10-31-2018

Remote Estimation of Surface Water $pCO_2$ in the Gulf of Mexico

Shuangling Chen

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Remote Estimation of Surface Water $pCO_2$ in the Gulf of Mexico

by

Shuangling Chen

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Date of Approval:
September 24, 2018

Keywords: surface $pCO_2$, sea surface salinity, remote sensing, dominant controls

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DEDICATION

This dissertation is dedicated to my parents Yufen and Wen. Thank you for your cheerful encouragement and selfless love. Thanks also to my uncle Hequn and my siblings Yunxia and Jianbei for their concerns and spiritual support.
ACKNOWLEDGEMENTS

This dissertation would not have been possible without the guidance of Dr. Chuanmin Hu. Thank you for mentoring and supporting me throughout this work. I am very grateful for your enthusiasm, persistence, and dedication to scientific research. Thank you also to my committee members, Dr. Byrne, Dr. Robbins, Dr. Luther, and Dr. Naar for their help and support throughout this dissertation work.

Many individuals and groups were instrumental towards completion of this dissertation. In particular, I would like to thank my coauthors (especially Wei-Jun Cai, Rik Wanninkhof, and Bo Yang), as well as friends and colleagues within the Optical Oceanography Lab (especially Jen Cannizzaro, David English, Brian Barnes, Brock Murch, Mengqiu Wang, and Shaojie Sun) and the College of Marine Science.

This research was made possible, in part, by a grant from the U.S. Geological Survey (USGS). Endowed fellowships from the College of Marine Science, University of South Florida (Gulf Oceanographic Charitable Trust Fellowship, Tampa Bay Parrot Head Fellowship, and George Lorton Fellowship) also provided immeasurable support for this research. Of particular importance was access to the large datasets collected and shared by many groups over the past decades. I wish to emphasis the great efforts and contributions of NOAA and several colleges and institutes (Columbia University, Texas A and M University, University of Delaware, University of South Florida, Florida Fish and Wildlife Conservation Commission) for their data (both ship-based and buoy data time series), and to thank all the researchers who collected and contributed
data used in this research – their efforts are much appreciated. Also I want to thank NASA for providing the MODIS satellite data, without which, this research would not have been possible.
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ABSTRACT

Surface ocean partial pressure of CO$_2$ ($p$CO$_2$) is a critical parameter in the quantification of air-sea CO$_2$ flux, which further plays an important role in quantifying the global carbon budget and understanding ocean acidification. The demand for a clearer understanding of how, and how fast, the ocean is changing due to atmospheric CO$_2$ absorption, requires accurate and synoptic estimation of surface $p$CO$_2$.

Surface ocean $p$CO$_2$ is mainly controlled by four oceanic processes – thermodynamics, ocean mixing, biological activities, and air-sea CO$_2$ exchange. Surface ocean $p$CO$_2$ is therefore closely related to environmental variables that characterize each oceanic process. These variables include sea surface temperature (SST), sea surface salinity (SSS), chlorophyll-a concentration (Chl), diffuse attenuation of downwelling irradiance ($K_d$), and wind speed. Ocean color satellites provide a means by which the relationship between these environmental variables and surface $p$CO$_2$ can be developed. Yet, remote estimation of surface $p$CO$_2$ in coastal oceans has been difficult due to the dynamic and complex biogeochemical processes. To date, most of the published satellite-based $p$CO$_2$ models are developed for single-process dominated regions, therefore having poor applicability in other oceanic regions. Particularly, there is no unified approach, let alone unified model, to remotely estimate surface $p$CO$_2$ in oceanic regions that are dominated by different oceanic processes.

This work provides solutions to these challenging issues for the remote estimation of surface $p$CO$_2$ in the Gulf of Mexico (GOM), with the following objectives: 1) Develop satellite-
based surface $p$CO$_2$ models and data products for single-process dominated subregions of the GOM, and quantify the sensitivities of the $p$CO$_2$ algorithms to the input environmental variables; 2) Quantify the oceanic processes in controlling surface $p$CO$_2$ in the GOM, analyze the relationships between environmental variables and surface $p$CO$_2$, and understand the mechanisms of seasonal and interannual variations of surface $p$CO$_2$ and its driving factors; 3) Develop an improved SSS model and data products for most GOM waters, and quantify the sensitivities of the SSS model to the input variables; 4) Develop a unified $p$CO$_2$ model and data products for the GOM waters, and quantify the sensitivities of the $p$CO$_2$ model to the input environmental variables and their relationships; 5) Quantify the temperature and non-temperature effects on surface $p$CO$_2$ at different latitudes, analyze the dominant controls and the corresponding the driving factors of surface $p$CO$_2$. The data used in this dissertation include those from extensive cruise surveys, buoy measurements, and long-term measurements by the Moderate Resolution Imaging Spectroradiometer (MODIS).

Specifically, for single-process dominated regions, two separate algorithms are developed and validated, respectively, from MODIS measurements. One is focused on the ocean current-dominated West Florida Shelf (WFS) (Appendix A), and the other is on the river-dominated northern GOM (Appendix B). The former utilizes a multi-variate nonlinear regression approach to establish the relationship between surface $p$CO$_2$ and environmental variables of SST, Chl, and K$_d$. The latter relies on a mechanistic semi-analytical approach (MeSAA), modified from an existing algorithm published earlier. Both algorithms show satisfactory performance, yet the latter requires SSS as the model input, which is difficult to obtain from ocean color satellite measurements. Therefore, a multilayer perceptron neural network-based (MPNN) SSS model is developed and validated, which generates SSS maps at 1-km resolution for the GOM using MODIS.
measurements (Appendix C). Finally, with the availability of SSS from MODIS for the GOM, a unified $pCO_2$ algorithm is developed and validated. The machine-learning algorithm is based on a random forest regression ensemble (RFRE), which is able to estimate surface $pCO_2$ from MODIS measurements with a Root Mean Square Error (RMSE) of $< 10 \mu atm$ and $R^2$ of 0.95 for $pCO_2$ ranging between 145 and 550 $\mu atm$ (Appendix D). Using this approach, The RFRE algorithm is shown to be applicable to the Gulf of Maine (a contrasting oceanic region to GOM) after local model tuning. The results show significant improvement over other models, suggesting that the RFRE approach may serve as a template for other oceanic regions once sufficient field-measured $pCO_2$ data are available for local model tuning.

To further improve the accuracy of satellite-derived surface $pCO_2$ from coastal oceans and to increase its capability in capturing the interannual variations of surface $pCO_2$ resulting from anthropogenic forcing, the dominant controls of surface $pCO_2$ over seasonal and interannual time scales need to be better understood. As such, *in situ* $pCO_2$ time series data along the coasts of the United States of America at different latitudes are analyzed (Appendix E). On a seasonal time scale, surface $pCO_2$ tends to be dominated by the temperature effect ($pCO_2\_T$) through SST and wind speed (with some exceptions) in tropical and subtropical oceans, but appears to be dominated by the non-temperature effect ($pCO_2\_nonT$) in subpolar regions. In contrast, in tropical and subtropical waters on interannual time scales, surface $pCO_2$ is primarily moderated by the non-temperature effect (through air-sea $CO_2$ exchange via atmospheric $pCO_2$), but conversely dominated by the temperature effect (i.e., SST increase) in subpolar regions. The effects of biological activities (i.e., algal blooms) need to be further investigated in the future.

Overall, this dissertation has developed several algorithms to estimate SSS and surface $pCO_2$, among which the unified $pCO_2$ algorithm for multi-processes dominated regions appears to
be able to serve as a template for many other regions after local model tuning. The derived surface $p\text{CO}_2$ data products for the GOM provide a fundamental basis to assess air-sea exchange of CO$_2$ and understand the carbon chemistry under a changing climate.
CHAPTER 1:
INTRODUCTION

1. Surface ocean $p$CO$_2$ and environmental controls

When CO$_2$ from the atmosphere enters seawater, a chain of reactions can occur, which can produce carbonic acid, bicarbonate, and carbonate (Kanwisher, 1960). The free aqueous CO$_2$ in seawater is quantified as partial pressure of CO$_2$ ($p$CO$_2$), which refers to the fugacity in most cases (Pilson, 2012). The term fugacity expresses the tendency of CO$_2$ to escape from the seawater.

Knowledge of spatial and temporal distributions of $p$CO$_2$ in surface ocean waters is essential to understanding of carbon cycling and ocean acidification (Borges, 2005; Bauer et al., 2013). Since the industrialization era, ocean acidity has increased by 30% (~0.1 decrease in pH units), corresponding to a 40% increase in atmospheric CO$_2$ (Sabine et al., 2004; Solomon et al., 2007; Feely et al., 2009; Pachauri and Meyer, 2014). As a result, a degradation of ecological environment and a decrease in marine biodiversity have been observed (Reynaud et al., 2003; Orr et al., 2005; Kleypas et al., 2006; Kleypas and Yates, 2009). Knowledge of surface $p$CO$_2$ also helps to quantify air-sea CO$_2$ flux (Borges et al., 2005; 2006; Cai et al., 2006). The benefits of quantifying air-sea CO$_2$ flux are twofold: 1) it can help to better understand the ocean acidification process; and 2) it can provide insight into carbon cycling. Synoptic and frequent surface $p$CO$_2$ measurements are critical to quantifying the air-sea CO$_2$ flux and ocean acidity.

The variation of surface $p$CO$_2$ is complex, being closely related to the carbonate parameters: pH, total dissolved inorganic carbon (DIC, $\mu$mol kg$^{-1}$) and total alkalinity (TA, $\mu$mol kg$^{-1}$) (Pilson,
In a carbonate system, once sea surface temperature (SST, °C), sea surface salinity (SSS, practical salinity unit) and pressure are known, any two parameters of TA, DIC, pCO₂, and pH can be used to calculate the other two and CO₂ speciation (i.e., [CO₃²⁻] and thus the carbonate mineral saturation state) using the CO₂ System Program (CO2SYS) (Pierrot and Wallace 2006). In principle, surface water pCO₂ in the ocean is mainly controlled by four processes: physical mixing, thermodynamic effects, biological activities, and air-sea CO₂ exchange (Fennel et al., 2008; Ikawa et al., 2013; Xue et al., 2016). These processes usually do not affect surface pCO₂ independently, but in an interrelated fashion (Murata, 2006).

1.1. Thermodynamic effects

Ocean thermodynamic effect on surface pCO₂ is dependent on SST, which influences the solubility of gaseous CO₂ (Weiss, 1974). The relationship between surface pCO₂ and SST can be estimated with an exponential function ($pCO₂_{T2} = pCO₂_{T1} \times e^{0.0423 \times (T_2 - T_1)}$) (Takahashi et al., 2002; 2009) although the exact parameter can deviate slightly from 0.0423 in coastal waters (Bai et al., 2015; Joesoef et al., 2015). The equation shows that an increase of SST increases surface pCO₂, and vice versa. SST is primarily regulated by several physical processes such as solar energy radiation, air-sea heat exchanges, and vertical oceanic mixing (Takahashi et al., 2002). Studies show that SST is the dominant factor in controlling seasonal variations of surface pCO₂ in the subtropical oligotrophic ocean waters (Takahashi et al., 2002; Fay and McKinley, 2017).
1.2. Biological activities

Biological activities in the ocean such as photosynthesis, respiration, and calcification have direct effects on surface $p$CO$_2$ because photosynthesis consumes CO$_2$, respiration produces CO$_2$, and calcification depletes both TA and DIC in a 2 to 1 ratio (Murata and Takizawa, 2002).

