May 8th, 2016

Dear Editor and Reviewers:

First of all, we would like to thank you for your constructive and detailed 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) explained why there is relatively large gap between the model-estimated flux in the open ocean and those estimated by Robbins et al. (2014), in which a monthly mean condition of wind fields and $pCO_2$ concentration was applied; 2) added information of the Net Community Productivity (Section 4.3, Figs. 8 and 9) as well as its contribution to carbon removal (Fig. 11); 3) added the DIC-salinity curve as well as the river end member derived by Cai et al. (2011a) to the $pCO_2$-salinity curve in the Northern Gulf of Mexico shelf, which helps to clarify the discussion of the river plume's impact on the region's $CO_2$ dynamics in Section 5.1; 4) added details of the biogeochemical model as well as formulas used for carbon model initial condition setup, and 5) responded to all other comments from the two reviewers.

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.

Regards,

Z. George Xue and co-authors

**Responses to Comments from Reviewer #1**

*The over-all results seem reasonable in that the modeled surface pco2 and air-sea CO2 fluxes agree reasonably well with available data. The open ocean flux, however, is about 2-3 times of the estimate by Robbins et al. (2014). In addition, it seems the model is unable to reproduce the large inter-annual variability of surface pCO2 (hence likely air-sea flux as well) as seen in the pco2 data, also reported by Huang et al. (2013, 2015a,b).*

**We understand there is a discrepancy, mainly in the open ocean, between our model simulated flux and those estimated by Robbins et al. (2014). We re-examined the flux calculation method used by Robbins et al. (2014) and determined that they indeed used monthly mean conditions in their $CO_2$ flux estimation. In other words, for each subregion, there was only one data point for each month. Following their method, we averaged our model solution as well as the wind fields and got a comparable flux (0.12 mol C $m^{-2}$ $yr^{-1}$). However, we think our flux calculation (0.79 mol C $m^{-2}$ $yr^{-1}$) based on daily model outputs is more reasonable when considering a balance among the air-sea $CO_2$ flux, riverine inorganic carbon input, and carbon export via loop current as proposed by Wang et al. (2013). We also embedded this discussion into the revised manuscript. For comparison against the results in Huang et al. (2015), our model is capable of reproducing the seasonal cycle of observed $pCO_2$, and Huang et al. (2015) also acknowledge a large variability in their flux calculation, which was 0.96 ± 3.7 mol $m^{-2}$ $yr^{-1}$.**

*1)Page 5-8, description of the model setup is not detailed enough and at times, confusing. For example, there is no description of how carbon is being cycled through the food web and in the water column (uptake, sinking, remineralization etc.). Also is organic carbon input included in the river discharges or along the open boundaries? And if yes, what are the data sources and processing details?*

**We added the details of the nitrogen and carbon cycling modules, including model components, treatment of remineralization and denitrification, in the "Method" section. We also added the description of the organic carbon input associated with the river discharge and along the open boundaries.**

*2) Page 10-13, it will be helpful to include some information regarding the spatial distribution and seasonal cycle of new productivity (or net community productivity) since it is concluded that biological removal is the dominant driver for air-sea CO2 flux in the gulf (see, e.g. abstract). In order to evaluate the impacts of biological removal, a map showing the differences of pco2 and air-sea flux between exp1 and exp2 (similar to Figure 8) will be useful as well.*

**We added one section as well as two figures (spatial map, Fig.8 and time series, Fig.9) about Net Community Production (NCP) to the revision. We also added the $pCO_2$ difference map between exp1 and exp2 (Fig. 10) as well as their correlation with NCP (Fig. 11).**

*3) Page 10, section 4.1. In addition to temporal comparison, a spatial comparison is needed to verify the spatial pco2 pattern, e.g., by binning the data into 0.5x0.5 boxes and then making a 1 to 1 correlation analysis.*

**We followed the reviewer's suggestion and tried to interpolate the available measurements**

**into 0.5*0.5 grids, yet as shown in Fig. 5 (distribution of observational data), there are still large spatial gaps in the open ocean, the western Gulf of Mexico, and the Mexico Shelf, so we have to forego such grid-grid comparisons in this revision and leave it for the future when more in-situ measurements are available.**

*4) Page 18, for the carbon budget, some calculation of production, respiration (it was asserted respiration is the dominant process within the Mississippi river plume), and export (vertical and horizontal) for NGoM or entire gulf will be useful as well.*

**Following the reviewer's suggestion #2, we included NCP (maps and time series) in the revision and tried to correlate NCP with $CO_2$ removal in the surface water. We discuss the lateral export of inorganic and organic matter in Xue et al., 2013 and provided a detailed budget there. We have added a citation to this paper in the discussion.**

*5) Page 14-17, section 5.1. This is a rather long section but the discussion is rather meandering and sometime contradicting. For example (line 359-360), why the high pco2 in the plume and on the shelf is a result of respiration? Just two paragraphs above (lines 333-334), the authors also state that there is rich DIC input from the river, which would presumably bring high pco2 along with the plume. The bottom line is that there is a lack of quantitative information regarding the roles of biological production/removal and respiration. Also, why is the river plume "light-limited"?*

**To further illuminate the impact of high DIC from the river plume, we revised Fig.10 (now Fig.14). We added the DIC-salinity curve as well as the river end member derived by Cai et al. (2011a) using in-situ data from spring and summer seasons. This new figure is a clear illustration that the high DIC from river decreases when biological processes are included in our model. Higher DIC on the Texas Shelf, could be linked to benthic respiration as previously reported by DiMarco and Hetland (2008). To address the impact of NCP on carbon removal, we also added the $pCO_2$-NCP scatter plot in Fig.11a. The light limitation was the result of the high suspended sediment concentration in the river plume and we also added an explanation for this in the text.**

*6) Page 17, lines 368-370. This statement appears to conflict with Figure 6 (bottom panel), which indicates the biological removal strongly affects surface pco2 and air-sea flux throughout the year.*

**In line with our response to comment #5, this conflict has been resolved.**

*7) Page 18, last paragraph, what exactly are model uncertainties?*

**We added some details about model uncertainties, which address issues related to parameterizations of remineralization, denitrification, organic particles, and others.**

The writing seems confusing or prone to grammatical errors. Here are some examples,

*1) page 5, line 95, pco2 -> CO2,* **corrected**
*2) page 6, line 123, we found -> we found that,* **corrected**

*3) page 6, line 124, were -> was,* **corrected**
*4) page 6, line 126, limited in -> limited to,* **corrected**
*5) page 8, line 155, Talk+50 is assigned as river DIC. This sounds like a strong assumption that needs to have a better justification;*

**We followed Guo et al., 2012, which is an observational study.**

*6) Page 8, line 160-167. Grammar error.* **Corrected.**

*7) Page 8, line 165-168. I assume the authors simply mapped the 1904-1910 conditions to 2004-2010 with a day to day match (e.g. Jan 20, 1904 will be corresponding to Jan 20, 2004). But, yes or no, this needs to be explicitly stated. Also, why 1904-1910? Any special reason to choose this period?*

**We have explained this experimental setup in more detail in this revision. We chose the 1904-1910 period as a comparison between the first ten years of the 20$^{th}$ century and that of the 21$^{st}$ century.**

*8) Page 9, line 178-182. How exactly is the data being processed? I assume the author use a 10-day binning for temporal processing. How about spatial means? Were the data within one domain (say NGoM) being summed up and divided by the total number of valid data points?*

**The data points falling in each sub-region were initially grouped in 10-day temporal bins and then spatially averaged over each sub-region to get a mean value. We added this explanation to the text as well.**

*9) Page 9, line 188, fell in -> fell within* **Corrected.**

*10) Page 10, line 217-218. I think this statement is not accurate. The pco2 maxima in the NGoM appear to be about 50 ppm higher. But this does not seem to be the case for low end pco2.*

