Nov 15th, 2015

Dear Editor and Reviewers:

First of all, we would like to thank you for your constructive comments and suggestions, which guided us to improve this manuscript We believe we have satisfactorily addressed your questions and comments in this revision. Specifically, we

1. Further investigated model sensitivity to various initial and boundary condition information and largely improved model results.

2. Updated air pCO_2 using satellite observation by NASA ARIS sensor. Due to the relative coarse resolution of the gridded data (2.5*2 degree), we fit the pCO_2 curve based on the mean value of all available grid points within the Gulf of Mexico and applied the air pCO2 in the CO2 flux calculation;

3. Performed experiments to test the model's sensitivity to the DIC/Alkalinity boundary conditions and found our model was less sensitive to boundary conditions (<5% variability) than the initial conditions;

4. Added details and formulas of the carbonate calculation, including how seawater pCO_2 and air-sea CO_2 flux was calculated in the supplementary materials;

5. Updated the model validation source suing the most updated version of the LDEO database (V2014). Simulated pCO_2 time series is able to capture 21 out of the 26 data groups on the Northern Gulf of Mexico Shelf and 24 out of the 26 data groups gulf-wide;

6. Added one more sensitivity test using river condition simulated by DLEM model for the period of 1904-1910 to connect coastal ecosystem with climate and land use changes within the Mississippi River basin;

7. Added seven new figures for model domain (now Fig.1), DIC/alkalinity initial conditions (Fig.2), air pCO2 curve (Fig.3), riverine inputs (Fig.4), distribution of available measurements (Fig.5), results condition of the 1904-1910 simulation (Fig.8), and salinity-pCO2 curve on the shelf (Fig. 10);

8. Updated all contexts and tables accordingly.

We hope you will find this revision satisfactory for publication in Biogeosciences. Attached please find (1) our responses (in bold) to the reviewers' comments (in italic), as enclosed below; and (2) a copy of our revised manuscript with all revisions since the last submission marked out.

Regards,

Z. George Xue

Response to Comments from Reviewer #1

1. The initial and boundary conditions for DIC simulation are questionable. The model uses empirical relationships between carbon terms and temperature or salinity to estimate initial and boundary conditions for DIC, which could somehow confound the anthropogenic CO2 signal in the model. For the initial condition, this kind of estimation should come from the relationship derived in the initial model year, that is, if the model starts in 2004, then the DIC-Temp or DIC-Salt-Temp relationship needs to come from 2004. Climatological DIC-Temp or DIC-Salt-Temp relationships are not appropriate for anthropogenic CO2 simulation, especially when the model tries to resolve interannual variations. If you use climatological relationships, you need to spin up the model much longer instead of one year. This is even more important for boundary conditions. Using a fixed relationship between DIC and temperature or salinity for boundary cannot accurately resolve the anthropogenic signal coming into the model domain, which can further introduce large errors for pCO2 and CO2 flux calculations. I believe the authors already realize the importance of initial conditions for DIC and alkalinity in the biological model simulation.

We notice that the model results were sensitive to DIC and alkalinity initial and boundary conditions. Indeed we also pointed out this in last submission. Although there are many historical measurements in the Gulf, the majority of these data points were limited to the northern Gulf regions and thus are insufficient to initialize the model. In our revision, 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) provided the best model-data comparison. For the open boundary condition, we found simulated surface pCO2 exhibited very limited variance (<5%) regardless 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). In addition, although the salinity-temperature-DIC-alkalinity was fixed through the simulation period, the salinity and temperature were extract from a global model and were time-dependent.

2. The model uses a fitting curve to represent atmospheric pCO2. Although the spatial variability of atmospheric pCO2 is much smaller the oceanic pCO2, has this relationship ever been verified in the GoM? I ask this question because the accuracy of the sea-air CO2 flux depends on the quality of atmospheric pCO2 used in the model.

In this revised manuscript, we have updated air pCO2 using satellite observations from the NASA ARIS sensor. Due to the relative coarse resolution of the gridded data (2.5*2 degree), we fit the pCO2 curve based on the mean value of all available grid points within the Gulf of Mexico and applied the air pCO2 in the CO2 flux calculation. We also added one figure showing the comparison between satellite-observed CO2 curve and the one we used in the CO2 flux calculation.

3. The modeled-data comparison for pCO2 seems not quite well. In Fig.1a on Louisiana shelf, there is only one measurement point in summer showing high value but with a large std. From the rest of years' measurements, it is really hard to see a summer pCO2 peak, while the model produces a clear and strong summer peak. The Gulf-wide pCO2 looks a little better, but still the model indicates stronger seasonal variability than observations. I think reproducing the seasonal variability not just the meanlevel is quite important when evaluating a model, and is usually

considered as the first priority while tuning a model. The authors already mentioned the model resolution and the structure of biological model could be the error sources, so I suggest the authors to continue refining the model.

With updated air pCO_2, we carried out a series of model experiments and refined the model solution. We also incorporated more ship-measurements from the updated LDEO database as well as the newly published paper by one of our co-authors (Huang et al., 2015). Now our model is able to capture 21 out of the 26 data groups in the Northern Gulf of Mexico and 24 out of 26 data groups gulf-wide.

4. The modeled-data comparison for CO2 flux seems not well either. Almost all of the CO2 flux differences between model results and observations are larger than a factor of 2, except one on Louisiana shelf. For example, in table 1, modeled annual values are 1.09 and 0.06 for Mexico shelf and Texas shelf, while observed values are 0.09 and 0.18.

The updated CO_2 flux showed a better agreement with estimations based on in-situ measurements-specifically in the four shelf sub-regions. We acknowledge there still is some model-observation mismatch in the open ocean and we ascribe that to the skewed data distribution. We also added one figure (Fig. 5) showing the distribution of available ship measurements.

Response to Comments from Reviewer #2

1. I'd like to see a brief description of the biogeochemical module that is the key to this paper, instead of having to read 3 other papers to learn about it. Likewise, since the paper focuses on pCO2, more detail as to how it was computed from DIC and TA should be provided.

We have added the details of the method and formulae used for carbon and air-sea CO2 flux calculation in the supplementary materials.

2. The authors use secular air pCO2 for their model, but they are trying to look at seasonal and spatial variability, not long-term trends. What is the advantage of using secular pCO2 in this case? Authors should justify in their paper why they are using it. When they compute air-sea CO2 fluxes and compare them with observation-based estimates, what air pCO2 has been used in the observations?

In the revised manuscript, we first derived a pCO_2 curve for air pCO_2 using satellite-based observation from the NASA AIRS mission, and then we used the air pCO_2 for the CO_2 flux calculation. The detailed method has been added into the context as well as a figure of the air pCO_2 curve.

