Modeling $pCO_2$ Variability in the Gulf of Mexico

Zuo (George) Xue$^{1,2,3}$, Ruoying He$^4$, Katja Fennel$^5$, Wei-Jun Cai$^6$, Steven Lohrenz$^7$, Wen-Jen Huang$^8$, Hanqin Tian$^9$, Wei Ren$^{10}$, Zhengchen Zang$^1$

1. Dept. of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA, United States
2. Center for Computation and Technology, Louisiana State University, Baton Rouge, LA, United States
3. Coastal Studies Institute, Louisiana State University, Baton Rouge, LA, United States
4. Dept. of Marine, Earth & Atmospheric Sciences, North Carolina State University, Raleigh, NC, United States
5. Dept. of Oceanography, Dalhousie University, Halifax, Canada
6. School of Marine Science and Policy, University of Delaware, Newark, DE, United States
7. School for Marine Science and Technology, University of Massachusetts Dartmouth, New Bedford, MA, United States
8. Department of Oceanography, National Sun Yat-sen University, Kaohsiung, Taiwan
9. School of Forestry and Wildlife Sciences, Auburn University, AL, United States
10. Department of Plant and Soil Sciences, University of Kentucky, Lexington, KY, United States
Abstract

A three-dimensional coupled physical-biogeochemical model was used to simulate and examine temporal and spatial variability of sea surface $p$CO$_2$ in the Gulf of Mexico (GoM). The model was driven by realistic atmospheric forcing, open boundary conditions from a data-assimilative global ocean circulation model, and observed freshwater and terrestrial nutrient and carbon input from major rivers. A seven-year model hindcast (2004–2010) was performed and validated against ship measurements. Model results revealed clear seasonality in surface $p$CO$_2$ and were used to estimate carbon budgets in the Gulf. Based on the average of model simulations, the GoM was a net CO$_2$ sink with a flux of $1.11 \pm 0.84 \times 10^{12}$ mol C yr$^{-1}$, which, together with the enormous fluvial inorganic carbon input, was comparable to the inorganic carbon export through the Loop Current. Two model sensitivity experiments were performed: one without biological sources and sinks and the other using river input from the 1904-1910 period as simulated by the Dynamic Terrestrial Ecosystem Model (DLEM). It was found that biological uptake was the primary driver making GoM an overall CO$_2$ sink and that the carbon flux in the northern GoM was very susceptible to changes in river forcing. Large uncertainties in model simulations warrant further process-based investigations.
1. Introduction

Human consumption of fossil fuels has resulted in continuously increasing levels of atmospheric CO$_2$ since the Industrial Revolution began around 1750. If the increasing trend continues, the projected $p$CO$_2$ by the end of the 21st century (970 ppm, in A1F1 scenario, Stocker et al., 2014) could be nearly triple the present level. In the face of different climate scenarios, a better understanding of the oceans’ role in regulating the global carbon cycle is crucial, because oceans not only act as receivers of the enormous carbon loading from coastal rivers (Cai et al., 2011a; Bauer et al. 2013), but also as vast carbon reservoirs via the “carbon pump” mechanism (Sabine et al., 2004; Sabine and Tanhua, 2010). On regional scales, the marine carbon cycle tends to be more complicated and shows contrasting behaviors in different areas (coastal vs. open ocean, low latitude vs. high latitude, etc.) and during different seasons (e.g., Lohrenz et al., 2010 for the northern Gulf of Mexico; Jiang et al., 2008 for the South Atlantic Bight; Signorini et al., 2013 for the North American east coast; Tsunogai et al., 1999 for the East China Sea). Quantifying the ocean carbon budget is therefore a difficult task. Coupled physical and biological models are useful tools for understanding complex biogeochemical processes and estimating carbon and nutrient fluxes in coastal oceans where spatial and temporal heterogeneities are high and data are sparse (e.g. Fennel and Wilkin, 2009; Fennel 2010; Fennel et al., 2011; and He et al., 2011).

Our study focuses on the carbon cycle in the Gulf of Mexico (GoM). One unique feature of the Gulf is that it receives enormous riverine nutrient and carbon inputs, both organic and inorganic, the majority of which are from the Mississippi-Atchafalaya River system. Excessive nutrient loading causes coastal eutrophication, which triggers not only
the well-known hypoxia phenomenon (a.k.a. the “Dead Zone”, Rabalais et al., 2002), but also a newly revealed coastal ocean acidification problem (Cai et al, 2011b). However, the carbon cycling associated with such enormous terrestrial carbon and nutrient inputs remains unclear: on the one hand extensive riverine carbon input results in CO₂ over-saturation in coastal waters, which serve as a CO₂ source to the atmosphere (e.g. Lohrenz et al., 2010; Guo et al., 2012); on the other hand, enhanced primary production in the river plume due to significant inputs of inorganic nutrients induces a net influx of CO₂ although the Mississippi River Plume region is an overall heterotrophic system that breaks down organic carbon (Murrell et al., 2013; Huang et al., 2013 and 2015). Further offshore, the circulation in the GoM is largely influenced by the energetic Loop Current. Large anticyclonic eddies aperiodically pinch off from the Loop Current (Sturges and Leben, 2000), which, along with the wind-driven cross-shelf circulation and other meso-scale and sub-mesoscale processes, enhance material exchanges between the eutrophic coastal waters and oligotrophic deep-ocean waters (e.g., Toner et al., 2003). Indeed, a recent observational study suggested a significant dissolved inorganic carbon export (DIC, \( \sim 3.30 \times 10^{12} \) mol C yr\(^{-1} \)) from the GoM shelves to the Loop Current waters (Wang et al., 2013).

While global inorganic carbon budgets have been made available through joint seawater CO₂ observations (e.g. World Ocean Circulation Experiment and Joint Global Ocean Flux study, Sabine et al., 2004; Feely et al., 2004; Orr et al., 2005), they are too coarse to represent CO₂ variability in the GoM (Gledhill et al., 2008). Other recent efforts were able to provide GoM sub-regional carbon assessments based on limited in situ observations (e.g. Cai et al., 2003, Lohrenz et al., 2010, Huang et al., 2013, 2015a and
2015b focused on the Mississippi River plume and the Louisiana Shelf; Wang et al., 2013 covered three cross-shelf transects in the northeastern GoM but only for one summer). Significant uncertainties exist in such budget estimations due to large temporal and spatial gaps presented in the observations (e.g. Coble et al., 2010; Hofmann et al., 2011; Robbins et al., 2014). In this regard, coupled physical-biogeochemical models are capable of representing the biogeochemical cycle with realistic physical settings (e.g., ocean mixing and advection) and providing an alternative means for a Gulf-wide carbon budget estimation.

Here we present a GoM $p$CO$_2$ analysis based on the results of a coupled physical-biogeochemical model simulation. Our objective was to simulate the CO$_2$ flux at the air-sea interface (which at present is based on observational analyses alone and subject to large uncertainty), as well as its variability in relationship with river plume dynamics and dominant oceanic processes in different regions of the GoM.