**Here, as we pointed out, was the difference between multiyear means for the "Control Run" and "No-biology Run" experiments rather than a direct daily comparison spanning over 2005-2010.**

*11) Page 13, line 271, wrong numbers.*
**Similar to #10, we compared a multiyear mean value.**

*12) Page 13, line 287, were simulated -> were,* **Corrected.**

*13) page 15, line 333-334, why this is true? What is the correlation relationship between Talk-sal (henceforth DIC-sal), Talk-DIN, and DIN-sal in the MS river?*

**We added the DIC-salinity curve in Fig.14. Please refer to our response to comment #5.**

*14) Page 16, line 354-355. What does the bifurcation exactly imply?*

**We re-examined the $pCO_2$ and DIC distribution around the Mississippi Delta and found that the scatter around the DIC-salinity curve is the result of the DIC inputs from different channels along the delta. We removed the misleading "bifurcation" expression.**

**Response to Comments from Reviewer #2**

*-I was surprised by the data presented in Figure 4, specifically the Mississippi/Atchafalaya River DIC input for the 1904-1910 and modern time periods. The river DIC flux appears largely similar, on average, between the two time periods. It was my understanding from the paper by Raymond et al. (Nature 2008) that DIC flux from the Mississippi increased substantially over the preceding century- an increase that the DLEM model used in this work does not seem to capture. This contrast is worth noting and discussing, although the discussion of results from the 1904-1910 simulation was very limited.*

**The DLEM model estimated a 0.19 $\times 10^{12}$ mol C increase between the mean of 1904-1910 and that of 2004-2010, which is consistent with the increase between the beginning and end of the 20$^{th}$ century (0.24 $\times 10^{12}$ mol C for an average discharge year) reported by Raymond et al. (2008). We added this information to the text and references.**

*-The validation data for the WGoM and MX regions, and to a lesser extent the WF regions, are extremely sparse. Also, there is a very large region of the south/western Open Ocean region with little to no validation data. I acknowledge that the utility of a model lies in the opportunity to estimate conditions in unsampled times/regions, but all those empty spaces leave a lot of uncertainty. The WGoM, MX and WF regions are not specifically addressed at all in the Discussion section. I imagine that the overall Gulf of Mexico results/fluxes would not change substantially if these three regions were excluded from the totals, and just the Open Ocean and NGoM results were used. This comparison (Open Ocean+NGoM vs. the entire GoM) would be useful to present.*

**The reasons that we focused on NGoM and Open Ocean in the discussion section are 1) as listed in Table 1, the area of the Open Ocean and NGoM sub-regions together account for ~75% of the Gulf; 2) as pointed out by the reviewer, compared with the NGoM sub-region, the data availability in the MX, WGoM and WF regions are still very limited, which prevents a comprehensive model-data comparison; 3) there are contrasting processes affecting the NGoM and Open Ocean region, the former is dominated by riverine inputs and the latter is influenced by water from the Caribbean.**

-The model presented in this manuscript relies on the empirical relationships of Lee et al. (2006) to determine total alkalinity and Lee et al. (2000) to determine total inorganic carbon boundary conditions. However, these relationships specifically exclude all of the Gulf of Mexico for total alkalinity, and about half of the Gulf of Mexico for inorganic carbon. The authors should explicitly describe which relationship/region from each Lee et al. paper was used in this work, and justify the choice to use these relationships. The authors should also explicitly describe that total alkalinity was parameterized from salinity and surface temperature (Lee et al. 2006), while inorganic carbon was presumably parameterized from just surface temperature (and not temperature and nitrate, Lee et al. 2000). This helps explain the larger apparent variability in DIC when compared to total alkalinity in Figure 9.

**We noticed that the relationship derived by Lee et al., 2000 and 2006 was for the Atlantic Ocean. Yet as we stated, we tried three sets of initial/boundary combinations, including the relationships from Cai et al., 2011, Wang et al., 2013, as well as those from Lee et al. 2000/2006. The Lee et al. relationships produced the most reasonable results. We have provided details of the formulas in Lee et al., 2000/2006 in the supplementary materials (S3).**

*-Section 4.1 discusses Mississippi River discharge and pCO2 results, yet pCO2 is not shown in*

*Fig. 4 where it is referenced. Instead NO3 is shown. This needs to be fixed.*

**The *p*CO2 time series was shown in Fig.6, which used the same time scale as that in Fig.4.**

Minor Comments

*-The manuscript could use another proof-read. Some instances: Abstract L32 change to "Two model sensitivity"; P3L44 "In the face"; sP6L124 change were to was; P7L133 change to 'regardless of which'; P7L138 change to calculations; P7L149 change to relatively; P8L173 change composed to compiled; P10L204 change to 'model results in shallow'; P12L259 change to "uniform"; P12L268 change was to were; P13L271 change to 'rest of the seasons'; P13L291 change to pCO2; P14L293 change to pCO2; P15L325 change to times; P18L390 change were to was; P19L425 change to relatively*
**We thank reviewer #2 for his/her detailed suggestions, and all the points have been addressed in the revision.**

-I echo the sentiment of the Anonymous Reviewer #2 that details of the biogeochemical component of the model are needed.

**Please see our responses to reviewer #2's comment #3. Details of the biogeochemical model have been added in the revision.**

*-P3L63: the authors may want to elaborate on how the loading of carbon causes eutrophication. I generally associate the term eutrophication with nutrient loading; the contributions of carbon (presumable organic) are more indirect that nutrient additions.*
**We changed the sentence to "excessive nutrient loading causes coastal eutrophication…."**

*-P4L65-70 and throughout: I believe the authors are generally using the term 'carbon' in this paper to refer to inorganic carbon. If so, this should be made explicit, and care should be taken when describing total or organic carbon, as I presume this section does. Another example is P13L284: presumably the authors are talking about a CO2 sink, instead of an inorganic or total carbon sink.*

**Our model indeed accounts both particular organic carbon (detritus) and dissolved inorganic carbon. The details of the model component have been added.**

*-P4L71-76: Please show the Loop Current in Figure 1, for those like myself who are less familiar with Gulf of Mexico circulation.*
**We added the information about the loop current in Fig. 1**

*-P5L95: This is a nitpick, but I believe one does not quantify pCO2 fluxes, as pCO2 refers to the partial pressure. Instead it is the CO2 flux which was quantified.* **Corrected**

*-P5L107-108: Please explain exactly what the terms "realistic atmospheric forcing" and "open boundary conditions" refer to.*
**Details of the atmospheric forcing as well as the open boundary condition were added in the revision.**
*-P7L154: Please list the major rivers whose observations were taken from USGS data.*

**Information about major rivers in the Gulf, which has alkalinity measurement, was added.**

-*P8L167: Should be Exp3.* **Corrected.**
-P9L187: Specifically name the model simulation as the control (Exp1). **Corrected.**

-P9L187-197: Why not show the model pCO2 results from all sub-regions in a table, as the fluxes are shown in Table 1?

**The mean $pCO_2$ varied from time to time, so the time series in Fig. 6 is more informative.**

-P10L222-223 and throughout: Please add uncertainties to the average fluxes listed here, as variability is quite important in understanding these results.

**Model uncertainties we estimated as well as those from Robbins et al., 2014 were included in Table 1 and in the text.**

-P15L329-336: This is a very nice section of the discussion, and would benefit even more from additional description of the biogeochemical component of the model, as mentioned earlier in my review.
**Please see our responses to reviewer #1's comment #1.**

-Figure 2: Panel A is labeled TIC (total inorganic carbon), while the manuscript discussed DIC. **Corrected.**

-Figure 3: Is there a way to show the 1904-1910 atmospheric pCO2 used in the model? Perhaps as an inset?
**We added the 1904-1910 $pCO_2$ conditions in Fig. 3.**

-Figure 6: The shading showing the model uncertainty is very light, and may not print well. Can it be darkened?