3. The authors state that their model captures the measured pCO2 in 6 out of 11 cruises for the Louisiana Shelf, but that is basically 50% of the times, so hit or miss results and they consistently overestimate pCO2 values. Since the model has high resolution, and the Louisiana shelf is so complex due to the influence of the river plume, it would be interesting to see if a more detailed data-model comparison (instead of a one point mean) provides more information on how to fine-tune the model for future exercises.

Our model results have been improved. Please see our responses to reviewer #1's question 3.

4. These are not LDEO in-situ data. They are data gathered by several institutions, most notably NOAA, that were shared in the LDEO database. Please refer to it as a database. In this database there are very few points outside the northern Gulf of Mexico, particularly in the TX and MX regions.

We clarified the usage of LDEO database throughout the manuscript.

5. That makes observation means heavily biased toward behavior in the northern Gulf and, in my opinion, make model-data validation Gulf wide a subject for discussion that has been ignored in this paper. Differences observed between data and model results in regions with few observations are less "problematic" than in areas with high data, and in fact, models might do a better job in those poorly sampled regions than data-based estimates.

We agree that the available ship measurements are still very limited, specifically in regions such as the western Gulf and Mexican Shelf. We have separated the model validation into an independent section and added more details for model validation. We found that the more measurement we have for a sub-region, the better model-data agreement we can expect.

6. since pCO2 was calculated from DIC and TA model estimates, it makes sense that these parameters correlate well, I'm more intrigued about how pCO2 calculated from DIC and TA in shelf waters during the spring correlates so poorly with DIC. Would the authors like to elaborate a bit more on what they think could be the reasons for this? Would this be an indication that DIC model estimates are off in this case?

Our updated model results have a much better agreement with ship measurements. However we notice that the model tends to over-estimated pCO2 during summer in the northern Gulf. We added in more analysis of relationship between DIC, pCO2, and salinity (Fig.10). Our model indicated that the relative high pCO2 simulated by our model is a results of respiration on the Texas shelf, where ship measurements are relative sporadic as compared with the deltaic region. For instance, in the summer of 2010 when more ship measurements were available in the northern Gulf, both model and observations indicated a high pCO_2 in the summer.

7. Technical corrections: In the introduction, why do the authors reference projections from IPCC 2001 instead of using more recent projections, such as the latest IPCC report? There are some typos scattered in the text. The use of English could be improved (e.g. all of section 3.3, but in any case, have another read with fresh eyes of all the paper). In Figure 1, the in-situ observations are in black, not red.

We corrected the above problems and improved the usage of English.

Biogeosciences

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 quantify temporal and spatial variability of sea surface pCO_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 pCO_2 and were used to compute carbon budgets in the Gulf. On average, the GoM was found to be a CO_2 sink with a flux of 1.11×10^{12} mol C yr^{-1}, which, together with the enormous fluvial carbon input, was balanced by the carbon export through the Loop Current. Two sensitivity model 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 sub-regional carbon budget was susceptible to changes in river forcing. When the 1904-1910 river conditions were applied, the northern GoM became a CO_2 source instead.

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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 pCO_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 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 el 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 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

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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 budget associated with such enormous terrestrial carbon and nutrient inputs remains unclear: on the one hand extensive riverine carbon input results in CO_2 over-saturation in 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 an overall 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 induce a net influx of CO_2. 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, ~ 3.30×10^{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 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 represent CO_2 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

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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 assessment.

Here we present a GoM pCO_2 analysis 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 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). A seven-year (January 1, 2004–December 31, 2010) model hindcast was performed, driven by realistic atmospheric forcing (North America Regional Reanalysis, www.cdc.noaa.gov), open boundary conditions from a data-

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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 have been reported in Xue et al. (2013).

In this study we focus 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 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). Details of the formulas used in simulation are provided in the supplementary materials S1.

Similar to the results reported by Hofmann et al. (2011), we found the model-simulated DIC concentration in the water column were very sensitive to the initial conditions. Although there are many historical measurements in the GoM, these data are limited in the northern GoM shelf regions and thus are 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) provided the best model-data comparison. For the open boundary

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condition, we found simulated surface pCO_2 exhibited very limited variance (<5%) regardless 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).

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 calculation we followed the formulas in Wanninkhof (1992, details see supplementary materials S2). 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:

$$pCO_{2air} = D0 + D1*t + D2*(t^2) + D3*\sin(pi2*t) + D4*\cos(pi2*t) + D5*\sin(pi2*2*t) + D6*\cos(pi2*2*t) \quad (1)$$

where pCO_{2air} represents the monthly air pCO_2; t represents the number of months since January 2004 divided by 12, $pi2$ is a constant set to 6.28, $D0$=375.96, $D1$=2.23, $D2$=-0.007, $D3$=1.31, $D4$=-0.64, $D5$= -0.13, $D6$=0.21, and $D7$=0.09. Due to the relative 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. Because direct riverine DIC measurements were not available, we

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approximated riverine DIC inputs using the corresponding alkalinity value plus 50, following Guo et al. (2012). The fluvial DIC input to the GoM was estimated as ~ 2.18 × 10^{12} mol C yr^{-1}, the majority of which was delivered by the Mississippi-Atchafalaya River (~ 1.80 × 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. Experiment 1 (Exp1): Control run, with observed riverine inputs from USGS and biological sources and sinks of DIC and alkalinity in the water column; Experiment 2 (Exp2): 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); Experiment 3 (Exp3): 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). Also in Exp2 the air pCO_2 was set to the 1904-1910 condition derived by formula (1). The purpose of Exp2 is to examine roles of biological processes in regulating regional pCO_2 variability, whereas Exp3 is to connect variability of coastal carbon dynamics with historical climate and land-use changes within the Mississippi watershed.

3. Validation of the control run

We utilized the ship-based sea surface pCO_2 database composed 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;

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January, April, July, November 2009; and March 2010, respectively and contains > 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 window, and then compared them with model-simulated pCO_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).

On the NGoM Shelf, the model simulation was able to capture the measured pCO_2 in 21 out of the 26 data groups (the mean value of in-situ measurements fell in 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 pCO_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.

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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 large pCO_2 gradients were found in both in-situ measurements and model in shallow waters, areas that are 10m deep and shallower 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 large values (~ 500 ppm) around August and smallest values (~ 300 ppm) around February (Fig.6a). Notably, spatial averaged pCO_2 on the NGoM Shelf were not coincident with high river carbon and nutrient inputs (Fig.3). Simulated pCO_2 peaks were generally two to three months later than maximum river input in a year. 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 pCO_2 on the NGoM Shelf was generally 50 ppm higher than that in the entire gulf.

4.2 Air-Sea CO_2 flux

The carbon flux was calculated based on a multi-year model mean (2005-2010). We found the GoM overall was a CO_2 sink with a mean flux rate of 0.71 mol C m^{-2} yr^{-1} (~ 1.11 × 10^{12} mol C yr^{-1}, Table 1 and Fig.7). Examining region by region, we found that

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Moved up [1]: variations in observed pCO_2, allowing us to use this seven-year hindcast to further characterize the air-sea CO_2 flux.
To facilitate our description of the air-sea CO_2 flux, 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).