2. Method

Our analysis uses solutions from a coupled physical-biogeochemical model covering the GoM and South Atlantic Bight waters (Xue et al., 2013, model domain see Fig.1). The circulation component of the coupled model is the Regional Ocean Modeling System (ROMS, Haidvogel et al. 2008, Shchepetkin and McWilliams, 2005; Hyun and He, 2010) and is coupled with the biogeochemical module described in Fennel et al. (2006, 2008, and 2011). The nitrogen cycling parameterization has seven state variables: two species of dissolved inorganic nitrogen (DIN hereafter, nitrate [NO$_3$] and ammonium [NH$_4$]), one functional phytoplankton group, chlorophyll as a separate state variable to
allow for photoacclimation, one functional zooplankton group, and two pools of detritus representing large, fast-sinking particles, and suspended, small particles. The carbon cycle is connected to the nitrogen cycle via a C to N ratio of 6.625 for the organic components (phytoplankton, zooplankton, large and small detritus). The sediment component of the biogeochemical model is a simplified representation of benthic remineralization processes, where the flux of sinking organic matter out of the bottommost grid box results immediately in a corresponding influx of ammonium and DIC at the sediment/water interface. The parameterization accounts for the loss of fixed nitrogen through sediment denitrification based on the linear relationship between sediment oxygen consumption and denitrification reported by Seitzinger and Giblin (1996) and only accounts for the portion of denitrification that is supported by nitrification of ammonium in the sediment (referred to as coupled nitrification/denitrification.

A seven-year (January 1, 2004–December 31, 2010) model hindcast was performed, driven by NCEP’s high resolution combined model and assimilated atmospheric dataset (North American Regional Reanalysis, www.cdc.noaa.gov), open boundary conditions for ocean model (temperature, salinity, water level, and velocity) from a data-assimilative global ocean circulation model (HYCOM/NCODA, Chassignet et al., 2007), and observed freshwater and terrestrial nutrient input from 63 major rivers (Aulenbach et al., 2007; Milliman and Farnsworth, 2011; Fuentes-Yaco et al., 2001; and Nixon, 1996). Model validations (physics, nutrients and chlorophyll) and a nitrogen budget were reported in Xue et al. (2013).
In this study, we have focused on the carbon cycle in the GoM. As in Xue et al. (2013), we considered the first year of the simulation (2004) as model spin-up; all results presented here use model output from 2005 to 2010. The carbonate chemistry of the coupled model is based on the standard defined by the Ocean Carbon Cycle Model Intercomparison Project Phase 2 (Orr et al., 2000). There are two active tracers, DIC and alkalinity, to determine the other four variables of the carbonate system (i.e. \( p\text{CO}_2 \), carbonate ion concentration, bicarbonate ion concentration, and pH; Zeebe and Wolf-Gladrow, 2001). Details of the formulas used in the simulation are provided in the supplementary materials S1.

Similar to the results reported by Hofmann et al. (2011), we found that the model-simulated DIC concentration in the water column was very sensitive to the initial conditions. Although there were many historical measurements in the GoM, these data were limited to the northern GoM shelf regions and thus were insufficient to initialize the model. Instead, we tested model sensitivity using three sets of initial and open boundary conditions, which were derived using the empirical salinity-temperature-DIC-alkalinity relationships described in Lee et al. (2000 and 2006), Cai et al. (2011a), and Wang et al. (2013), respectively. Among them, the initial condition prescribed following Lee et al. (2000 and 2006, Fig.2, details see supplementary materials S2) provided the best model-data comparison. For the open boundary condition, we found simulated surface \( p\text{CO}_2 \) exhibited very limited variance (<5%) regardless of which conditions were applied. To be consistent with the setup of the initial condition, the results presented here were driven by boundary conditions derived from Lee et al., (2000 and 2006). For particular organic
carbon, we set a small, positive value for both phytoplankton and zooplankton along the open boundaries.

The carbon cycle parameterizations used in this study followed the same approach and values as in Fennel et al. (2008), Fennel and Wilkin (2009), and Fennel (2010). For gas exchange calculations we followed the formulas in Wanninkhof (1992, details see supplementary materials S3). For air $pCO_2$, we utilized the Atmospheric Infrared Sounder (AIRS, 2008) monthly gridded observation dataset and averaged them over the study area. We applied the curve-fitting method using a C language program named CCGCRV (http://www.esrl.noaa.gov/gmd/ccgg/mbl/crvfit/crvfit.html, Fig.3), and the air $pCO_2$ in the gas exchange calculation was prescribed as:

$$pCO_{2air} = D_0 + D_1 \times t + D_2 \times (t^2) + D_3 \times \sin(p\ i2 \times t) + D_4 \times \cos(p\ i2 \times t)$$

$$+ D_5 \times \sin(p\ i2 \times 2 \times t) + D_6 \times \cos(p\ i2 \times 2 \times t)$$

(1)

where $pCO_{2air}$ represents the monthly air $pCO_2$; $t$ represents the number of months since January 2004 divided by 12, $p\ i2$ is a constant set to 6.28, $D_0$=375.96, $D_1$=2.23, $D_2$=-0.007, $D_3$=1.31, $D_4$=-0.64, $D_5$ = -0.13, $D_6$=0.21, and $D_7$=0.09. Due to the relatively low horizontal resolution of the AIRS data (2.5*2 degree), air $pCO_2$ was set to be spatially uniform.

To account for riverine inputs, we constructed climatological monthly alkalinity time series by averaging all available U.S. Geological Survey (USGS) observations for each major river, including the Mississippi, Atchafalaya, Mobile, and Brazos in the GoM. Because direct riverine DIC measurements were not available, we approximated riverine DIC inputs using the corresponding alkalinity value plus 50, following the observational
study by Guo et al. (2012). The fluvial DIC input to the GoM was estimated as $\sim 2.18 \times 10^{12}$ mol C yr$^{-1}$, the majority of which was delivered by the Mississippi-Atchafalaya River ($\sim 1.80 \times 10^{12}$ mol C yr$^{-1}$, Fig.4, comparable with the estimation in Cai et al., 2003).

