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Key Points:

- *p*CO₂ varied along the salinity gradient, showing low values in middle salinities
- \bullet This study region was generally a $\rm CO_2$ sink or was neutral (relative to the air)
- Biological and mixing processes dominated sea surface pCO₂ variations

Supporting Information:

Supporting Information S1

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The carbon dioxide system on the Mississippi River-dominated continental shelf in the northern Gulf of Mexico: 1. Distribution and air-sea CO₂ flux

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Abstract River-dominated continental shelf environments are active sites of air-sea CO₂ exchange. We conducted 13 cruises in the northern Gulf of Mexico, a region strongly influenced by fresh water and nutrients delivered from the Mississippi and Atchafalaya River system. The sea surface partial pressure of carbon dioxide (pCO₂) was measured, and the air-sea CO₂ flux was calculated. Results show that CO₂ exchange exhibited a distinct seasonality: the study area was a net sink of atmospheric CO_2 during spring and early summer, and it was neutral or a weak source of CO₂ to the atmosphere during midsummer, fall, and winter. Along the salinity gradient, across the shelf, the sea surface shifted from a source of CO_2 in lowsalinity zones ($0 \le S \le 17$) to a strong CO₂ sink in the middle-to-high-salinity zones ($17 \le S \le 33$), and finally was a near-neutral state in the high-salinity areas ($33 \le S \le 35$) and in the open gulf ($S \ge 35$). High pCO₂ values were only observed in narrow regions near freshwater sources, and the distribution of undersaturated pCO_2 generally reflected the influence of freshwater inputs along the shelf. Systematic analyses of pCO_2 variation demonstrated the importance of riverine nitrogen export; that is, riverine nitrogen-enhanced biological removal, along with mixing processes, dominated pCO_2 variation along the salinity gradient. In addition, extreme or unusual weather events were observed to alter the alongshore pCO_2 distribution and to affect regional air-sea CO $_2$ flux estimates. Overall, the study region acted as a net CO $_2$ sink of 0.96 \pm 3.7 mol m $^{-2}$ yr^{-1} (1.15 ± 4.4 Tg C yr^{-1}).

1. Introduction

The continental shelf accounts for about ~30% of oceanic net ecosystem production [*Ducklow and McCallister*, 2005] and 15–21% of the net annual carbon dioxide (CO₂) sink of the global ocean [*Borges*, 2011; *Cai*, 2011; *Cai et al.*, 2006; *Chen and Borges*, 2009] even though it accounts for only 7% of the area of the sea surface. Despite continental margins' importance in the global carbon budget and the fact that they are sensitive to impacts of both anthropogenic perturbation and climate-related changes, insufficient attention has been given to carbon cycle research in continental shelf systems [*Bauer et al.*, 2013]. Past studies have shown substantial spatial and temporal heterogeneity of air-sea CO₂ fluxes on continental shelves that experience moderate river impacts [*Jiang et al.*, 2008; *Salisbury et al.*, 2008]. For continental shelves receiving large freshwater discharge and nutrient fluxes, coastal eutrophication has been shown to affect the CO₂ system [*Borges and Gypens*, 2010; *Cai et al.*, 2011; *Chou et al.*, 2011; *Chen et al.*, 2012]. Moreover, circulation can be complex on continental shelves [*Lentz and Fewings*, 2012], and thus sharp variations in partial pressure of CO₂ (*p*CO₂) are expected in river plumes and surrounding areas due to strong gradients in biological and physical processes [*Cai*, 2003; *Chou et al.*, 2013; *Cooley et al.*, 2007; *Kortzinger*, 2003; *Ternon et al.*, 2000; *Tseng et al.*, 2011; *Tsunogai et al.*, 1997; *Zhai and Dai*, 2009]. Therefore, a better understanding of CO₂ distributions and air-sea CO₂ fluxes in river-dominated continental shelves is needed to improve global carbon budgets.

The Mississippi and Atchafalaya River System is one of the world's largest rivers, ranking sixth in freshwater discharge (18,400 m³ s⁻¹) [*Milliman and Meade*, 1983]. Seventy percent of the discharge is through the Mississippi River to the northern Gulf of Mexico, while the remaining ~30% is via the Atchafalaya River (Figure 1) [*Walker et al.*, 2005]. Each river contributes similar amounts of freshwater discharge to the Louisiana shelf and adjacent areas that are the focus of this study, because all freshwater from the Atchafalaya River flows onto the shelf, but

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Figure 1. Study area and cruise tracks. The study area was in the northern Gulf of Mexico (the gray rectangular in plot) which was enlarged in plot (b) to display geographic setting of the Mississippi and Atchafalaya River system and various coastal bays and estuaries. The cross-shelf area (light blue lines) was surveyed during 2009–2010 (c). The shelf-wide area (green lines) was surveyed during June 2006–2007 (c), and this area was used as a reference area to unify the shelf-wide and cross-shelf survey areas when discussing air-sea CO₂ fluxes. The Louisiana Bight and its adjacent areas (red lines) were surveyed from 2004 to June 2006 (c). The inner shelf (dark blue lines) was surveyed in 2008 (c).

only about half of the freshwater discharge from the Mississippi River (approximately 35% of the total) is transported westward to the Louisiana shelf [*Dinnel and Wiseman*, 1986; *Etter et al.*, 2004; *Lehrter et al.*, 2013]. Overall, the Mississippi and Atchafalaya River System delivers 1 to 1.5 Tg (Tg = 10^{12} g) of nitrogen, about two-thirds of it as nitrate N [*Goolsby et al.*, 2000; *Lehrter et al.*, 2013] and ~17 Tg as bicarbonate C annually to the northern Gulf of Mexico [*Raymond et al.*, 2008; *Lohrenz et al.*, 2013].

The large freshwater discharge and nitrogen loading contribute to distinct river-ocean mixing dynamics that are associated with enhanced biological production, both leading to low pCO_2 in the plume and the adjacent coastal system [*Cooley and Yager*, 2006; *Salisbury et al.*, 2008; *Cai et al.*, 2013; *Tseng et al.*, 2011]. Prior studies in this region provide evidence of strong nutrient enhancement of biological production [*Dagg et al.*, 2007; *Green et al.*, 2008; *Murrell et al.*, 2013; *Turner and Rabalais*, 2013] that contribute to strong drawdown of CO_2 in the moderate salinity region coinciding with the location of maximum nutrient removal [*Guo et al.*, 2012; *Huang et al.*, 2012].