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the open ocean, occupying ~ 65% of the GoM in area, acted as a CO_2 sink (1.04 mol m^{-2} yr^{-1} of C) during most of the year except in summer. The greatest carbon uptake occurred in winter (2.44 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 carbon sink in winter and spring (1.46 and 0.97 mol C m^{-2} yr^{-1}) and then a carbon source in summer and fall (-0.96 and -0.76 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 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, -1.69 and -1.06 mol C m^{-2} yr^{-1}) and a strong carbon sink during winter (1.62 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 mol C m^{-2} yr^{-1}.

The NGoM Shelf shifted from acting as a CO_2 source in summer and fall (-1.42 and -0.79 mol C m^{-2} yr^{-1}) to a sink in winter and spring (1.01 and 2.49 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 mol C m^{-2} yr^{-1}). Similarly,

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the WF Shelf also shifted from acting as a CO_2 source in summer and fall (-1.26 and -1.73 mol C m^{-2} yr^{-1}) to a sink in winter and spring (1.19 and 0.28 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 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 agreed 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, which can be attributed to 1) the spatial and temporal heterogeneity of the in-situ dataset and 2) the spatially uniformed air pCO_2 used by our model.

4.3 Model Sensitivity experiments: No-bio simulation (Exp2)

To test the role of biological processes 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). The experiment produced higher surface pCO_2. The multi-year mean sea surface pCO_2 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). Such pCO_2 increase was not temporally uniform. On the NGoM Shelf, pCO_2 increases in the no-bio simulation was clearly higher during spring-summer (84.1 and 95.6 ppm) than during fall-winter (57.3

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and 56.0 ppm). On the Gulf-wide scale, the pCO_2 increase was stronger during summer (97.1 ppm) than the rest 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 2.09 mol C m^{-2} yr^{-1} (Table 1).

4.4 Model Sensitivity experiments: historical river forcing (Exp3)

Fig.4 shows that river discharge and DIC inputs during years 1904-1910 as simulated by the DLEM model were 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 1.51×10^{12} mol C yr^{-1} during 1904-1910 and 1.70×10^{12} mol C yr^{-1} during 2004-2010. However, NO_3 inputs during 1904-1910 was < 30% of current inputs (18.12 vs. 63.18 $\times10^9$ mol N yr^{-1}). Limited N input led to a decrease of primary production not only on the NGoM Shelf, but also the adjacent waters on the WGoM and WF Shelves. Reduced primary production resulted in the coastal ocean being a weaker carbon sink during spring and summer (Fig. 8) 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 condition on the NGoM Shelf showed that differences in primary production between Exp1 and Exp3 were simulated mainly along the Texas and Louisiana coasts. Primary production was significantly elevated in the control run because of enhanced NO_3 inputs (Fig. 8a and c). Elevated primary production brought down the sea surface pCO_2. During spring, enhanced primary production and decreased CO_2 was simulated along the Louisiana and Texas coast (Fig.

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8b), while during summer when coastal circulation was influenced by the westerly wind forcing, the decreased CO_2 was more confined within waters along the Louisiana coast.

5. Discussion

So far, the carbon dynamics in the GoM were poorly characterized and represented a large uncertainty. This study provides one of the first attempts to quantify GoM-wide carbon fluxes and exchanges using a coupled physical-biogeochemical model. Here, we discuss the factors controlling sea surface pCO_2 variability on the river-influenced NGoM Shelf and the Loop Current-influenced open ocean. The relationship between pCO_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 pCO_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 pCO_2 (e.g. Lohrenz et al., 2010; Guo et al., 2012; Huang et al., 2013 and 2015). Such biological removal of CO_2 was also confirmed by the elevated pCO_2 values in the no-bio simulation in this study. Although the river plume's influence on CO_2 flux has been addressed by prior observational studies, large uncertainties were also found regarding whether the NGoM 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

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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 CO_2 sink, but with a large uncertainty (influx rate: 0.96 ±3.7 mol m^{-2} 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. 9a), accompanied by low salinity (Fig. 9c), high Dissolved Inorganic Nitrogen (DIN) and high DIC (Figs. 9d and 9e). The pCO_2 value was significantly lower as water became deeper, where the ocean acted as a CO_2 sink during most time 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 correlation 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 condition 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.

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To further link pCO_2 dynamics with biological processes on the NGoM shelf, we plotted the seasonal mean pCO_2 against surface salinity of the control and no-bio runs in Fig.10. Seawater pCO_2 decreased almost linearly as salinity increased in the no-bio simulation in all seasons (right panels). For most seasons of the year (except winter), the NGoM shelf acted as a source of CO_2 if no biological mixing was involved. During summer when discharge and river DIC input were high, the high pCO_2 low salinity waters around the Mississippi River Delta (86-88°W, reddish points) can be easily differentiated from the high salinity low pCO_2 waters on the Texas Shelf (92-95°W, bluish points).

When biological processes were included, the shelf water exhibited large spatial and seasonal variability (left panels). A pCO_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-bio run, pCO_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 throughout a year. The difference in pCO_2 between waters around the delta and the Texas Shelf became more salient. The surface pCO_2 was in general higher in the Texas Shelf region than around the delta. Intriguingly, the pCO_2-salinity curve of waters around the Mississippi Delta exhibited a bifurcated feature in spring and summer. We further examined the relationship between salinity and variables other than pCO_2 and found a similar pattern in the DIC-salinity curve (not shown here), which was also reported by Guo et al., 2012 based on ship measurements. The similarity between the DIC-salinity and pCO_2-salinity curves indicates that the elevated pCO_2 water in the plume and on the

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Texas Shelf is a result of respiration, which is usually linked with hypoxia. We note that Hetland and DiMarco (2007) also suggested that hypoxia on the NGoM Shelf happened both in the deltaic region due to plume-dependent respiration, and on the Texas Shelf due to benthic respiration.

5.2 Open Ocean

In the open ocean, the distribution of surface pCO_2 was largely determined by that of 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), while the influence from DIN and primary production was limited to fall and winter months when wind-induced upwelling is strong (Xue et al., 2013). The dependence of pCO_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.9b 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. 9e and 9f). Surface pCO_2 in this warm water mass was significantly lower than surrounding shelf waters (Fig. 9a), making the Loop Current a strong carbon 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.