The results of three model experiments covering the period of 2004-2010 are presented in this study, in which, Experiment 1 (Exp1) was a “control run”, with observed riverine inputs from USGS and biological sources and sinks of DIC and alkalinity in the water column; Experiment 2 (Exp2) was a “no-biology run”, where all biological sources and sinks of DIC and alkalinity were disabled, similar to the experiment described in Fennel and Wilkin (2009); and Experiment 3 (Exp3) had the same set up as Exp1, but the riverine inputs (water, nutrients, and carbon of the Mississippi-Atchafalaya river) were taken from the Dynamic Land Ecosystem Model (DLEM, Tian et al., 2015) simulation for the period of 1904-1910 (Fig. 4). Specifically, we used the monthly model outputs of water, NO$_3$, NH$_4$, and alkalinity from DLEM as riverine inputs to drive the ocean model in Exp1. Also in Exp3 the air $p$CO$_2$ was set to the 1904-1910 condition derived by formula (1). The purpose of Exp2 was to qualitatively examine the role of biological processes in regulating regional $p$CO$_2$ variability, whereas Exp3 examined the coastal carbon cycle’s response to alternations in river inputs as a result of land-use change within the Mississippi watershed (the first ten years of the 20$^{th}$ century vs. that of the 21$^{st}$ century) . Although we applied riverine and air $p$CO$_2$ estimated for the period of 1904-1910, the purpose of Exp3 was not to reproduce the $p$CO$_2$ for that period as changes of other variables over the past 100 years were not considered (e.g. air temperature, ocean and food web conditions).
3. Validation of the control run

We utilized the ship-based sea surface $p$CO$_2$ database compiled by the Lamont-Doherty Earth Observatory (LDEO Version 2014, >180,000 data points in the Gulf over 2005-2010, Takahashi et al., 2015) and Huang et al. (2015a and b) for model validation (see locations of ship measurements in Fig.5). The ship measurements by Huang et al. (2015a and b) were taken in October 2005; April, June, August 2006; May, August 2007; January, April, July, November 2009; and March 2010, respectively and contain > 78,000 data points. To alleviate the spatial and temporal mismatches associated with these in-situ measurements, we computed their temporal and spatial mean using a 10-day temporal binning for temporal processing, and then compared them with model-simulated $p$CO$_2$ time series (Fig.6). To facilitate our analysis, the GoM was divided into five sub-regions: 1) Mexico Shelf (MX Shelf), 2) West Gulf of Mexico Shelf (WGoM Shelf), 3) Northern Gulf of Mexico Shelf (NGoM Shelf), 4) West Florida Shelf (WF Shelf), and 5) the open ocean, which is > 200m water depth (regional definitions followed Benway and Coble, 2014, maps of sub-regions see Fig.1). The data points falling in each of the sub-regions was first grouped by a 10-day temporal binning and then spatially averaged to get a mean value for each sub-region.

On the NGoM Shelf, the control simulation was able to capture the measured $p$CO$_2$ in 21 out of the 26 data groups (the mean value of in-situ measurements fell within one standard deviation of the model mean). Specifically, agreement between model and observations was better during spring, fall, and winter, than during summer. The model overestimated $p$CO$_2$ in June 2006, August 2007, and July 2009. These discrepancies will
be discussed in later sections. On the Gulf-wide scale, the control run reproduced the observed seasonality. Decent model-data agreements were found in 24 out of the 26 data groups. These sub-regional and Gulf-wide comparisons indicate that the coupled physical-biogeochemical model is generally capable of resolving temporal and spatial variations in observed $pCO_2$, allowing us to use this seven-year hindcast to further characterize the air-sea $CO_2$ flux.

4. Results

In this section, we present model-simulated sea surface $pCO_2$ and air-sea $CO_2$ flux in the five sub-regions. Because few data existed and large $pCO_2$ gradients were found in both in-situ measurements and model simulation in shallow waters, areas that are shallower than 10 m were excluded from our analysis.

4.1 Temporal variability of Sea Surface $pCO_2$

Spatially averaged model-simulated $pCO_2$ on the NGoM Shelf exhibited clear seasonality, with highest values (~ 500 ppm) around August and lowest values (~ 300 ppm) around February (Fig.6a). Notably, spatially averaged $pCO_2$ on the NGoM Shelf was not coincident with high river carbon and nutrient inputs (Fig.3). Peaks in $pCO_2$ generally occurred two to three months later than the annual maximum in river input. The maximum riverine input during 2005-2010 was observed in June 2008 when a major flood occurred (Fig. 4a), yet no significant elevation of $pCO_2$ was seen in the model simulation. Gulf-wide spatially averaged $pCO_2$ (Fig.4b) had a temporal pattern similar to that on the NGoM Shelf, with high $pCO_2$ values (~ 425 ppm) in August and low values
(~ 350 ppm) in February. Averaged $p$CO$_2$ on the NGoM Shelf was generally 50 ppm higher than that in the entire Gulf.

4.2 Model Simulations of Air-Sea CO$_2$ flux

The simulated carbon flux was calculated from a multi-year model mean (2005-2010). We found that the GoM overall was a CO$_2$ sink with a mean flux rate of $0.71 \pm 0.54$ mol C m$^{-2}$ yr$^{-1}$ ($\sim 1.11 \pm 0.84 \times 10^{12}$ mol C yr$^{-1}$, Table 1 and Fig.7). Examining region by region, we found that the open ocean, occupying ~ 65% of the GoM by area, acted as a CO$_2$ sink ($1.04 \pm 0.46$ mol m$^{-2}$ yr$^{-1}$ of C) during most of the year except in summer. The greatest carbon uptake occurred in winter ($2.44 \pm 0.49$ mol C m$^{-2}$ yr$^{-1}$). It is evident that waters around the Loop Current act as a sink throughout the year, whereas the western part of the open ocean waters shifted from acting as a CO$_2$ source in summer and fall to a sink in winter and spring.

Compared with the open ocean, air-sea flux on the continental shelf was more location-dependent and varied from season to season. Among the four shelf sub-regions, the MX Shelf has the largest area. It acted as a strong CO$_2$ sink in winter and spring ($0.49 \pm 0.28$ and $0.97 \pm 0.28$ mol C m$^{-2}$ yr$^{-1}$) and then a carbon source in summer and fall ($-0.96 \pm 0.38$ and $-0.76 \pm 0.45$ mol C m$^{-2}$ yr$^{-1}$). Waters along the eastern side of the MX Shelf were a sink during most of the year, while to the west the shelf was a source in summer and fall. On an annual scale, this region was a sink with an air-sea flux of $0.19 \pm 0.35$ mol C m$^{-2}$ yr$^{-1}$. To the north, the WGoM Shelf has the smallest area among the four shelf sub-regions. It acted as a CO$_2$ source during spring, summer, and fall ($-0.24 \pm 0.59$, $-1.69 \pm 0.43$ and $-1.06 \pm 0.34$ mol C m$^{-2}$ yr$^{-1}$) and a strong CO$_2$ sink during winter ($1.62 \pm 0.32$ mol C m$^{-2}$ yr$^{-1}$).
On an annual scale the WGoM region was a CO$_2$ source with a degassing rate of 0.34±0.42 mol C m$^{-2}$ yr$^{-1}$.

The NGoM Shelf shifted from acting as a CO$_2$ source in summer and fall (-1.42±0.74 and -0.79±0.63 mol C m$^{-2}$ yr$^{-1}$) to a sink in winter and spring (1.01±0.89 and 2.49±0.70 mol C m$^{-2}$ yr$^{-1}$). The most prominent feature here was the continuous, strong degassing in the coastal waters around the Mississippi-Atchafalaya River mouths. However, as the water becomes deeper, the NGoM Shelf water shifted from acting as a sink during winter and spring to a source during summer and fall. Despite of the extensive degassing in the coastal water, the NGoM Shelf overall was a CO$_2$ sink on a yearly basis (0.32±0.74 mol C m$^{-2}$ yr$^{-1}$). Similarly, the WF Shelf also shifted from acting as a CO$_2$ source in summer and fall (-1.26±0.53 and -1.73±0.67 mol C m$^{-2}$ yr$^{-1}$) to a sink in winter and spring (1.19±0.38 and 0.28±0.33 mol C m$^{-2}$ yr$^{-1}$). The degassing in the inner shelf was strong enough to make the WF Shelf a CO$_2$ source on a yearly basis (-0.38±0.48 mol C m$^{-2}$ yr$^{-1}$).

