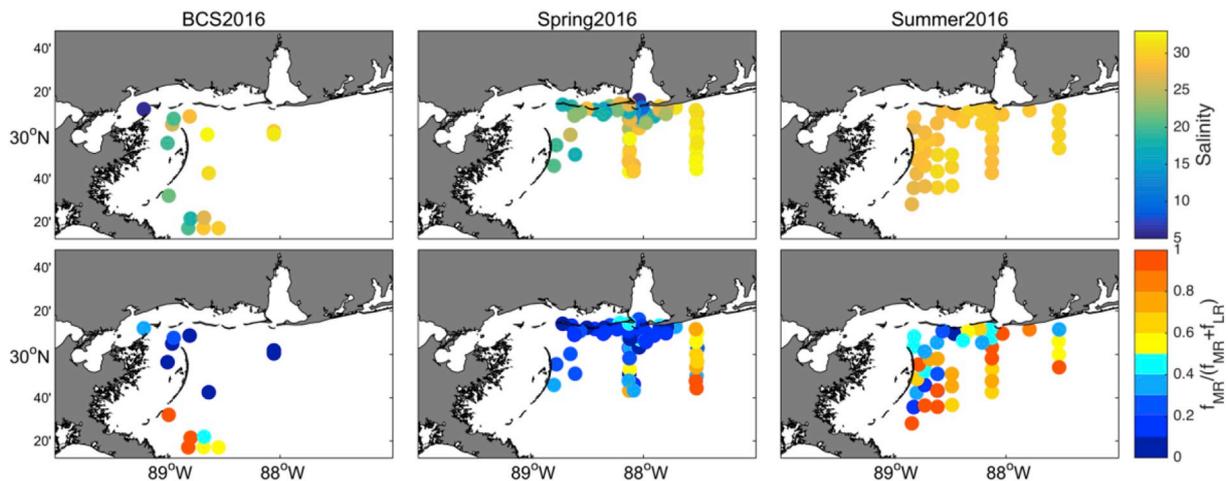


Fig. 7. Spatial distribution of surface water salinity (top) and river source fraction $f_{\text{MR}}/(f_{\text{MR}} + f_{\text{LR}})$ (bottom) from the CONCORDE cruises conducted in Spring 2016, Summer 2016, and after the opening of the Bonnet Carré Spillway (BCS2016). The shades of red/orange highlight a dominant contribution from the Mississippi River (f_{MR}) while the shades of blue highlight a dominant contribution from the local rivers (f_{LR}). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

in the Atchafalaya River, the difference is not significant. Similarly, [Strauss et al. \(2012\)](#) observed a regression line in the Atchafalaya River plume with an intercept at salinity zero of $-4.3 \pm 0.2\text{‰}$ in August 2008. They concluded that there was no significant influence from evaporation/precipitation processes and they attributed the variation of $\delta^{18}\text{O}$ values in the river to seasonal variability.

For the Mississippi Bight data, the residuals from equation (5) (ε_3) were below 5%, suggesting that the equation system were relatively well constrained. For the NGI transect data, the residual ε_3 averaged $< 0.2\%$. For the Louisiana Shelf samples, the largest residual ε_3 was approximately 8%. The following discussion on the spatial and temporal variations of the river fraction utilizes the fraction of fresh water derived from the Mississippi River, that is $f_{\text{MR}}/(f_{\text{MR}} + f_{\text{LR}})$ in the Mississippi Bight and $f_{\text{MR}}/(f_{\text{MR}} + f_{\text{AR}})$ for the Louisiana Shelf. A Monte-Carlo analysis conducted on the $\delta^{18}\text{O}$ end-member of the local river and Mississippi River showed uncertainties of maximum 10% on the river fraction ratios. Because of the linear relationship between $\delta^{18}\text{O}$ and salinity that converged towards the Gulf of Mexico end-member, the uncertainties on the river fraction ratios are the highest for high salinity. Assuming that the largest uncertainties are due to the uncertainties on the measurement of $\delta^{18}\text{O}$, the propagation of the analytical uncertainties suggests that the $f_{\text{MR}}/(f_{\text{MR}} + f_{\text{LR}})$ provides meaningful information on the extent of the Mississippi River for coastal waters with a salinity below 33. Thus, the river fraction ratios will be discussed only for salinity below 33.