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781 **5.3 Carbon budget estimation and model uncertainty**

782 Based on our model-simulations, we conclude that the GoM is an overall CO_2
783 sink, taking up 1.11 × 10^{12} mol C yr^{-1} from the air. This estimation is comparable to those
784 based on in situ observations, e.g. 1.48 × 10^{12} mol C yr^{-1}, (Coble et al., 2010) and 0.30 ×
785 10^{12} mol C yr^{-1} (Robbins et al. 2014). These recent estimates are in stark contrast to the
786 earlier SOCCR report (Takahashi et al. 2007), which found the GoM to be a CO_2 source
787 (1.58× 10^{12} mol C yr^{-1}, the GoM and Caribbean Sea combined). In addition, we estimated
788 that the GoM received ~ 2.18 × 10^{12} mol C yr^{-1} from rivers, the majority of which were
789 from the Mississippi-Atchafalaya River (~1.80 × 10^{12} mol C yr^{-1}). These two DIC
790 sources (air: ~1.11 × 10^{12} mol C yr^{-1} plus river: ~2.18 × 10^{12} mol C yr^{-1}) largely balance
791 the DIC transported out of the GoM by the Loop Current (~ 3.30 × 10^{12} mol C yr^{-1}, Wang
792 et al., 2013).

793 We notice that, during summer months, our model simulated a higher surface
794 pCO_2 than ship measurements on the NGoM Shelf (Fig.6a). As discussed in Section 5.1,
795 a large part of the strong CO_2 degassing simulated by our model was from respiration on
796 the Texas Shelf. Yet a close examination of the distribution of available ship
797 measurements indicates that data points on the Texas Shelf are fairly sparse and sporadic
798 (Fig.5), which may partially explain the mismatch between model and ship measurements
799 in Fig.6a. For instance, in the summer of 2010 when more ship measurements were
800 available on the NGoM shelf, both model and observation indicated a high pCO_2 in the
801 summer. In addition, the current model resolution (~5 km) may not be high enough to
802 reproduce small-scale circulation patterns associated with the Mississippi River plume.
803 The complexity of the food web and uncertainty in model parameterization (e.g.

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rudimentarily represented 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 pCO_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 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 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-bio simulation). 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 driven by river conditions from the 1904-1910 period (reduced NO_3 and comparable DIC) indicates the NGoM shelf could have been a CO_2 source with an outflux rate of 0.61 mol C m^{-2} yr^{-1} under those conditions.

The Mississippi-Atchafalaya River plume is the dominant factor controlling the pCO_2 distribution on the NGoM Shelf. Although the NGoM Shelf is overall a CO_2 sink, high surface pCO_2 was simulated in relative shallow waters, induced by both oversaturated plume water and respiration on different parts of the shelf. pCO_2 in the open ocean is controlled largely by the low DIC high alkalinity Loop Current water from the Caribbean Sea.

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Our model simulations characterize the GoM as an overall CO_2 sink, taking up ~ 1.11 × 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 was largely balanced by carbon 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 model DIC initial conditions, and further refinements in model parameterizations 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 and OCE-0752110); NOAA Grant NA11NOS0120033; and GRI GISR grant SA/GoMRI-006 and GOMRI-020 is much appreciated. The operational mode of the SABGOM model is located at http://omgsrv1.meas.ncsu.edu:8080/ocean-circulation/. Data of daily nowcast/forecast model output is hosted at http://omgsrv1.meas.ncsu.edu:8080/thredds/sabgom_catalog.html. Data used in all figures for the hindcast simulation can be obtained by contacting the corresponding author.

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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*.

		Sub-regions					
		Mexico Shelf	Texas Shelf	Louisiana Shelf	West Florida Shelf	Open Ocean	Gulf-wide**
Subregion Area (10^{12} m^2)		0.18	0.08	0.15	0.15	1.01	1.56
Simulation 1 (control run)*	Spring	0.97	-0.24	1.01	0.28	1.51	1.23
	Summer	-0.96	-1.69	-1.42	-1.26	-0.33	-0.62
	Fall	-0.76	-1.06	-0.79	-1.73	0.56	0.06
	Winter	1.49	1.62	2.49	1.19	2.44	2.21
	Annual	**0.19**	**-0.34**	**0.32**	**-0.38**	**1.04**	**0.71**
Robbins et al., 2014	**Annual**	**0.09**	**-0.18**	**0.44**	**-0.37**	**0.48**	**0.19**
Simulation 2 (no-bio)	Annual	-2.77	-2.02	-1.64	-1.79	-2.08	-2.10
Simulation 3 1904-1910	Annual	0.08	-0.77	-0.61	-0.55	0.86	0.50

*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.

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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	-0.24	**-0.81**	-0.12	**0.86**	-0.77	0.36
	Summer	0.63	**-0.65**	0.65	**0.66**	-0.17	0.35
	Fall	-0.66	**-0.87**	0.86	**0.78**	0.17	0.58
	Winter	-0.67	**-0.89**	0.45	**0.89**	-0.90	0.23
	Annual	-0.64	**-0.82**	0.63	**0.82**	-0.65	0.47
pCO_2 in open ocean	Spring	0.11	0.17	**0.76**	-0.27	**-0.70**	-0.41
	Summer	-0.11	-0.11	**0.99**	-0.29	**-0.91**	-0.43
	Fall	0.04	0.08	**0.96**	-0.77	**-0.88**	-0.76
	Winter	0.04	-0.05	**0.75**	-0.49	**-0.69**	-0.55
	Annual	-0.17	0.05	**0.93**	-0.50	**-0.85**	-0.59

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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.

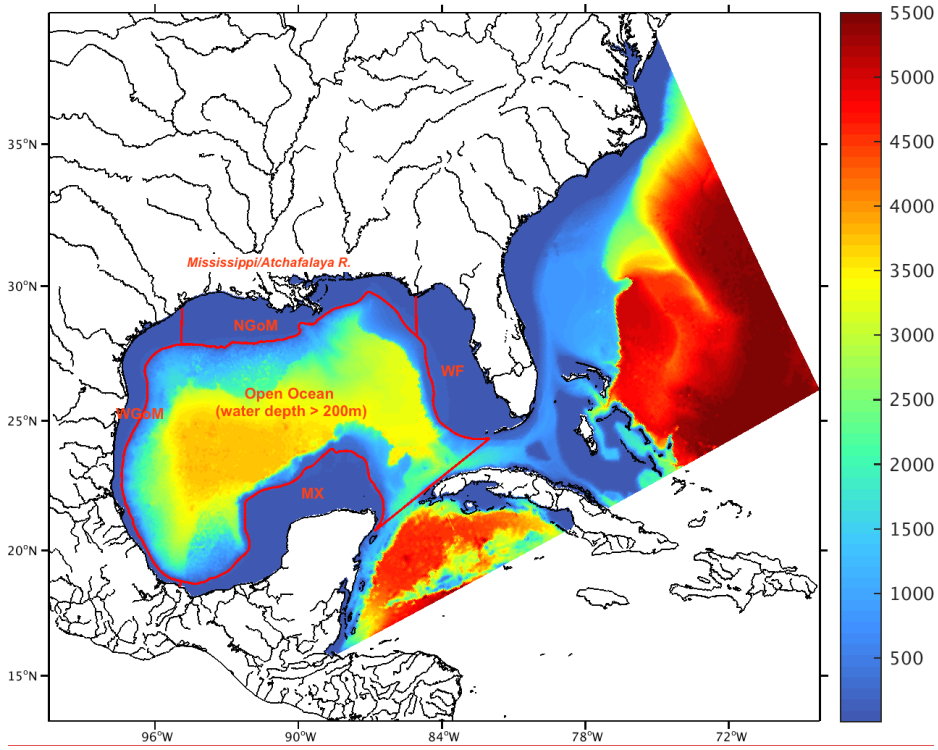


Figure 2. DIC and alkalinity initial conditions derived from the empirical relationship by Lee et al., (2000 and 2006).