Despite the salient spatial and temporal variability, the GoM was an overall CO$_2$ sink, mainly because of the strong uptake in the open ocean. For validation purposes, we compared (in Table 1) model-simulated air-sea flux against an estimation based on observations, which utilized all available measurements collected within the GoM from 2005 to 2010 (Robbins et al., 2014). Our control-run estimations generally agree with in-situ measurements in all five sub-regions in terms of the ocean’s role as a CO$_2$ source or sink. There is some discrepancy in the magnitude of the estimated flux, specifically in the Open Ocean sub-region. We note that Robbins et al. (2014) used monthly mean $p$CO$_2$ and wind fields in their calculation as opposed to the 10-day interval we used here.
Therefore, to facilitate the comparison of results, we recalculated the flux using a monthly mean $pCO_2$ and wind fields and obtained a flux estimate of $0.31 \pm 0.35$ mol C m$^{-2}$ yr$^{-1}$ for the Open Ocean sub-region, and $0.12 \pm 0.23$ mol C m$^{-2}$ yr$^{-1}$ for the entire GoM. These values are comparable to those in Robbins et al. (2014, $0.48 \pm 0.07$ mol C m$^{-2}$ yr$^{-1}$ for the Open Ocean and $0.19 \pm 0.08$ mol C m$^{-2}$ yr$^{-1}$ for the entire GoM).

### 4.3 Net Community Production

As Net Community Production (NCP) plays an important role in regulating water $CO_2$ concentration, we generated maps of seasonal mean surface NCP as well as time series of spatially averaged surface NCP for the NGoM and Open Ocean in Figs. 8 and 9. High NCP was simulated in the surface NGoM water and near the eastern tip of the MX shelf during most time of the year. For the NGoM shelf, surface NCP peaks in the late spring and early summer, with the highest value (2.62 mmol N/m$^3$) simulated in summer 2008 when there was a major flooding event. Compared with the NGoM condition (0.53 mmol N/m$^3$), mean surface NCP in the Open Ocean was relatively small, with a multi-year mean value of 0.11 mmol N/m$^3$. In addition, the Gulf-wide mean surface NCP exhibited peaks in late winter and early spring, mainly incurred by the strong upwelling along the west side of the Yucatan Strait (Figs. 8a and 8d). Compared with the surface NCP, the magnitude of bottom NCP was found to be small and is thus not shown.

### 4.4 Model Sensitivity experiments: No-biology simulation (Exp2)

To qualitatively test the role of biological processes in regional $CO_2$ variability, a no-biology run was conducted, where all biology sources and sinks of DIC and alkalinity were disabled similar to the experiment described in Fennel and Wilkin (2009). The experiment produced higher surface $pCO_2$ than the control run. $pCO_2$ is strongly elevated
around the Mississippi River Delta on the NGoM shelf during spring and summer. For
the Open Ocean, the $pCO_2$ increase was mainly confined within the loop current and was
strongly impacted by Caribbean waters flowing in through the Yucatan Channel (Fig. 10).
To assess the influence of NCP on CO$_2$ variation, we plotted the $pCO_2$ difference between
the Control run (Exp1) and No-biology run (Exp2) against the surface NCP from the
Control run in Fig. 11. In the NGoM, the $pCO_2$ difference between the Control run and
No-biology run was strongly correlated with NCP ($r=0.80$), indicating a regional
biological carbon removal. For the Open Ocean, the $pCO_2$ difference shows no
correlation with NCP, and we speculate that the biological carbon removal in this region
was incurred not only by local NCP, but also remote processes. As shown in Fig. 9, the
poor correlation between $pCO_2$ and local NCP could be the result of the high $pCO_2$ water
from the Caribbean, which will be discussed in Section 5.2.

The multi-year mean sea surface $pCO_2$ from the no-biology run was elevated by
88.0 ppm (from 393.1 to 466.5 ppm) for the NGoM Shelf and 56.0 ppm (from 375.1 to
463.1 ppm) for the entire Gulf (Fig. 6, spatially averaged over the sub-regions). This
$pCO_2$ increase was not temporally uniform. On the NGoM Shelf, $pCO_2$ increases in the
no-biology run were clearly higher during spring-summer (with increases of 84.1 and
95.6 ppm) than during fall-winter (with increases of 57.3 and 56.0 ppm). On the Gulf-
wide scale, the $pCO_2$ increase was stronger during summer (97.1 ppm) than the other
seasons (86.5, 87.6, and 80.9 ppm for spring, fall, and winter). For air-sea flux, the
elevated surface $pCO_2$ turns all five sub-regions into a carbon source throughout the year,
resulting in a net outflux rate of $2.10 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Table 1).

4.5 Model Sensitivity experiments: historical river forcing (Exp3)
The purpose of Exp3 was to examine coastal carbon dynamics’ response to different river conditions. Fig. 4 shows that river discharge and DIC inputs during years 1904-1910 as simulated by the DLEM model are comparable with those at present (2004-2010). The multi-year mean value of freshwater discharge is 25,700 m$^3$/s for 1904-1910 and 23,900 m$^3$/s for 2004-2010. The Mississippi-Atchafalaya delivered $1.51 \times 10^{12}$ mol C yr$^{-1}$ during 1904-1910 and $1.70 \times 10^{12}$ mol C yr$^{-1}$ during 2004-2010, which is comparable to the increase over the preceding century reported by Raymond et al. (2008), i.e., a $0.24 \times 10^{12}$ mol C yr$^{-1}$ increase in an average discharge year. However, NO$_3$ inputs during 1904-1910 were $<30\%$ of current inputs ($18.12$ vs. $63.18 \times 10^9$ mol N yr$^{-1}$). Limited N input led to a smaller primary production not only on the NGoM Shelf, but also the adjacent waters on the WGoM and WF Shelves. Due to the smaller primary production the coastal ocean was a weaker CO$_2$ sink during spring and summer (Fig. 12) and the NGoM Shelf a year-long carbon source with a net outflux rate of 0.61 mol C m$^{-2}$ yr$^{-1}$ (Table 1). A close examination of the spring and summer conditions on the NGoM Shelf shows that differences in primary production between Exp1 and Exp3 occur mainly along the Texas and Louisiana coasts. Primary production was significantly elevated in the control run because of enhanced NO$_3$ inputs (Fig. 12a and c). Elevated primary production brought down the sea surface $p$CO$_2$. During spring, enhanced primary production and decreased CO$_2$ was simulated along the Louisiana and Texas coast (Fig. 12b), while during summer, when coastal circulation was influenced by westerly winds, the decreased $p$CO$_2$ was more confined within waters along the Louisiana coast.