Photosynthesis by phytoplankton is mainly controlled by the concentrations of surface nutrients (i.e., $[NO_3^-]$, $[SO_4^{2-}]$, $[Fe^{2+}]$), SST, and light availability, which are all set by the physical environment (Fay and McKinley, 2017). Under optimal conditions (i.e., sufficient nutrients and sunlight at proper water temperatures, usually in spring and fall), phytoplankton blooms occur. In most cases, phytoplankton blooms (e.g., cyanobacteria blooms) would bring a distinct decrease in surface $p$CO$_2$ due to the great consumption of CO$_2$ in the production of organic carbons (Schneider et al., 2006; Martz et al., 2009). However, there are some exceptions. For example, Shadwick et al. (2011) found that spring blooms could introduce a sharp drop of surface $p$CO$_2$ by ~ 180 µatm, while the blooms in fall did not appear to change the surface $p$CO$_2$. This lack of change has been mainly attributed to the competing effect of decreasing SST, though the bloom can be clearly detected from satellite images. Furthermore, for phytoplankton blooms that also produce calcium carbonate (e.g., coccolithophorid, *E. huxleyi*), it was found that such phytoplankton blooms could result in an increase in surface $p$CO$_2$ (Murata and Takizawa, 2002; Murata, 2006). In these type of algal blooms, both DIC and TA would decrease during the bloom. It has been observed that if the ratio of calcification to photosynthesis during the bloom is between 1:1 and 2:1, the production of CO$_2$ via calcification would balance and exceed the consumption of CO$_2$ through photosynthesis (Murata and Takizawa, 2002; Murata, 2006).

In general, the overall effect of biological activities on surface $p$CO$_2$ is quite complex. Currently, the most common proxies for this biological term include chlorophyll concentrations.
(Chl, mg m$^{-3}$) and light attenuation coefficients (Salisbury et al., 2008; Zhu et al., 2009; Hales et al., 2012; Signorini et al., 2013; Fay and McKinley, 2017). In addition, studies show that the biologic effect on surface $p$CO$_2$ only dominates in high-latitude waters greater than 40° latitude in both hemispheres (Takahashi et al., 2002; Fay and McKinley, 2017).

### 1.3. Ocean mixing

Different water masses have specific carbonate characteristics such as TA and DIC. The horizontal and vertical mixing among these water masses can affect the surface $p$CO$_2$ distribution in a dynamic way. For example, the mixing between the ice meltwater (typically with a low DIC value) with the surrounding seawater in the Arctic Ocean would reduce $p$CO$_2$ by 50-60 µatm, which compensates the increase of $p$CO$_2$ caused by the water warming in summer (Cai et al., 2010). In river-dominated coastal oceans (e.g., the northern Gulf of Mexico and the East China Sea), the riverine water mass (i.e., river plume) has distinct water properties (i.e., SST, SSS, TA, DIC, and nutrients) relative to those of the seawater. The mixing between the fresh/brackish riverine waters and seawater have great impact on the variation of surface $p$CO$_2$, in terms of the conservative mixing of the carbonate properties (i.e., TA and DIC), as well as the nutrient-enhanced phytoplankton blooms (e.g., Lohrenz and Cai, 2006; Lohrenz et al., 2010; Bai et al., 2015). In addition, the surface cooling-induced, or wind-induced, vertical mixing and ocean upwelling also varies surface $p$CO$_2$. This is because vertical mixing and upwelling transport DIC enriched (mostly CO$_2$ enriched) waters to the surface where they generally release CO$_2$ into the atmosphere. However, in the presence of nutrient-enriched surface waters, phytoplankton production would be enhanced and uptake of atmospheric CO$_2$ would occur (e.g., Hales et al., 2005; Ikawa et al., 2013; Norman et al., 2013; Huang et al., 2015).
Oceanic water masses derived from melted ice and river sources typically have low SST and SSS. Oceanic water masses brought to the surface via vertical mixing and upwelling usually have lower temperature and salinity values. Therefore, SST and SSS are commonly used as proxies to quantify the effect of ocean mixing on surface $p$CO$_2$ (e.g., Lohrenz and Cai, 2006; Lohrenz et al., 2010; 2018; Hales et al., 2012; Signorini et al., 2013; Bai et al., 2015). In addition to SST and SSS, wind speed and the mixed layer depth was also used in some studies (Jamet et al., 2007; Chierici et al., 2009; Shadwick et al., 2010; Nakaoka et al., 2013).

### 1.4. Air-Sea CO$_2$ exchange

The difference between the surface ocean $p$CO$_2$ and atmospheric $p$CO$_2$ at the air-sea interface represents the thermodynamic driving potential for the CO$_2$ to transfer across the air-sea interface (Takahashi et al., 2002). The direction of the net CO$_2$ transfer is governed by the $p$CO$_2$ differences between the ocean’s surface and its overlying atmosphere. On seasonal time scales, Lu et al. (2012) found that air-sea CO$_2$ exchange exceeded the role of SST and dominated the seasonal variations of surface $p$CO$_2$ in the northern South China Sea. On short time scales (i.e., a few days up to 3 weeks), extreme weather events such as hurricanes also have strong impact on surface $p$CO$_2$, via air-sea CO$_2$ exchange. It’s known that the rate of air-sea CO$_2$ exchange depends on the gas transfer velocity, which is a function of wind speed. During high-wind events (i.e., hurricanes, and strong storms), the wind speed is usually greater than 10 m s$^{-1}$. Bates et al. (1998) found that hurricanes in the Sargasso Sea could greatly increase the outgassing of CO$_2$ from the ocean surface to the atmosphere and decrease the surface $p$CO$_2$ further, despite the strong cooling effect during the events (which would also decrease surface $p$CO$_2$ by ~60 µatm). However, Turk et al. (2013) shows that episodic high wind events would increase surface $p$CO$_2$ by 30-50 µatm, regardless of
the pre-event conditions of the upper ocean water mass (either stratified, non-stratified, oversaturated, or under-saturated).

In most cases (except extreme events), air-sea CO$_2$ exchange has little effect on the surface $p$CO$_2$ during short-time scales, mainly due to buffering of the carbonate system (Murata et al., 2002; Bai et al., 2015). However, during long-time scales, surface $p$CO$_2$ has changed with time, especially during the anthropogenic increase of atmospheric $p$CO$_2$ (Takahashi et al., 2002; 2009), and atmospheric $p$CO$_2$ can be used as a proxy to quantify how air-sea CO$_2$ exchange affects surface $p$CO$_2$ (Lefèvre and Taylor, 2002).

2. Satellite estimation of surface ocean $p$CO$_2$

Synoptic and frequent surface $p$CO$_2$ measurements are critical to quantifying the air-sea CO$_2$ flux and ocean acidification. Due to data scarcities of surface $p$CO$_2$ from ship-based measurements and their limitations in spatial and temporal coverages, large uncertainties exist in the resultant air-sea CO$_2$ fluxes (e.g., Takahashi et al., 2002; 2009; Tseng et al., 2011; Vandemark et al., 2011; Geilfus et al., 2012). Numerical models have been used to estimate surface $p$CO$_2$ (Xue et al., 2014; Arruda et al., 2015), however the model results are strongly dependent on the assumption of the initial conditions. In contrast, recent advances in satellite ocean color remote sensing have shown its capacity in synoptic and frequent mapping of surface $p$CO$_2$ through developing relationships between environmental variables and surface $p$CO$_2$.

2.1. Satellite-derived environmental variables

Although surface $p$CO$_2$ is mainly controlled by the four processes as described in Section 1, in practice, it is hard to accurately quantify each of them separately due to the interactions among
them. Therefore, most of the satellite mapping models of surface \( p\text{CO}_2 \) are empirical (see Section 2.2 for details), and the most commonly used environmental variables include SST, SSS, Chl (e.g., Lohrenz and Cai, 2006; Lohrenz et al., 2010; 2018; Hales et al., 2012; Signorini et al., 2013; Bai et al., 2015). SST and SSS are proxies for the thermodynamic and ocean mixing effects, and Chl is a proxy for biological activities. In addition to these variables, some studies also used a beam attenuation coefficient, absorption of the Colored Dissolved Organic Matter (CDOM), Mixed Layer Depth (MLD), and wind speed as auxiliary variables to quantify surface \( p\text{CO}_2 \) in some oceanic regions (e.g., Jamet et al., 2007; Salisbury et al., 2008; Chierici et al., 2009; Shadwick et al., 2010; Nakaoka et al., 2013; Parard et al., 2014).

Of the commonly used environmental variables, SST and ocean color data products (i.e., Chl, CDOM, diffuse attenuation coefficient of the downwelling irradiance \( K_d, \text{m}^{-1} \)) are available from the ocean color satellites such as Moderate Resolution Imaging Spectroradiometer (MODIS). However, currently there is no standard SSS data from these ocean color satellites.

The satellites designed to “measure” SSS, such as the ESA SMOS (the Soil Moisture and Ocean Salinity) and NASA Aquarius/SAC-D, lack sufficient spatial (30-100 km) and temporal resolution (≥ 3days revisit period), and they are not designed for dynamic coastal waters (Lagerloef et al., 2008; Font et al., 2010). Since CDOM is a good tracer of SSS in coastal oceans (e.g., Hu et al., 2003; Coble et al., 2004; Del Vecchio and Blough, 2004), several studies have demonstrated the potentials of ocean color satellites in deriving SSS via empirical models (e.g., Bai et al., 2013; Geiger et al., 2013; Qing et al., 2013; Vandermeulen et al., 2014; Zhao et al., 2017). However, these models are region-dependent and may have poor applicability in other coastal waters, considering the difference of optical complexities among coastal regions. Therefore, in order to
map the surface $p$CO$_2$ from satellites in different coastal ocean settings, SSS data products from ocean color need to be developed first.

2.2. Satellite mapping of surface $p$CO$_2$: current status

At present, most of the published literature correlate surface $p$CO$_2$ to the environmental variables (SST, SSS, Chl, etc.) via traditional empirical regression and machine learning approaches (i.e., neural network) with variable performance in different oceanic regions (e.g., Stephens et al., 1995; Rangama et al., 2005; Wanninkhof et al., 2007; Zhu et al., 2009; Chierici et al., 2009; Friedrich and Oschlies, 2009; Telszewski et al., 2009; Signorini et al., 2013; Nakaoka et al., 2013; Parard et al., 2014). Specifically, for the open oceans, the satellite $p$CO$_2$ models often yield results with Root Mean Square Error (RMSE) between 10 and 20 µatm (e.g., Table 1), while for the coastal oceans, the model RMSE is > 20 µatm in most cases (Table 2). Some studies also proposed semi-analytical approaches to estimate surface $p$CO$_2$, but with larger error (RMSE > 30 µatm) (Hales et al., 2012; Bai et al., 2015; Song et al., 2016).