**We adjusted the shading level.**

-Figure 10: I'm not quite sure what this figure is showing. What does each data point represent: one grid cell in each sub-region? The caption describes seasonal means from 2005-2010, but that would produce 24 data points for each sub-region, and there are many more data points shown here. Are these data points averaged over some sort of longitude range?

**We revised this figure (now Figure 14). Each of the data points represents one grid cell in the sub-region. And we averaged the spring and summer conditions (high flow from the river, also to be consistent with the river end member in Cai et al., 2011a) over the 2005-2010 period. There was no averaging along the longitude scale and the color of the scatter indicates the longitude of the grid cell presented.**

-*P41L700: Isn't salinity technically unit-less?* **Corrected.**

-P42L713: I believe Alk should be in units of micro-equivalents per liter, or milli-equivalents per cubic meter) **Corrected.**

*Biogeosciences*

# 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

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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 $1.11 \pm 0.84 \times 10^{12}$ mol C $yr^{-1}$, which, together with the enormous fluvial carbon input, was balanced by the carbon export through the Loop Current. Two 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 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 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

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68 the well-known hypoxia phenomenon (a.k.a. the "Dead Zone", Rabalais et al., 2002), but
69 also a newly revealed coastal ocean acidification problem (Cai et al, 2011b). However,
70 the carbon budget associated with such enormous terrestrial carbon and nutrient inputs
71 remains unclear: on the one hand extensive riverine carbon input results in $CO_2$ over-
72 saturation in coastal waters, which serve as a $CO_2$ source to the atmosphere (e.g. Lohrenz
73 et al., 2010; Guo et al., 2012); on the other hand, although the Mississippi River Plume
74 region is an overall heterotrophic system that breaks down organic carbon (Murrell et al.,
75 2013), enhanced primary production in the river plume due to significant inputs of
76 inorganic nutrients induces a net influx of $CO_2$. Further offshore, the circulation in the
77 GoM is largely influenced by the energetic Loop Current. Large anticyclonic eddies
78 aperiodically pinch off from the Loop Current (Sturges and Leben, 2000), which, along
79 with the wind-driven cross-shelf circulation and other meso-scale and sub-mesoscale
80 processes, enhance material exchanges between the eutrophic coastal waters and
81 oligotrophic deep-ocean waters (e.g., Toner et al., 2003). Indeed, a recent observational
82 study suggested a significant dissolved inorganic carbon export (DIC, ~ $3.30 \times 10^{12}$ mol
83 C $yr^{-1}$) from the GoM shelves to the Loop Current waters (Wang et al., 2013).

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84 While global inorganic carbon budgets have been made available through joint
85 seawater $CO_2$ observations (e.g. World Ocean Circulation Experiment and Joint Global
86 Ocean Flux study, Sabine et al., 2004; Feely et al., 2004; Orr et al., 2005), they are too
87 coarse to represent $CO_2$ variability in the GoM (Gledhill et al., 2008). Other recent efforts
88 were able to provide GoM sub-regional carbon assessments based on limited in situ
89 observations (e.g. Cai et al., 2003, Lohrenz et al., 2010, Huang et al., 2013, 2015a and
90 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 $CO_2$ 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

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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

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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. $pCO_2$, 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 are many historical measurements in the GoM, these data are limited to 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, details see supplementary materials S2) provided the best model-data comparison. For the open boundary condition, we found simulated surface $pCO_2$ 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.

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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:

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

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 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 ~ 2.18 ×

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$10^{12}$ mol C $yr^{-1}$, the majority of which was delivered by the Mississippi-Atchafalaya River (~ $1.80 \times 10^{12}$ 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 $pCO_2$ was set to the 1904-1910 condition derived by formula (1). The purpose of Exp2 was to examine the role of biological processes in regulating regional $pCO_2$ variability, whereas Exp3 examined connections between variability of coastal carbon dynamics and historical climate (the first ten years of the 20th century vs. that of the 21st century) and land-use changes within the Mississippi watershed.

**3. Validation of the control run**

We utilized the ship-based sea surface $pCO_2$ 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

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(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 $pCO_2$ 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). 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 $pCO_2$ 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 $pCO_2$ 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

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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 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 large values (~ 500 ppm) around August and smallest 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 $pCO_2$ were generally simulated 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 $pCO_2$ on the NGoM Shelf was generally 50 ppm higher than that in the entire Gulf.

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### 4.2 Air-Sea $CO_2$ flux

The 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±0.54 mol C $m^{-2}$ $yr^{-1}$ (~ 1.11±0.84 × $10^{12}$ 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±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±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±0.28 and 0.97±0.28 mol C $m^{-2}$ $yr^{-1}$) and then a carbon source in summer and fall (-0.96±0.38 and -0.76±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±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±0.59, -1.69±0.43 and -1.06±0.34 mol C $m^{-2}$ $yr^{-1}$) and a strong $CO_2$ sink during winter (1.62±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 $m^{-2}$ $yr^{-1}$.

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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 $pCO_2$ 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±0.35 mol C $m^{-2}$

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346 $yr^{-1}$ for the Open Ocean sub-region, and 0.12±0.23 mol C $m^{-2}$ $yr^{-1}$ for the entire GoM.
347 These values are comparable to those in Robbins et al. (2014, 0.48±0.07 mol C $m^{-2}$ $yr^{-1}$
348 for the Open Ocean and 0.19±0.08 mol C $m^{-2}$ $yr^{-1}$ for the entire GoM).
349
350 **4.3 Net Community Production**
351 As Net Community Production (NCP) plays an important role in regulating water
352 $CO_2$ concentration, we generated maps of seasonal mean surface NCP as well as time
353 series of spatially averaged surface NCP for the NGoM and Open Ocean in Figs. 8 and 9.
354 High NCP was simulated in the surface NGoM water and near the eastern tip of the MX
355 shelf for of the year. For the NGoM shelf, surface NCP peaks in the late spring and early
356 summer, with the highest value (2.62 mmol N/$m^3$) simulated in summer 2008 when there
357 was a major flooding event. Compared with the NGoM condition (0.53 mmol N/$m^3$),
358 mean surface NCP in the Open Ocean was relatively small, with a multi-year mean value
359 of 0.11 mmol N/$m^3$. In addition, the Gulf-wide mean surface NCP exhibited peaks in late
360 winter and early spring, mainly incurred by the strong upwelling along the west side of
361 the Yucatan Strait (Figs. 8a and 8d). Compared with the surface NCP, bottom NCP was
362 found to be small (0.05 mmol N/$m^3$ for the NGoM) and is thus not shown.
363
364 **4.4 Model Sensitivity experiments: No-biology simulation (Exp2)**
365 To test the role of biological processes in regional $CO_2$ variability, a no-biology
366 run was conducted, where all biology sources and sinks of DIC and alkalinity were
367 disabled similar to the experiment described in Fennel and Wilkin (2009). The
368 experiment produced higher surface $pCO_2$ than the control run. $pCO2$ is strongly elevated

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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 $pCO_2$ 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 2.09 mol C $m^{-2}$ $yr^{-1}$ (Table 1).

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**4.5 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 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 $1.51\times10^{12}$ mol C $yr^{-1}$ during 1904-1910 and $1.70\times10^{12}$ 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 $0.24\times10^{12}$ 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 $\times10^9$ 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 $pCO_2$. 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 $pCO_2$ was more confined within waters along the Louisiana coast.



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## 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 quantify GoM-wide carbon fluxes and exchanges using a coupled physical-biogeochemical model. We next 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-biology run 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 $pCO_2$ 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

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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. 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

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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 $pCO_2$ and low salinity waters around the Mississippi River Delta (86-88°W, reddish points) can be easily differentiated from the high salinity and low $pCO_2$ 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 $pCO_2$ 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-biology 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. The difference in $pCO_2$ 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

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**Deleted:** 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 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.

