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Modeling pCO_2 variability in the Gulf of Mexico

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Abstract

A three-dimensional coupled physical–biogeochemical model was used to simulate and examine temporal and spatial variability of surface pCO_2 in the Gulf of Mexico (GoM). The model is 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 was validated against in situ measurements. The model revealed clear seasonality in surface pCO_2. Based on the multi-year mean of the model results, the GoM is an overall CO_2 sink with a flux of 1.34×10^{12} mol C yr^{-1}, which, together with the enormous fluvial carbon input, is balanced by the carbon export through the Loop Current. A sensitivity experiment was performed where all biological sources and sinks of carbon were disabled. In this simulation surface pCO_2 was elevated by ~70 ppm, providing the evidence that biological uptake is a primary driver for the observed CO_2 sink. The model also provided insights about factors influencing the spatial distribution of surface pCO_2 and sources of uncertainty in the carbon budget.

1 Introduction

Human consumption of fossil fuels has induced a continuous increase of atmospheric CO_2 concentration, since the Industrial Revolution began around 1750. Projected pCO_2 by the end of 21st century (970 ppm, in A1F1 scenario, IPCC 2001) could be nearly triple the present level. Oceans play an important role in regulating the global carbon cycle not only as receivers of the enormous carbon loading from coastal rivers (Cai, 2011; 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 is rather complicated and shows contrasting behaviors in different locations (coastal vs. open ocean, low latitude vs. high latitude, etc.) and during dif-

ferent 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.

Our study focuses on the carbon cycle in the Gulf of Mexico (GoM). One unique feature of the gulf environment is that it receives enormous riverine nutrient and carbon inputs, the majority of which are from the Mississippi/Atchafalaya River system. Excessive nutrient and carbon 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., 2011). However, the carbon budget associated with such enormous terrestrial carbon and nutrient inputs still remains unclear: on the one hand extensive riverine carbon input results in over-saturated coastal waters, which serve as a CO_2 source to the atmosphere (e.g. Lohrenz et al., 2010; Guo et al., 2012); on the other hand, although the Mississippi River Plume region is a heterotrophic system that breaks down organic carbon (Murrell et al., 2013), enhanced primary production in the river plume due to significant inputs of inorganic nutrients would introduce a net influx of CO_2. Further offshore, the circulation in the GoM is largely influenced by the energetic Loop Current. Large anticyclonic eddies periodically pinch off from the Loop Current (Sturges and Leben, 2000) and, along with the cross-shelf circulation driven by wind and other meso-scale and submesco-scale coastal 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 significant dissolved inorganic carbon (DIC, $\sim 3.30 \times 10^{12}\,\mathrm{mol\,C\,yr^{-1}}$) export from the GoM shelf to the Loop Current waters (Wang et al., 2013).

While global inorganic carbon budgets have been made available through joint seawater CO_2 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 resolve the GoM (Gledhill et al., 2008). Regional carbon assessments for the

GoM were made recently based on limited in situ observations (e.g. Cai, 2003; Lohrenz et al., 2010; Huang, 2013 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 present in the observations (e.g. Coble et al., 2010; Hofmann et al., 2011; Robbins et al., 2014). In this regard, coupled physical–biogeochemical models capable of representing the biogeochemical cycle with realistic physical settings (e.g., ocean mixing and advection) provide an alternative means for the budget assessment.

Here we present a pCO_2 analysis for the GoM based on the results of a coupled physical–biogeochemical model simulation. Our objective is to quantify the pCO_2 flux at the air–sea interface (which at present is highly uncertain when based on observational analyses alone), with specific emphasis on 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). The circulation component of the coupled model is the Regional Ocean Modeling System (ROMS, Haidvogel et al., 2008; Shchepetkin and McWilliams, 2005) and is coupled with the biogeochemical module described in Fennel et al. (2006, 2008, and 2011). A seven year (1 January 2004–31 December 2010) hindcast was performed with the system, driven by realistic atmospheric forcing (North America Regional Reanalysis, www.cdc.noaa.gov), open boundary conditions 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; Nixon, 1996). Model validations (physics, nutrients and chlorophyll) and a nitrogen budget have been reported in Xue et al. (2013).