3.3.1. Sources of fresh water to the Mississippi Bight

During the spring 2016 survey, the surface water $\delta^{18}\text{O}$ -salinity trend ([Fig. 7](#)) suggests that local rivers were the dominant source of fresh water to the Mississippi Bight. The spatial heterogeneity of salinity in the Mississippi Sound near the Mobile Bay estuary showed the dynamic mixing between freshwater from the Mississippi Sound and more saline water from the Mississippi Bight consistent with in situ measurement of currents and satellite chlorophyll analysis of this area ([Cambazoglu et al., 2017](#)). The river fraction analysis confirmed the dominant freshwater source was from local Mississippi/Alabama rivers to most of the Mississippi Bight area. It is interesting to note that while the salinity of the eastern corridor during the spring 2016 survey was high ($\sim 31\text{--}32$), the river fraction analysis showed that the small contribution of freshwater largely originated from the Mississippi River.

During the summer 2016 survey, Mississippi Bight surface water salinity was relatively high and in a smaller range of variation in comparison with the spring survey. Interestingly, the fresh water fraction calculations indicate that the local rivers were the main source of freshwater to the northern part of the Mississippi Bight, while the Mississippi River was the principal source of freshwater to the southwestern part of the Bight. River discharge and its nutrient load stimulate the primary production, and a clear link between satellite-derived chlorophyll-a images and river inputs is established over the Louisiana Shelf ([Walker and Rabalais, 2006](#)). During the summer survey, chlorophyll-a satellite images suggest the intrusion of a freshwater plume from the Mississippi River Delta into the Bight ([Dzwonkowski et al. submitted](#)). This Mississippi River plume entering the Bight from the south is in agreement with the river fraction analysis conducted in this study, suggesting at least occasional significant influence of the Mississippi River on the southern part of the Bight. This extension of the Mississippi River plume towards the Mississippi Bight is also consistent with the eastward transport observed in summer season by [Morey et al. \(2003\)](#).

The winter 2016 cruise (February 10–12) was motivated by the opening of the Bonnet Carré Spillway on January 10, 2016 to keep the Mississippi River discharge at New Orleans below $3.5 \times 10^4 \text{ m}^3 \text{ s}^{-1}$ ([Fig. 2](#)). The spillway remained open for 22 days and resulted in a substantial flux of Mississippi River water into Lake Pontchartrain (6.9 km^3), which then empties into Lake Borgne and the western end of Mississippi Sound. Lake Pontchartrain is typically composed of brackish water with salinity in the range of 2–9 ([White et al., 2009](#)) and a

flushing time on the order of 56 days ([Turner et al., 2004](#)). The BCS2016 dataset gave us the opportunity to investigate the extent of the diverted Mississippi River water in the Mississippi Bight after the opening of the BCS. We note, however, that of the 12 openings of the spillway since 1937, the 2016 opening was one of the smallest in terms of volume discharged into Lake Pontchartrain ($\sim 6.6 \text{ km}^3$; US Army Corps of Engineers, Pers. Com.). Additionally, discharge of the local rivers was high at this time ([Fig. 2](#)). After the opening of the BCS, the local Mississippi/Alabama rivers seemed to remain the main source of freshwater to the northern part of the Mississippi Bight while the Mississippi River was the dominant source of freshwater south of Chandeleur Sound, near the birdfoot delta ([Fig. 7](#)). Together, the comparatively low BCS discharge with the high local discharge may partly account for the surprisingly low influence of the Mississippi River on the freshwater in the northwestern Bight and even in the western Mississippi Sound ([Fig. 7](#)). The fate of Mississippi River water is also greatly influenced by the wind regimes resulting in westward-flowing currents most of the year except in summer when wind reverse causing the Mississippi River plume to reverse direction and to flow eastward ([Walker et al., 2005](#)). However, river plumes are also influenced by eddies and short strong wind episodes due to, for instance, the passage of cold fronts ([Walker et al., 2005](#)). A good example is the heterogeneity of the stations located south of the Chandeleur Islands, near the birdfoot delta, that displayed various Mississippi River water contributions while being very close to each other. Dilution of the Mississippi River water and small-scale circulation likely explain the heterogeneity of the stations near the birdfoot delta.