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 $pCO_2$ 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 $pCO_2$ 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 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 $pCO_2$ 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 $pCO_2$ difference between the control run and no-biology run in Fig. 10 as well as the poor correlation between the $pCO_2$ drop (difference between control and no-biology runs) and NCP in the Open Ocean (Fig. 11b).

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588 **5.3 Carbon budget estimation and model uncertainty**

589 Based on our model-simulations, we conclude that the GoM is an overall $CO_2$
590 sink, taking up $1.11 \pm 0.84 \times 10^{12}$ mol C $yr^{-1}$ from the air. This estimation is comparable to
591 those based on in situ observations, e.g. $1.48 \times 10^{12}$ mol C $yr^{-1}$, (Coble et al., 2010) and
592 $0.30 \times 10^{12}$ mol C $yr^{-1}$ (Robbins et al. 2014). These recent estimates are in stark contrast
593 to the earlier SOCCR report (Takahashi et al. 2007), which found the GoM to be a $CO_2$
594 source ($1.58 \times 10^{12}$ mol C $yr^{-1}$, the GoM and Caribbean Sea combined). In addition, we
595 estimated that the GoM received ~ $2.18 \times 10^{12}$ mol C $yr^{-1}$ from rivers, the majority of
596 which was from the Mississippi-Atchafalaya River (~$1.80 \times 10^{12}$ mol C $yr^{-1}$). These two
597 DIC sources (air: ~$1.11 \times 10^{12}$ mol C $yr^{-1}$ plus river: ~$2.18 \times 10^{12}$ mol C $yr^{-1}$) largely
598 balance the DIC transported out of the GoM by the Loop Current (~ $3.30 \times 10^{12}$ mol C $yr^{-1}$,
599 Wang et al., 2013). However, such a balance cannot be achieved using the $CO_2$ flux
600 estimated by Robbins et al., (2014).

601 We notice that, during summer months, our model simulated a higher surface
602 $pCO_2$ than ship measurements on the NGoM Shelf (Fig.6a). As discussed in Section 5.1,
603 a large part of the strong $CO_2$ degassing was simulated on the Texas Shelf. Yet a close
604 examination of the distribution of available ship measurements indicates that data points
605 on the Texas Shelf are fairly sparse and sporadic (Fig.5), which may partially explain the
606 mismatch between model and ship measurements in Fig.6a. For instance, in the summer
607 of 2010 when more ship measurements were available on the NGoM shelf, both model
608 and observation indicated a high $pCO_2$ in the summer. In addition, the current model
609 resolution (~5 km) may not be high enough to reproduce small-scale circulation patterns
610 associated with the Mississippi River plume. The complexity of the food web and

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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 $pCO_2$ 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-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 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 relatively shallow waters, induced by both oversaturated plume water. $pCO_2$ 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±0.84 × $10^{12}$ 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

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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** | **Western Gulf** | **Northern Gulf** | **West Florida Shelf** | **Open Ocean** |
| **Subregion Area ($10^{12}$ $m^2$)** | | 0.18 | 0.08 | 0.15 | 0.15 | 1.01 |
| **Simulation 1 (control run)*** | Spring | 0.97±0.29 | -0.24±0.59 | 1.01±0.89 | 0.28±0.33 | 1.51±0.41 |
| | Summer | -0.96±0.38 | -1.69±0.43 | -1.42±0.74 | -1.26±0.53 | -0.33±0.33 |
| | Fall | -0.76±0.45 | -1.06±0.34 | -0.79±0.63 | -1.73±0.67 | 0.56±0.61 |
| | Winter | 0.49±0.28 | 1.62±0.32 | 2.49±0.70 | 1.19±0.38 | 2.44±0.49 |
| | **Annual** | **0.19±0.35** | **-0.34±0.42** | **0.32±0.74** | **-0.38±0.48** | **1.04±0.46** |
| **Robbins et al., 2014** | **Annual** | **0.09±0.05** | **-0.18±0.05** | **0.44±0.37** | **-0.37±0.11** | **0.48±0.07** |
| **Simulation 2 (no-bio)** | Annual | -2.77±0.36 | -2.02±0.36 | -1.64±0.68 | -1.79±0.36 | -2.08±0.39 |
| **Simulation 3 1904-1910** | Annual | 0.08±0.35 | -0.77±0.77 | 0.61±1.07 | 0.55±0.46 | 0.86±0.46 |

*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 NGoM** | 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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1297 Figure 1. Domain of the South Atlantic Bight and Gulf of Mexico (SABGOM) ROMS
1298 model with water depth in color (unit: m). Also shown are the five sub-regions used in
1299 this study, which are Mexico Shelf (MX), Western Gulf of Mexico Shelf (WGoM),
1300 Northern Gulf of Mexico Shelf (NGoM), West Florida Shelf (WF), and open ocean. Also
1301 shown is a schematic for the Loop Current.
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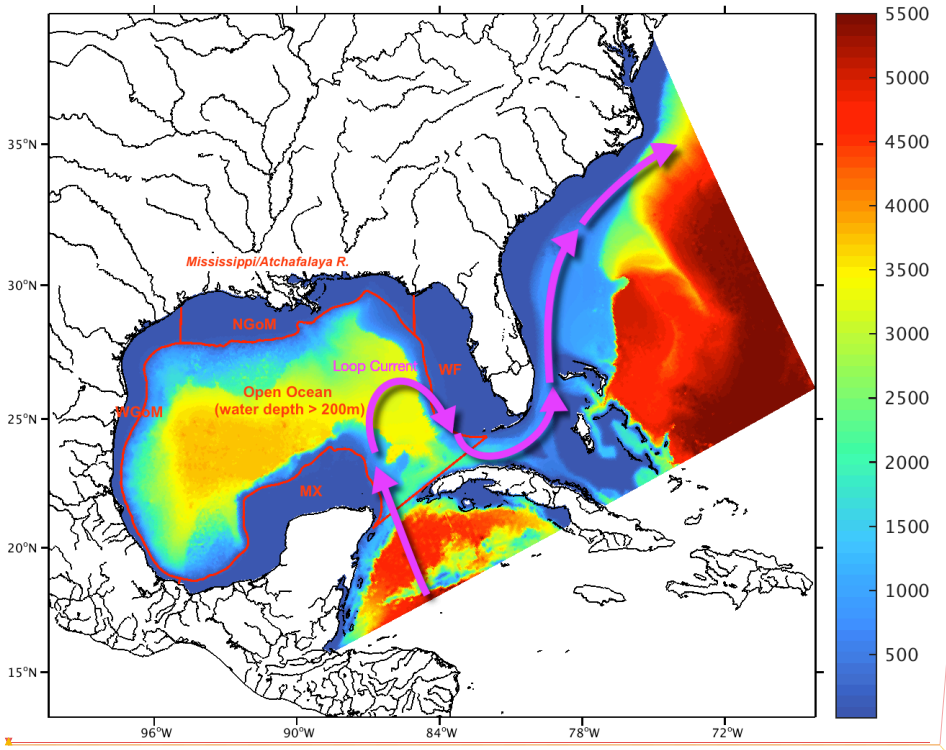


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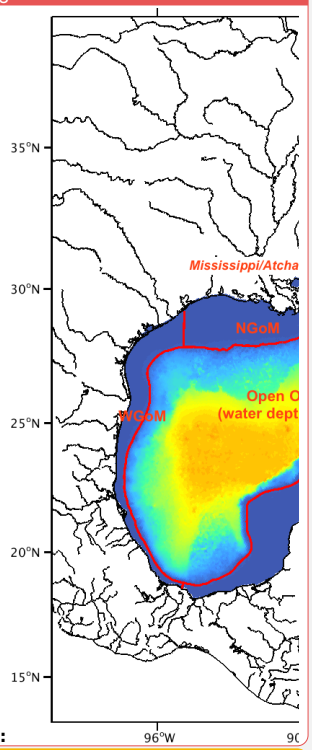


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Figure 2. DIC and alkalinity initial conditions derived from the empirical relationship by Lee et al. (2000 and 2006).