Previous measurements have shown a strong cross-shelf pCO_2 gradient with the inner shelf being undersaturated with respect to atmospheric CO₂ and the outer shelf being oversaturated [*Cai*, 2003; *Lohrenz and*

				Coverage Area	River Discharge ^c	$NO_3 + NO_2 Flux^c$	Air CO ₂
Year	Date ^a	Ship	Survey Region ^b	10 ³ km ²	$10^3 m^3 s^{-1}$	10^9 g N month ⁻¹	μ atm
2004	9 Aug to 12 Aug	Pelican	LAB	9.2	12.9	42.5	380
2005	4 Oct to 7 Oct ^d	Pelican	LAB	4.4	7.9	19.9	387.6
2006	27 Apr to 1 May	Pelican	LAB	7.2	17.3	96.0	375
2006	6 Jun to 11 Jun	Bold	nGOM	34.1	12.2	60.2	386
2006	6 Sep to 11 Sep	Bold	nGOM	34.7	7.5	19.7	369.5
2007	2 May to 7 May	Bold	nGOM	39.1	25.4	148	379
2007	18 Aug to 24 Aug	Bold	nGOM	41.4	12.1	31.2	384
2008	17 Jul to 20 Jul	Pelican	in-LAs	14.9	28.4	138.0	385
2009	9 Jan to 20 Jan	Cape Hatteras	nGOM	41.4	23.9	92.6	371.7
2009	20 Apr to 1 May	Cape Hatteras	nGOM	41.4	30.9	151.0	386
2009	19 Jul to 29 Jul ^d	Cape Hatteras	nGOM	41.4	18.9	73.5	387.3
2009	28 Oct to 7 Nov	Hugh R. Sharp	nGOM	41.4	25.6	52.4	371.8
2010	9 Mar to 21 Mar ^d	Cape Hatteras	nGOM	40.9	27.8	121.0	379

Table 1. Summary of Survey Cruises

^aSpring was from March to May, summer was from June to August, fall was from September to November, and winter was from December to February in this study.

^bLAB: the Louisiana Bight and its adjacent area; nGOM: the northern Gulf of Mexico; in-LAs: the inner Louisiana shelf.

^cRiver discharge and monthly NO₃+NO₂ flux data were in Mississippi and Atchafalaya Rivers. Data from the U.S. Geological Survey (USGS) "Hypoxia in the Gulf of Mexico studies."

^dCruise affected by weather events.

Cai, 2006; *Lohrenz et al.*, 2010], along with a distinct temporal variation of air-sea CO_2 fluxes near the Mississippi River delta [*Lohrenz et al.*, 2010]. Air-sea CO_2 fluxes in the Gulf of Mexico reported in "The First State of the Carbon Cycle Report (SOCCR)" [*Chavez et al.* 2007] were based on very limited observations and were insufficient to characterize seasonal variations of sea surface pCO_2 and to quantify the annual air-sea CO_2 flux. Thus, more comprehensive field measurements with sufficient seasonal and shelf coverage are needed to more fully describe the pCO_2 variations over the northern Gulf of Mexico and to understand the role of riverine nitrogen in sea surface pCO_2 variations.

The major objectives of this study were to determine the spatial and temporal distributions of surface water pCO_2 , to identify surface pCO_2 features along the salinity gradient or across the shelf, and to quantify the air-sea CO_2 fluxes over this study area. We also discuss the factors controlling pCO_2 and provide a surface CO_2 budget for the study area. In a companion paper, we will examine surface water CO_2 and oxygen dynamics.

2. Methods

2.1. Field Measurement

Data for this study were acquired from thirteen cruises conducted in the northern Gulf of Mexico (Figure 1 and Table 1). Four shelf-wide cruises (2006–2007) covered the area very likely to develop summer bottom-water hypoxia (dissolved oxygen concentration less than 2 mg L⁻¹) (Figure 1), similar to the region sampled during a hypoxia study in the past 30 years (http://www.gulfhypoxia.net/). A wider area across the shelf was surveyed during five cruises from 2009 to 2010 (Figure 1). Three earlier cruises (April 2006 and before) also surveyed the shelf, with a focus on the Louisiana Bight and the adjacent area immediately west of the Mississippi River birdfoot delta (Figure 1). Finally, one cruise (August 2008) surveyed the inner Louisiana shelf (Figure 1).

Throughout the course of our sampling, freshwater discharge and nitrate plus nitrite fluxes (U.S. Geological Survey, USGS data) were seasonally variable: they were generally high during spring and low during late summer and fall (Figure 2). Note that the October 2005 cruise coincided with a period of low discharge and was also about 1 month after Hurricane Katrina (23–30 August 2005) and 2 weeks after Hurricane Rita (18–26 September 2005).

Surface water pCO_2 was measured by pumping surface water continuously through an underway pCO_2 analyzer installed in the shipboard laboratory. On cruises from 2003 to 2007, the system included a gaswater equilibrator and CO_2 detection via an infrared gas analyzer (LI-COR[®] 7000) as described by *Jiang et al.* [2008]. On cruises from 2008 to 2010, we used an upgraded system that included a Global Positioning System, a Seabird thermosalinograph (SBE-45), and a water-gas equilibrator with an



Figure 2. The variations of monthly river discharge and nitrate plus nitrite fluxes for the Mississippi and Atchafalaya rivers from 2004 to May 2010. River discharge (black line) and nitrate plus nitrite fluxes (red line) were usually low in fall and high in winter or spring. The vertical gray line indicates the first day of each survey cruise. Data source: U.S. Geological Survey (USGS, "Hypoxia in the Gulf of Mexico studies", http://toxics.usgs.gov/hypoxia/index.html).

improved spray head, a temperature sensor, and a pressure sensor (Setra 270). This underway pCO_2 system (AS-P2, Apollo SciTech, USA) also had an improved water vapor trap via sequential Peltier cooling and Nafion dryers. The upgraded system yielded more reliable and consistent results and was similar to the NOAA (National Oceanic and Atmospheric Administration) system [*Pierrot et al.*, 2009]. However, both systems had similar accuracy and precision (better than 2 ppm). Periodically, the CO_2 analyzer was calibrated against certificated CO_2 gas standards of 0, 197.5, 400.6, and 594.7, and 975.3 ppm referenced against standards traceable to those of the National Institute of Standards and Technology. Atmospheric CO_2 values were measured every 6 or 12 h on cruises from 2004 to 2007, and every 3 to 4 h during the 2008–2010 cruises. Sea surface salinity (SSS) and temperature (SST) were measured using a Seabird SBE-45 flow-through thermosalinograph from 2004 to 2010.