A salinity gradient was observed along the NGI transect during that six-month time series ([Fig. 8](#)). Salinities were significantly fresher in the Mississippi Sound than in the Mississippi Bight suggesting a permanent influence of rivers in the Sound between June and November when the time series was conducted. Coastal waters were relatively fresher in summer 2011 (especially in June and July) than they were in summer 2016. This was at least partly due to the opening of the BCS for 42 days in late spring (May 9 – June 20, 2011) resulting in approximately three times greater total discharge through the spillway in 2011 (21.9 km^3) than 2016. Although local rivers still seemed to be the main source of freshwater in the Mississippi Sound; a higher fraction of Mississippi River water was found in the Sound in June and July, consistent with the opening of the BCS. The Mississippi River appeared to be the main source of freshwater to the offshore section of the NGI transect, especially in summer 2011. However, the salinity in the Bight remained relatively high, leading to an overall relatively small contribution of the freshwater from the Mississippi River. By August 2011, the freshwater in the Sound was again largely dominated by local rivers. In September 2011, the river fraction analysis suggested a significant contribution of the Mississippi River in the Sound and a contribution of the local rivers further offshore into the Mississippi Bight than usual. The presence of Mississippi River water in the Sound could have been caused by the passage of a tropical storm (“Lee”) on the coast of Louisiana on September 2th-5th 2011. The Mississippi Sound waters were again under the influence of the local rivers in October 2011, suggesting a relaxation to normal conditions within a few weeks.

Overall, our isotopic analysis of Mississippi Sound and Bight waters suggests limited influence of Mississippi River water in this region, with most of the freshwater derived from local sources including Mobile Bay. Even during the openings of the Bonnet Carré Spillway, which delivers Mississippi River more directly to the study area, this major river’s influence can still be limited east of the birdfoot delta. On the one hand, this is surprising given the proximity of this major freshwater source and crevasses in the birdfoot delta region that should allow significant quantities of Mississippi River water to flow east. However, satellite imagery shows that this river plume is generally directed south, and then west ([Allison et al., 2012](#)). Through modeling and studies of chlorophyll imagery, [Androulidakis and Kourafalou \(2013\)](#) showed that transport of Mississippi River water to the Bight is episodic and