### Table 1: List of published satellite $p$CO$_2$ remote sensing algorithms for open ocean waters. It should include most, if not all, the published studies of surface $p$CO$_2$ from remote sensing in the open oceans.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Study area</th>
<th>Model input</th>
<th>Model</th>
<th>Model uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stephens et al. (1995)</td>
<td>North Pacific</td>
<td>SST, LON</td>
<td>MPR</td>
<td>RMSE=$\pm$17 µatm (subtropical), RMSE=$\pm$40µatm (subpolar)</td>
</tr>
<tr>
<td>Sarma (2003)</td>
<td>Arabian Sea</td>
<td>SST, SSS, CHL</td>
<td>MLR for DIC and TA</td>
<td>errors=$\pm$5-30 µatm</td>
</tr>
<tr>
<td>Lefevre and Taylor (2002)</td>
<td>Atlantic Gyre</td>
<td>SST, LAT, LON, atmospheric $p$CO$_2$</td>
<td>MLR</td>
<td>R=0.95–0.99</td>
</tr>
<tr>
<td>Olsen et al. (2004)</td>
<td>Caribbean Sea</td>
<td>SST, LAT, LON</td>
<td>MLR</td>
<td>RMSE=9.5 µatm, $R^2$=0.8</td>
</tr>
<tr>
<td>Ono et al. (2004)</td>
<td>North Pacific</td>
<td>SST, CHL</td>
<td>MPR</td>
<td>RMSE=$\pm$14 µatm (subtropical), RMSE=$\pm$17 µatm (subpolar)</td>
</tr>
<tr>
<td>Rangama et al. (2005)</td>
<td>Southern ocean</td>
<td>SST, CHL</td>
<td>MLR</td>
<td>STD=2.6–7.9 µatm</td>
</tr>
<tr>
<td>Sarma et al. (2006)</td>
<td>North Pacific</td>
<td>SST, SSS, CHL</td>
<td>MLR for DIC and TA</td>
<td>RMSE=17–23 µatm</td>
</tr>
</tbody>
</table>
Table 1 (Continued)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Study area</th>
<th>Model input</th>
<th>Model</th>
<th>Model uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jamet et al. (2007)</td>
<td>North Atlantic</td>
<td>SST, CHL, MLD</td>
<td>MLR</td>
<td>$R=0.45$–$0.86$, RMSE = 8.98–15.01 µatm</td>
</tr>
<tr>
<td>Berryman et al. (2008)</td>
<td>Central Pacific</td>
<td>SST, SSS, CHL</td>
<td>MLR</td>
<td>$R^2=0.59$, $p&lt;0.02$</td>
</tr>
<tr>
<td>Chierici et al. (2009)</td>
<td>Northern North Atlantic</td>
<td>SST, CHL, MLD</td>
<td>MPR</td>
<td>RMSE=10.8 µatm, $R^2=0.72$</td>
</tr>
<tr>
<td>Telszewski et al. (2009)</td>
<td>North Atlantic</td>
<td>SST, CHL, MLD</td>
<td>SOM</td>
<td>RMSE=11.6 µatm</td>
</tr>
<tr>
<td>Friedrich and Oschlies (2009)</td>
<td>North Atlantic</td>
<td>SST, CHL</td>
<td>KFM</td>
<td>RMSE=19 µatm</td>
</tr>
<tr>
<td>Chen et al. (2011)</td>
<td>Southern Atlantic and Indian Ocean</td>
<td>SST, CHL</td>
<td>MLR</td>
<td>$R^2=0.77$, 0.85, STD=1.21, 21.0 µatm</td>
</tr>
<tr>
<td>Nakaoka et al. (2013)</td>
<td>North Pacific</td>
<td>SST, SSS, CHL, MLD</td>
<td>SOM</td>
<td>RMSE=17.6–20.2 µatm</td>
</tr>
<tr>
<td>Moussa et al. (2016)</td>
<td>Tropical Atlantic</td>
<td>SST, SSS, CHL</td>
<td>FNN</td>
<td>RMSE=8.7–9.6 µatm</td>
</tr>
<tr>
<td>Xu et al. (2017)</td>
<td>Southern Ocean</td>
<td>SST, CHL</td>
<td>MLR</td>
<td>RMSE=13.6–21.3 µatm</td>
</tr>
</tbody>
</table>

Note: MLR=Multiple Linear Regression; MPR=Multiple Polynomial Regression; SOM=Self Organising Map; KFM=Kohonen Feature Map; FNN=Feedforward Neural Network; STD=Standard Deviation; $R=Correlation$ Coefficient; SST=Surface Temperature, CHL=Chlorophyll concentration; MLD=Mixed Layer Depth; LAT=Latitude; LON=Longitude; TA=Total Alkalinity; DIC=Dissolved Inorganic Carbon.

Table 2: List of published satellite $pCO_2$ remote sensing algorithms for coastal ocean waters. It should include most, if not all, the published studies of surface $pCO_2$ from remote sensing in the coastal oceans.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Study area</th>
<th>Model input</th>
<th>Model</th>
<th>Model uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lefevre et al. (2002)</td>
<td>Coast off Chile</td>
<td>SST, SSS, CHL</td>
<td>MLR</td>
<td>STD=35 µatm, $R^2=0.65$</td>
</tr>
<tr>
<td>Lohrenz and Cai (2006)</td>
<td>Mississippi River delta</td>
<td>SST, SSS, CHL</td>
<td>PCA and MLR</td>
<td>$R^2=0.743$, RMSE=50.2 µatm</td>
</tr>
<tr>
<td>Evans et al. (2008)</td>
<td>Oregon and Washington Shelf</td>
<td>SST, CHL</td>
<td>Not available</td>
<td>Not available</td>
</tr>
<tr>
<td>Zhu et al. (2009)</td>
<td>Northern South China Sea</td>
<td>SST, CHL</td>
<td>MPR</td>
<td>$R^2=0.66$–0.68, RMSE=4.6–25.1 µatm</td>
</tr>
<tr>
<td>Shadwick et al. (2010)</td>
<td>Scotian Shelf</td>
<td>SST, CHL, wind speed</td>
<td>MLR</td>
<td>STD=13 µatm, $R^2=0.81$</td>
</tr>
<tr>
<td>Borges et al. (2010)</td>
<td>Belgian coastal zone</td>
<td>SST, CHL</td>
<td>MPR</td>
<td>Not available</td>
</tr>
<tr>
<td>Lohrenz et al. (2010)</td>
<td>Mississippi River delta</td>
<td>SST, SSS, CHL</td>
<td>PCA and MLR</td>
<td>$R^2=0.165$–0.976, $p&lt;0.001$</td>
</tr>
<tr>
<td>Karagali et al. (2010)</td>
<td>Peru and Namibia</td>
<td>SST, CHL</td>
<td>MPR</td>
<td>$R^2=0.67$–0.72</td>
</tr>
<tr>
<td>Wipf et al. (2012)</td>
<td>Santa Barbara Channel</td>
<td>SST, CHL, NO$_3$</td>
<td>MLR</td>
<td>Not available</td>
</tr>
<tr>
<td>Jo et al. (2012)</td>
<td>Northern South China Sea</td>
<td>SST, CHL, LAT, LON</td>
<td>FFBP</td>
<td>RMSE=6.9 µatm, $R^2=0.98$</td>
</tr>
<tr>
<td>Hales et al. (2012)</td>
<td>North American West Coast</td>
<td>SST, CHL</td>
<td>Quasi-mechanistic model</td>
<td>$R=0.61$–0.93, RMSE=6.6–65 µatm</td>
</tr>
<tr>
<td>Tao et al. (2012)</td>
<td>Huanghai Sea and Bohai Sea</td>
<td>SST, CHL</td>
<td>MPR</td>
<td>RMSE=15.82–31.74 µatm</td>
</tr>
<tr>
<td>Signorini et al. (2013)</td>
<td>North American East Coast</td>
<td>SST, SSS, CHL, Jday</td>
<td>MLR</td>
<td>$R^2=0.42$–0.82, RMSE=22.4–36.9 µatm</td>
</tr>
<tr>
<td>Marrec et al. (2014)</td>
<td>Western English Channel</td>
<td>SST, SSS, CHL, MLD, Jday, LAT, LON</td>
<td>MLR</td>
<td>RMSE=17.2, 21.5 µatm, $R^2=0.71$–0.79</td>
</tr>
<tr>
<td>Parard et al. (2014)</td>
<td>Baltic Sea</td>
<td>SST, CHL, CDOM, NPP, MLD, Jday</td>
<td>MLR and SOM</td>
<td>RMSE=35 µatm, $R^2=0.93$</td>
</tr>
</tbody>
</table>
Regardless if an empirical or semi-analytical approach is used, the resulting published satellite $p$CO$_2$ model depends on the assumptions made for a specific oceanic region (e.g., river dominated, ocean-current dominated, or upwelling dominated). To date, there is no unified $p$CO$_2$ approach, let alone a unified $p$CO$_2$ model with region-specific parameterization, available to estimate surface $p$CO$_2$ from satellites for a large oceanic domain (e.g., the Gulf of Mexico) that contains several different oceanic processes. The difficulty in obtaining a unified approach to estimate surface $p$CO$_2$ from satellites with relatively lower uncertainties is due mostly to the complexity and dynamics of the biogeochemical and physical processes in such regions.

In some of the published satellite-based $p$CO$_2$ models, the monthly mean satellite products or climatology for Chl are used as model inputs to compensate for the scarcities of concurrent and co-located satellite measurements of Chl. These satellite measurements are paired with *in situ* $p$CO$_2$ to develop a model. As a result, significant uncertainties could exist in the nonlinear $p$CO$_2$ models (Zhu et al., 2009; Jo et al., 2012; Hale et al., 2012; Signorini et al., 2013; Parard et al., 2014). Likewise, the sensitivity of the established models to each input variable has rarely been

### Table 2 (Continued)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Study area</th>
<th>Model input</th>
<th>Model</th>
<th>Model uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qin et al. (2014)</td>
<td>Yellow Sea</td>
<td>SST, CHL</td>
<td>MPR</td>
<td>RMSE=16.68–21.46 µatm</td>
</tr>
<tr>
<td>Bai et al. (2015)</td>
<td>East China Sea</td>
<td>TA, DIC, CHL</td>
<td>MeSAA</td>
<td>Not available, but large data scattering in validation</td>
</tr>
<tr>
<td>Marrec et al. (2015)</td>
<td>European shelf</td>
<td>SST, CHL, wind speed, PAR, MLD</td>
<td>MLR</td>
<td>RMSE=16, 17 µatm</td>
</tr>
<tr>
<td>Padhy et al. (2015)</td>
<td>Hooghly Estuary</td>
<td>SST, CHL</td>
<td>MPR</td>
<td>RMSE=18 µatm</td>
</tr>
<tr>
<td>Song et al. (2016)</td>
<td>Bering Sea</td>
<td>SST, CHL</td>
<td>MeSAA</td>
<td>STD=17.67–74.8 µatm</td>
</tr>
<tr>
<td>Lohrenz et al. (2018)</td>
<td>Mississippi River delta</td>
<td>SST, CDOM, CHL</td>
<td>Regression tree</td>
<td>RMSE = 30.8 µatm</td>
</tr>
<tr>
<td>Joshi et al. (2018)</td>
<td>Apalachicola Bay</td>
<td>SST, CDOM, CHL</td>
<td>MLR</td>
<td>Uncertainty = ±101 ppm and ±643 ppm</td>
</tr>
</tbody>
</table>

Note: MLR=Multiple Linear Regression; MPR=Multiple Polynomial Regression; SOM=Self Organising Map; KFM=Kohonenn Feature Map; FNN=Feedforward Neural Network; FFBP= Feed Forward Back Propagation; MeSAA=Mechanistic Semi-Analytical Algorithm; PCA=Principal Component Analysis; STD=Standard Deviation; R=Correlation Coefficient; SST=Sea Surface Temperature; SSS=Sea Surface Salinity; CHL=Chlorophyll concentration; MLD=Mixed Layer Depth; LAT=Latitude; LON=Longitude; TA=Total Alkalinity; DIC=Dissolved Inorganic Carbon; CDOM=Colored Dissolved Organic Matter; NPP=Net Primary Production; PAR=Photosynthetically Active Radiation; Jday=Julian day.
studied (Lefèvre et al., 2002; Olsen et al., 2004; Zhu et al., 2009; Lohrenz and Cai, 2006; Lohrenz et al., 2010; Borges et al., 2010; Parard et al., 2014). As satellite-derived variables (i.e., SST, SSS, and Chl) have inherent uncertainties (Hu et al., 2009; Cannizzaro et al., 2013), error propagation in model-derived $p$CO$_2$ needs to be understood, especially for regions with potentially large uncertainties in these satellite-derived variables. Therefore, in this study, the uncertainties in satellite products used in the $p$CO$_2$ model will be quantified to better understand their error propagations.