2.2. Air-Sea CO₂ Flux Calculation

The instrument records the mole fraction of CO_2 in the dry air flow (xCO₂), which then is converted to the pCO_2 inside the equilibrator at 100% water saturation via the equation:

$$pCO_{2(eq)} = xCO_{2(eq)} \times (P_b - P_{weq}), \tag{1}$$

where $xCO_{2(eq)}$ is the mole fraction (ppm) of CO_2 in the dried sample gas; P_b is the barometric or total pressure inside the equilibrator; and P_{weq} is the equilibrium water vapor pressure at the equilibrated temperature, T_{eq} , (°C) and salinity [*Weiss and Price*, 1980]. The $pCO_{2(eq)}$ was further converted to pCO_2 in water at SST [*Takahashi et al.*, 1993] using:

$$pCO_{2(water)} = pCO_{2(eq)} \times exp[0.0423 \times (SST-T_{eq})]$$
⁽²⁾

For data from before 2008, we estimated that the equilibrator temperature was $0.4^{\circ}C$ lower than sea surface temperature from a comparison with water column temperature data from the ship's CTD (conductivity, temperature, and depth) package. The atmospheric pCO_2 (pCO_{2air}) was corrected by the water vapor pressure with:

$$pCO_{2(air)} = xCO_{2(air)} \times (P_{b} - P_{w})$$
(3)

where Pw is the surface seawater vapor pressure at SST and SSS [Weiss and Price, 1980].

To calculate the air-sea CO₂ exchange flux, SSS, SST, $pCO_{2(water)}$, and $pCO_{2(air)}$ were gridded at a resolution of $0.1^{\circ} \times 0.1^{\circ}$ (by applying the grid data function in Matlab[®]). The $pCO_{2(air)}$ value was set at a uniform value for each cruise over the Louisiana shelf from 2004 to 2007, as we have insufficient data to quantify its full spatial and temporal variability. After 2008, we used intensively measured $pCO_{2(air)}$ data to interpolate $pCO_{2(air)}$ values for each $pCO_{2(air)}$.

(4)

Finally, air-sea CO₂ flux (F) was calculated as:

 $F = k \times K_0 \times [pCO_{2(water)} - pCO_{2(air)}]$

where k is the gas transfer velocity of CO₂; K₀ is the CO₂ solubility coefficient at the ambient temperature and salinity [Weiss, 1974]. To calculate k, we adopted the updated coefficient given by Ho et al. [2006], which is very close to the commonly used coefficients given by Wanninkhof [1992] and the more recent coefficients recommended by Sweeney et al. [2007] and Wanninkhof et al. [2009] (i.e., the coefficient is 0.27, 0.31, 0.26, and 0.25, respectively, in the equation: $k \approx a \times U_{10}^2$, where a is the coefficient and U_{10} is the wind speed at 10 m). Monthly satellite products QuikSCAT wind data (12.5 km resolution) were adopted (from a Live Access Server provided by NOAA Coastwatch and SWFSC/Environmental Research Division, http://las. pfeg.noaa.gov/) and were interpolated to 0.1° by 0.1° to calculate the areal-integrated air-sea CO₂ fluxes. In addition, we followed the approach given by Jiang et al. [2008] who suggested using instantaneous wind speeds from coastal buoy stations to deal with the non-Gaussian distribution of wind speeds over a month [Wanninkhof et al., 2002]. By this approach, a nonlinearity coefficient, C₂ (roughly 1.2), was calculated from buoy wind data and the gas transfer velocity equation is expanded to $k \approx a imes C_2 imes U_{monthly}^2$ where $U_{monthly}$ is the monthly average wind speed. Buoy wind data were taken from the following stations: 42362, 42364, PSTL, LUML1, FGBL1, CAPL1, 42002, 42001, 42039, 42035 in the northern Gulf of Mexico. Thus, the buoy stations provided high temporal resolution for a limited area, while satellite products provided lower temporal resolution and high spatial resolution.

The monthly mean air-sea CO₂ flux was averaged from the areal-integrated CO₂ fluxes interpolated to 0.1° \times 0.1° grid. To systematically compare these monthly mean CO₂ fluxes among surveys, we designated a reference area for comparison based on the smaller area surveyed during the period between June 2006 and August 2007 (Figure 1), as the area surveyed during 2009–2010 were larger. Results from the three surveys focusing on the Louisiana Bight from 2004 to April 2006 were not used to estimate a shelf-wide CO₂ flux, but instead only the CO₂ flux for the Louisiana Bight and its adjacent areas. The inner shelf region had larger spatial variations in sea surface salinity, temperature, and pCO_2 , and thus also had more highly variable CO₂ fluxes than the outer shelf. To better account for this variability, an additional inner shelf alongshore track was added in later cruises.

2.3. The Uncertainties in Air-Sea CO₂ Fluxes

As we have no precise way to assess the uncertainties of the calculated air-sea CO_2 flux, we adopt the methods described by *Jiang et al.* [2008] and consider three uncertainties. For the first of these, we calculated the standard deviation of the CO_2 flux using six available gas transfer velocities (including *Ho et al.* [2006], *Liss and Merlivat* [1986]; *Wanninkhof* [1992]; *Wanninkhof and McGillis* [1999]; *Nightingale et al.*, [2000a]; *Nightingale et al.*, [2000b]). This approach resulted in 11%–15% relative variability in monthly mean gas transfer velocity, with an average of 12%, in this study. This variation of 12% is reasonable under usual wind speed distributions, but can be as much as doubled when wind speeds are extremely high or low [*Ho et al.*, 2006; *Wanninkhof et al.*, 2009]. The second source of uncertainty was assessed as the standard deviation due to the spatial and temporal variation of atmospheric CO_2 (6 μ atm) that was based on our measurements during 2008 and 2010. For the third of the three uncertainties considered, we determined the error associated with a small temperature difference (deltaT) between the equilibrator and surface seawater during 2006 and 2007. The above three uncertainties were then used to calculate the uncertainty of air-sea CO_2 flux for each cruise [*Taylor*, 1997]:

Uncertainty=F ×
$$(0.12^{2} + (6/(pCO_{2w} - pCO_{2a}))^{2} + (deltaT/SST)^{2})^{0.5}$$
 (5)

Thus, we determined the average uncertainty for each cruise was in the range \pm 0.05 to \pm 2.98 mmol m⁻² d⁻¹ (the average is \pm 1.15 mmol m⁻² d⁻¹), similar to the uncertainty estimated in the South Atlantic Bight [*Jiang et al.*, 2008].