In this study we focus on the carbon cycle in the GoM. As before, we considered the first year of the simulation (2004) as model spin-up; all results presented here are for 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. pCO_2, carbonate ion concentration, bicarbonate ion concentration, and pH; Zeebe and Wolf-Gladrow, 2001). The initial and open boundary conditions of DIC and alkalinity in the open ocean (> 200 m water depth) are prescribed based on their relationship with salinity and temperature as derived by Lee et al. (2000, 2006). In the coastal and shelf waters (< 200 m), initial values of DIC and alkalinity were defined using a relationship among salinity, DIC and alkalinity based on data collected on the Louisiana Shelf (Cai, 2011). The carbon cycle parameterization used in the hindcast followed the same approach and values as in Fennel et al. (2008), Fennel and Wilkin (2009) and Fennel (2010).

To account for riverine input into the model domain, we constructed climatological monthly time series of alkalinity by averaging all available US Geological Survey alkalinity observations for each major river. Because direct riverine DIC measurements were not available, we approximated river DIC input using the corresponding alkalinity value plus 50, following 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}, comparable with the estimation in Cai, 2003). The gas exchange calculation followes Wanninkhof (1992). The temporal variation of air pCO_2 is prescribed using the following curve-fitting model provided by the Cooperative Global Atmospheric Data Integration Project:

$$pCO_{2\,air}\_secular = 282.6 + 0.125 \times pmonth \times 12 - 7.18 \times \sin(pi2 \times pmonth + 0.86) - 0.99 \times \sin(pi2 \times pmonth + 0.28) - 0.80 \times \sin(pi2 \times pmonth + 0.06) \quad (1)$$

where $pCO_{2\,air}$_secular represents the secular monthly air pCO_2; pmonth represents the months since January 1951, and pi2 is a constant equal to 6.28. Air pCO_2 was set to be spatially uniform.

3 Results

In this section, we present model-simulated sea surface pCO_2 and model-estimated air–sea CO_2 flux in different sub-regions of the GoM. In situ data from various sources were included for model validation. Because large pCO_2 gradients were found in both in-situ data and model in shallow waters, in-situ and model data for waters with < 10 m depth were excluded.

3.1 Sea surface pCO_2

Spatially averaged model-simulated pCO_2 on the Louisiana Shelf exhibited clear seasonality, with large values (~ 500 ppm) around August and smallest values (~ 350 ppm) around February (Fig. 1a, area map see Fig. 2). Gulf-wide spatially averaged pCO_2 (Fig. 1b) had a temporal pattern similar to that on the Louisiana Shelf, with high pCO_2 values (~ 450 ppm) in August and low values (~ 250 ppm) in February. The pCO_2 on the Louisiana Shelf was generally 100 ppm higher than that in the entire gulf.

For model validation, we used in situ measurements collected on the Louisiana Shelf (Huang, 2013; Huang et al., 2013). These ship-based observations were taken in October 2005; April, June, August 2006; May, August 2007; January, April, July, November 2009; and March 2010, respectively. To alleviate the spatial and temporal heterogeneity associated with these in-situ data (see Huang, 2013 for data distribution), we overlaid the mean value of in situ measurements during each survey over the model-simulated pCO_2 time series (Fig. 1a). On the Louisiana Shelf, our model was able to capture the measured pCO_2 in 6 out of the 11 cruises. Specifically, agreement between model and observations was better during spring, including April 2006, May 2007,

April 2009, and March 2010, than summer, including June 2006, August 2007, and July 2009, when pCO_2 was overestimated. The overall overestimated pCO_2 during summer months will be discussed later.

On a gulf-wide extent, the LDEO in situ data were grouped by a 10 day temporal window (> 180 000 data points gulf-wide during 2005–2010; Takahashi et al., 2013) and overlaid on the spatially averaged pCO_2 time series for the entire gulf (Fig. 1b). The in situ data exhibited a similar seasonality with that reproduced by the model and 32 out of the 40 data groups were within one standard deviation of the modeled time series. The above-mentioned comparisons indicate that our coupled physical–biogeochemical model is capable of resolving gulf-wide seasonal and intra-annual variations in observed pCO_2, allowing us to use this seven-year hindcast to further characterize the air–sea CO_2 flux.