3. Study area

As the largest semi-enclosed marginal sea of the western Atlantic, the Gulf of Mexico (GOM) encompasses the West Florida Shelf (WFS), Louisiana Shelf, Texas Shelf, Mexican Shelf, the Cuban Shelf, and the open Gulf, with a surface area of 1.6 million km$^2$, as shown in Figure 1.1. Each of these regions is dominated by different oceanic processes. The WFS is a broad carbonate-based shelf with gentle slope. It is mainly controlled by the coastal currents with little freshwater inputs. The offshore area of the WFS is also affected by the Loop current. The Louisiana Shelf is the most dynamic region of the GOM, with larger amounts of freshwater discharges from the Mississippi-Atchafalaya River system (MARS). Texas Shelf is very narrow and usually receives lots of freshwater from the MARS during spring. Mexican Shelf is also broad which is characterized by the coastal upwelling along the carbonate Campeche Bank. The Cuban shelf is narrow and is mainly affected by the Loop Current in the Florida Strait. The open Gulf is the mainly controlled by the Loop Current, and mesoscale eddies.

The GOM is a very productive marine ecosystem (estimated at 150-300 g C m$^{-2}$ yr$^{-1}$; Heileman and Rabalais, 2008) and an important global reservoir of biodiversity and biomass of
fish, sea birds, and marine mammals (Widdicombe and Spicer, 2008; Xue et al., 2013), thus, it is important to quantify the role of the GOM in modulating CO$_2$ flux and ocean acidification through estimating surface $p$CO$_2$.

![Map of the Gulf of Mexico](image)

**Figure 1.1:** Study region of the Gulf of Mexico. The Gulf of Mexico encompasses the West Florida Shelf (WFS), Louisiana Shelf (LA), Texas Shelf (TX), Mexican Shelf (MX), Cuban Shelf, and the open Gulf.

In previous studies, contradictory results about the air-sea CO$_2$ flux in the GOM were obtained. For instance, based on field measurements, Takahashi et al. (2009) estimated the GOM to be a CO$_2$ source (CO$_2$ flux = 0.21 mol C/m$^2$/year). On the other hand, Xue et al. (2014) estimated the GOM to be a CO$_2$ sink (CO$_2$ flux = -0.84 mol C/m$^2$/year) using a 3-dimensional numerical model. Benway and Coble (2014) also concluded that the GOM is a CO$_2$ sink but with a smaller flux (CO$_2$ flux = -0.19 mol C/m$^2$/year). These discrepancies resulting from these studies show that...
new methods need to be developed to better quantify the air-sea CO₂ flux and understand carbon cycling and ocean acidification in the GOM. Synoptic and frequent mapping of surface pCO₂ from satellites should play an important role in developing new methods.

In the northern GOM near the MARS, Lohrenz and Cai (2006) and Lohrenz et al. (2010; 2018) developed empirical pCO₂ models using satellite-derived SST, SSS and Chl. However, due to the complexities and dynamics of the northern GOM waters, these models all showed relatively large errors (i.e., RMSE > 30 µatm). Such errors would introduce large uncertainties in the quantification of air-sea CO₂ flux. Thus, model improvements are needed. In other GOM waters, uncertainties are greater because there are no satellite pCO₂ models or data products available.

4. Objectives

The overarching goals of this research are to advance satellite remote sensing technology by developing surface pCO₂ models and data products for most of the GOM waters, and to improve our understanding of the mechanisms and dominant factors in controlling surface pCO₂. Towards these goals, the specific research objectives are:

1) Develop satellite-based surface pCO₂ models and data products for single-process dominated subregions of the GOM, and quantify the sensitivities of the pCO₂ algorithms to the input environmental variables.

2) Quantify the oceanic processes in controlling surface pCO₂ in the GOM, analyze the relationships between environmental variables and surface pCO₂, and understand the mechanisms of seasonal and interannual variations of surface pCO₂ and its driving factors.
3) Develop an improved SSS model and data products for most GOM waters, and quantify the sensitivities of the SSS model to the input variables.

4) Develop a unified $pCO_2$ model and data products for the GOM waters, and quantify the sensitivities of the $pCO_2$ model to the input environmental variables.

5) Quantify the temperature and non-temperature effects on surface $pCO_2$ at different latitudes, analyze the dominant controls and the corresponding the driving factors of surface $pCO_2$.

5. Data sources

5.1. Field data

In the years between 2002 and 2017, over 220 cruise surveys have been conducted to collect flow-through surface $pCO_2$ data during different seasons in the GOM as well as one buoy time series data from the Coastal Mississippi Buoy. Most of these $pCO_2$ data were obtained from the NOAA National Centers for Environmental Information (NCEI) (https://www.nodc.noaa.gov/ocads/), and several cruise data were obtained from University of Columbia, Texas A andM University, and University of Delaware. All these surface $pCO_2$ data sources were compiled and quality controlled for the development of surface $pCO_2$ remote sensing algorithms in this research. Details of these data can be found in Appendixes of A, B, and D. It should be clarified that data collected before July 2002 were not used mainly because there is no MODIS data available for that period.

In addition to surface $pCO_2$, SSS was also measured and collected in all the field surveys mentioned above. To develop the SSS remote sensing algorithm for the GOM, the SSS data
collected from these field surveys was compiled and quality controlled. Other cruises that measured SSS but not surface $pCO_2$ were also used. Specifically, ship-based cruise data collected in the GOM by College of Marine Science University of South Florida, Florida Fish and Wildlife Conservation Commission (FWC), and buoy-based time series data collected in the GOM from NOAA National Data Buoy Center (NDBC) buoys were also compiled and quality controlled, and merged with the SSS datasets from the $pCO_2$ data surveys. Details of these data can be found in Appendix C.

To analyze the driving mechanisms of surface $pCO_2$ in different coastal ocean environments, *in situ* surface $pCO_2$ time series data collected from buoys located at different latitudes along the coasts of U. S. and its territories were compiled and quality controlled. These data were obtained from the NOAA NCEI. Details of these can be found in Appendix E.

### 5.2. Satellite data

NASA standard daily Level-2 data products (version R2014.0) for the period of Jul. 2002 – Dec. 2017 with a spatial resolution of ~1 km were downloaded from the NASA Goddard Space Flight Center (GSFC) ([https://oceancolor.gsfc.nasa.gov/](https://oceancolor.gsfc.nasa.gov/)). These Level-2 data products were derived from measurements by the Moderate Resolution Imaging Spectroradiometer (MODIS) on the Aqua satellite, and they included Chl, SST, and spectral remote sensing reflectance (Rrs, $sr^{-1}$) in 7 bands between 412 and 678 nm. The spectral Rrs data were used to calculate $K_a$ using the semi-analytical algorithm developed by Lee et al. (2005). The MODIS-derived environmental variables including Chl, $K_a$, SST, and SSS were used as inputs for the development of $pCO_2$ remote sensing algorithms. The spectral Rrs data and SST were used to develop the SSS remote sensing algorithm.
6. Approach and dissertation structure

This dissertation is arranged in chapters that detail the research conducted to fulfill these objectives. Chapters 2 and 3 focus on the estimation of surface $pCO_2$ from MODIS in single-process dominated regions of the GOM: the WFS and the northern GOM, respectively (Objective 1). For the WFS, a multi-variate nonlinear regression (MNR) model is developed to estimate surface $pCO_2$ from MODIS, and in the northern GOM, a previously developed mechanistic semi-analytical algorithm (MeSAA) is evaluated and locally-tuned, and compared with the performance of regression-based models. For both regions, the sensitivity of the developed $pCO_2$ models to the input environmental variables and their relationships are analyzed. The MeSAA model is developed through quantifying different oceanic processes that affect surface $pCO_2$ variations (Objective 2). The driving mechanisms of the seasonal and interannual variations of surface $pCO_2$ on the WFS are analyzed (Objective 2).

The satellite mapping of surface $pCO_2$ in the northern GOM waters requires the development of SSS data products from ocean color remote sensing (Objective 3). This work is completed using MODIS and SeaWiFS data, as described in Chapter 4. Briefly, a multilayer perceptron neural network (MPNN) is developed to estimate SSS from satellite-derived SST and remote sensing reflectance (Rrs(λ), m$^{-1}$) in the visible bands. The sensitivity of the model to realistic model input errors is analyzed and quantified.

Most of the published satellite-based $pCO_2$ models are developed for single-process dominated oceanic regions, as described in Chapters 2 and 3. The availability of SSS data products from remote sensing in the GOM (Chapter 4) makes it possible to test the feasibility of developing a unified $pCO_2$ model for the multi-process dominated GOM (Objective 4). Chapter 5 details the
development of such a unified $pCO_2$ model for the GOM, which proves the possibility of using the proposed approach for other oceanic regions (e.g., Gulf of Maine). The seasonal and interannual variability of surface $pCO_2$ in the GOM, and the relationships between $pCO_2$ and environmental variables, as well as the underlying driving mechanisms, are also analyzed in Chapter 5 (Objective 2).

Chapter 6 details the decomposition of the effects of temperature and non-temperature on surface $pCO_2$ variations, based on buoy time series data at different latitudes in both open oceans and coastal oceans (Objective 5). The underlying driving mechanisms of the seasonal variations of surface $pCO_2$ as well as their temperature and non-temperature components are analyzed, where the relationships between surface $pCO_2$ and environmental variables are also quantified.

Finally, Chapter 7 summarizes the works and findings in the previous chapters, with particular focus on the implications of the dissertation as a whole. Overall implications are presented on both the successes and lessons learned from this work. Furthermore, Chapter 7 also discusses future research directions to broaden the findings of this work and to study $CO_2$ flux, carbon cycling, and ocean acidification using satellite data.

7. Literature cited


Pacific using a self-organizing map neural network technique. Biogeosciences, 10(9), 6093-6106.


air CO$_2$ flux based on climatological surface ocean $p$CO$_2$, and seasonal biological and temperature effects. Deep Sea Research Part II: Topical Studies in Oceanography, 49(9-10), 1601-1622.