2.4. Data Analysis

We use two scenarios to examine mixing and biological effects on pCO_2 variations: conservative mixing (pCO_{2Mix}) , and conservative mixing plus biological removal $(pCO_{2Mix+Bio})$. We first simulated the abiotic mixing of pCO_2 along the salinity gradient between the Mississippi River and seawater. The fraction from each

end-member was solved by equations (6) and (7) to estimate the conservative mixing values of total alkalinity (TA) and dissolved inorganic carbon (DIC) as equations (8) and (9) in one-unit salinity interval (end-members were listed in supporting information, Table S1):

$$1 = f_{\rm R} + f_{\rm S} \tag{6}$$

$$Sal = S_R \times f_R + S_S \times f_S$$
(7)

$$TA_{Mix} = TA_R \times f_R + TA_S \times f_S$$
(8)

$$DIC_{Mix} = DIC_R \times f_R + DIC_S \times f_S$$
(9)

where Sal is our desired salinity, S is the salinity and f is the fraction of end-members from the Mississippi River (subscripted R) and seawater (subscripted S), respectively, "Mix" represents the conservative mixing values for its affiliated parameters. These TA_{Mix} and DIC_{Mix} values were converted to pCO_2 (pCO_{2Mix}) at the measured temperature by using CO2SYS program (from Carbon Dioxide Information Analysis Center, http:// cdiac.ornl.gov/ftp/co2sys/, K1, K2 from *Mehrbach et al.* [1973] refit by *Dickson and Millero* [1987] were adopted). To simulate the effects of biotic activity on pCO_2 along the salinity gradient, we estimated the net biological NO₃ removal (NO_{3Bio}) by the difference between the measured NO₃ data (NO₃) during our cruises (data from *Lehrter et al.* [2013]) and the conservative mixing values (NO_{3Mix}) derived from the river and ocean end-members (supporting information, Table S1):

$$NO_{3Mix} = NO_{3R} \times f_{R} + NO_{3S} \times f_{S}$$
(10)

$$NO_{3Bio} = NO_{3Mix} - NO_3$$
(11)

We converted net biological NO₃ removal to estimate TA_{Mix+Bio} by the following equation;

$$TA_{Mix+Bio} = TA_R \times f_R + TA_S \times f_S - NO_{3Bio}$$
(12)

and also to estimate DIC consumption by assuming that Redfield stoichiometry [*Redfield*, 1958] is applicable in this river dominated shelf [*Huang et al.*, 2012] as the following equation:

$$DIC_{Mix+Bio} = DIC_R \times f_R + DIC_S \times f_{S-} NO_{3Bio} \times 106/16$$
(13)

TA_{Mix+Bio} and DIC_{Mix+Bio} were converted to pCO_2 ($pCO_{2Mix+Bio}$) by using CO2SYS. Furthermore, to examine the effect of temperature, $pCO_{2Mix+Bio}$ was modeled for both binned temperature and the seasonal average temperature along the salinity gradient. Finally, as air-sea gas exchanges also affect pCO_2 variation (we will discuss this effect later), this estimated biological effect is only a conservative result to demonstrate the importance of biological uptake of CO₂ in determining plume pCO_2 .

3. Results

3.1. pCO₂ in Lower Rivers and Bays

The Mississippi River and Atchafalaya Bay waters had characteristically highly supersaturated pCO_2 values ranging between 977 and 2220 μ atm (Table 2) with noticeable seasonality, being lower in the winter and higher in the summer, with the highest value in July 2009. The pCO_2 values decreased rapidly from extremely high values in rivers and bays to below the atmospheric value along the river-ocean mixing gradient extending out onto the shelf. Water pCO_2 values in Terrebonne Bay and Calcasieu Lake, which only have limited freshwater inputs, however, were much lower than values in the two major river systems (less than 800 μ atm) (Table 2). The lower pCO_2 values in these bays are likely caused by a lower turbidity and water mixing rates, allowing biological removal of CO_2 , in them than the two river mouths. Furthermore, water pCO_2 values in Calcasieu Lake showed a larger variation (171.5 and 768.8 μ atm) than the change in Terrebonne Bay (257– 532 μ atm) (Table 2). While these differences are interesting, we cease the discussion about them as the CO_2 exchange fluxes from these bays had minor contributions to the overall regional flux due to their small area.

3.2. The Plume Trajectory Reflected by Sea Surface Salinity

Distributions of sea surface salinity demonstrated an alongshore Mississippi-and-Atchafalaya-Rivers plume trajectory in most of our surveys (Figure 3). Such an alongshore freshwater trajectory was similar to those described in previous studies, which documented low salinities close to the Mississippi River mouth,

		Salin	ity	pCO ₂ (µatm)			
Year	Month	Mean	s.d.	Mean	s.d.	n	
Lower Mississi	opi River						
2004	August	2.0	0.2	1628.3	18.0	32	
2005	October	5.9	0.4	1348.8	32.3	62	
2006	June	1.9	0.7	1708.6	281.4	153	
2006	September	6.2	0.8	1209.8	52.9	72	
2007	May	1.2	1.0	1732.9	39.2	74	
2007	August	5.0	0.7	1362.7	103.6	143	
2009	January	0.1	0.0	977.4	77.7	46	
2009	April	0.1	0.1	1663.2	53.2	86	
2009	July	1.4	0.4	2222.4	57.2	91	
2009	November	0.2	0.1	1611.9	78.5	63	
2010	March	0.2	0.1	1407.5	164.6	76	
Atchafalaya Ba	у						
2009	January	0.1	0.1	1361.6	142.6	55	
2009	April	1.2	1.7	1310.3	553.8	42	
2009	July	0.5	0.7	2072.8	402.4	84	
2009	November	0.6	0.8	1813.7	208.2	23	
2010	March	0.1	0.0	1682.4	111.9	45	
Terrebonne Ba	у						
2009	January	30.7	1.0	532.4	95.3	55	
2009	April	26.1	0.6	257.3	15.0	46	
2009	July	28.6	0.3	486.4	52.5	66	
2009	November	27.0	1.0	314.4	29.7	44	
2010	March	23.1	0.7	293.6	23.7	56	
Calcasieu Lake							
2007	May	22.8	0.1	171.5	5.0	20	
2007	August	17.9	0.9	768.8	264.7	228	

Table 2. Surface Water pCO₂ Values on the Lower Mississippi and Atchafalaya Rivers, Terrebonne Bay and Calcasieu Lake

increasing salinities along the Louisiana coast toward Texas, and a localized region of freshwater near the Atchafalaya Bay. An exception was in October 2005 when both low and high salinities were observed in the Louisiana Bight and the adjacent area shortly after two hurricanes (Figure 3b). Another exception was in July 2009, when the freshwater plume was largely confined to the eastern Louisiana and Mississippi shelf regions (Figure 3k). In March 2010, the freshwater plume was widely dispersed, extending across the shelf southward of 28°N (Figure 3m), and low temperature waters (less than 19°C) were also observed offshore. These weather-related exceptions will be discussed later.