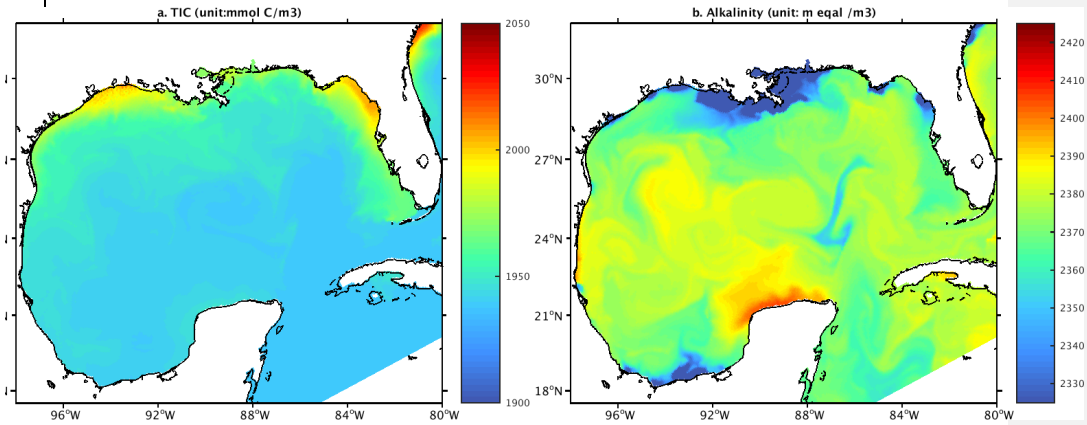


Figure 3. Satellite observed monthly pCO_2 (AIRS) averaged over the Gulf of Mexico (red stars) and the pCO_2 air used in model air-sea CO_2 flux calculation (blue line), which is generated using the curve-fitting software CCGCRV.

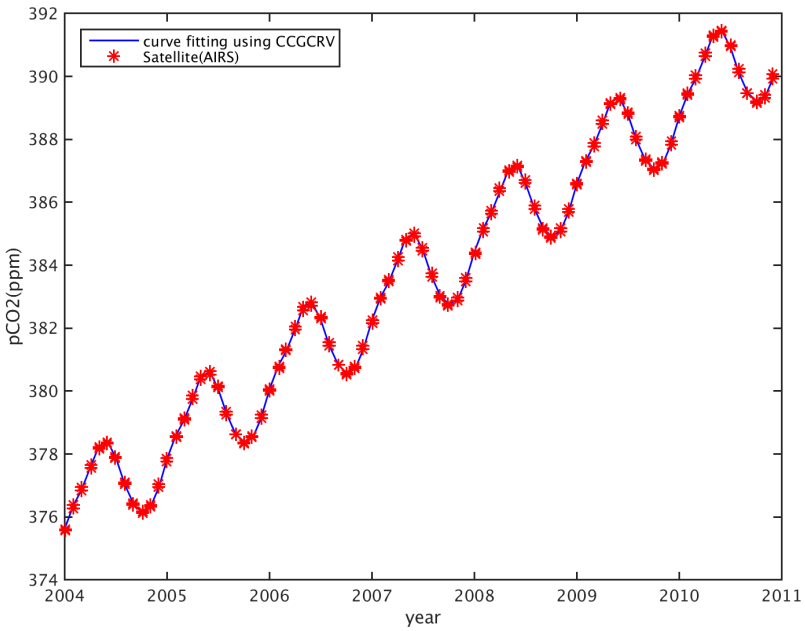


Figure 4. Comparisons between the 2005-2010 riverine DIC and NO_3 conditions observed by USGS (red line) and the 1904-1910 river condition simulated by the Dynamic Land Ecosystem Model (black line, Tian et al., 2015).

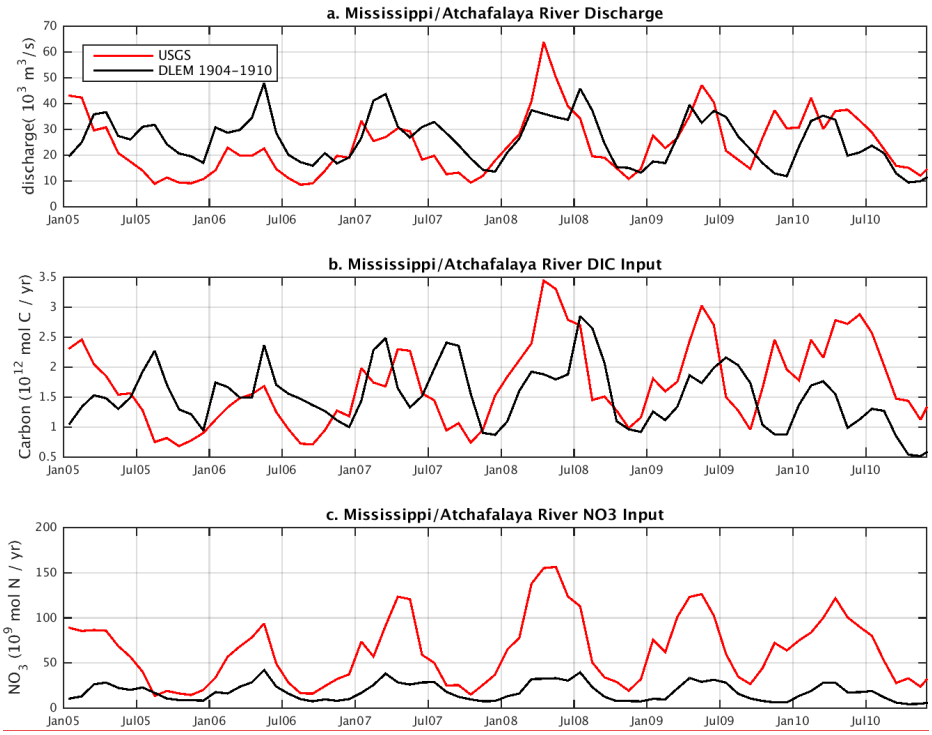


Figure 5. Locations of in-situ measurements from the LDEO database (blue) and Huang et al. (2015, grey) in the period of 2005-2010.