CHAPTER 2:

ESTIMATING SURFACE $pCO_2$ IN SINGLE-PROCESS DOMINATED REGION FROM SATELLITES: THE WEST FLORIDA SHELF

Note to Reader

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1. Research overview

Appendix A – Remote estimation of surface $pCO_2$ on the West Florida Shelf (Chen et al., 2016)

As one of the broadest continental shelves of the U. S., the West Florida Shelf (WFS) should play a big role in modulating CO$_2$ flux in the Gulf of Mexico (GOM). However, despite significant efforts to collect surface $pCO_2$ data through numerous ship surveys, synoptic mapping of surface $pCO_2$ from satellites is available for the WFS. In this study, a multi-variable empirical surface $pCO_2$ model was firstly developed for satellite mapping of surface $pCO_2$ over the WFS, with a Root Mean Square Error (RMSE) of $< 12 \mu atm$ and a $R^2$ of 0.88 for $pCO_2$ ranging from 300 to 550 $\mu atm$ ($N = 1,516$). This model was based on concurrent MODIS estimates of surface chlorophyll concentrations, diffuse light attenuation at 490 nm, and sea surface temperature. The first spatial and temporal estimate of distributions of surface $pCO_2$ on the WFS were investigated and discussed in this study. However, while the general approach of empirical regression may work for waters in other
areas of the GOM, model coefficients will most likely need to be empirically determined in a similar fashion.
CHAPTER 3:
ESTIMATING SURFACE $pCO_2$ IN SINGLE-PROCESS DOMINATED REGION FROM SATELLITES: THE NORTHERN GOM

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1. Research overview

Appendix B – Estimating surface $pCO_2$ in the northern Gulf of Mexico: Which remote sensing model to use? (Chen et al., 2017a)

Various approaches and models have been proposed to remotely estimate surface $pCO_2$ in the ocean, with variable performance as they were designed for different environments. Among these, a recently developed mechanistic semi-analytical approach (MeSAA) has shown an advantage for its explicit inclusion of physical and biological forcing in the model, yet its general applicability is unknown. Here, with extensive in situ measurements of surface $pCO_2$, the MeSAA was tested in the northern GOM where river plumes dominate the coastal water’s biogeochemical properties during summer. Specifically, the MeSAA-predicted surface $pCO_2$ was estimated by combining the dominating effects of thermodynamics, river-ocean mixing and biological activities on the surface $pCO_2$. The RMSE (root mean square error) was 22.94 µatm (5.91 %) and $R^2$ was 0.25 for $pCO_2$ ranging between 316 and 452 µatm (N=676). A locally-tuned MeSAA and regression
models showed a RMSE of 12.36 µatm (3.14 %) and 10.66 µatm (2.68%), and $R^2$ of 0.78 and 0.84, respectively. These results suggest that the locally-tuned MeSAA worked better in the river-dominated northern GOM than the original MeSAA, with slightly worse statistics but more meaningful physical and biogeochemical interpretations than the empirical regression model. Because data from abnormal upwelling are not used to train the models, the models are not applicable for waters with strong upwelling, yet the empirical regression approach has the potential to be further tuned to adapt to such cases.
CHAPTER 4:
REMOTE ESTIMATION OF SEA SURFACE SALINITY IN THE GOM

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1. Research overview

SSS is an important input to $pCO_2$ remote sensing models, but currently there is no satellite-based SSS data product covering coastal waters with 1-km resolution. Therefore, an important step in developing $pCO_2$ models is developing a model to estimate SSS from ocean color measurements. This work is presented in Appendix C below.

Appendix C – Estimating sea surface salinity in the northern Gulf of Mexico from satellite ocean color measurements (Chen and Hu, 2017b)

Sea surface salinity (SSS) is an important parameter to characterize physical and biogeochemical processes, and it is also an important parameter to quantify the surface $pCO_2$ variation especially in the river-dominated regions, yet its remote estimation in coastal waters has been difficult because satellite sensors designed to “measure” SSS lack sufficient resolution, and higher-resolution ocean color measurements suffer from optical and biogeochemical complexity when used to estimate SSS. In the northern Gulf of Mexico (GOM), this challenge is addressed through modeling, validation, and extensive tests in contrasting environments. Specifically, using extensive SSS datasets collected by many
groups spanning > 10 years and MODIS (Moderate Resolution Imaging Spectroradiometer) and SeaWiFS (Sea-Viewing Wide Field-of-View Sensor) estimated remote sensing reflectance (Rrs(λ), m⁻¹) at 412, 443, 488 (490), 555, and 667 (670) nm and sea surface temperature (SST), a multilayer perceptron neural network-based (MPNN) SSS model has been developed and validated with a spatial resolution of ~1km. The model showed an overall performance of root mean square error (RMSE) = 1.2, with coefficient of determination (R²) = 0.86, mean bias (MB) = 0.0, and mean ratio (MR) = 1.0 for SSS ranging between ~1 and ~37 (N=3640). The model was thoroughly evaluated under different scenarios with reasonable performance. The sensitivity of the model to realistic model input errors from satellite-derived SST and Rrs was also thoroughly examined, with uncertainties in the model-derived SSS being always < 1 for SSS > 30. The extensive validation, evaluation, and sensitivity test all indicated the robustness of the MPNN model in estimating SSS in most, if not all, coastal waters and offshore plumes in the northern GOM. Thus, the model provided a basis for generating near real-time 1-km resolution SSS maps from satellite measurements. However, the model showed limitations when applied to regions with known algal blooms or upwelling as they both led to low Rrs in the blue bands that may be falsely recognized as caused by low SSS.
CHAPTER 5:  
A UNIFIED APPROACH TO ESTIMATE SURFACE OCEAN $pCO_2$ FROM  
SATELLITE MEASUREMENTS  

1. Research overview  

With all satellite-derived variables (SST, SSS, Chl, $K_d$) available as the model inputs, this chapter details the effort in using these variables to develop a unified approach to estimated $pCO_2$ in multi-process dominated regions. The steps and results are all presented in Appendix D below.  

Appendix D – A machine learning approach to estimate surface ocean $pCO_2$ from satellite measurements (Chen et al., submitted)  

Surface ocean $pCO_2$ is a critical parameter in the quantification of air-sea CO$_2$ flux, which further plays an important role in quantifying the global carbon budget and understanding ocean acidification. Yet, to date there is no unified approach, let alone unified model, to remotely estimate surface $pCO_2$ in oceanic regions that are dominated by different oceanic processes. In the study area of the Gulf of Mexico (GOM), this challenge is addressed through the evaluation of different approaches, including multi-linear regression (MLR), multi-nonlinear regression (MNR), principle component regression (PCR), decision tree, supporting vector machines (SVMs), multilayer perceptron neural network (MPNN), and random forest based regression ensemble (RFRE). After modeling, validation, and extensive tests under different scenarios, the RFRE model performed the best. The RFRE model showed an overall performance of a root mean square error (RMSE) of 9.1 µatm,
with $R^2$ of 0.95, a unbiased percentage difference (UPD) of 0.07%, and a mean ratio difference (MRD) of 0.12% for $pCO_2$ ranging between 145 and 550 µatm. The model, with its original parameterization, has been tested with independent datasets collected over the entire GOM, with satisfactory performance in each case. The sensitivity of the RFRE-based $pCO_2$ model to input errors of each environmental variable was also thoroughly examined. The extensive validation, evaluation, and sensitivity analysis indicate the robustness of the RFRE model in estimating surface $pCO_2$ in most, if not all, GOM waters. The RFRE model approach was applied to the Gulf of Maine (a contrasting oceanic region to GOM), with local model training. The results showed significant improvement over other models for that area, suggesting that the RFRE may serve as a robust approach for other regions once sufficient field-measured $pCO_2$ data are available for model training.

While most results are presented in a submitted manuscript, further analysis of surface $pCO_2$ climatology and the $pCO_2$ model sensitivity to input variables (i.e., SST, SSS, Chl, and $K_d$) is presented below.

Specifically, the monthly $pCO_2$ maps derived from MODIS between July 2002 and December 2017 were averaged to derive the climatological $pCO_2$ monthly mean. Meanwhile, the standard deviations of the monthly surface $pCO_2$, as well as the monthly maxima and minima of surface $pCO_2$ over the study period were also quantified to express the variations of surface $pCO_2$ in each month. Figs. 5.1-5.5 are the monthly mean, monthly mean with two standard deviation added, monthly mean with two standard deviations subtracted, monthly maxima, and monthly minima, of surface $pCO_2$ in the GOM, respectively. These monthly surface $pCO_2$ maps should represent the typical variation range of surface $pCO_2$ in each month, and thus can be used as
references during the field surveys of surface $pCO_2$ in the GOM in the future. It should be noted that, there is some patchiness in the monthly mean $pCO_2$ maps; specifically where two standard deviation are added (Fig. 5.2), where two standard deviations are subtracted (Fig. 5.3), and monthly maxima (Fig. 5.4) and minima (Fig. 5.5). These extreme high (or low) $pCO_2$ values are mainly caused by the large variations of the monthly surface $pCO_2$ from year to year in those regions.

Figure 5.1: Surface $pCO_2$ climatology in the GOM: monthly mean. They are based on MODIS-derived surface $pCO_2$ between July 2002 and December 2017.
Figure 5.2: Surface $pCO_2$ climatology in the GOM: monthly mean minus two standard deviations. They are based on MODIS-derived surface $pCO_2$ between July 2002 and December 2017.
**Figure 5.3:** Surface $pCO_2$ climatology in the GOM: monthly mean plus two standard deviations. They are based on MODIS-derived surface $pCO_2$ between July 2002 and December 2017.
Figure 5.4: Surface $p$CO$_2$ climatology in the GOM: monthly minima. They are based on MODIS-derived surface $p$CO$_2$ between July 2002 and December 2017.
Figure 5.5: Surface $pCO_2$ climatology in the GOM: monthly maxima. They are based on MODIS-derived surface $pCO_2$ between July 2002 and December 2017.

In the manuscript, the sensitivity of the $pCO_2$ remote sensing algorithm to the input variables was quantified based on the training dataset used to develop the algorithm. This sensitivity analysis was conducted by varying one of the input variables by a certain amount while keeping the other variables unchanged (see Appendix D). Here I did a 3-dimensional (3D) sensitivity analysis via data simulation. For example, to examine the model sensitivity to both SST and SSS, a 2-dimensional (2D) arrays for both SST and SSS were generated by varying SST and
SSS within a typical range of each input (i.e., SST within 0~35 °C, and SSS within 0~40); thus, each value of SST corresponds to different SSS values in the SSS range, and each pair of SST and SSS values was referred to as a grid cell. Further, each grid cell was assigned fixed Chl and $K_d$ values (e.g., Chl = 1.0 mg m$^{-3}$, $K_d = 0.1$ m$^{-1}$). A data matrix was generated, and each grid cell of the data matrix represented a data sample associated with SST, SSS, Chl, and $K_d$. Finally, the developed $pCO_2$ model was applied to this data matrix to calculate the surface $pCO_2$ value for each grid cell. Following the above steps, Fig. 5.6-5.12 are the 3D plots of the sensitivity of the developed $pCO_2$ model to environmental variable pairs of Chl and $K_d$, Chl and SSS, Chl and SST, $K_d$ and SSS, $K_d$ and SST, SST and SSS, respectively. These 3D plots allow the visualization of model-predicted $pCO_2$ varied against any other two of the four environmental variables (i.e., SST, SSS, Chl, and $K_d$). Similar to the sensitivity analysis in Appendix D, the $pCO_2$ algorithm is more sensitive to SST and SSS than to Chl and $K_d$. Surface $pCO_2$ showed large increase with an increase in SST and SSS, while the changes in surface $pCO_2$, in response to Chl and $K_d$ variations, were gradual with smaller amplitudes.

Figure 5.6: Sensitivity of the $pCO_2$ remote sensing algorithm to Chl and $K_d$. SST and SSS are fixed with a certain value.
**Figure 5.7:** Sensitivity of the $p$CO$_2$ remote sensing algorithm to Chl and SSS. $K_d$ and SST are fixed with a certain value.

**Figure 5.8:** Sensitivity of the $p$CO$_2$ remote sensing algorithm to Chl and SST. $K_d$ and SSS are fixed with a certain value.
Figure 5.9: Sensitivity of the $pCO_2$ remote sensing algorithm to $K_d$ and SSS. Chl and SST are fixed with a certain value.