3.3. Distributions of Shelf pCO₂ and Air-Sea CO₂ Flux

3.3.1. CO₂ Gradients Across Inner, Middle, and Outer Shelves

The sea surface pCO_2 distribution (Figure 4) revealed sharp gradients from inner to outer shelves. To illustrate this variation better, we considered two example transects (Figure 1): Transect B, starting from the northern Louisiana Bight along longitude 89.7°W (Figure 5a); and Transect E, from Atchafalaya Bay along longitude 91.6°W (Figure 5b). In general, both transects displayed a similar pattern across the shelf: near the coast, water pCO_2 decreased sharply from highly oversaturated to undersaturated with respect to the atmospheric CO₂ across the inner shelf, and pCO_2 increased gradually to near atmospheric values when moving toward open ocean waters. The locations of lowest pCO_2 varied among these cruises from inner shelf to middle shelf. Furthermore, higher variability in surface water pCO_2 values was observed on the inner shelf (\pm 200 ppm) compared to the outer shelf (\pm 100 ppm) for both transects (Figures 5a and 5b).

Our overall estimates of air-sea CO_2 flux further revealed that the inner shelf (where bottom depth was less than 20 m but excluding river mouths and bays) and the middle shelf (20–45 m depth) acted as atmospheric CO_2 sinks (-3.35 mmol m⁻² d⁻¹ and -2.14 mmol m⁻² d⁻¹, respectively), while the outer shelf (45–200 m) and the open gulf (depth deeper than 200 m) varied from neutral to weak sources (i.e., 0.08 mmol m⁻² d⁻¹ and 1.46 mmol m⁻² d⁻¹, respectively). The specific CO_2 fluxes for different subregions in each cruise are given in Table 3. Transects B and E illustrate the cross-shelf variation of the CO_2 flux: the inner shelf was not only an atmospheric CO_2 sink, but it also showed larger air-sea CO_2 flux variations than the outer shelf (Figures 5c and 5d).



Figure 3. Sea surface salinity distributions. Contour maps are adopted to present the freshwater distribution in August 2004 (a), October 2005 (b), April 2006 (c), June 2006 (d), September 2006 (e), May 2007 (f), August 2007 (g), July 2008 (h), January 2009 (i), April 2009 (j), July 2009 (k), November 2009 (l), and March 2010 (m). The freshwater plume was usually distributed alongshore, but it was confined to the eastern shelf in July 2009, and extended to the open gulf in March 2010.

3.3.2. Overall Spatial and Temporal Distribution

In addition to the cross-shelf variation, an important aspect of the complex spatial pCO_2 variation was that the distribution of waters undersaturated in pCO_2 generally mirrored the freshwater distribution on shelf-wide scales. For example, the plume trajectories were alongshore for the majority of surveys (Figures 4d, 4e, 4f, 4g, 4i, and 4j) and undersaturated pCO_2 values were also observed in those regions. When the freshwater was confined to the east in July 2009, undersaturated pCO_2 values were also observed on the eastern shelf but not the western shelf (Figure 4k). For the wide plume extending across the shelf in March 2010, undersaturated pCO_2 values also expanded to the off-shore and open gulf (Figure 4m). Among these varied plume trajectories, there was a gradient in pCO_2 values, where they increased progressively as the low-salinity plume traveled downstream to middle and to high salinities. We will discuss this pCO_2 versus salinity pattern in the next section. An exception to this pattern occurred in November (Figure 4l), when pCO_2 values remained close to the atmospheric level along the entire trajectory of fresh water. To sum up, three types of pCO_2 spatial variation were observed, including high oversaturated values in river end-members, clear cross-shelf variations when plume trajectories were alongshore, and undersaturated values that mirrored the freshwater distribution over the shelf.



Figure 4. Sea surface pCO_2 distributions. pCO_2 values are presented along the cruise tracks for the corresponding plots shown in Figure 3. Under saturated pCO_2 usually mirrored the freshwater distribution along the plume trajectories, whether the trajectories were alongshore (in most cases) or not (in July 2009 and March 2010). The exception was in November 2009, when we observed pCO_2 values generally close to the atmospheric values.

Monthly averaged properties for $0.1^{\circ} \times 0.1^{\circ}$ pixels gridded over the entire study area displayed seasonality in various environmental variables, including water temperature, wind speed, *p*CO₂, and air-sea CO₂ flux (Figure 6). Water temperature was lower in winter and early spring, and it could be as high as 30°C in summer and fall (Figure 6a). Stronger wind speed was observed in winter and spring, and weaker wind speed was observed in summer and fall (Figure 6b). *p*CO₂ was generally <300 µatm during spring and summer, and it increased to oversaturation during fall (Figure 6c). Finally, this study area acted as a strong sink for atmospheric CO₂ in spring, a weak sink in summer, a source in fall, and was nearly neutral in winter (Figure 6d). Specifically, the strong sink from spring to June was mainly due to the inner and middle shelf contributions (Table 3). Moreover, two extreme conditions were observed, comprising a strong CO₂ source in October 2005 and a strong sink in March 2010. These unusual periods are considered further in sections 4.2 and 4.3, respectively. Overall, this study area acted as a sink of atmospheric CO₂ (overall mean plus standard deviation of -0.963 ± 3.7 mmol m⁻² d⁻¹) and within it, the Louisiana Bight and the adjacent area acted as a particularly strong sink (-4.89 mmol m⁻² d⁻¹).

3.3.3. CO₂ Distribution Along the Salinity Gradient

To further examine the pattern of pCO_2 variations along the plume trajectory, we describe the variation of pCO_2 along the salinity gradient. By binning pCO_2 values into salinity intervals, it became evident that pCO_2



Figure 5. Variations of sea surface pCO_2 values and air-sea CO_2 fluxes across the shelf. For both transects (labeled in Figure 1) B, on longitude 89.7°W (a), and E, on longitude 91.6°W (b), water pCO_2 showed larger variations on the inner shelf than the outer shelf during 2009 to 2010. Air-sea CO_2 fluxes are binned by 0.1° latitude, and error bars represent the standard deviation in each 0.1° latitude bin. Larger variations of CO_2 fluxes were observed on the inner shelf than on the middle, outer shelves, and the open gulf (c,d). Water pCO_2 was not only under saturated on the inner shelf but also on the middle and outer shelves in March 2010 (c,d), resulting a significantly strong sink of CO_2 with respect to the atmosphere in the northern Gulf of Mexico.