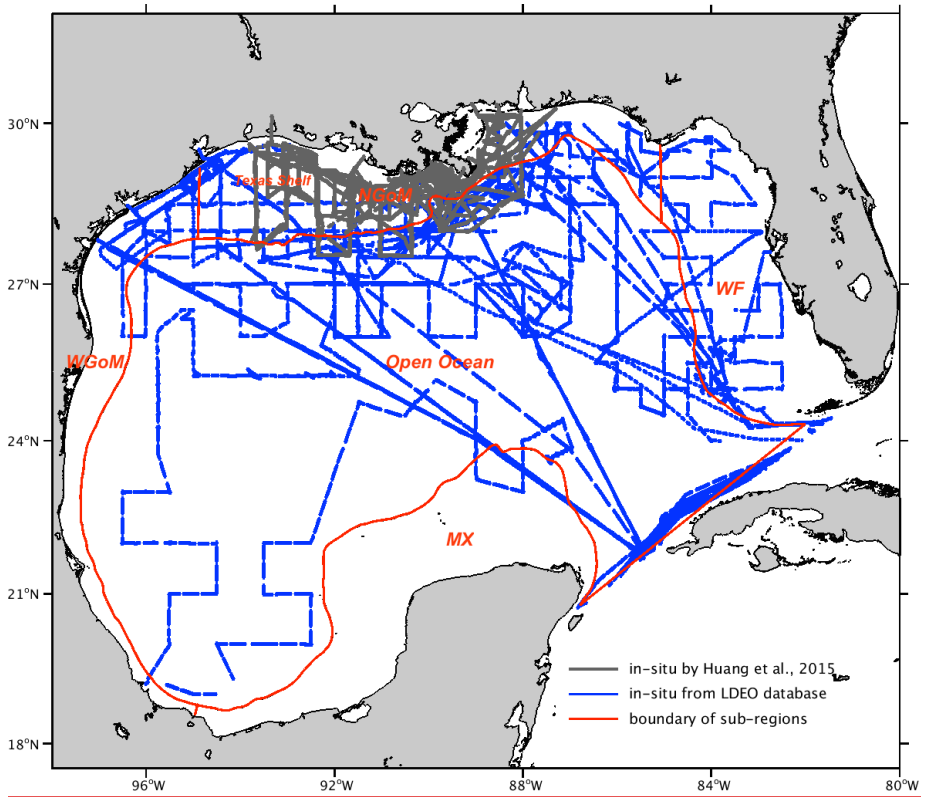
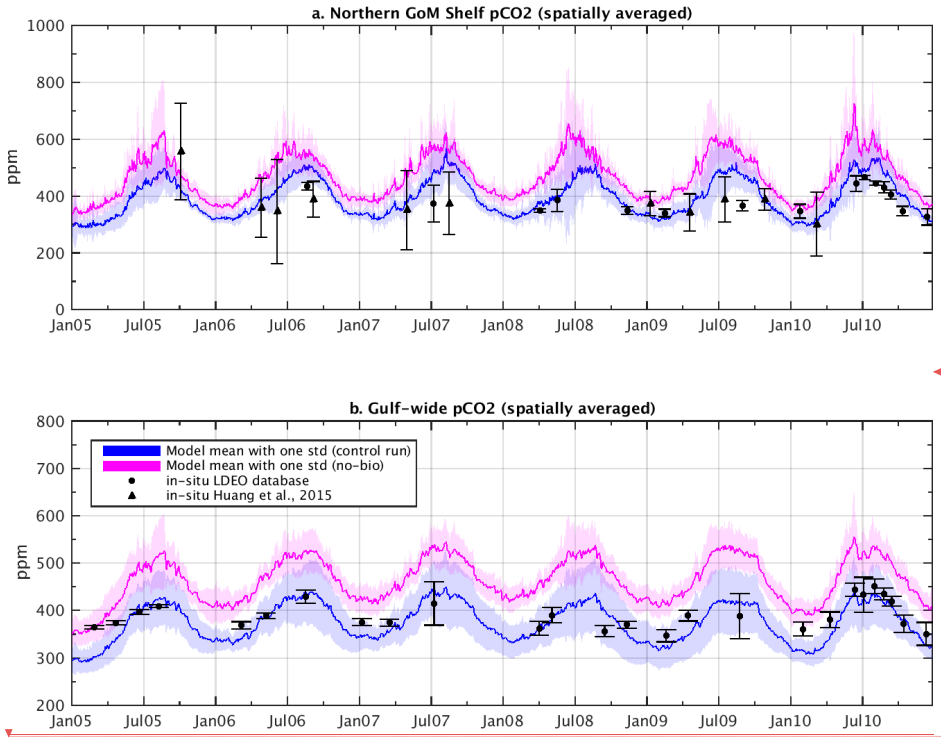


Figure 6. Time series of spatially averaged pCO_2 (control run in blue and no-bio simulation in red) (a) on the Louisiana shelf, and (b) in the entire Gulf of Mexico, overlaid with in situ observations (in black) from Huang et al. (2015a and b), and Takahashi et al. (2015).



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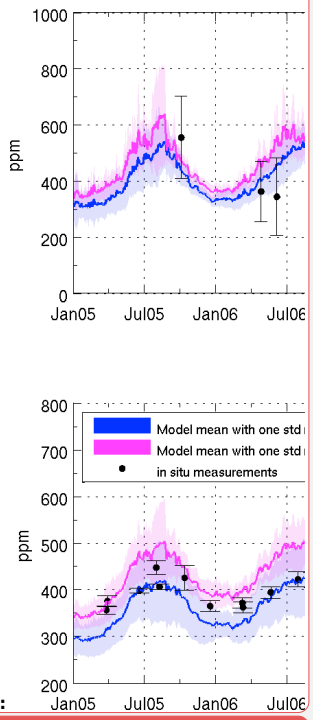