Figure 5.10: Sensitivity of the $pCO_2$ remote sensing algorithm to $K_d$ and SST. Chl and SSS are fixed with a certain value.
Figure 5.11: Sensitivity of the pCO$_2$ remote sensing algorithm to SSS and SST. Chl and $K_d$ are fixed with a certain value.
CHAPTER 6:
DOMINANT CONTROLS OF SURFACE OCEAN pCO₂ IN COASTAL OCEANS:
ANALYSIS OF IN SITU TIME SERIES DATA

1. Research overview

Appendix E – Dominant controls of surface water pCO₂ in different coastal environments (Chen and Hu, prepared)

Atmospheric pCO₂ has increased continuously since global industrialization. Satellite measurements allow for synoptic estimation of surface ocean pCO₂, which can be further used to quantify air-sea CO₂ flux and to understand ocean acidification under anthropogenic forcing. To improve the accuracy of satellite-derived surface pCO₂, the dominant controls of surface pCO₂ over seasonal and interannual time scales need to be better understood. As such, a time series of in situ pCO₂ data, together with other environmental variables from field or satellite measurements along the U. S coasts at different latitudes, are analyzed. On seasonal time scales, surface pCO₂ tends to be dominated by the temperature effect (pCO₂_T) through SST and wind speed (with exceptions in river-dominated, upwelling-dominated, or coral reef dominated regions) in tropical and subtropical oceanic waters, but by the non-temperature effect (pCO₂_nonT) in subpolar regions. At high latitudes, despite the covariations between pCO₂_nonT and atmospheric pCO₂ on seasonal scales, no statistically significant correlation is found between the two or between pCO₂_nonT and the environmental proxies of ocean mixing and biological activities. On interannual time scales, corresponding to the significant
increasing trends in atmospheric $p$CO$_2$ over the study period, surface $p$CO$_2$ also shows significant increasing trends (again with exceptions in river-dominated, upwelling-dominated, or coral reef dominated regions). In contrast to the dominant controls of the seasonal variations, interannual variability of surface $p$CO$_2$ is mainly controlled by the non-temperature effect (through air-sea CO$_2$ exchange via atmospheric $p$CO$_2$) in tropical and subtropical waters but by temperature effect (warming effect of SST) in subpolar regions. In river-dominated and upwelling-dominated coastal ocean systems where biological activities are expected to be intensive, surprisingly, no significant correlation is found between $p$CO$_2$\textsubscript{nonT} and biological proxies (i.e., Chlorophyll concentration (Chl), diffuse attenuation coefficient of downwelling irradiance ($K_d$)). This may be mainly attributed to the data scarcities and large uncertainties in the satellite-derived Chl and $K_d$, and more importantly to the complexities of the dynamic physical and biogeochemical processes in such coastal environments. Therefore, the effects of biological activities (e.g., algal blooms) need to be further investigated.
1. Summary of findings

Due to the dynamic and complex physical and biogeochemical processes in coastal oceans, large uncertainties (i.e., Root Mean Square Error (RMSE) ≥ 20µatm) exist in satellite-derived surface $pCO_2$ (e.g., Lohrenz et al., 2010; 2018; Hales et al., 2012; Signorini et al., 2013; Bai et al., 2015). Most of the published satellite-based $pCO_2$ models are region specific and thus having poor applicability in other regions. In the Gulf of Mexico (GOM), no satellite-based $pCO_2$ models or data products are available except for a few preliminary attempts in the northern GOM waters around the Mississippi river delta (Lohrenz and Cai, 2006; Lohrenz et al., 2010; 2018), yet these attempts all show relatively large uncertainties (i.e., RMSE > 30 µatm). Here, an empirical surface $pCO_2$ remote sensing algorithm, based on multi-variate nonlinear regression (MNR), was developed for the West Florida Shelf (WFS) with RMSE of 10.98 µatm and $R^2$ of 0.86 for $pCO_2$ between 300 and 550 µatm. (Chen et al., 2016). For the northern GOM waters, a mechanistic semi-analytical approach (MeSAA) was attempted and the same MNR approach used for the WFS was also locally tuned for this region (Chen et al., 2017a). The MNR shows better performance with RMSE of 10.66 µatm and $R^2$ of 0.84 than the best MeSAA results (RMSE = 12.36 µatm, and $R^2 = 0.78$) for $pCO_2$ range of 315~450 µatm. Clearly studies of both the WFS and the northern GOM show greatly reduced errors when compared to the published studies. It should be clarified that, while a multi-variate nonlinear regression model was developed from this work, the MeSAA model was adapted from a previously published work
(Bai et al., 2015) but tuned using local parameterization. While they both appear to be able to estimate surface $pCO_2$ using satellite measurements, their advantages and disadvantages are discussed in Chen et al. (2017a). Specifically, while the MeSAA model can address the individual processes more explicitly, it also leads to higher uncertainties than the empirical model. On the other hand, because the complex and often unknown processes may be implicitly included in the model coefficients, empirical models often lead to lower uncertainties than MeSAA models, but at the price of being unable to explain the processes explicitly. One limitation of both models is their requirement of SSS as the model input (Chen et al., 2017a), where SSS at 1-km resolution is not readily available from satellite measurements.

To overcome this difficulty, a multilayer perceptron neural network (MPNN) is developed to estimate SSS from MODIS and SeaWiFS (Chen et al., 2017b). This SSS model is mainly based on the optical properties of the colored dissolved organic matter (CDOM) and its relationship with SSS (Vodacek et al., 1997; Hu et al., 2003; Coble et al., 2004; Del Vecchio and Blough, 2004). However, the CDOM characteristics depend on individual rivers, and the CDOM-SSS relationship also varies with space and time (Chen, 1999; Hu et al., 2003; Del Vecchio and Blough, 2004; Bowers and Brett, 2008; Bai et al., 2013; Geiger et al., 2013). To overcome these difficulties, the MPNN model developed in Chen et al. (2017b) bypasses the need of CDOM as an intermediate step, but estimates SSS directly from satellite-derived SST and remote sensing reflectance ($Rrs(\lambda)$, m$^{-1}$) in the visible bands. This model shows a RMSE of 1.2 PSU and $R^2$ of 0.86 for a wide range of SSS (i.e., 1~37) with uncertainties always < 1 PSU for SSS > 30, and therefore is being able to generate SSS data products at 1-km resolution to be used in surface $pCO_2$ models.
Most of the published satellite-based $p$CO$_2$ models (e.g., Hales et al., 2012; Signorini et al., 2013), as well as the models described in Chapters 2 and 3, are developed for single-process dominated regions. These regional $p$CO$_2$ models are developed using various approaches and different combinations of environmental variables. With the available SSS data products from ocean color remote sensing in the GOM (Chapter 4), the feasibility of developing a unified $p$CO$_2$ model for multi-process dominated regions (GOM, Gulf of Maine) is demonstrated (Chapter 5). Such a $p$CO$_2$ model leads to spatial and temporal (e.g., seasonal and interannual) distribution patterns of surface $p$CO$_2$ in the GOM that can be interpreted as being driven by different physical and biological processes. This unified satellite $p$CO$_2$ model has a RMSE of 9.1 µatm and $R^2$ of 0.95 for $p$CO$_2$ between 145 and 550 µatm.

Finally, to improve the accuracy of satellite mapping of surface $p$CO$_2$ in the complex coastal waters, the mechanisms and dominant controls of the variations in surface $p$CO$_2$ on seasonal and interannual time scales are further investigated using *in situ* time series data along the coasts of U. S. and its territories (Chapter 6). It is found that, in tropical and subtropical coastal waters, the seasonal variations of surface $p$CO$_2$ are mainly controlled by SST (with a few exceptions in the river-dominated, upwelling-dominated, and coral-reef-dominated systems), while in the subpolar or high latitude regions, the seasonal variations of surface $p$CO$_2$ are mainly dominated by non-temperature effects. In contrast, on interannual time scale, with the increase of the atmospheric $p$CO$_2$, surface $p$CO$_2$ also shows increasing trends over most of the sites selected for this study. In the tropical and subtropical coastal waters, the increasing trends in surface $p$CO$_2$ are mainly attributed to non-temperature effect, while in the subpolar or high latitude regions, they are mainly caused by the effect of SST. More biological data are required to better understand the biological effects on surface $p$CO$_2$ variations.
2. Research implications

2.1. Satellite mapping of surface $p$CO$_2$

In principle, surface ocean $p$CO$_2$ is mainly controlled by four oceanic processes: thermodynamics, ocean mixing, air-sea CO$_2$ exchange, and biological activities (Fennel et al., 2008; Ikawa et al., 2013; Xue et al., 2016). Therefore, any environmental variables related to these processes can be used to remotely estimate surface $p$CO$_2$. In practice, SST, SSS, Chl and $K_d$ are determined to be the best variables to model surface $p$CO$_2$ in the GOM. The selection of these variables (except $K_d$) concurs with many of the published studies (e.g., Lohrenz and Cai, 2006; Lohrenz et al., 2010; 2018; Hales et al., 2012; Signorini et al., 2013; Bai et al., 2015). In this study, $K_d$ is found to be an important biological proxy. More importantly, although the GOM encompasses several sub-regions that are dominated by distinct and complex physical and biogeochemical processes (Figure 1.1), SST, SSS, Chl and $K_d$ are found to be the common environmental variables in affecting surface $p$CO$_2$ over the GOM. However, it is known that, in addition to these variables, other variables (e.g., mixed layer depth and wind speed) can also affect surface $p$CO$_2$ (e.g., Jamet et al., 2007; Salisbury et al., 2008; Chierici et al. 2009; Shadwick et al., 2010; Nakaoka et al., 2013; Parard et al., 2014). Therefore, in order to apply the developed $p$CO$_2$ model on a global scale, further investigations need to be conducted to examine the sufficiency of these four environmental variables (SST, SSS, Chl, and $K_d$) in estimating surface $p$CO$_2$. The significantly improved model performance from this effort suggest that many of the published $p$CO$_2$ models may need to be revisited.

Due to the dynamic and complex characteristics of the coastal oceans and prior to this work, the satellite estimated $p$CO$_2$ always showed relatively large uncertainties (e.g., RMSE >
20 µatm, or RMSE > 30 µatm in river-dominated regions). Furthermore, due to the lack of sufficient surface $pCO_2$ data, contradictory results about the air-sea CO$_2$ flux in the GOM have also been reported (Takahashi et al., 2009; Xue et al., 2014; Benway and Coble, 2014). In this dissertation, the considerable gaps of available synoptic $pCO_2$ data in the GOM are filled through extensive algorithm development effort. Various approaches, such as multi-nonlinear regression, principle component analysis and regression, neural network, supporting vector machines, regression tree, and random forest, are all thoroughly tested and compared toward an improved accuracy (e.g., RMSE < 10 µatm) in the satellite-derived $pCO_2$. With the synoptic surface $pCO_2$ at relatively high spatial and temporal resolutions available from satellites, it is now straightforward to calculate air-sea CO$_2$ flux in future works. This will lead to an improved understanding of the carbon budget and carbon cycling in the GOM. More importantly, the unified $pCO_2$ approach demonstrated here shows potentials for other regions (e.g., Gulf of Maine), and thus may greatly facilitate carbon-flux studies in other region.