versus salinity exhibited a concave upward curve and varied seasonally (Figure 7). In spring, low and undersaturated pCO_2 was observed at moderate salinities around 20–25 and gradually increased toward saturation with increasing salinity (Figure 7a). In summer, undersaturated pCO_2 values were observed over a wider salinity range from 9 to 31 (Figure 7b). In fall, undersaturated pCO_2 values were restricted to a salinity range smaller than that in spring or summer (Figure 7c). Finally, pCO_2 values were close to atmospheric values along the salinity gradient in winter (Figure 7d). To systematically organize the data and describe larger features, we further group pCO_2 and air-sea CO_2 fluxes by five salinity zones: $0 \le S < 17$, $17 \le S < 25$, $25 \le S < 33$, $33 \le S < 35$, and $S \ge 35$ for each cruise (Table 4) and for each season (Table 5). Note that whereas the low-salinity region ($0 \le S < 17$) acted as a strong CO_2 source, it only covered a relatively small proportion of the study area and thus its contribution to the overall regional flux is small. In contrast, the two middle

Year	Month	Survev Area	Reference Area	Inner	Middle	Outer	Open Gulf	Louisiana Bight
2004	August	-5.9	-6.2	-6.1	-6.3	N.A.	N.A.	-5.6
2005	October	13.1	13.0	13.0	N.A.	N.A.	N.A.	10.1
2006	April	-4.5	-6.4	-8.7	-3.5	N.A.	N.A.	-6.6
2006	June	-3.2	-3.4	-6.3	-1.3	2.1	N.A.	-7.7
2006	September	-0.8	-0.9	-1.6	-0.5	1.5	N.A.	-2.0
2007	May	-8.1	-8.3	-12.8	-4.0	-2.5	N.A.	-14.3
2007	August	-2.0	-2.0	-1.8	-2.2	-0.7	N.A.	-4.0
2008	July	-2.3	-2.3	-0.2	-5.3	N.A.	N.A.	N.A.
2009	January	-2.3	-2.4	-0.6	-4.0	-5.0	-10.8	-0.2
2009	April	-4.8	-6.5	-6.8	-6.6	0.1	-1.3	-11.4
2009	July	0.4	1.4	1.5	1.4	1.1	0.8	-0.6
2009	November	0.2	-0.1	0.5	-0.6	-1.2	-0.6	-4.8
2010	March	-14.3	-17.7	-17.3	-18.3	-15.3	-4.1	-124

 a CO₂ fluxes were calculated for various regions: for the cruise survey area, the reference area (the gray area in Figure 1), the inner shelf (bottom depth less than 20 m), the middle shelf (20 to 45 m), the outer shelf (45 to 200 m), and the open gulf (depth deeper than 200 m), and the Louisiana Bight and its adjacent area. N.A.: no available data.



Figure 6. Seasonal variations of average (a) temperature, (b) wind speed, (c) sea surface pCO_2 , and (d) air-sea CO_2 flux in the reference area. The error bars in Figures 6a–6c showed ± 1 standard deviation of each data point. In Figure 6, the bar showed the uncertainties of the data point. The line on Figure 6c represents the atmospheric CO_2 value.

salinity regions ($17 \le S < 33$) with undersaturated pCO_2 values covered the majority of this area (Table 4). Thus, the northern Gulf of Mexico as a whole was still a CO_2 sink.

4. Discussion

4.1. Factors Controlling pCO₂ Variations From the river mouth to the inner shelf, the outer shelf, and beyond, both physical and biological conditions changed greatly. Mechanistic analysis in sections 2.4 and 3.3.3 demonstrates that biological removal and mixing were the two dominant factors influencing pCO_2 along the salinity gradient. As predicted from carbon dynamics during river-to-sea mixing, the conservative mixing lines of pCO_2 are concave upward along the salinity gradient [Cai et al., 2013] (Figure 7). Along this concave-upward curve, the pCO₂ difference between salinities 18 and 36 (salinity regions which covered the majority of this study area) was 124, 346, 185, and 117 μ atm in spring, summer, fall, and winter, respectively. However, the majority of pCO₂ values calculated from conservative mixing were still much higher than observed values, implying mixing is not the only factor controlling pCO_2 . The exception was in October 2005, when observed pCO₂ values were close to mixing-only simulated results (Figure 7c). We believe this represented an extreme case when the water column was well mixed following two major storm events.

Simulations that included biological activity as well as mixing produced results much closer to our observed pCO_2 values (Figure 7). From salinities 18–36, the maximum pCO_2 values induced by biological removal (i.e., the difference between pCO_{2Mix} and $pCO_{2Mix+Bio}$ at the salinity binned temperature) were 322, 527, 397, and 141 μ atm in spring, summer, fall, and winter, respectively. The strong biological carbon uptake inferred from nitrate

removal along the salinity gradient in $pCO_{2Mix+Bio}$ was consistent with that observed during our previous studies on the Louisiana Bight and the adjacent region [*Cai* 2003; *Guo et al.*, 2012; *Huang et al.*, 2012]. While the majority of pCO_2 observations agreed with $pCO_{2Mix+Bio}$ in spring, summer, and fall (Figures 7a, 7b, and 7c), a few pCO_2 observations fell midway between the mixing-only and mixing-plus-biology simulated values in fall and winter (Figures 7c and 7d). Some observed data in winter between salinities 28 and 35 also agreed with mixing-only values (Figure 7d). The above two facts led us to conclude that along salinities 18–36,



Figure 7. Observed and modeled relationships between pCO_2 and salinity in each season. The measured pCO_2 values are binned by 1-unit salinity intervals (circle) and the error bars indicate ± 1 standard deviation of the point in each interval. Each plot focuses on $pCO_2 < 900$ μ atm, but the inserted plots show the plots' full scales. The comparison of mixing only (blue lines) and mixing plus biology (green lines) under the same temperature (the binned temperature in each salinity interval) suggests that biological activity is the dominant factor controlling pCO_2 while abiotic mixing could not be ignored in spring (a), summer (b), and fall (c). Mixing became important in winter at higher salinities (d). The comparison of two temperatures under mixing plus biology, i.e., the binned temperature in each 1- unit salinity interval (green lines) versus the seasonal average (red triangle markers), suggests that temperature is less important than biological and mixing processes. The observations in October 2005 (blue triangle markers in (c) affected by the remaining effects of hurricanes were close to abiotic mixing. Black lines represent the atmospheric CO₂ value.