5. Discussion
Prior to this investigation, the carbon dynamics in the GoM have been poorly characterized and had a high degree of uncertainty. This study provides one of the first attempts to simulate GoM-wide carbon fluxes and exchanges using a coupled physical-biogeochemical model. We next discuss the factors controlling sea surface $p\text{CO}_2$ variability on the river-influenced NGoM Shelf and the Loop Current-influenced open ocean. The relationship between $p\text{CO}_2$ and other hydrographic variables as well as model uncertainty are also considered.

### 5.1 NGoM Shelf

The Mississippi-Atchafalaya River and associated plume play the most important role in determining the $p\text{CO}_2$ distribution on the NGoM Shelf. The large input of fluvial DIC and alkalinity introduces carbonate saturation in the coastal waters, conversely, nutrients from the river enhance local primary production, which results in DIC removal and thus reduces sea surface $p\text{CO}_2$ (e.g. Lohrenz et al., 2010; Guo et al., 2012; Huang et al., 2013 and 2015). Such biological removal of $\text{CO}_2$ was also confirmed by the elevated $p\text{CO}_2$ values in the no-biology run in this study. Although the river plume’s influence on $\text{CO}_2$ flux has been addressed by prior observational studies, large uncertainties were also found regarding whether the NGoM Shelf is a $\text{CO}_2$ sink or source over a longer time period. For instance, Huang et al. (2013) found a large difference between the $p\text{CO}_2$ distributions in April 2009 and in March 2010. Such a difference was attributed to the variations in river plume extension influenced by local wind conditions and river discharge. In a later communication, based on ship-measurements from 11 cruises, Huang et al. (2015a) concluded that the NGoM Shelf acted as a net $\text{CO}_2$ sink, but with a large uncertainty (influx rate: $0.96 \pm 3.7 \text{ mol m}^{-2} \text{ yr}^{-1}$).
Model results in this study revealed significant spatial and temporal gradients in sea surface $pCO_2$ as well. The multi-year mean (2005-2010) $pCO_2$ distribution was characterized by high values in the coastal waters (Fig. 13a), accompanied by low salinity (Fig. 13c), high Dissolved Inorganic Nitrogen (DIN) and high DIC (Figs. 13d and 13e). The $pCO_2$ value was significantly lower as water became deeper, where the ocean acted as a CO$_2$ sink during most times of the year (Figs. 7a through d). The surface $pCO_2$ distribution on the NGoM Shelf was highly correlated with surface salinity ($r$ value: -0.81) and DIN concentration ($r$ value: 0.80) throughout the year, while its correlations with surface temperature and DIC concentration were significant only for part of the year (for detailed season-by-season correlations see Table 2). Although our model suggests that the shelf-wide $pCO_2$ distribution was positively correlated with DIN concentration, this is not contrary to findings of the above-mentioned observational studies, that is, the high DIN stimulates primary production should be negatively correlated with sea surface $pCO_2$. Instead, the high DIN concentration, together with the low salinity, was a signal of rich DIC from the riverine inputs and, potentially, the light-limited conditions due to the high suspended sediment and dissolved organic matter concentrations within the river plume. In other words, CO$_2$ outgassing from oversaturated plume water overwhelmed the CO$_2$ influx induced by “biological pump” in the areas near the river mouths.

To further link $pCO_2$ dynamics with biological processes stimulated by river inputs, we plotted the $pCO_2$ and DIC averaged over spring and summer seasons (high flow from the Mississippi) against surface salinity of the control run and no-biology run in Fig. 14. Seawater $pCO_2$ decreased almost linearly as salinity increased in the no-biology run (Fig. 14b). During spring and summer when river discharge and DIC inputs
were high, the high $p$CO$_2$ and low salinity waters around the Mississippi River Delta (86-88°W, reddish points) can be easily differentiated from the high salinity and low $p$CO$_2$ waters on the Texas Shelf (92-95°W, bluish points). The DIC-salinity relationship for waters around the Mississippi Delta (reddish points in Fig. 14d) fell below the conservative mixing relationship for the river end member calculated using in-situ data collected in the spring and summer of 2008 by Cai et al. (2011a). For locations to the west, the DIC-salinity relationship reflected a mixture of waters from the Texas shelf (bluish points) and those from the Atchafalaya river (yellowish-greenish points) likely with differing end members.

When biological processes were included, the shelf water exhibited large spatial and seasonal variability (left panels). A $p$CO$_2$ minimum was simulated in mid-salinity waters (30-33 psu) during spring and summer, which is consistent with the curve derived by Huang et al., 2015a using ship measurements. Compared with the no-biology run, $p$CO$_2$ was reduced significantly and exhibited a wider range in the control run. The biological removal of sea surface CO$_2$ was most salient in waters around the Mississippi River Delta. The difference in $p$CO$_2$ between waters around the delta and the Texas Shelf became more salient. The DIC-salinity relationship for locations around the Mississippi River delta (reddish points in Fig. 14c) indicated a significant carbon removal along the salinity gradient. For waters on the Texas Shelf, the DIC-salinity relationship was confined to higher salinities and slightly increased compared with the no-biology run (bluish points in Fig.14c). The DIC increase on the Texas Shelf in the control run could be linked with the benthic respiration in this region proposed by Hetland and DiMarco (2007).
5.2 Open Ocean

In the open ocean, the distribution of surface $p$CO$_2$ was strongly related to the surface DIC (r value: 0.93) and alkalinity throughout the year (r value: -0.85, for detailed season-by-season correlations see Table 2). An influence of DIN and primary production was evident in fall and winter months when wind-induced upwelling was strong (Xue et al., 2013). The dependence of $p$CO$_2$ on DIC and alkalinity makes the Loop Current an important factor controlling the regional air-sea CO$_2$ flux. In addition to a relatively high temperature, the Loop Current water is also characterized by low DIC and high alkalinity (Wang et al., 2013 and references therein). The multi-year mean sea surface temperature in Fig.13b shows persistent warm water mass in the form of the Loop Current, which carries the carbonate characteristics of the Caribbean water (i.e. low DIC and high alkalinity, Figs. 13e and 13f). Surface $p$CO$_2$ in this warm water mass was significantly lower than surrounding shelf waters (Fig. 13a), making the Loop Current a strong CO$_2$ sink throughout the year (Figs.7a-d). Any changes in the Caribbean water’s carbonate characteristics will affect the carbon budget in the GoM as well as waters further downstream in the Gulf Stream. This is also illustrated by the high $p$CO$_2$ difference between the control run and no-biology run in Fig. 10 as well as the poor correlation between the $p$CO$_2$ drop (difference between control and no-biology runs) and NCP in the Open Ocean (Fig. 11b).