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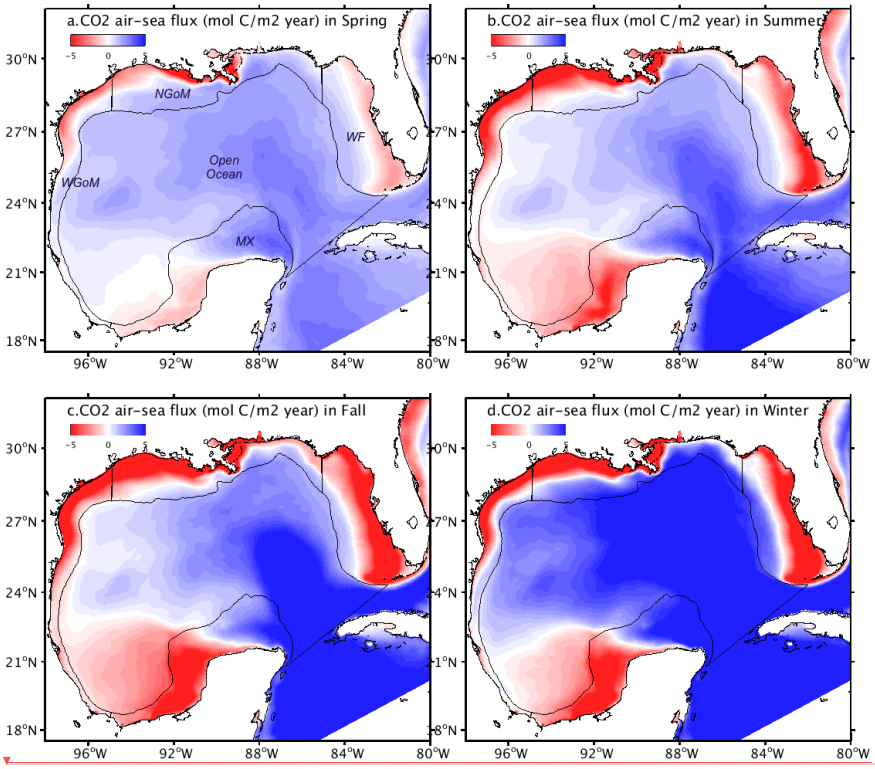
Figure 7. Seven-year (2005-2010) model (control run) mean air-sea CO_2 flux in the Gulf of Mexico during (a) spring, (b) summer, (c) autumn, and (d) winter. Blue color indicates where the ocean is a sink for CO_2; red color indicates where the ocean is a source.



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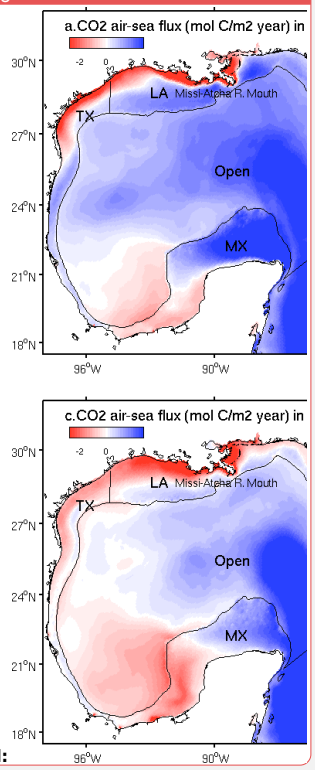

Figure 8. Differences in model simulated primary production and pCO_2 between the 2004-2010 and the 1904-1910 periods (2005-2010 minus 1905-1910 seasonal mean condition). For a) and c) blue color indicates increased primary production during 2004-2010, for b) and d) red color indicates reduced pCO_2 during 2004-2010.

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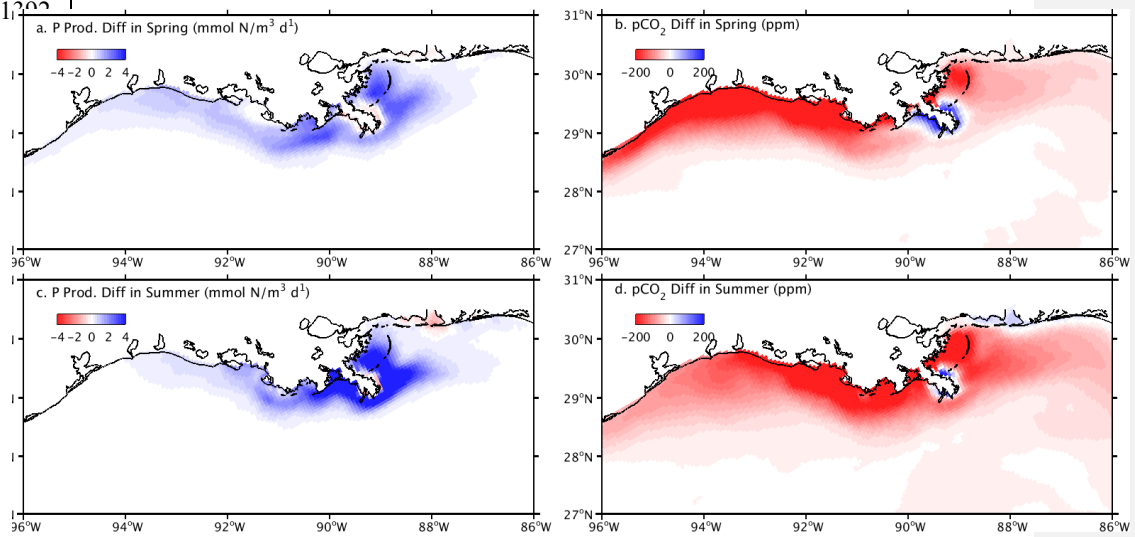

Figure 9. Seven-year mean (2005-2010) surface conditions simulated by the model for a) pCO_2 (ppm), b) temperature (degree C), c) salinity (psu), d) dissolved inorganic carbon (mmol C m^{-3}), e) dissolved inorganic nitrogen (NO_3+NH_4) (mmol N m^{-3}), and f) alkalinity (mEq m^{-3}).