3.2 Air–sea CO_2 flux

To facilitate our description of the air–sea CO_2 flux, the GoM was divided into five sub-regions: (1) Mexico Shelf, (2) Texas Shelf, (3) Louisiana Shelf, (4) West Florida Shelf, and (5) open ocean (Fig. 2; following the regional definitions in Benway and Coble, 2014).

Based on model simulations, the GoM was characterized as an overall CO_2 sink with a multi-year mean (2005–2010) carbon flux rate of 0.86 mol C m^{-2} yr^{-1} ($\sim 1.34 \times 10^{12}$ mol C yr^{-1}, Table 1 and Fig. 2). Examining region by region, we see that the open ocean, occupying ~ 65 % of the GoM in area, acts as a CO_2 sink (1.06 mol m^{-2} yr^{-1} of C) during most of the year except in summer. The greatest carbon uptake occurred in winter (2.24 mol C m^{-2} yr^{-1}). From a closer examination of the CO_2 flux map, it was evident waters around the Loop Current were a continuous sink, while the western part of the open ocean shifted between acting as a source in summer and fall and 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 Mexico Shelf has the largest area. It acted as a strong carbon sink in winter and spring (2.25 and 1.76 mol C m^{-2} yr^{-1}) and a weaker sink in summer and fall (0.03 and 0.31 mol C m^{-2} yr^{-1}). Waters along the eastern side of the Mexico Shelf were a sink during most of the year, while to the west the ocean was a source in summer and fall. On a yearly scale, this region was a sink with an air–sea flux of 1.09 mol C m^{-2} yr^{-1}. To the north, the Texas Shelf has the smallest area among the four shelf sub-regions. It acted as a CO_2 source during spring, summer, and fall (−0.03, −1.15 and −0.46 mol C m^{-2} yr^{-1}) and a strong sink during winter (1.89 mol C m^{-2} yr^{-1}). On a yearly scale this region was a weak CO_2 sink with an air–sea flux of 0.06 mol C m^{-2} yr^{-1}.

The Louisiana Shelf shifted between acting as a CO_2 source in summer and fall (−1.47 and −0.41 mol C m^{-2} yr^{-1}) and a sink in winter and spring (2.59 and 0.99 mol C m^{-2} yr^{-1}). The most prominent feature here is the continuous, strong degassing in the coastal waters around the Mississippi–Atchafalaya River mouths. The open shelf shiftedfrom acting as a sink during winter and spring to a source during summer and fall. Despite the extensive degassing in the coastal water, the Louisiana Shelf overall was a CO_2 sink on a yearly basis (0.42 mol C m^{-2} yr^{-1}). Similarly, the West Florida Shelf also shifted from acting as a CO_2 source in summer and fall (−1.06 and −1.28 mol C m^{-2} yr^{-1}) to a sink in winter and spring (1.41 and 0.49 mol C m^{-2} yr^{-1}). The degassing in the inner shelf is strong enough to make the West Florida Shelf a CO_2 source on a yearly basis (−0.11 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) the 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 estimation agrees with the 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 on the Mexico Shelf and in the open ocean, which can be attributed to the spatial and

temporal heterogeneity of the in situ dataset (see distributions in Takahashi et al., 2013) and warrants further investigation.

3.3 No-bio simulation

To test biological processes' role in regional pCO_2 variability, a no-bio simulation was conducted, where all biology sources and sinks of DIC and alkalinity were disabled similar to the experiment described in Fennel and Wilkin (2009). Surface pCO_2 was elevated in the no-bio simulation where the biological sources and sinks of carbon were disabled. The multi-year mean pCO_2 was increased from 402.1 to 453.3 ppm for the Louisiana Shelf and from 358.0 to 428.2 ppm for the entire gulf (Fig. 1). Nevertheless, such pCO_2 increase was not temporally uniform. Specifically on the Louisiana Shelf, pCO_2 increases in the no-bio simulation was clear higher during spring-summer than during fall-winter. For air–sea flux, the elevated surface pCO_2 (~ 70 ppm for the entire gulf) turn all five sub-regions into to a strong carbon source, resulting in a net outflux of 1.57 mol C m^{-2} yr^{-1} (Table 1).