5.3 Carbon budget estimation and model uncertainty
Based on our model-simulations, we conclude that the GoM is an overall CO$_2$ sink, taking up $1.11 \pm 0.84 \times 10^{12}$ mol C yr$^{-1}$ from the air. This estimation is comparable to those based on in situ observations, e.g. $1.48 \times 10^{12}$ mol C yr$^{-1}$, (Coble et al., 2010) and $0.30 \times 10^{12}$ mol C yr$^{-1}$ (Robbins et al. 2014). These recent estimates are in stark contrast to the earlier SOCCR report (Takahashi et al. 2007), which found the GoM to be a CO$_2$ source ($1.58 \times 10^{12}$ mol C yr$^{-1}$, the GoM and Caribbean Sea combined). In addition, we estimated that the GoM received $\sim 2.18 \times 10^{12}$ mol C yr$^{-1}$ from rivers, the majority of which was from the Mississippi-Atchafalaya River ($\sim 1.80 \times 10^{12}$ mol C yr$^{-1}$). These two DIC sources (air: $\sim 1.11 \times 10^{12}$ mol C yr$^{-1}$ plus river: $\sim 2.18 \times 10^{12}$ mol C yr$^{-1}$) is comparable to the DIC transported out of the GoM by the Loop Current ($\sim 3.30 \times 10^{12}$ mol C yr$^{-1}$, Wang et al., 2013). Such a balance cannot be achieved using the CO$_2$ flux estimated by Robbins et al., (2014). Nevertheless, here our intent is not to close the carbon budget, considering the large uncertainties involved and discussed below. Indeed, the ultimate CO$_2$ source and/or sink term would be dependent on the relative contribution of both DIC and nutrients to the upper layer of the ocean as well as the biogeochemical alteration therein (Dai et al., 2013).

We notice that, during summer months, our model simulated a higher surface $p$CO$_2$ than ship measurements on the NGoM Shelf (Fig.6a). As discussed in Section 5.1, a large part of the strong CO$_2$ degassing was simulated on the Texas Shelf. Yet a close examination of the distribution of available ship measurements indicates that data points on the Texas Shelf are fairly sparse and sporadic (Fig.5), which may partially explain the mismatch between model and ship measurements in Fig.6a. For instance, in the summer of 2010 when more ship measurements were available on the NGoM shelf, both model...
and observation indicated a high $p\text{CO}_2$ in the summer. In addition, $p\text{CO}_2$ in the Mississippi plume was very sensitive to river DIC inputs. Our specification of riverine DIC (e.g. alkalinity plus 50) was based on limited measurements and may not reflect the true seasonal and inter-annual variability of alkalinity-DIC relationship. The current model resolution (~5 km) may not be high enough to reproduce small-scale circulation patterns associated with the Mississippi River plume. The complexity of the food web and uncertainty in model parameterization (e.g. rudimentarily represented denitrification, remineralization, particular organic matters, the lack of phosphate and silicate components, etc.) warrants further investigation.

6. Summary

A coupled physical-biogeochemical model was used to hindcast surface $p\text{CO}_2$ in the GoM from January 2004 to December 2010. Favorable comparisons were found when validating model solutions against ship measurements on the Gulf-wide scale, indicating that this coupled model can reproduce observed $p\text{CO}_2$ variability in the GoM. Time series of spatially averaged $p\text{CO}_2$ for both shelf and open ocean waters exhibit significant seasonal variability, with high values in August and low values in February. Model-simulated $p\text{CO}_2$ values were elevated by 56 and 88 ppm for the entire Gulf and the NGoM shelf, respectively, when the biological sources and sinks of carbon were disabled (i.e., the no-biology run). Without biological processes, the GoM shifts to a strong carbon source with a outflux rate of 2.10 mol C m$^{-2}$ yr$^{-1}$. Another sensitivity test examining river conditions from the 1904-1910 period (reduced NO$_3$ and comparable DIC) supported the view that the impact of river inputs were mainly limited to the NGoM.
shelf, which under the conditions of the simulation acted as a CO\textsubscript{2} source with an outflux rate of 0.61 mol C m\textsuperscript{-2} yr\textsuperscript{-1}.

The Mississippi-Atchafalaya River plume is the dominant factor controlling the pCO\textsubscript{2} distribution on the NGOM Shelf. Although the NGOM Shelf is overall a CO\textsubscript{2} sink, high surface pCO\textsubscript{2} was simulated in relatively shallow waters, induced by both oversaturated plume water. pCO\textsubscript{2} in the open ocean is controlled largely by the low DIC high alkalinity Loop Current water from the Caribbean Sea.

Our model simulations characterize the GoM as an overall CO\textsubscript{2} sink, taking up \(1.11\pm0.84 \times 10^{12}\) mol C yr\textsuperscript{-1} from the air. Together with the enormous riverine input (\(2.18 \times 10^{12}\) mol C yr\textsuperscript{-1}), this inorganic carbon influx was comparable with the DIC export through the Loop Current estimated by an earlier study. More accurate model predictions of water column DIC concentration will require more in-situ data for improved specification of riverine DIC inputs, model DIC initial conditions, and further process studies to refine model parameterizations so as to better account for complex carbon dynamics in the coastal ocean.

Acknowledgement

Research support provided through the National Aeronautics and Space Administration (NNX10AU06G, NNX12AP84G, NNX14AO73G, and NNH13ZDA001N); National Science Foundation (OCE-0752254, OCE-0752110 and OCE-1559279); NOAA Grant NA11NOS0120033. The operational mode of the SABGOM model is located at [http://omgsrv1.meas.ncsu.edu:8080/ocean-circulation/](http://omgsrv1.meas.ncsu.edu:8080/ocean-circulation/). Data of daily nowcast/forecast model output is hosted at
Data used in all figures for the hindcast simulation can be obtained by contacting the corresponding author.


Fennel, K., Hetland, R., Feng, Y., and DiMarco, S.: A coupled physical-biological model of the Northern Gulf of Mexico shelf: model description, validation and analysis of phytoplankton variability, Biogeosciences, 8, 1881-1899, 2011.


Tsunogai, S., Watanabe, S., and Sato, T.: Is there a "continental shelf pump" for the

Uppström, L. R.: The boron/chlorinity ratio of deep-sea water from the Pacific Ocean, Deep Sea Research and Oceanographic Abstracts, 1974, 161-162,


Tables and Figures

Table 1. Comparison between observed and modeled air-sea CO$_2$ flux. Observations are taken from Robins et al (2014), whereas the model results are seven-year (2005-2010) model mean*.