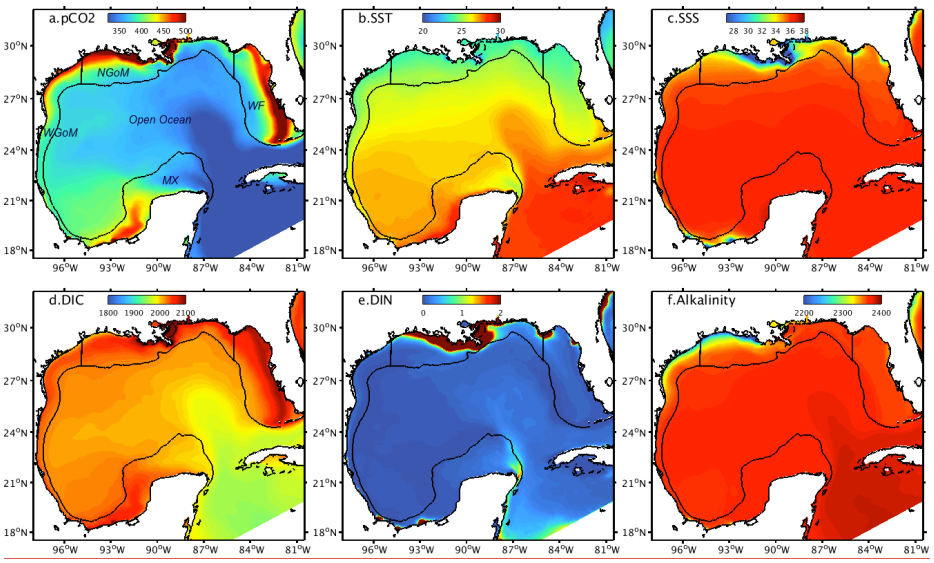

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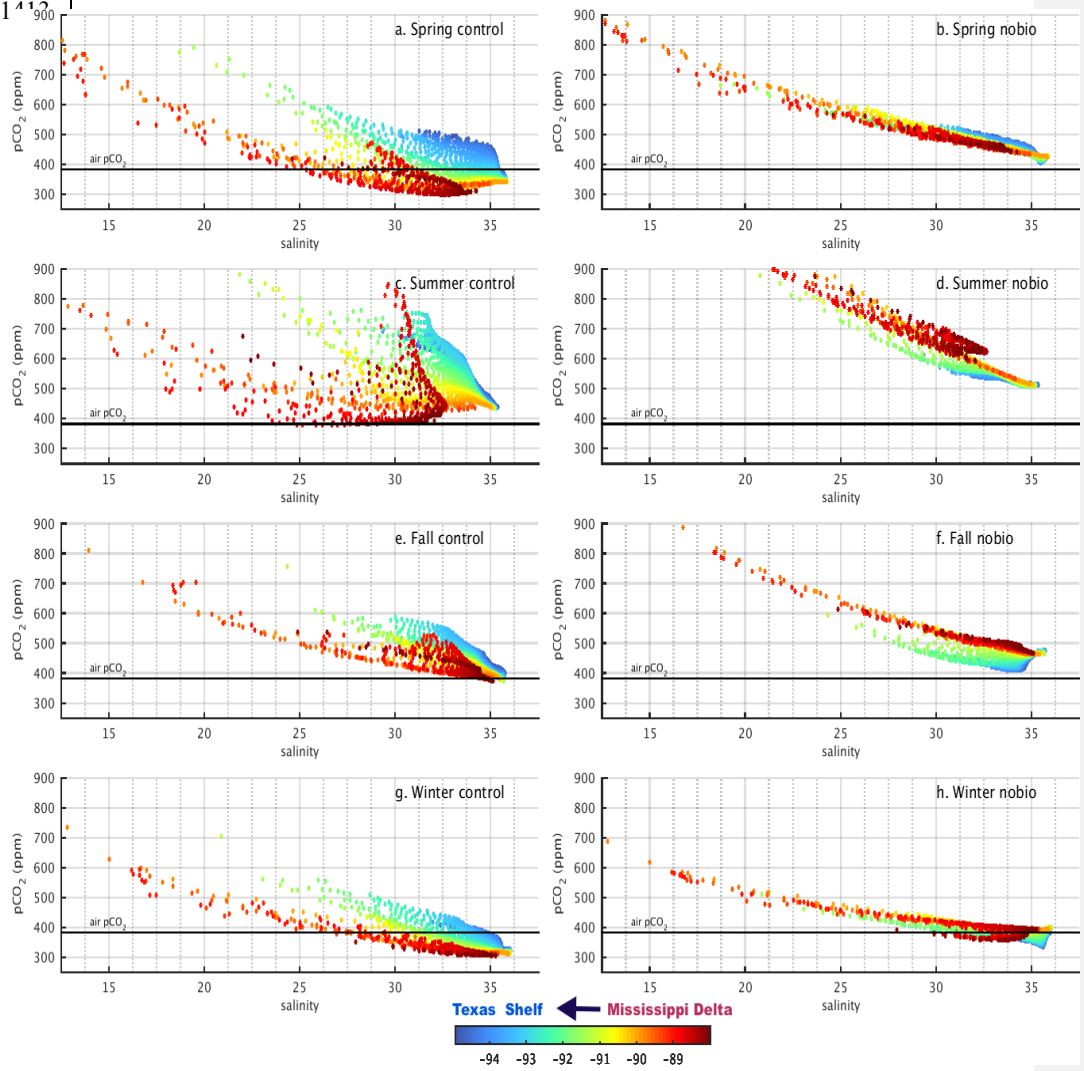
Figure 10. Seasonal mean (2005-2010) of model simulated sea surface pCO_2 against salinity for the control (a, c, e and g) and no-bio experiment (b, d, f and h) on the Louisiana Shelf; also shown are longitude with colors, note the Mississippi river delta is located around 89°W.



Supplementary Materials

S1. Calculation of seawater pCO_2

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

$$pCO_2=DIC*[H^+]^2/([H^+]^2+K_1*[H^+]+K_1*K_2)/f \quad (1)$$

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 following:

$$logK_1=62.008-1/T*3670.7-logT*9.7944+S*(0.0118-S*0.000116) \quad (2)$$

$$logK_2=-4.777-1/T*1394.7-logT*9.7944+S*(0.0184-S*0.000118) \quad (3)$$

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

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:

$$p5=1; \quad (4)$$

$$p4=-Alk-K_b-K_1; \quad (5)$$

$$p3=DIC*K_1-Alk*(K_b+K_1)+K_b*borate+K_w-K_b*K_1-K_1*K_2; \quad (6)$$

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

$$p1=2*DIC*K_b*K_1*K_2-Alk*K_b*K_1*K_2+K_b*borate*K_1*K_2+ K_w*K_b*K_1+K_w*K_1*K_2; \quad (8)$$

$$p0=K_w*K_b*K_1*K_2; \quad (9)$$

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):

$$lnK_b=-8966.90+2890.51*S^{0.5}-77.942*S+1.726*S^{1.5}-0.0993*S^2)/T +(148.0248+137.194*S^{0.5}+1.62247*S +(-24.4344-25.085*S^{0.5}-0.2474*S)*lnT+0.053105*S^{0.5}*T) \quad (10)$$

$$lnK_w=148.9802-13847.26/T-23.6521*lnT +(-0.977+118.67/T+1.0495*lnT)*S^{0.5}-0.01615*S) \quad (11)$$

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

$$borate=0.000232*S/1.80655/10.811 \quad (12)$$

S2. Air-Sea CO_2 flux calculation

The air-sea CO2 flux was calculated following Wanninkhof (1992) as following:

$$F=K*(pCO_{2\ air}- pCO_{2\ water}) \quad (13)$$

where pCO_2 air is the air pCO_2, and $pCO_{2\ water}$ was calculated from (1); F is the air-sea CO_2 flux (unit: millimole C meter^{-2} day^{-1});

$$K=kL \quad (14)$$

where L is the solubility of CO_2 and was calculated following Weiss (1974) as following:

$$ln\ L= -60.2409+93.4517/T+23.3585*Log(T) +S*(0.023517+T*(-0.023656+0.0047036*T)) \quad (15)$$

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

$$k=0.31u^2(Sc/660)^{-0.5} \quad (16)$$

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

$$Sc=2073.1-125.62*T+36276*T^2-0.043219*T^3 \quad (17)$$