Finally, with rapidly increasing atmospheric $pCO_2$ resulting from anthropogenic forcing, it is expected that surface $pCO_2$ would also show a similar or detectable increasing rate (Takahashi et al., 2009; 2014). However, no such clear trends are observed in either the satellite-derived $pCO_2$ for the GOM or in situ time series of $pCO_2$ data in the northern GOM (e.g., buoy C3 in Chapter 6). In other words, based on the results presented in this study, currently it is difficult to conclude whether there is a significantly increasing trend in the surface $pCO_2$ in the GOM, despite the fact that the satellite-based surface $pCO_2$ does show slight increases after 2012. This is possibly due to 1) the buoy-based time series data may not be representative of the entire GOM, especially for the open GOM waters, and 2) if the model inputs (SST, SSS, Chl, and $K_d$) do not show apparent trend, the modeled $pCO_2$ would not show any trend either. Therefore, in
future studies of surface $p$CO$_2$, in order to capture the response of surface $p$CO$_2$ to the increased atmospheric $p$CO$_2$ on interannual time scale, the latter should be used as the model input as well.

### 2.2. Further implications

The SSS work presented in this dissertation has implications beyond its use in satellite mapping of surface $p$CO$_2$. Accurate estimation of SSS from ocean color remote sensing is critical to characterizing many physical and biogeochemical processes in coastal ocean waters (Fennel et al., 2011; Xue et al., 2013). It can not only be used to examine the mixing characteristics between different water masses (e.g., riverine freshwater versus oceanic water) (Hu et al., 2004; Horner-Devine et al., 2015; Yang et al., 2015), but it can also be used to trace the pathways of the terrestrial runoffs into the ocean as well as to characterize the optical properties of the ocean waters related to hypoxia and algal blooms (Rabalais et al., 1996; 2002; Weisberg et al., 2014; 2016; Le et al., 2016). The SSS algorithm developed here (Chen et al., 2017b) may also be implemented within near-real time applications in monitoring water properties in the near future. Likewise, the general approach of using neural network to implicitly address relationships between spectral reflectance and SSS may be applied to other coastal regions to derive SSS from ocean color measurements.

Similar to the neural network approach used on SSS estimation, the approaches proposed in this dissertation to estimate surface $p$CO$_2$ may be extended to other regions as well. Although the relative importance of the four processes (thermodynamics, physical ocean mixing, biological activities, air-sea CO$_2$ exchange) that control the variations of surface $p$CO$_2$ may vary in different oceanic ecosystems (e.g., upwelling-dominated, river-dominated, or current-dominated), for example at different latitudes, the proposed machine learning approach used to generate the $p$CO$_2$
model for the multi-process dominated GOM waters shows great potential for estimating surface $pCO_2$ from other oceanic waters (Chapter 5, Chen et al., submitted). At present, due to the lack of synoptic and accurate mapping of surface $pCO_2$ in coastal margins, it is still difficult to quantify the role of coastal oceans in cycling atmospheric $CO_2$ as either a source or a sink (e.g., Borges, 2005; Cai et al., 2006). As such, the proposed approach in this dissertation can be implemented and tested on global continental margins as well as in global open-ocean waters to improve our knowledge of global oceanic carbon cycling.

3. Future work

3.1. Research

In the past, controversial results have been reported on whether the GOM acts as a $CO_2$ source or sink (Takahashi et al., 2009; Xue et al., 2014; Benway and Coble, 2014). Based on the synoptic and long-term satellite-based $pCO_2$ data products provided in this work, an important next step is to estimate the air-sea $CO_2$ flux in the GOM waters. Subsequently, the variations of the air-sea $CO_2$ fluxes in the past years (e.g., at least > 15 years from MODIS) can be analyzed towards a better understanding of the carbon cycling in the GOM.

With the increases of atmospheric $pCO_2$ resulting from anthropogenic forcing, how the ocean responds to such increases is one of the top concerns in marine carbonate studies (e.g., Doney et al., 2009). Therefore, future works on $pCO_2$ remote sensing must improve the model capacity in capturing interannual variations surface $pCO_2$ in response to changes in atmospheric $pCO_2$. In particular, based on the in situ time series data, surface $pCO_2$ shows clear increasing trends in most of the study sites along the U. S. However, based on the remotely sensed $pCO_2$ from this work, surface $pCO_2$ trends in the GOM are less conclusive. Considering the dynamic
and complex oceanic processes in the GOM, it could be possible that surface $pCO_2$ did not increase much over this study period; it could also be possible that the interannual changes in surface $pCO_2$ were not captured well by the environmental variables used in the developed $pCO_2$ models. As such, further investigation and improvement of the developed $pCO_2$ models are needed, possibly through the use of the atmospheric $pCO_2$ as one of the input variables.

Finally, to better quantify surface $pCO_2$ from satellite measurements, the biological effects on surface $pCO_2$ must be investigated in greater detail in the future. At present, Chl and $K_d$ are used as general proxies of the biological activities in modulating surface $pCO_2$. However, due to the complex processes of the biological activities (e.g., photosynthesis, respiration, and calcification), the signals in Chl and $K_d$ may not co-vary with surface $pCO_2$ on the same time scales. For example, it was surprising to find that Chl and $K_d$ are insignificant to surface $pCO_2$ changes (Chapter 5). Such results could be caused by data scarcities and large uncertainties in the satellite-derived Chl and $K_d$, especially in coastal ocean waters. As such, more work is still needed to study the effects of biological activities on surface $pCO_2$. In particular, how surface $pCO_2$ changes, together with other environmental variables (e.g., apparent oxygen utilization, nutrients, dissolved oxygen, and Chl), before, during, and after algal blooms needs to be investigated.

### 3.2. Product delivery

Surface $pCO_2$ is a key parameter in assessing air-sea $CO_2$ flux and understanding ocean acidification. While algorithms and data products are developed in this study, effective delivery of these products to the end-users still requires more efforts, especially for a user groups of different needs. For example, the North American Carbon Program (NACP) is a multi-agency,
multidisciplinary scientific research program which focuses on carbon sources and sinks. The surface \( pCO_2 \) data products can be provided to researchers in this program to study carbon cycles. The NOAA Ocean Acidification Program (OAP) is dedicated to improving our understanding of how (and how fast) the ocean chemistry is changing. The interannual variations of the surface \( pCO_2 \) in different regions of the GOM (e.g., river-dominated northern GOM, WFS, and open GOM waters), after accounting for the anthropogenic factor, can help to understand the response of the GOM waters to anthropogenic forcing. Further, similar to the NOAA Pacific Marine Environmental Laboratory (PMEL) moored \( pCO_2 \) systems (Chapter 6), virtual buoy systems (VBS) presenting surface \( pCO_2 \) time series at pre-selected locations of the GOM may be developed (Hu et al., 2014) in coordination with the NOAA PMEL carbon program.

In addition to the major data products (surface \( pCO_2 \)) developed here, SSS estimated from ocean color satellite measurements is also an important data product for many applications, from water quality monitoring to ecosystem research. Currently, SSS data products have been generated in retrospective mode, which can be shared with many research and environmental groups. Once SSS data products are generated and updated in near real-time, these products may be delivered to various user groups through the common web portal established at the University of South Florida Optical Oceanography Lab (https://optics.marine.usf.edu).

4. Conclusions

Ocean color satellites provide synoptic and frequent measurements of the surface ocean to study the changing ocean chemistry. Integrating satellite data with traditional ship- and buoy-based measurements can provide further insights into understanding of variations of surface \( pCO_2 \) and \( CO_2 \) flux. Compared with previous efforts in mapping surface \( pCO_2 \) from satellite measurements,
the most significant outcome of this research is its use of machine learning to establish models to estimate SSS and surface $p$CO$_2$ resulting in greatly reduced uncertainties even for multi-process dominated complex regions. The accurate surface $p$CO$_2$ data products enable a better understanding of controlling mechanisms of their spatial, seasonal, and inter-annual variations. The developed datasets of SSS and surface $p$CO$_2$ are expected to facilitate more studies of carbon cycling between atmosphere and ocean, for example to better quantify the role of continental margins as potential CO$_2$ sources or sinks, and to better quantify the ocean’s role in absorbing atmosphere CO$_2$.

5. Literature cited


Takahashi, T., Sutherland, S. C., Chipman, D. W., Goddard, J. G., Ho, C., Newberger, T., Sweeney, C., and Munro, D. R. (2014). Climatological distributions of pH, pCO2, total CO2,
alkalinity, and CaCO$_3$ saturation in the global surface ocean, and temporal changes at
selected locations. Marine Chemistry, 164, 95-125.

variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and

red tide was observed on the West Florida Continental Shelf in 2010. Harmful Algae, 38,
119-126.

robust 2012 bloom and the nearly null 2013 event. Continental Shelf Research, 120, 106-
121.

circulation and biogeochemical variability in the Gulf of Mexico. Biogeosciences, 10(11),
7219-7234.

$pCO_2$ variability in the Gulf of Mexico, Biogeosciences Discussions, 11(8), 12673-12695.

APPENDIX A:

REMOTE ESTIMATION OF SURFACE pCO₂ ON THE WEST FLORIDA SHELF


pCO₂ on the West Florida Shelf. Continental Shelf Research, 128, 10-25.
Remote estimation of surface pCO₂ on the West Florida Shelf

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A R T I C L E   I N F O

Keywords:
Surface pCO₂, Satellite remote sensing, MODIS, Chlorophyll, SST, Kd, WFS

A B S T R A C T

Surface pCO₂ data from the West Florida Shelf (WFS) have been collected during 25 cruise surveys between 2003 and 2014. The data were scaled up using remote sensing measurements of surface water properties in order to provide a more nearly syoptic map of pCO₂ spatial distributions and describe their temporal variations. This investigation involved extensive tests of various model forms through parsimony and Principal Component Analysis, which led to the development of a multi-variable empirical surface pCO₂ model based on concurrent MODIS (Moderate Resolution Imaging Spectroradiometer) estimates of surface chlorophyll a concentrations (CHL, mg m⁻²), diffuse light attenuation at 490 nm (Kd, Lee m⁻¹), and sea surface temperature (SST, °C). Validation using an independent dataset showed a pCO₂ Root Mean Square Error (RMSE) of <12 µatm and a 0.88 coefficient of determination (R²) for measured and model-predicted pCO₂ ranging from 300 to 550 µatm. The model was more sensitive to SST than to CHL and Kd, Lee, with a 1°C change in SST leading to a ~16 µatm change in the predicted pCO₂. Application of the model to the entire WFS MODIS time series between 2002 and 2014 showed clear seasonality, with maxima (~450 µatm) in summer and minima (~350 µatm) in winter. The seasonality was positively correlated to SST (high in summer and low in winter) and negatively correlated to CHL and Kd, Lee (high in winter and low in summer). Inter-annual variations of pCO₂ were consistent with inter-annual variations of SST, CHL, and Kd, Lee. These results suggest that surface water pCO₂ of the WFS can be estimated, with known uncertainties, from remote sensing. However, while the general approach of empirical regression may work for waters from other areas of the Gulf of Mexico, model coefficients need to be empirically determined in a similar fashion.

1. Introduction

Atmospheric CO₂ has increased by 40% since the industrialization era (Sabine et al., 2004; Solomon et al., 2007). Correspondingly, oceanic uptake of CO₂ has resulted in ocean acidification and decreased surface water pH (by ~0.1 units) (Gan et al., 2012; Pachepsky and Meyron, 2014), leading to ecological degradation and a decrease of marine biodiversity (Wildi and Walker, 2000; Goll et al., 2005; Feely et al., 2012). Due to large spatial and temporal variations in surface water CO₂ partial pressure (pCO₂), the magnitude and even the sign of air/seas CO₂ fluxes can be highly variable (Takahashi et al., 2002, 2009, 2014; Sarma, 2005; Borup et al., 2005; Hofmann et al., 2011; Sarma et al., 2012; Chen et al., 2013; Wanninkhof et al., 2013). Accurate knowledge of surface pCO₂ distributions is therefore essential to quantify the ocean’s role in carbon cycling.