<table>
<thead>
<tr>
<th>Subregions</th>
<th>Mexico Shelf</th>
<th>Western Gulf</th>
<th>Northern Gulf</th>
<th>West Florida Shelf</th>
<th>Open Ocean</th>
<th>Gulf-wide**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subregion Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(10$^{12}$ m$^2$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>0.97±0.29</td>
<td>-0.24±0.59</td>
<td>1.01±0.89</td>
<td>0.28±0.33</td>
<td>1.51±0.41</td>
<td>1.23±0.48</td>
</tr>
<tr>
<td>Summer</td>
<td>-0.96±0.38</td>
<td>-1.69±0.43</td>
<td>-1.42±0.74</td>
<td>-1.26±0.53</td>
<td>-0.33±0.33</td>
<td>-0.62±0.52</td>
</tr>
<tr>
<td>Fall</td>
<td>-0.76±0.45</td>
<td>-1.06±0.34</td>
<td>-0.79±0.63</td>
<td>-1.73±0.67</td>
<td>0.56±0.61</td>
<td>0.06±0.66</td>
</tr>
<tr>
<td>Winter</td>
<td>0.49±0.28</td>
<td>1.62±0.32</td>
<td>2.49±0.70</td>
<td>1.19±0.38</td>
<td>2.44±0.49</td>
<td>2.21±0.40</td>
</tr>
<tr>
<td>Annual</td>
<td>0.19±0.35</td>
<td>-0.34±0.42</td>
<td>0.32±0.74</td>
<td>-0.38±0.48</td>
<td>1.04±0.46</td>
<td>0.71±0.54</td>
</tr>
</tbody>
</table>

Robbins et al., 2014

<table>
<thead>
<tr>
<th></th>
<th>Annual</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.09±0.05</td>
<td>-0.18±0.05</td>
<td>0.44±0.37</td>
<td>-0.37±0.11</td>
<td>0.48±0.07</td>
<td>0.19±0.08</td>
</tr>
</tbody>
</table>

Simulation 2 (no-bio)

<table>
<thead>
<tr>
<th></th>
<th>Annual</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-2.77±0.36</td>
<td>-2.02±0.36</td>
<td>-1.64±0.68</td>
<td>-1.79±0.36</td>
<td>-2.08±0.39</td>
<td>-2.10±0.46</td>
</tr>
</tbody>
</table>

Simulation 3 1904-1910

<table>
<thead>
<tr>
<th></th>
<th>Annual</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.08±0.35</td>
<td>-0.77±0.77</td>
<td>0.61±1.07</td>
<td>0.55±0.46</td>
<td>0.86±0.46</td>
<td>0.50±0.65</td>
</tr>
</tbody>
</table>

*unit: mol m$^{-2}$ yr$^{-1}$, + indicates ocean is an air CO$_2$ sink; - indicates a CO$_2$ source to the atmosphere

**Gulf-wide value is a sum of all sub-regions.
Table 2. Spatial correlation coefficients between $pCO_2$, sea surface temperature (SST), sea surface salinity (SSS), dissolved inorganic nitrate (DIN: $NO_3^-+NH_4^+$), dissolved inorganic carbon (DIC), alkalinity (ALK), and primary production (P-Prod) on the Louisiana Shelf and in the open ocean (multi-year mean of 2005-2010, control run).

<table>
<thead>
<tr>
<th>Correlation Coefficient (R value)</th>
<th>SST</th>
<th>SSS</th>
<th>DIC</th>
<th>DIN</th>
<th>ALK</th>
<th>P-Prod</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$pCO_2$ on the NGoM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>-0.24</td>
<td>-0.81</td>
<td>-0.12</td>
<td>0.86</td>
<td>-0.77</td>
<td>0.36</td>
</tr>
<tr>
<td>Summer</td>
<td>0.63</td>
<td>-0.65</td>
<td>0.65</td>
<td>0.66</td>
<td>-0.17</td>
<td>0.35</td>
</tr>
<tr>
<td>Fall</td>
<td>-0.66</td>
<td>-0.87</td>
<td>0.86</td>
<td>0.78</td>
<td>0.17</td>
<td>0.58</td>
</tr>
<tr>
<td>Winter</td>
<td>-0.67</td>
<td>-0.89</td>
<td>0.45</td>
<td>0.89</td>
<td>-0.90</td>
<td>0.23</td>
</tr>
<tr>
<td>Annual</td>
<td>-0.64</td>
<td>-0.82</td>
<td>0.63</td>
<td>0.82</td>
<td>-0.65</td>
<td>0.47</td>
</tr>
<tr>
<td><strong>$pCO_2$ in open ocean</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>0.11</td>
<td>0.17</td>
<td>0.76</td>
<td>-0.27</td>
<td>-0.70</td>
<td>-0.41</td>
</tr>
<tr>
<td>Summer</td>
<td>-0.11</td>
<td>-0.11</td>
<td>0.99</td>
<td>-0.29</td>
<td>-0.91</td>
<td>-0.43</td>
</tr>
<tr>
<td>Fall</td>
<td>0.04</td>
<td>0.08</td>
<td>0.96</td>
<td>-0.77</td>
<td>-0.88</td>
<td>-0.76</td>
</tr>
<tr>
<td>Winter</td>
<td>0.04</td>
<td>-0.05</td>
<td>0.75</td>
<td>-0.49</td>
<td>-0.69</td>
<td>-0.55</td>
</tr>
<tr>
<td>Annual</td>
<td>-0.17</td>
<td>0.05</td>
<td>0.93</td>
<td>-0.50</td>
<td>-0.85</td>
<td>-0.59</td>
</tr>
</tbody>
</table>
Figure 1. Domain of the South Atlantic Bight and Gulf of Mexico (SABGOM) ROMS model with water depth in color (unit: m). Also shown are the five sub-regions used in this study, which are Mexico Shelf (MX), Western Gulf of Mexico Shelf (WGoM), Northern Gulf of Mexico Shelf (NGoM), West Florida Shelf (WF), and open ocean. Also shown is a schematic for the Loop Current.
Figure 2. DIC and alkalinity initial conditions derived from the empirical relationship by Lee et al. (2000 and 2006).
Figure 3. Satellite observed monthly $pCO_2$ (AIRS) averaged over the Gulf of Mexico (red stars) and the $pCO_2$ air used in model air-sea CO$_2$ flux calculation (blue line), which is generated using the curve-fitting software CCGCRV.
Figure 4. Comparisons between the 2005-2010 riverine DIC and NO$_3$ conditions observed by USGS (red line) and the 1904-1910 river condition simulated by the Dynamic Land Ecosystem Model (black line, Tian et al., 2015).
Figure 5. Locations of in-situ measurements from the LDEO database (blue) and Huang et al. (2015, grey) in the period of 2005-2010.
Figure 6. Time series of spatially averaged $p$CO$_2$ (control run in blue and no-biology run in red) (a) on the Northern Gulf of Mexico shelf, and (b) in the entire Gulf of Mexico, overlaid with in situ observations (in black) from Huang et al. (2015a and b), and Takahashi et al. (2015).
Figure 7. Six-year (2005-2010) model (control run) mean air-sea CO\textsubscript{2} flux in the Gulf of Mexico during (a) spring, (b) summer, (c) fall, and (d) winter. Blue color indicates where the ocean is a sink for CO\textsubscript{2}; red color indicates where the ocean is a source.
Figure 8. Six-year (2005-2010) model (control run) mean surface Net Community Production (NCP) in the Gulf of Mexico during (a) spring, (b) summer, (c) fall, and (d) winter.
Figure 9. Time series of spatially averaged Net Community Production (a) on the Northern Gulf of Mexico shelf, and (b) in the entire Gulf of Mexico (unit: mmol N/m$^3$).
Figure 10. Multiyear (2005-2010) seasonal mean $p\text{CO}_2$ elevation (No-biology run minus control run, in the Gulf of Mexico during (a) spring, (b) summer, (c) fall, and (d) winter.
Figure 11. Scatter plots of the multiyear mean $p$CO$_2$ drop (No-biology run minus Control run) and surface NCP in NGoM (left) and Open Ocean (right).
Figure 12. Differences in model simulated primary production and $pCO_2$ between the 2004-2010 and the 1904-1910 periods (2005-2010 minus 1905-1910 seasonal mean condition). For a) and c) blue color indicates increased primary production during 2004-2010, for b) and d) red color indicates reduced $pCO_2$ during 2004-2010.
Figure 13. Six-year mean (2005-2010) surface conditions simulated by the model for a) $p$CO$_2$ (ppm), b) temperature (degree C), c) salinity, d) dissolved inorganic carbon (mmol C m$^{-3}$), e) dissolved inorganic nitrogen (NO$_3$+NH$_4$) (mmol N m$^{-3}$), and f) alkalinity (mEq m$^{-3}$).
Figure 14. Six-year (2005-2010) spring-summer mean condition of model simulated sea surface \( pCO_2 \) and DIC against salinity for the control run (a and c) and no-biology run (b and d) on the NGoM Shelf; also shown are longitude with colors (note that the Mississippi river delta is located around 89°W and Atchafalaya river delta is located around 91°W). Also shown in c) and d) are conservative mixing relationships for river end members from Cai et al. (2011a).
Supplementary Materials