lable 4. Avera	age pCO_2 , Are	a, and CO_2 flu	ux on the Lou	lisiana Shelf L	Juring Each C	ruise							
Salinity	Aug 2004	Oct 2005	Apr 2006	Jun 2006	Sep 2006	May 2007	Aug 2007	Jul 2008	Jan 2009	Apr 2009	Jul 2009	Nov 2009	Mar 2010
Average pCO ₂	(µatm)												
$0 \leq S < 17$	N.A.	506.9	N.A.	305.3	297.2	316.2	616.0	286.1	375.6	465.1	440.7	431.3	427.1
$17 \le S \le 25$	285.6	539.2	283.0	199.0	323.8	199.5	390.9	350.7	367.3	300.2	299.0	405.4	262.6
$25 \le S \le 33$	304.3	445.6	287.7	295.4	364.6	253.0	328.1	410.1	387.2	303.3	347.5	371.0	267.4
$33 \le S \le 35$	N.A.	457.4	332.3	380.6	394.6	336.7	380.8	N.A.	386.4	353.9	423.6	376.5	326.0
$35 \le S \le 37$	N.A.	N.A.	373.9	423.7	402.8	364.6	N.A.	N.A.	343.9	379.6	435.8	393.3	358.8
Area (10 ³ km ²))												
$0 \leq S < 17$	N.A.	0.4	N.A.	0.9	0.5	1.4	0.3	4.1	1.4	2.1	2.1	2.3	2.8
$17 \le S \le 25$	2.8	0.4	1.0	3.5	0.5	4.3	1.8	7.0	3.1	9.2	6.9	12.9	15.6
$25 \le S \le 33$	7.2	3.5	3.9	18.4	27.3	13.3	28.8	3.8	21.1	28.4	54.7	31.6	53.7
$33 \le S \le 35$	N.A.	0.3	1.3	5.8	2.9	7.6	10.5	N.A.	13.8	9.5	19.9	18.7	19.9
$35 \le S \le 37$	N.A.	N.A.	4.5	8.1	4.8	13.7	N.A.	N.A.	63.9	50.4	16.4	40.6	12.3
Average CO ₂ f	lux (mmol m ⁻	⁻² d ⁻¹)											
$0 \leq S < 17$	N.A.	24.2	N.A.	-5.9	-9.3	-8.1	27.8	-6.0	-0.3	12.7	3.4	6.8	7.3
$17 \le S \le 25$	-8.4	23.0	-8.9	-10.3	-5.2	-20.4	0.8	-2.0	-1.9	-11.7	-5.2	2.5	-20.0
$25 \le S \le 33$	-4.9	10.4	-8.0	-5.1	-1.2	-13.1	-3.1	1.4	-0.2	-11.4	-1.1	-2.2	-17.9
$33 \le S < 35$	N.A.	13.8	-3.8	0.0	1.0	-4.1	-0.2	N.A.	0.2	-4.6	3.0	-1.2	-9.1
$35 \le S < 37$	N.A.	N.A.	-0.9	2.0	1.7	-1.8	N.A.	N.A.	-4.7	-0.8	3.8	1.5	-4.2

^aN.A.: no available data.

biological activity drove pCO₂ variation and was more important than mixing. But mixing was a nonnegligible factor to estimate biological removal (equations (6–13)) in spring, summer, and fall and mixing became a dominant factor in winter at higher salinities.

In the carbonate system, pCO₂ variation is theoretically related to variations of DIC, TA, and temperature [Sarmiento and Gruber, 2006]. To explore the role of mixing and biology, we have set our simulations at the salinity binned temperature. To explore the role of temperature, we also run the pCO_{2Mix+Bio} simulation at the seasonal average temperature (Figure 7). The maximum differences of $pCO_{2Mix+Bio}$ between the two temperatures were only 41, 27, 16, and 64 μ atm for spring, summer, fall, and winter, respectively. These pCO_{2Mix+Bio} differences due to temperature variations were much smaller than the differences due to biological uptake between pCO_{2Mix} and pCO_{2Mix+Bio} at the same temperature. The temperature effect was only notable when mixing dominated in the moderate to high salinities (27 to 36) during winter (Figure 7d). This result highlights the importance of non-temperature effects, e.g., biological activity and mixing, on pCO₂ variation in this river-influenced system.

Finally, air-sea CO_2 exchange also plays a role in determining plume pCO_2 values although it is generally minor. For example, in the Mississippi River plume, net community production (NCP) estimated by DIC deficient were 83 to -233 mmol m⁻² d⁻¹ (1 to -2.8 g C m⁻² d⁻¹) in salinity ranges 0–18, 275–616 mmol m⁻² d^{-1} (3.3–7.4 g C m⁻² d⁻¹) in salinity ranges 18–27, 32–80 mmol m⁻² d⁻¹ (0.38–0.96 g C m⁻² d⁻¹) in salinity ranges 27–32, and 25–48 mmol m⁻² d⁻¹ (0.3–0.53 g C m⁻² d⁻¹) in salinity ranges 32–34.5 [*Guo et al.*, 2012]. Mean CO₂ gas exchange rates in similar salinity ranges (Table 5) were only <6.2%, <2.3%, 6.8-17%, and <6.8% of these estimated NCP values, respectively. Thus, the effect of air-sea exchanges on pCO_2 variations was rather small in this enhanced primary production area.

4.2. Disturbance of River Plume Trajectories by Weather Events

Weather events may have a strong influence on spatial distributions of pCO₂ in this study area. Two weather events considered here included wind-driven shifts in plume trajectory in March 2010 and July 2009. When northerly winds and high river discharge dominated in March 2010 [Huang et al., 2013], the trajectory of the alongshore plume became wider and extended over the area between 28°N and 25°N (Figure 3m), and as a result, low pCO_2 values also extended to the middle and outer shelves (Figures 4m, 5a and 5b). In this case, the extensive strong CO₂ uptake in the middle and outer shelves encompassed areas that would be

Table 5. Average Air-Sea CO ₂ Flux (mmol m	1 ⁻² d ⁻¹) by Season and Salinity Region
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	Spring	Summer	Fall	Winter	Annual	Area (10 ³ km ²)	Annual (10 ⁹ g C yr ⁻¹)
$0 \le S < 17$	9.6	-4.1	11.1	4.1	5.2	1.7	38.7
$17 \le S \le 25$	-16.6	-8.0	-2.7	1.7	-6.4	6.7	-189.6
$25 \le S \le 33$	-15.3	-3.6	-1.8	-1.4	-5.5	29.5	-713.4
$33 \le S \le 35$	-7.5	0.9	0.4	-0.6	-1.7	12.2	-90.9
$35 \le S < 37$	-1.4	1.4	1.7	-2.3	-0.1	24.7	-14.6

normally nearly net zero CO_2 uptake and resulted in a strong CO_2 sink in March 2010 than the averages along transects B and E (Figures 5c and 5d).