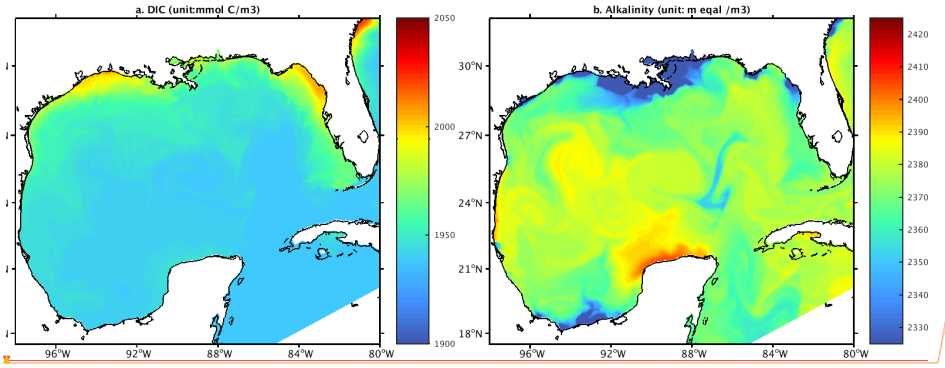


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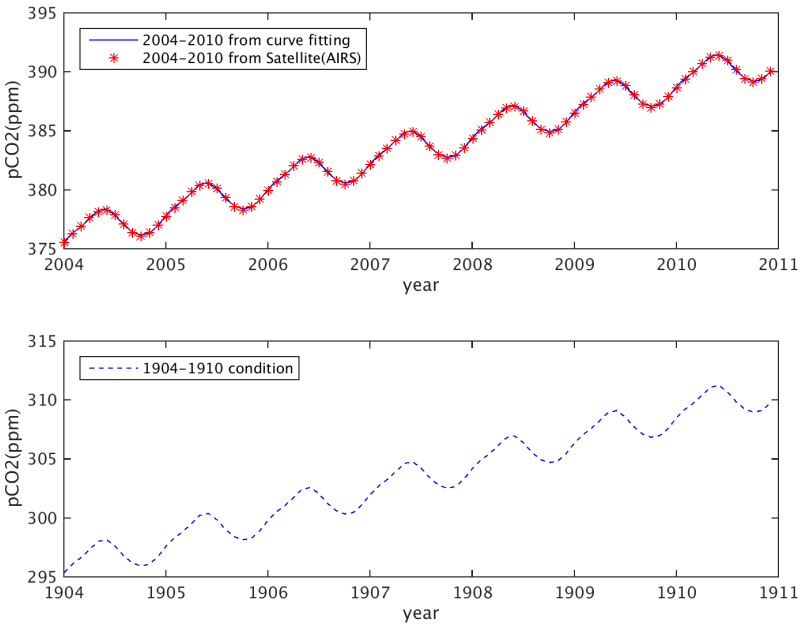
Figure 3. Satellite observed monthly $pCO_2$ (AIRS) averaged over the Gulf of Mexico (red stars) and the $pCO_2$ air used in model air-sea $CO_2$ flux calculation (blue line), which is generated using the curve-fitting software CCGCRV.

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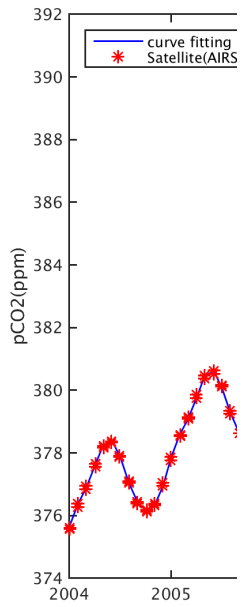


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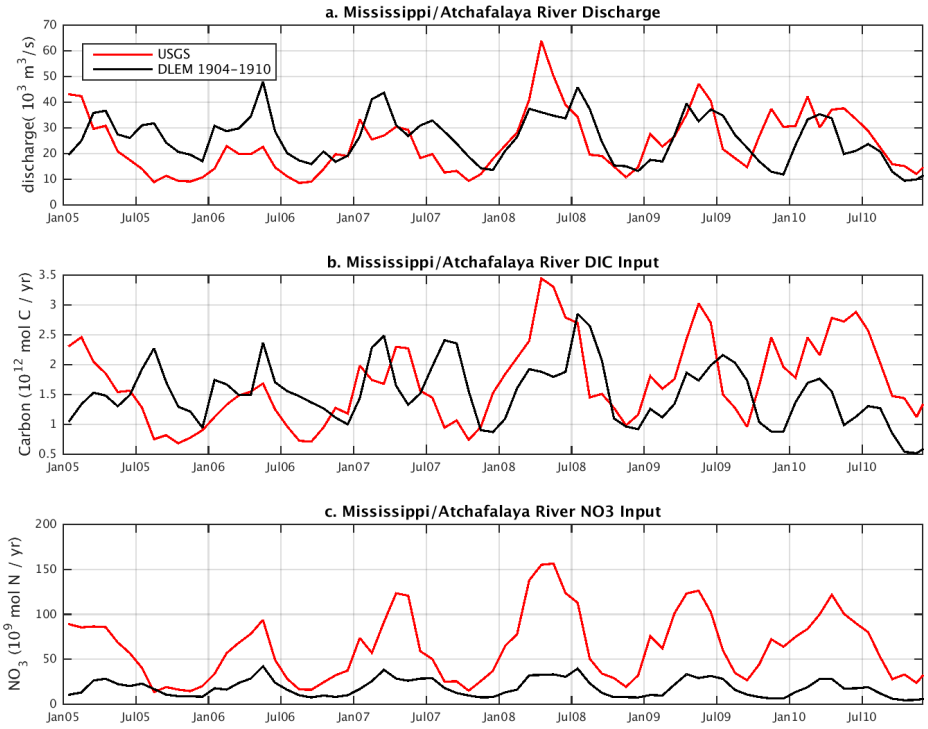
1317 Figure 4. Comparisons between the 2005-2010 riverine DIC and $NO_3$ conditions
1318 observed by USGS (red line) and the 1904-1910 river condition simulated by the
1319 Dynamic Land Ecosystem Model (black line, Tian et al., 2015).
1320



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1322 Figure 5. Locations of in-situ measurements from the LDEO database (blue) and Huang

1323 et al. (2015, grey) in the period of 2005-2010.

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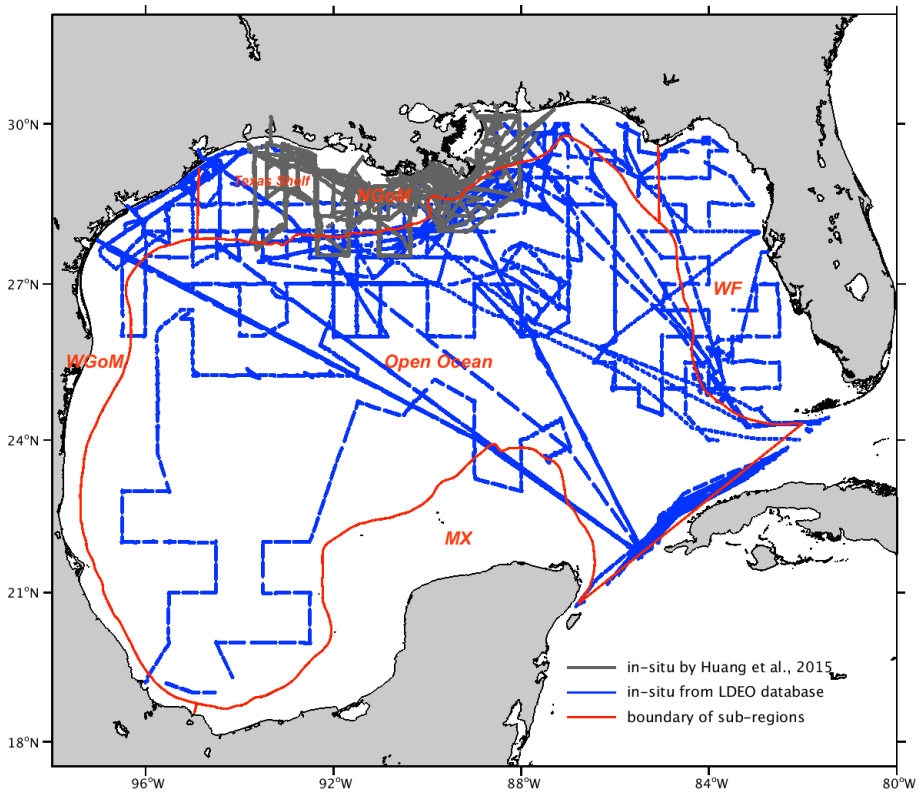