4 Discussion

This study provides an unprecedented model simulation of carbon fluxes and exchanges in the Gulf of Mexico. Until recently, carbon dynamics in the Gulf of Mexico have been poorly characterized and represented a large source of uncertainty in regional carbon budgets. Here, we examine the model-simulated spatial and temporal patterns in air–sea flux of CO_2 and discuss the factors controlling pCO_2 variability in different subregions of the GoM with specific focus on the river-influenced Louisiana Shelf and the Loop Current-influenced open ocean. The relationship between pCO_2 and other hydrographic variables are also considered.

4.1 Factors controlling spatial distribution of surface pCO_2

The Mississippi–Atchafalaya River and associated plume play the most important role in determining the pCO_2 distribution on the Louisiana Shelf. A large input of fluvial DIC and alkalinity introduce carbonate saturation in the coastal waters, conversely, nutrients from the river enhance local primary production, which results in DIC removal and thus reduces seawater pCO_2 (e.g. Lohrenz et al., 2010; Guo et al., 2012; Huang, 2013; Huang et al., 2013). Although the river plume's influence on the CO_2 flux has been addressed by observational studies, large uncertainties, mainly resulting from the relatively sporadic measurement, were also found regarding whether the Louisiana Shelf is a CO_2 sink or source over a longer time period. For instance, Huang et al. (2013) found a large difference between the pCO_2 distributions in April 2009 and in March 2010, which was attributed to the variations in river plume extent influenced by different local wind conditions.

Model results in this study reveal significant spatial and temporal gradients in pCO_2 as well. Our model-simulated multi-year mean (2005–2010) distribution of pCO_2 was characterized by relatively high values in the coastal waters on the Louisiana Shelf (Fig. 3a) accompanied by low salinities (Fig. 3c), high DIN and high DIC (Fig. 3d and e). In contrast, the pCO_2 value on the open shelf was significantly lower, thus making it a CO_2 sink during most time of the year (Fig. 2a–d). On the shelf-scale the pCO_2 distribution was highly correlated with surface salinity (r value: −0.81) and DIN concentration (r value: 0.80) throughout the year, while relationships to surface temperature and DIC concentration were significant only for part of the year (detailed season-by-season correlation see Table 2). Previous studies have reported that during high flow seasons, high concentrations of nutrients in the plume water stimulate primary production, resulting in a pCO_2 removal through the biological pump (e.g., Lohrenz et al., 2010), which was confirmed by the elevated pCO_2 value in the no-bio simulation in this study. Although our model suggests that on the Louisiana Shelf the pCO_2 distribution was positively correlated with DIN concentration, this is not contrary to findings of

the above-mentioned observational studies; the high DIN concentration, together with the low salinity, is a signal of the river plume. In other words, on a yearly scale model results indicate the spatial distribution of surface pCO_2 is mostly dominated by the extent of the oversaturated plume water (low salinity and high DIN), which degases more CO_2 despite high primary production. This also explains why our model suggests the Louisiana Shelf is a CO_2 source instead of a sink during summer months when primary production is high (Table 1 and Fig. 2). However, caution should be taken as our model seems to overestimate surface pCO_2 during summer months (Fig. 1a), which can be attributed to: (1) the spatial and temporal heterogeneity of the in situ measurements, (2) current model solution (~ 5 km) may not be high enough to reproduce small scale circulation patterns associated with the Mississippi River plume; and (3) the complexity of the food web and uncertainty in model parameterization (e.g. rudimentarily represented particular organic matters, the lack of phosphate and silicate components, etc.).

In the open ocean, the distribution of surface pCO_2 is largely determined by that of DIC (r value: 0.96) and alkalinity throughout the year (r value: −0.81, detailed season-by-season correlation see Table 2), while the influence from DIN and primary production is limited to fall and winter months when wind-induced upwelling is strong (Xue et al., 2013 and references therein). The dependence of pCO_2 on DIC and alkalinity makes the transport of water from the Caribbean Sea through the Yucatan Channel an important factor in the regional air–sea CO_2 flux. In addition to high temperature, the Caribbean waters are also characterized by low DIC and high alkalinity (Wang et al., 2013 and references therein). In the GoM, the multi-year mean sea surface temperature shows a persistent warm water mass in the form of the LC (Fig. 3b), which carries the signal of carbonate characteristics of Caribbean water (i.e. low DIC and high alkalinity, Fig. 3e and f). Surface pCO_2 in this warm water mass is significantly lower than in the surrounding waters (Fig. 3a), making the Loop Current a strong carbon sink throughout the year (Fig. 2a–d). In other words, any changes in the Caribbean water's

carbonate characteristics will affect the carbon budget in the GoM as well as waters further downstream along the Gulf Stream.