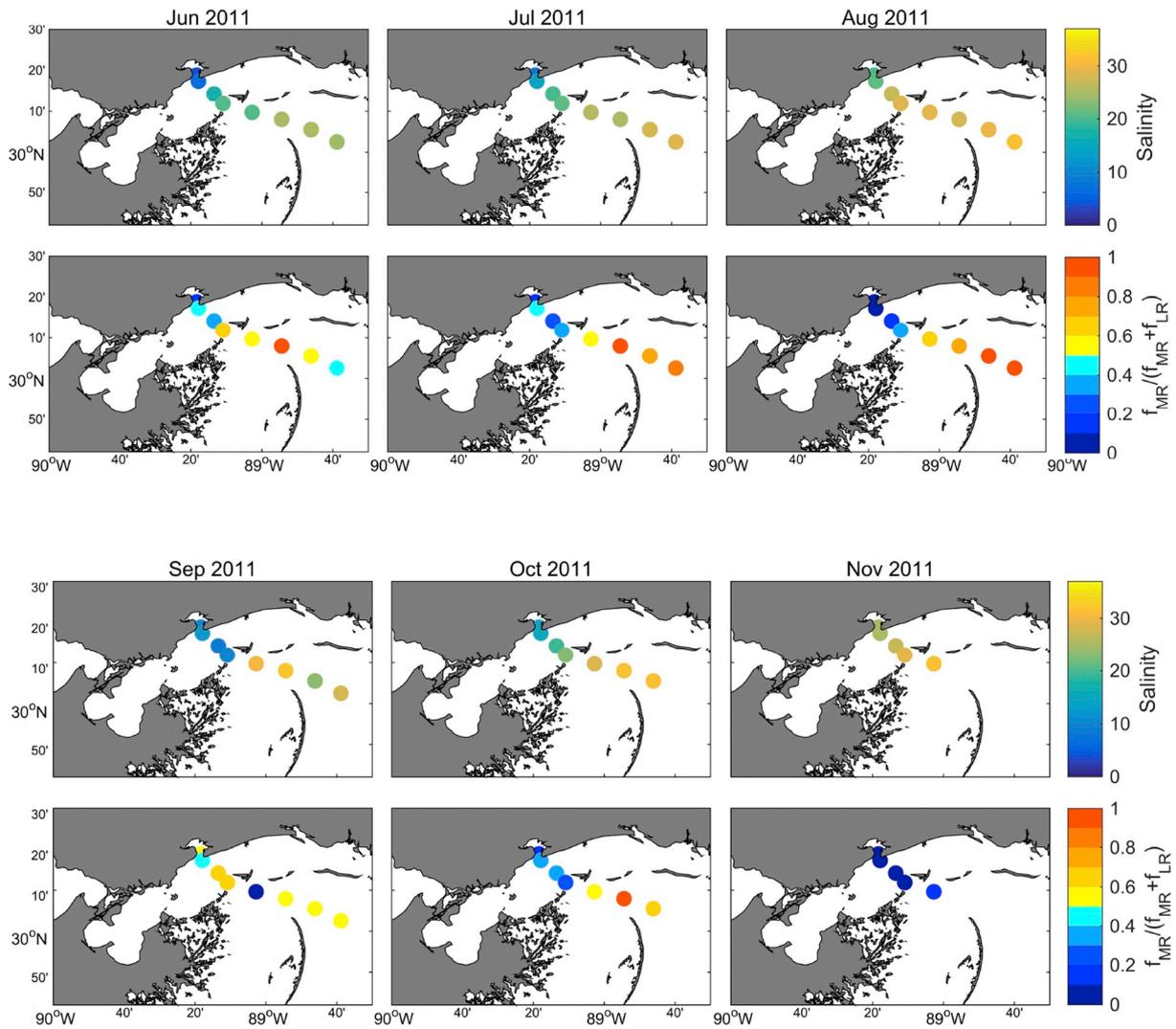


Fig. 8. Spatial distribution of surface water salinity (top) and of the river fractions $f_{MR}/(f_{MR} + f_{LR})$ (bottom) for the NGI transect between June 2011 and November 2011. The red/orange shades highlight a dominant contribution from Mississippi River (f_{MR}) while the blue shades highlight a dominant contribution from the local rivers (f_{LR}). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