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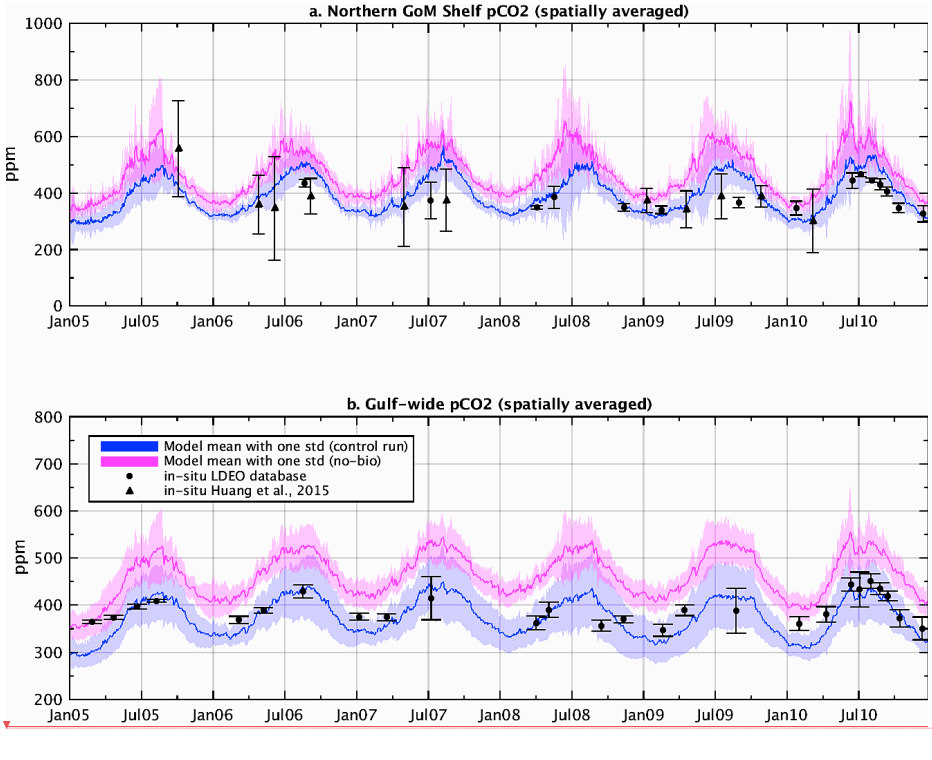
Figure 6. Time series of spatially averaged $pCO_2$ (control run in blue and no-biology run in red) (a) on the Northern Gulf of Mexico shelf, and (b) in the entire Gulf of Mexico, overlaid with in situ observations (in black) from Huang et al. (2015a and b), and Takahashi et al. (2015).

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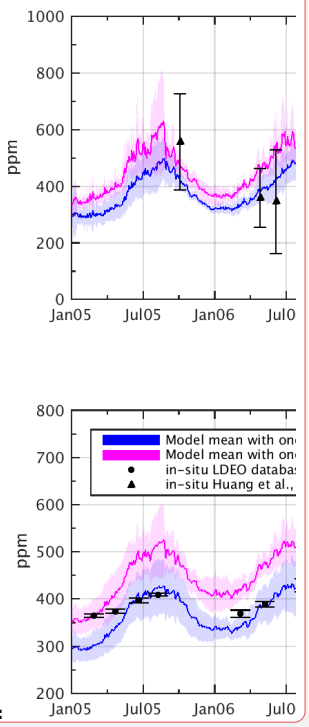


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Figure 7. Six-year (2005-2010) model (control run) mean air-sea $CO_2$ flux in the Gulf of Mexico during (a) spring, (b) summer, (c) fall, and (d) winter. Blue color indicates where the ocean is a sink for $CO_2$; red color indicates where the ocean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

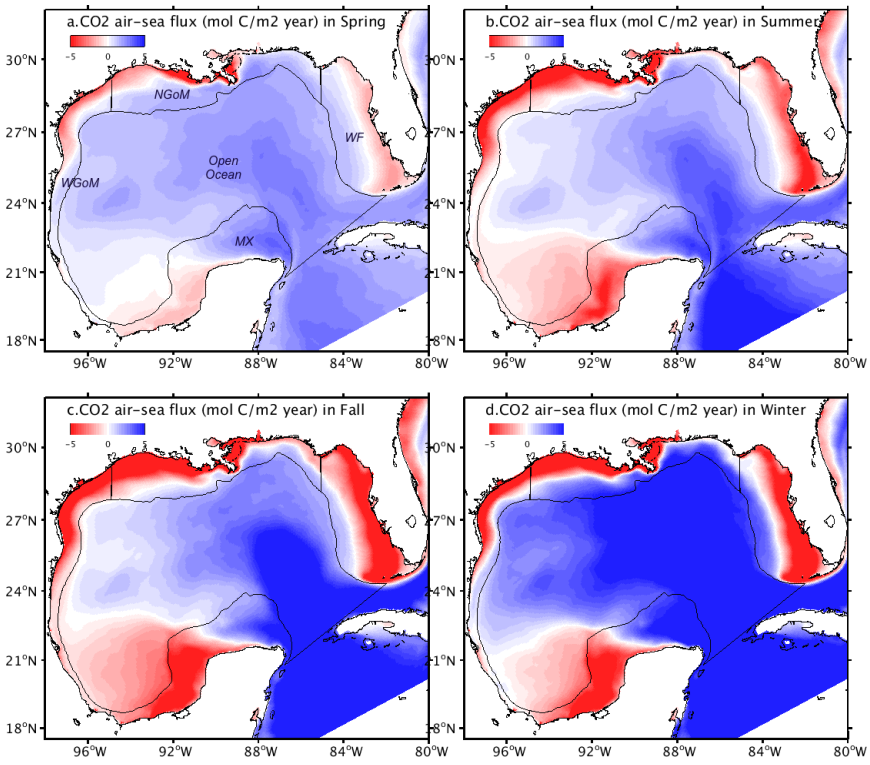


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Figure 8. Six-year (2005-2010) model (control run) mean surface Net Community Production (NCP) in the Gulf of Mexico during (a) spring, (b) summer, (c) fall, and (d) winter.