4.2 Uncertainty in carbon budget estimation

Based on our model-simulations, we conclude that the GoM is an overall CO_2 sink, taking up 1.34×10^{12} mol C yr^{-1} from the air. This estimation is comparable to those based on in situ observations, e.g. 1.48×10^{12} mol C yr^{-1}, (Coble et al., 2010) and 0.30×10^{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 (1.58×10^{12} mol C yr^{-1}, the GoM and Caribbean Sea combined). In addition, we estimate that the GoM receives $\sim 2.18 \times 10^{12}$ mol C yr^{-1} from rivers ($\sim 1.80 \times 10^{12}$ mol C yr^{-1} from the Mississippi/Atchafalaya River). These two DIC sources (air: $\sim 1.34 \times 10^{12}$ mol C yr^{-1} plus river: $\sim 2.18 \times 10^{12}$ mol C yr^{-1}) largely balance 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).

We note that although the model generates estimates of the DIC flux through the Yucatan Channel and Florida Straits, large uncertainties remain with regard to quantifying the DIC concentration in the water column. Similar to the situation reported by Hofmann et al. (2011), we found the model-simulated DIC concentration in the water column to be very sensitive to the initial conditions. Although there are historical measurements in the GoM, the majority of these data are limited to the Louisiana Shelf. In our model, we calculated the initial and open boundary conditions of DIC and alkalinity for the open ocean using the empirical relationship in Lee et al. (2000 and 2006), which was derived based on measurements of the surface ocean. In addition, the large gradient in observed pCO_2 in the shallow water as well as the discrepancy between simulated and observed values during summer months on the Louisiana Shelf warrants further investigation.

5 Summary

A coupled physical–biogeochemical model was used to hindcast surface pCO_2 in the GoM from January 2004 to December 2010. Favorable comparisons were found when validating model solutions against in situ measurements on a gulf-wide extent, indicating that this coupled model can reproduce observed pCO_2 variability in the GoM. Time series of spatially averaged pCO_2 for both shelf and open ocean waters exhibit significant seasonal variability, with high values in August and low values in February. Model simulated pCO_2 is elevated by ~ 70 ppm when the biological sources and sinks of carbon were disabled (i.e., the no-bio simulation) and the GoM shifted to a strong carbon source with a outflux of 1.57 mol C m^{-2} yr^{-1}. Model-estimated air–sea CO_2 flux exhibited large spatial variability as well, with highest pCO_2 on the Louisiana shelf. While the Mississippi/Atchafalaya River plume is the dominant factor controlling the pCO_2 distribution on the Louisiana Shelf, pCO_2 in the open ocean is controlled mostly by DIC and alkalinity throughout the year as well as DIN and associated primary production during fall and winter months.

Our model simulations characterize the GoM as an overall CO_2 sink, taking up ~ 1.34×10^{12} mol C yr^{-1} from the air. Together with the enormous riverine input (~ 2.18×10^{12} mol C yr^{-1}), this carbon influx is largely balanced by carbon export through the Loop Current in agreement with estimates from previous observational studies. More accurate model predictions of water column DIC concentration will require more in-situ data for improved specification of model DIC initial conditions, and better model parameterizations accounting for complex carbon dynamics around the Mississippi River plume.

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Table 1. Multi-year mean (2005–2010) of model-simulated air–sea CO_2 flux against the estimation based on in situ measurements[a].