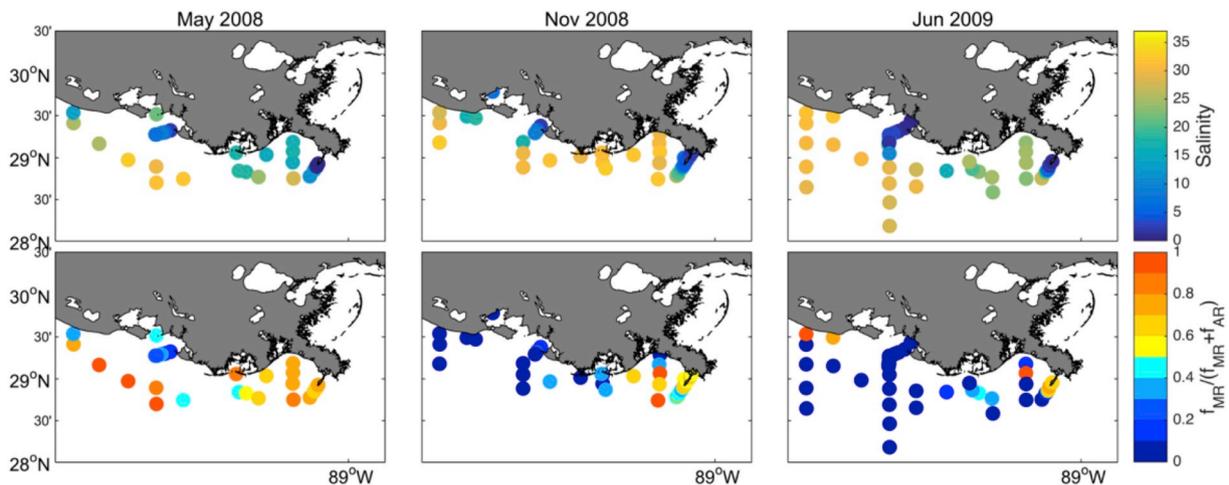


Fig. 9. Spatial distribution of surface water salinity (top) and of the river fractions $f_{MR}/(f_{MR} + f_{AR})$ (bottom) for the Louisiana shelf region. Water isotopes and salinity data are from [Joung and Shiller \(2014\)](#). The red/orange shades highlight a dominant contribution from Mississippi River (f_{MR}) while the blue shades highlight a dominant contribution from the Atchafalaya River (f_{AR}). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

modulated by regional circulation factors such as eddies. Both modeling and drifters (Morey et al., 2003) indicate that summer is when there is eastward coastal flow that can more consistently bring Mississippi River water to the Bight. Summer is also the time when we saw the greatest Mississippi River influence in our isotopic analysis despite the relatively high salinity.

The limited influence of the nutrient-rich Mississippi River outflow on the Mississippi Bight is intriguing in the context of coastal hypoxia. It is generally thought that the high nutrient load from the Mississippi River along with seasonal stratification, leads to the seasonal development of hypoxia in bottom waters of the Louisiana Shelf to the west of the birdfoot delta (e.g., Rabalais et al., 2007). However, the local rivers that dominate the freshwater supply to the Mississippi Bight, east of the delta, have much lower nutrient concentrations (Dortch et al., 2007; Dunn, 1996). Nonetheless, seasonal hypoxia has been observed in the Mississippi Bight (e.g., Brunner et al., 2006; Rakocinski and Menke, 2016), though surveys of the Bight have been far more limited than surveys of the Louisiana Shelf. Assuming that there is significant bottom water hypoxia in the Bight, our observations then beg the question of whether there is another nutrient source or other causative factor for hypoxia; however, this study cannot answer that question.

3.3.2. Sources of fresh water on the Louisiana Shelf

In May 2008, the Mississippi River seemed to be the dominant source of freshwater over the Louisiana Shelf (Fig. 9). The westward current over the shelf commonly observed in non-summer months (Cochrane and Kelly, 1986) is consistent with the Mississippi River plume being transported westward over the Louisiana Shelf. The Atchafalaya River plume appeared limited to the Atchafalaya Bay. Only a few samples with relatively high salinity located east of the Atchafalaya Bay and close to the coast displayed a dominant freshwater source from the Atchafalaya River.

In November 2008, the inputs of freshwater were generally low over the Louisiana Shelf based on the salinity distribution (Fig. 9) in agreement with seasonal trend (Fig. 2). This is consistent with the fact that the cumulative freshwater discharges from the Mississippi and Atchafalaya Rivers were relatively low during the November 2008 sampling trip (Joung and Shiller, 2014). The two river plumes were well identified by low salinity while surrounding waters remained relatively saline. Based on the salinity distribution, the Mississippi River plume seemed to be limited to the Louisiana Bight and the Atchafalaya River plume to coastal waters in the vicinity of the Atchafalaya Bay without significant apparent mixing between the two sources of freshwater. The river fraction analysis was in relatively good agreement with the salinity distribution because the results showed the dominant source of freshwater from the Mississippi River was limited to the Louisiana Bight.