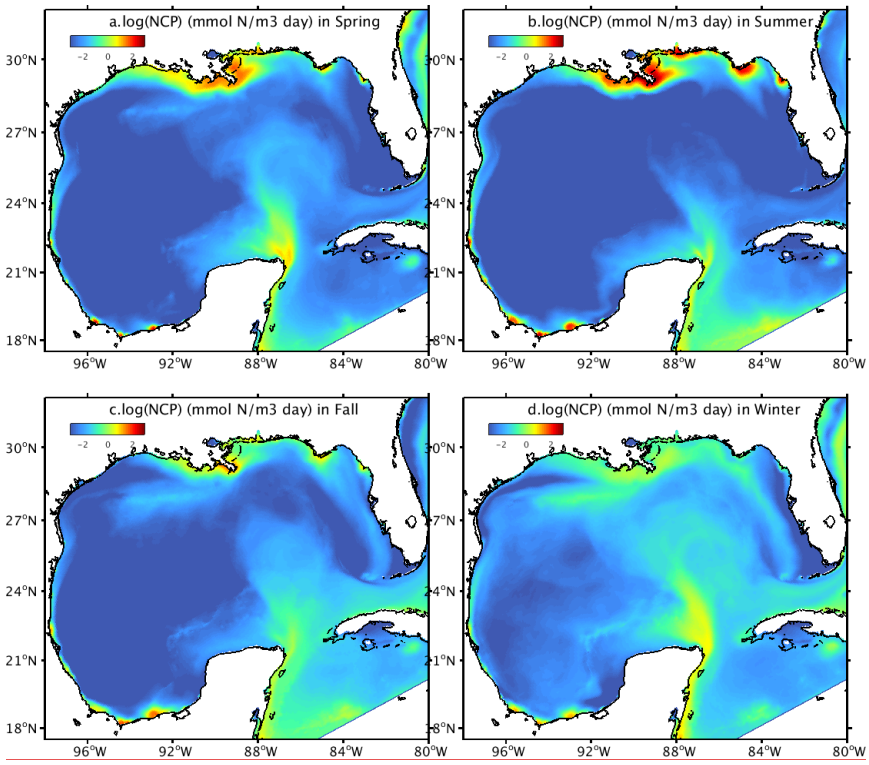

Figure 9. Time series of spatially averaged Net Community Production (a) on the Northern Gulf of Mexico shelf, and (b) in the entire Gulf of Mexico (unit: mmol N/m$^3$).

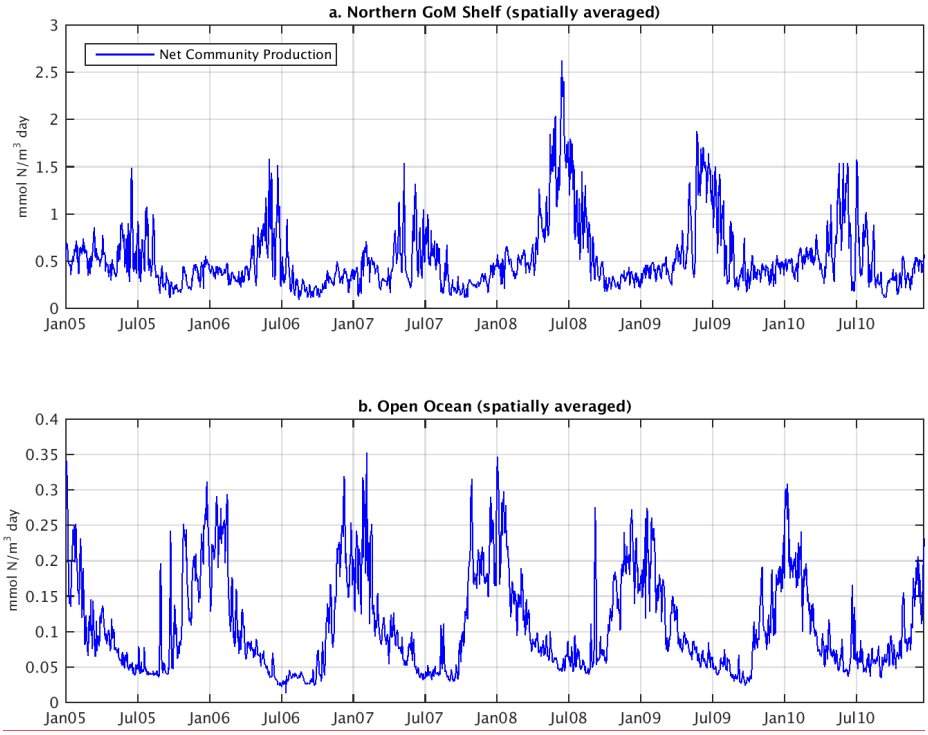

Figure 10. Multiyear (2005-2010) seasonal mean $pCO_2$ elevation (No-biology run minus control run, in the Gulf of Mexico during (a) spring, (b) summer, (c) fall, and (d) winter.

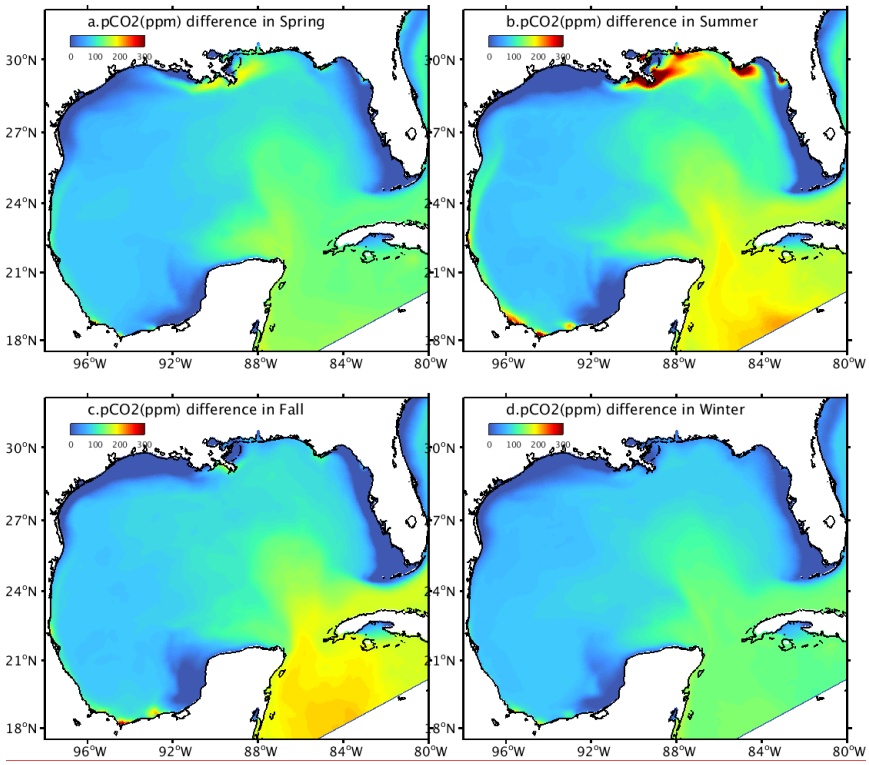

Figure 11. Scatter plots of the multiyear mean $pCO_2$ drop (No-biology run minus Control run) and surface NCP in NGoM (left) and Open Ocean (right).

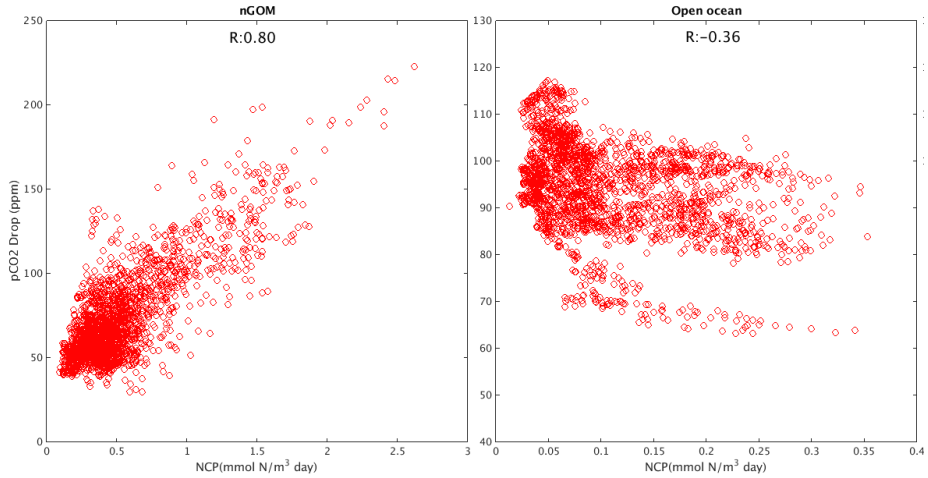

Figure 12. Differences in model simulated primary production and $pCO_2$ between the 2004-2010 and the 1904-1910 periods (2005-2010 minus 1905-1910 seasonal mean condition). For a) and c) blue color indicates increased primary production during 2004-2010, for b) and d) red color indicates reduced $pCO_2$ during 2004-2010.