		Sub-regions					Gulf-wide[b]
		Mexico Shelf	Texas Shelf	Louisiana Shelf	West Florida Shelf	Open Ocean	
Subregion Area (10^{12} m^2)		0.18	0.08	0.15	0.15	1.01	1.56
Model (control run)[a]	Spring	1.76	−0.03	0.99	0.49	1.36	1.23
	Summer	0.03	−1.15	−1.47	−1.06	−0.09	−0.39
	Fall	0.31	−0.46	−0.41	−1.28	0.81	0.42
	Winter	2.25	1.89	2.59	1.41	2.24	2.19
	Annual	**1.09**	**0.06**	**0.42**	**−0.11**	**1.06**	**0.86**
Observation[c]	**Annual**	**0.09**	**0.18**	**0.44**	**−0.37**	**0.48**	**0.19**
Model (no-bio simulation)	Annual	−1.43	−1.28	−0.97	−1.06	−1.75	−1.57

[a] Unit: mol m^{-2} yr^{-1}, + indicates ocean is a CO_2 sink.
[b] Gulf-wide value is a sum of all sub-regions.
[c] From Robbins et al. (2014).

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).

Correlation Coefficient (R value)		SST	SSS	DIC	DIN	ALK	P-Prod
pCO_2 on the Louisiana Shelf	Spring	−0.23	**−0.81**	−0.03	**0.84**	−0.79	0.38
	Summer	0.67	**−0.60**	0.67	**0.65**	−0.23	0.37
	Fall	−0.72	**−0.88**	0.86	**0.73**	−0.04	0.55
	Winter	−0.74	**−0.87**	0.51	**0.86**	−0.90	0.22
	Annual	−0.69	**−0.81**	0.66	**0.80**	−0.68	0.47
pCO_2 in open ocean	Spring	−0.03	0.06	**0.87**	−0.25	**−0.73**	−0.38
	Summer	−0.18	−0.16	**0.99**	−0.34	**−0.82**	−0.39
	Fall	−0.03	0.01	**0.98**	−0.79	**−0.82**	−0.78
	Winter	−0.16	−0.14	**0.88**	−0.53	**−0.76**	−0.62
	Annual	−0.25	−0.04	**0.96**	−0.52	**−0.81**	−0.60

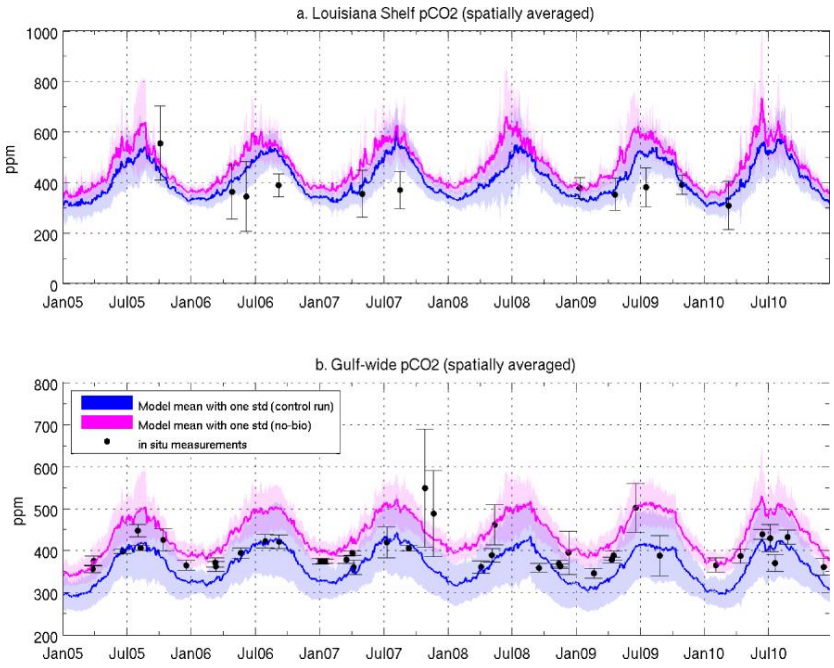

Figure 1. Time series of spatially averaged pCO_2 (control run in pink and no-bio simulation in blue) **(a)** on the Louisiana shelf, and **(b)** in the entire Gulf of Mexico, overlaid with in situ observations (in red) from Huang (2013), Huang et al. (2013), and Takahashi et al. (2013).