The plume trajectory and wind forcing in July 2009 were unusual [*Zhang et al.*, 2012; *Feng et al.*, 2014]. Our observations also showed high surface salinity on the western inner shelf while the low-salinity plume was confined to the eastern side (Figure 3k). Under these conditions, pCO_2 was oversaturated west of 90°W, especially on the inner shelf which typically had low pCO_2 ; areas east of 90°W were undersaturated, especially on the outer shelf (Figure 4k). This pattern can also be seen along the two transects in Figure 5; pCO_2 values were undersaturated in July 2009 on the outer shelf in Transect B and were oversaturated in the middle and outer shelves in Transect E. Thus, the entire shelf shifted from a normally weak CO_2 sink to a strong source in July 2009. To sum up, plume trajectory can be strongly influenced by wind forcing [*Cochrane and Kelly*, 1986; *Schiller et al.*, 2011; *Walker et al.*, 2005; *Zhang et al.*, 2012], and it can affect the spatial distributions of primary production [*Chen et al.*, 2000] and other biogeochemical processes [*Huang et al.*, 2013].

4.3. Disturbance by Hurricanes

The anomalously high surface water pCO_2 values observed in October 2005 were attributed to mixing effects of hurricanes Katrina (23–30 August 2005) and Rita (18–29 September 2005), as the water column was still nearly completely mixed during the survey as indicated by CTD and DIC data (not presented). The October pCO_2 values were higher than the mean values of the September 2006 and November 2009 surveys, which were considered to represent typical fall conditions (Figure 7c). As in situ pCO_2 measurements were limited on the inner shelf during this cruise, *Lohrenz et al.* [2010] extrapolated them across the Louisiana Bight and its adjacent area (~9000 km²) using remote sensing techniques and estimated an air-sea CO_2 flux of 5.4 mmol m⁻² d⁻¹ (0.21 Tg C yr⁻¹). Compared to the CO_2 fluxes from nonstorm months in September 2006 and November 2009 (average of 1.79 mmol m⁻² d⁻¹ or 0.07 Tg C yr⁻¹), the higher CO_2 flux (3.61 mmol m⁻² d⁻¹ or 0.14 Tg C yr⁻¹) in October 2005 can arguably be attributed to effects of storm-enhanced terrestrial inputs and bottom sediment resuspension by hurricanes [*Lohrenz et al.*, 2010]. In addition, winds were relatively high in October 2005 and the uncertainty of gas transfer velocity was large under high wind speeds [*Wanninkhof et al.*, 2009], resulting in larger uncertainty in air-sea CO_2 fluxes. Nonetheless, it is apparent, and perhaps not a surprising conclusion, that hurricanes can exert dramatic changes to normal sea surface pCO_2 distribution and thus the flux of air-sea CO_2 exchange.

4.4. Conceptual Model for CO₂ Dynamics in the River Plume

We conclude this paper with a conceptual model and a summary for the surface water inorganic carbon budget and dynamics of this river plume in the northern Gulf of Mexico (Figure 8). Annually, the Mississippi and Atchafalaya Rivers exported about 17 Tq C of bicarbonate to the coastal ocean [Cai et al., 2008; Lohrenz et al., 2013] while they also transported 1.57 Tg N of inorganic nitrogen [Goolsby et al., 2000]. In the subregion where salinity was 0–17 in the river plume, water transit time was short (2 days) [Green et al., 2006] and high turbidity inhibited light penetration that would support phytoplankton growth [Dagg et al., 2003; Lohrenz et al., 1990], with the result that this subregion was a intensive source of CO₂ to the atmosphere (5.2 mmol m⁻² d⁻¹, 39 \times 10⁹ g C yr⁻¹). Surface waters of salinity 17-24 and 25-33 covered a relatively large portion of the shelf and were characterized by reduced turbidity and thus higher light penetration, resulting in high primary production and nonconservative behavior in nutrients consistent with biological uptake [Dagg et al., 2007; Lohrenz et al., 1990; Lohrenz et al., 1999]. DIC mass balance analyses also pointed to strong biological DIC removal only in the middle salinity plume (salinity 18–27) [Guo et al., 2012]. Nitrate removal along the salinity gradient also showed patterns proportional to DIC removal [Cai 2003; Guo et al., 2012; Huang et al., 2012; Lehrter et al., 2013], supporting our pCO2 simulations based on nitrate plus nitrite removal in section 3.5. These middle salinity regions coincided with strong sinks of atmospheric CO₂ (6.4 mmol m⁻² d⁻¹, 190 \times 10⁹ g C yr⁻¹) for waters with salinity 17–24, and 5.5 mmol m⁻² d⁻¹, 713 \times 10⁹ g C yr⁻¹ for waters with salinity 25-33). Net DIC removal was close to zero at the high-salinity end of these intermediate salinity regions (S>32) [Guo et al., 2012]. In our high-salinity subregion ($33 \le S \le 35$), surface waters shifted from a CO₂ sink to a near neutral status, and this subregion was a weak sink of 90 \times 10⁹ g C yr⁻¹ (1.7 mmol m⁻² d⁻¹).

5. Summary

This study described spatial and seasonal variations of surface water pCO_2 in the northern Gulf of Mexico. The spatial distribution was characterized by: (1) water pCO_2 values of 1000–2000 μ atm in the Mississippi



Figure 8. The conceptual model of the CO₂ budget in the river plume. Blue-dashed lines separate the plume into five salinity divisions: 0 \leq salinity <17, 17 \leq salinity <25, 25 \leq salinity <33, 33 \leq salinity <35, and 35 \leq salinity <37.

and Atchafalaya river sources, (2) a strong cross-shelf CO_2 gradient, where the inner to middle shelf acted as a sink of atmospheric CO_2 and the outer shelf was near a neutral status, and (3) a concave upward curve of pCO_2 values versus salinity with high values at low salinities near the river sources, low at middle salinities, and increasing to near equilibrium or slight oversaturation in surface waters at high salinities. A quantitative budget to describe the CO_2 flux along the salinity gradient was also presented. The average pCO_2 values over this study area revealed seasonality: undersaturation in spring, near atmospheric CO_2 values in summer, oversaturation in fall, and a return to near atmospheric values in winter. Overall, the northern Gulf of Mexico acted as a sink of CO_2 with respect to the atmosphere, especially strong in the Louisiana Bight.

Analysis further indicated that variations in pCO_2 distribution and air-sea CO_2 flux were strongly influenced by biological activity, and to a lesser extent mixing processes. Finally, air-sea fluxes of CO_2 were also affected by weather events, implying that future climate-related changes in meteorological forcing may alter air-sea CO_2 fluxes on river-dominated continental shelves.

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