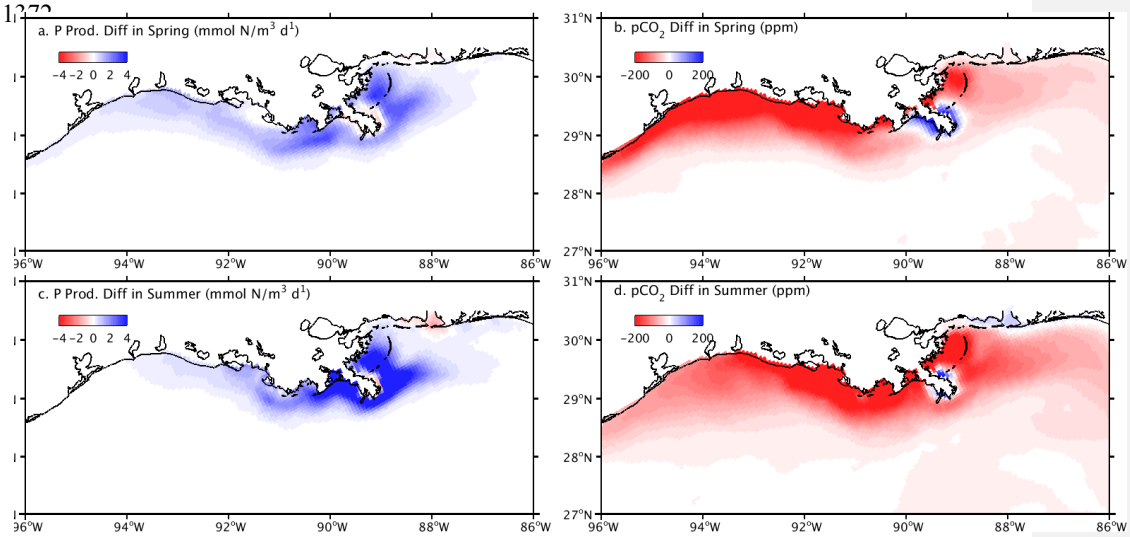

Figure 13. Six-year mean (2005-2010) surface conditions simulated by the model for a) $pCO_2$ (ppm), b) temperature (degree C), c) salinity, d) dissolved inorganic carbon (mmol C $m^{-3}$), e) dissolved inorganic nitrogen ($NO_3$+$NH_4$) (mmol N $m^{-3}$), and f) alkalinity (mEq $m^{-3}$).

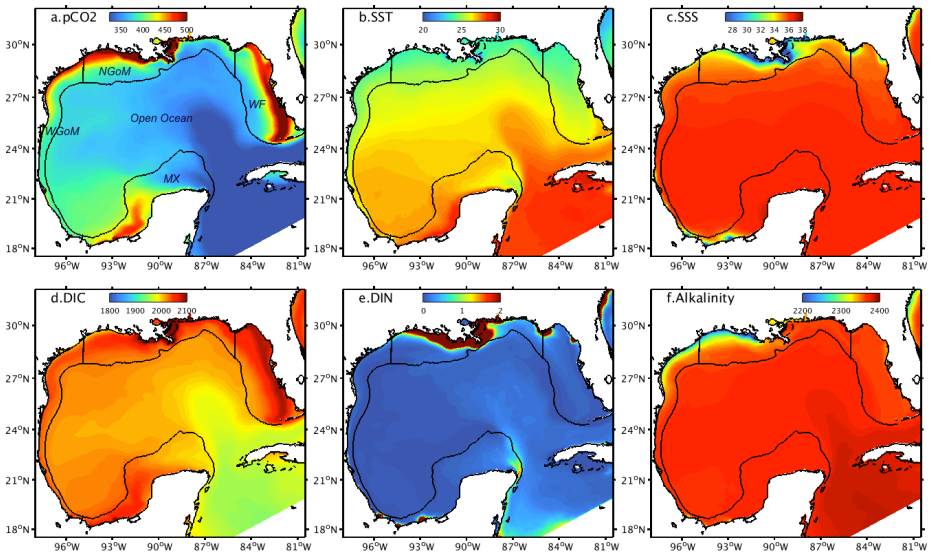


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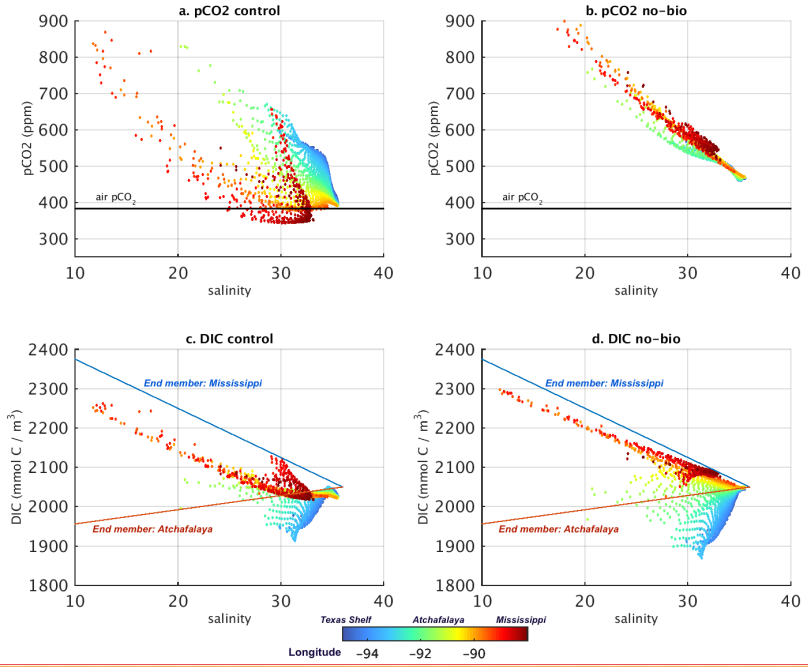
Figure 14. Six-year (2005-2010) spring-summer mean condition of model simulated sea surface $pCO_2$ and DIC against salinity for the control run (a and c) and no-biology run (b and d) on the NGoM Shelf; also shown are longitude with colors (note that the Mississippi river delta is located around 89°W 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).

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## Supplementary Materials

### S1. Calculation of seawater $pCO_2$

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

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

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 follows:

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

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

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

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:

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

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

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

$$p2=DIC*(K_b*K_1+2*K_1*K_2)-Alk*(K_b*K_1+K_1*K_2)+$$

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$$K_b*borate*K_1+(K_w*K_b+K_w*K_1-K_b*K_1*K_2); \quad (7)$$

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

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

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):

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

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**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:

$$DIC=1940+1.842*(SST-29)+0.468*(SST-29)^2 \quad (13)$$

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:

$$Alkalinity= 2305+58.66*(SSS-35)+2.32*(SSS-35)*(SSS-35)-1.41*(SST-20)+0.040*(SST-20)*(SST-20); \quad (14)$$

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## S3. Air-Sea $CO_2$ flux calculation

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

$$F=K*( pCO_{2\ air}- pCO_{2\ water}) \quad (15)$$

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$^{-1}$);

$$K=kL \quad (16)$$

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

$$ln\ L= -60.2409+93.4517/T+23.3585*Log(T) +S*(0.023517+T*(-0.023656+0.0047036*T)) \quad (17)$$

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

$$k=0.31u^2(Sc/660)^{-0.5} \quad (18)$$

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

$$Sc=2073.1-125.62*T+36276*T^2-0.043219*T^3 \quad (19)$$

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