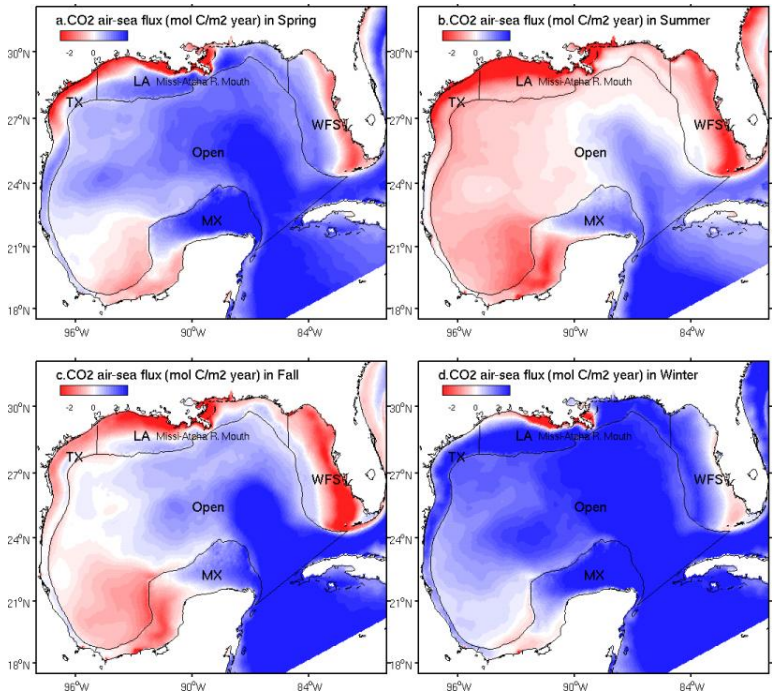

Figure 2. Multi-year mean (2005–2010) of model-simulated air–sea CO_2 flux in the Gulf of Mexico (control run) during **(a)** spring, **(b)** summer, **(c)** autumn, and **(d)** winter. Blue color indicates where the ocean is a sink for CO_2; red color indicates where the ocean is a source. TX = Texas Shelf, LA = Louisiana Shelf, WFS = West Florida Shelf, MX = Mexico Shelf, and Open = open ocean.

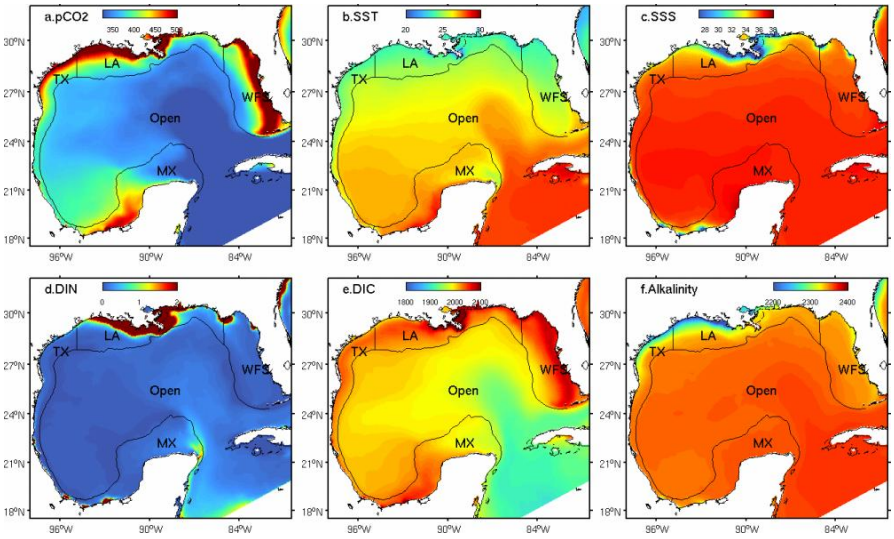

Figure 3. Multi-year mean (2005–2010) conditions simulated by the model for **(a)** pCO_2 (ppm), **(b)** sea surface temperature (degree C), **(c)** sea surface salinity (psu), **(d)** dissolved inorganic nitrogen ($NO_3 + NH_4$) (mmol N m^{-3}), **(e)** dissolved inorganic carbon (mmol C m^{-3}), and **(f)** alkalinity (mEq m^{-3}).