In June/July 2009, the total input of freshwater was greater than in November 2008 but less than in May 2008 (Fig. 2). The river fraction analysis suggested that there was a dominant contribution of freshwater from the Atchafalaya River over the Louisiana Shelf, and in particular in the Louisiana Bight west of the Mississippi River delta. This result would be consistent with a change of the general circulation in summer. Indeed, the Louisiana Shelf circulation is complex and results from the interaction between eddies formed by the Loop Current, river buoyancy, and wind (Oey, 1995). However, the mean circulation over the Louisiana Shelf is generally dominated by a westward flow (downcoast) except in July and August where the mean circulation is dominated by an eastward flow (upcoast) (Cochrane and Kelly, 1986), which can carry freshwater from the Atchafalaya River towards the Mississippi River Delta. The shelf current direction is driven by the annual cycle of alongshore winds that are relatively constant in summer but can be more variable for non-summer months (Wang et al., 1998). The higher instability observed during the non-summer season may also be resulted from the more frequent passages of cold fronts (Nowlin et al., 2005). Thus, there was a shift in the dominant source of freshwater over

the Louisiana Shelf and in particular in the Louisiana Bight. The dominant source of freshwater over the Louisiana Shelf (minus the Atchafalaya Bay) was the Mississippi River in spring, whereas the Atchafalaya River was the dominant source of freshwater in summer over the Louisiana Shelf including in the Louisiana Bight. This is also in agreement with the observations of Strauss et al. (2012).

4. Summary and conclusions

The oxygen isotopic signature ($\delta^{18}\text{O}$) of the Mississippi River ($-6.6 \pm 0.3\text{‰}$) was distinct from the signature of the Atchafalaya River ($-4.9 \pm 0.2\text{‰}$; Joung and Shiller, 2014), the local rivers discharging to the Mississippi Sound and Bight ($-3.6 \pm 0.2\text{‰}$), and seawater from the Gulf of Mexico ($1.1 \pm 0.05\text{‰}$ at salinity 36; (Wagner and Slowey, 2011)). The distribution of the oxygen isotope composition combined with salinity data provided key additional information on the origin of the freshwater that the sole use of salinity could not have provided. A three-endmember river mixing model was applied to shelf waters of the Mississippi Bight and Louisiana Shelf to better constrain the extent of the Mississippi River plume relative to the local rivers and to the Atchafalaya River, respectively. The river mixing model led to two major findings. First, the fraction of freshwater coming from the Mississippi River into the Mississippi Bight was generally not significant during the various study periods including after the opening of the Bonnet Carré Spillway (BCS) in January 2016 that diverted a fraction of the Mississippi River into the Lake Pontchartrain. Second, the dominant source of freshwater to the Louisiana Shelf is greatly influenced by the general shelf circulation and alternates between Mississippi River water and Atchafalaya River water.

Variations in the source of freshwater is of great interest in this region that is subjected to summertime bottom water hypoxia because of the difference in nutrient content of the freshwater sources. The limited extent of nutrient-rich Mississippi River water to the Mississippi Bight coastal area suggests that other mechanisms such as submarine groundwater discharge (SGD) may play a role in the development of hypoxia. Indeed, SGD has been recognized as a significant source of nutrients to some coastal regions (e.g., Rodellas et al., 2015) and there are buried paleo-channels stretching from the Mississippi-Alabama coast (Flocks et al., 2015), which may serve as a conduit for SGD. Additionally, recent work by Peterson et al. (2016) showed evidence of development of hypoxia off South Carolina due to the discharge of cold, salty, anoxic groundwater.

Conflicts of interest

The authors declare no conflict of interestsw

Acknowledgements

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All data are publicly available through the Gulf of Mexico Research Initiative Information & Data Cooperative (GRIIDC) at <https://data.gulfresearchinitiative.org> (Fall 2015 doi:10.7266/N7F769NC, BCS 2016 doi:10.7266/N75T3J3B, Spring 2016 doi:10.7266/n7-9wex-sg48, Summer 2016 doi:10.7266/n7-f91t-7725, NGI data doi:10.7266/n7-jwt7-0p03, River data doi:10.7266/n7-sps7-rq23). Collection and

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