S1. Calculation of seawater $pCO_2$

The seawater $pCO_2$ was calculated following Zeebe and Wolf-Gladrow (2001) as follows:

$$pCO_2 = \frac{DIC[H^+]}{([H^+]^2 + K_1[H^+] + K_1 K_2)/f}$$  \hspace{1cm} (1)

where DIC is the dissolved inorganic carbon and was given by model input. $K_1$ and $K_2$ are constant of carbonic acid, $K_1 = [H^+] [HCO_3^-]/[H_2CO_3]$, $K_2 = [H^+] [CO_3^{2-}]/[HCO_3^-]$ and were calculated following Millero (1995) using data from Mehrbach et al. (1973) as follows:

$$\log K_1 = 62.008 - 1/T \times 3670.7 - \log T \times 9.7944 + S \times (0.0118 - S \times 0.000116)$$  \hspace{1cm} (2)

$$\log K_2 = -4.777 - 1/T \times 1394.7 - \log T \times 9.7944 + S \times (0.0184 - S \times 0.000118)$$  \hspace{1cm} (3)

where in (2) and (3) the $T$ is for water temperature (unit: K) and $S$ is for salinity;

The $f$ in (1) is the correction term for non-ideality and was calculated from Weiss and Price (1980) using equation 13 with 6 values. $[H^+]$ is solved using the 5th order polynomial bracket and bisection method with the following 5 coefficients:

$$p5 = 1;$$  \hspace{1cm} (4)

$$p4 = -Alk - K_b - K_1;$$  \hspace{1cm} (5)

$$p3 = DIC * K_1 - Alk * (K_b + K_1) + K_b * borate + K_b *borate + K_1 * K_1 * K_2;$$  \hspace{1cm} (6)

$$p2 = DIC * (K_b * K_1 + 2 * K_1 * K_2) - Alk * (K_b * K_1 + K_1 * K_2) +$$
\( K_b*borate*K_1+(K_w*K_b+K_w*K_1-K_b*K_1*K_2); \) \( \text{ (7)} \)

\[ p1=2*DIC*K_b*K_1*K_2-Alk*K_b*K_1*K_2+K_b*borate*K_1*K_2+ \\
K_w*K_b*K_1+K_w*K_1*K_2; \] \( \text{ (8)} \)

\[ p0=K_w*K_b*K_1*K_2; \] \( \text{ (9)} \)

where \( Alk \) is for total alkalinity (unit: milli-equivalent per liter) and was given by model input; \( K_w \) is ion product of water \( ([H^+] *[OH^-]) \) and \( K_b \) is the constant of boric acid \( ([H^+] *[BO_2^-])/[HBO_2^-]) \), which were calculated following Millero (1995):

\[ \ln K_b = -8966.90+2890.51*S^{0.5}-77.942*S+1.726*S^{1.5}-0.0993*S^2/T \]

\[ + (148.0248+137.194*S^{0.5}+1.62247*S \]

\[ + (-24.4344-25.085*S^{0.5}-0.2474*S)*\ln T+0.053105*S^{0.5} \ln T) \] \( \text{ (10)} \)

\[ \ln K_w = 148.9802-13847.26/T-23.6521*\ln T \]

\[ + (-0.977+118.67/T+1.0495*\ln T)*S^{0.5}-0.01615*S) \] \( \text{ (11)} \)

and borate stands for the concentrations for borate and was calculated following Uppstrom (1974):

\[ borate=0.000232*S/1.80655/10.811 \] \( \text{ (12)} \)
S2. Model initial and boundary condition setup for Dissolved Inorganic Carbon (DIC) and alkalinity

The initial and boundary conditions for DIC follow the relationship between DIC and Sea Surface Temperature (SST) for the western (sub)tropical Atlantic waters described in Lee et al., 2000 as follows:

\[ DIC = 1940 + 1.842 \times (SST - 29) + 0.468 \times (SST - 29)^2 \]  \hspace{1cm} (13)

For alkalinity, we use the relationship among DIC and SST and Sea Surface Salinity (SSS) for the sub(tropical) waters described in Lee et al., 2006 as follows:

\[ Alkalinity = 2305 + 58.66 \times (SSS - 35) + 2.32 \times (SSS - 35) \times (SSS - 35) - 1.41 \times (SST - 20) + 0.040 \times (SST - 20) \times (SST - 20) \]  \hspace{1cm} (14)
**S3. Air-Sea CO\textsubscript{2} flux calculation**

The air-sea CO\textsubscript{2} flux was calculated following Wanninkhof (1992) as follows:

\[ F = K \cdot (pCO\textsubscript{2\ air} - pCO\textsubscript{2\ water}) \]  
(15)

where \( pCO\textsubscript{2\ air} \) is the air \( pCO\textsubscript{2} \), and \( pCO\textsubscript{2\ water} \) was calculated from (1); \( F \) is the air-sea CO\textsubscript{2} flux (unit: millimole C m\textsuperscript{-2} day\textsuperscript{-1});

\[ K = kL \]  
(16)

where \( L \) is the solubility of CO\textsubscript{2} and was calculated following Weiss (1974) as follows:

\[ \ln L = -60.2409 + 93.4517/T + 23.3585 \cdot \log(T) + S \cdot (0.023517 + T \cdot (-0.023656 + 0.0047036 \cdot T)) \]  
(17)

and the \( k \) in (14) is the gas transfer velocity and was calculated using

\[ k = 0.31 u^2 \cdot (Sc/660)^{-0.5} \]  
(18)

where \( u \) is the wind speed at 10 m above sea-level from the North America Regional Reanalysis dataset; \( Sc \) is the Schmidt number and was set to

\[ Sc = 2073.1 - 125.62 \cdot T + 36276 \cdot T^2 - 0.043219 \cdot T^3 \]  
(19)