A large number of studies have used field measurements to estimate air-sea CO₂ fluxes for both the open ocean and coastal sites (e.g., Takahashi et al., 2002, 2009, 2014; Tuong et al., 2011; Jiang et al., 2008; Geirra et al., 2012; Vandenbergh et al., 2011; Zhai et al., 2005). However, direct field observations are often limited in spatial and temporal coverage. While numerical models have also been used to estimate surface pCO₂ (e.g., Vare et al., 2014; Arruda et al., 2013), model results are strongly influenced by assumed initial conditions and can also be highly model-specific. In contrast, satellite remote sensing can provide frequent synoptic assessments of surface ocean properties, and in view of recent advances in surface pCO₂ algorithm development (e.g., Oono et al., 2004; Sarma et al., 2006; Jumet et al., 2007; Tolszewski et al., 2009; Hales et al., 2012; Nakaoka et al., 2013; Sigrist et al., 2015; Bai et al., 2015), there is potential for the use of satellite remote sensing to augment direct field assessments of air/seas CO₂ fluxes. Nevertheless, except for two studies that focused on nearshore waters off the Mississippi River delta (Loheren and Cai, 2006; Loheren et al., 2010), such remote sensing approaches have rarely been applied to major ocean basins such as the Gulf of Mexico (GOM), a semi-enclosed sea of environmental and economic importance.

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http://dx.doi.org/10.1016/j.car.2016.09.004
Received 5 December 2015; revised in revised form 26 July 2016; accepted 12 September 2016
Available online 13 September 2016
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With a surface area of 1.6 million km², the GOM encompasses the West Florida Shelf (WFS), Louisiana Shelf, Texas Shelf, Mexican Shelf, and the open Gulf (Robbins et al., 2009; Coble et al., 2010). As one of the most productive areas for fisheries in the world, it is essential habitat for numerous fish and wildlife species, and is likely to be strongly impacted by ocean acidification (Cai et al., 2011; Wanninkhof et al., 2015). Thus, it is important to quantify the role of the GOM in modulating CO₂ flux (Takahashi et al., 2009). Based on field measurements, Takahashi et al. (2009) estimated the GOM as a CO₂ source with a net flux of about 0.21 mol C/m²/year. However, with additional field observations, Robbins et al. (2014) reported that the GOM is a CO₂ sink with a net flux near −0.19 mol C/m²/year. Using a 3-dimensional numerical model, Xue et al. (2014) estimated the GOM as a sink with a flux of −0.84 mol C/m²/year. Clearly, such discrepancies necessitate additional studies to better quantify CO₂ flux and synoptic mapping of surface pCO₂ should play an important role. In particular, with continuous surface pCO₂ collections in the GOM in recent years (see below for data sources), the application of satellite remote sensing can strongly contribute to a better understanding of surface pCO₂ distributions and CO₂ flux.

Within the GOM, of particular importance is the WFS between 24°31'N and 80°–85°W (Fig. 1). The WFS is a broad carbonate-based shelf with a width of 220–275 km and a gently sloping, influenced by the Loop Current (LC) system as well as upwelling, river discharge, blooms of both harmful and non-harmful algae, summer and winter storms, and groundwater influx (Julliff et al., 2003; Weisberg and He, 2003; Liu et al., 2005; Liu et al., 2006; Walsh et al., 2006; Bebawy and Coble, 2014). Although the GOM is typically characterized as being oligotrophic, the WFS is one of the most productive continental shelves in the United States, supporting numerous fisheries and diverse organisms (Sanil et al., 2011; Chong et al., 2011). As one of the broadest continental shelves of the United States (He and Weisberg, 2002), the WFS may play a bigger role in modulating CO₂ flux in the GOM, and knowledge of synoptic surface pCO₂ distributions as well as their temporal changes can help to quantify air-sea CO₂ fluxes, biochemical and ocean acidification processes. However, despite significant efforts to collect surface pCO₂ data through numerous ship surveys, and one study (Xue et al., 2014) to model pCO₂ variability on the Louisiana Shelf and the GOM as a whole, little information is available for the WFS.

The objectives of this study are thus two-fold: (a) development of a remote sensing model to scale up ship-based surface pCO₂ observations in order to take advantage of the more synoptic and frequent remote sensing observations for the WFS, and (b) application of the model to long-term remote sensing data to examine spatial-temporal distributions of surface pCO₂ on the WFS. The present work is directed toward bridging knowledge gaps by providing, for the first time, monthly pCO₂ distribution maps at medium resolution (1-km) and their temporal variations on the WFS.

2. Data and methods

2.1. A brief review of pCO₂ remote sensing

While the details of different methods to estimate surface pCO₂...
Table 1
List of published works on remote sensing of surface ocean pCO₂, arranged in chronological order. Note that studies of surface ocean pCO₂ without the use of remote sensing are not listed here.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Study area</th>
<th>Model input</th>
<th>Model</th>
<th>Model uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stephens et al. (1995)</td>
<td>North Pacific</td>
<td>SST, LON</td>
<td>MPR</td>
<td>EMSE = 8.1 µatm (subtropical), RMSE = 18 µatm (subpolar)</td>
</tr>
<tr>
<td>Lorente et al. (2002)</td>
<td>Gulf of Calif.</td>
<td>SST, SST, Chlor, LON</td>
<td>MPR</td>
<td>STD = 35 µatm, R² = 0.63</td>
</tr>
<tr>
<td>Sarmiento (2003)</td>
<td>Caribbean Sea</td>
<td>SST, LON, LON, LON</td>
<td>MPR</td>
<td>EMSE = 5.5 µatm, R² = 0.6</td>
</tr>
<tr>
<td>Ogle et al. (2004)</td>
<td>North Pacific</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 11 µatm (subtropical), RMSE = 17 µatm (subpolar)</td>
</tr>
<tr>
<td>Bates et al. (2005)</td>
<td>Southern Ocean</td>
<td>SST, LON</td>
<td>MPR</td>
<td>STD = 2.6–7.9 µatm</td>
</tr>
<tr>
<td>Sarmiento et al. (2006)</td>
<td>North Pacific</td>
<td>SST, LON, LON</td>
<td>MPR</td>
<td>EMSE = 17.3 µatm</td>
</tr>
<tr>
<td>Lorentz and Sepulveda (2008)</td>
<td>Mississippi River delta</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 0.745, RMSE = 0.52 µatm</td>
</tr>
<tr>
<td>Ju et al. (2007)</td>
<td>North Atlantic</td>
<td>SST, LON, LON, LON, LON</td>
<td>MPR</td>
<td>STD = 4.5–6.8, RMSE = 8.98–15.01 µatm</td>
</tr>
<tr>
<td>Weiss et al. (2007)</td>
<td>East China Sea</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>Not available</td>
</tr>
<tr>
<td>Berryman et al. (2008)</td>
<td>Central Pacific</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 0.59, R² = 0.02</td>
</tr>
<tr>
<td>Erofeeva et al. (2009)</td>
<td>Oregon and Washington Shelf</td>
<td>SST, LON</td>
<td>MPR</td>
<td>STD = 2.6–7.9 µatm</td>
</tr>
<tr>
<td>Zhai et al. (2009)</td>
<td>Southern South China Sea</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 18.4 µatm, R² = 0.72</td>
</tr>
<tr>
<td>Trabasso et al. (2009)</td>
<td>North Atlantic</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 11.6 µatm</td>
</tr>
<tr>
<td>Friedrich and Osthoff (2009)</td>
<td>North Atlantic</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 19 µatm</td>
</tr>
<tr>
<td>Shadwick et al. (2010)</td>
<td>Southern South China Sea</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 8.9 µatm, R² = 0.78</td>
</tr>
<tr>
<td>Bugge et al. (2010)</td>
<td>Southern South China Sea</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 10.4 µatm, R² = 0.72</td>
</tr>
<tr>
<td>Lobenfeld et al. (2010)</td>
<td>Southern South China Sea</td>
<td>SST, SST, LON</td>
<td>MPR</td>
<td>EMSE = 11.6 µatm</td>
</tr>
<tr>
<td>Ittekott et al. (2010)</td>
<td>Baltic Sea</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 17.2, 21.5 µatm, R² = 0.72, 0.79</td>
</tr>
<tr>
<td>Lou et al. (2011)</td>
<td>South China Sea</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Xue et al. (2011)</td>
<td>South China Sea</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Wijffels et al. (2012)</td>
<td>South China Sea</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Cao et al. (2012)</td>
<td>South China Sea</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Håkkinen et al. (2012)</td>
<td>Northern North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 10.4 µatm, R² = 0.72</td>
</tr>
<tr>
<td>Tal et al. (2012)</td>
<td>Baltic Sea</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 17.2, 21.5 µatm, R² = 0.72, 0.79</td>
</tr>
<tr>
<td>Nakazato et al. (2013)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 17.2, 21.5 µatm, R² = 0.72, 0.79</td>
</tr>
<tr>
<td>Ogasawara et al. (2013)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 17.2, 21.5 µatm, R² = 0.72, 0.79</td>
</tr>
<tr>
<td>Ban et al. (2014)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Perez et al. (2014)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Qiu et al. (2014)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Zhang et al. (2014)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Marotzke et al. (2014)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Marotzke et al. (2015)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Palma et al. (2015)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Moore et al. (2016)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
<tr>
<td>Xue et al. (2016)</td>
<td>North Atlantic</td>
<td>SST, SST, SST</td>
<td>MPR</td>
<td>EMSE = 16.8–21.46 µatm</td>
</tr>
</tbody>
</table>

Note: MPR=Multiple Linear Regression; MPR=Multiple Polynomial Regression; PCA=Principal Component Analysis; SOM=Self-Organizing Map; FFP=Forward Forward Propagation; KFM=Kohonen Feature Map; IINN=Indirect Forward Neural Network; STD=Standard Deviation; CDOOM=Colored Dissolved Organic Matter; GPP=Net Primary Production; PAR=Photosynthetically Active Radiation; Jday=Julian day; K=Correlation Coefficient.
from remote measurements can be found in the literature (as listed in Table 1), for completeness the methods are briefly described here.

In terms of model inputs, most published works correlated surface $pCO_2$ to physical and biological parameters such as sea surface temperature (SST), sea surface salinity (SSS), mixed layer depth (MLD, m), and chlorophyll $a$ concentration (CHL, mg m$^{-2}$) (e.g., Siegel et al., 1995; Riebesell et al., 2000; Wanninkhof et al., 2007). Watanabe, 2007; Kerry et al., 2008; Zhu et al., 2009; Friedrich and Oschlies, 2008; Hales et al., 2012; Tuo et al., 2012; Signorini et al., 2013; Qiao et al., 2014; Bai et al., 2015; Murrell et al., 2015; Padhy et al., 2015; Meeza et al., 2016). These parameters all have the potential to affect surface $pCO_2$, because: 1) SST and SSS can influence the solubility of CO$_2$ and the dissociation constants of the carbonate system (Weiss, 1974; Lee et al., 1998; Millero et al., 2006); 2) CHL can be a good tracer of the influence of biological processes on surface $pCO_2$ as CHL increases (e.g., in algal blooms) can cause significant decreases in surface $pCO_2$ (Bama et al., 2006; Jamet et al., 2007; Friedrich and Oschlies, 2009); and 3) MLD can be a good indicator of wind stress and convective mixing, and as a result, carbonate properties of subsurface waters brought to surface by strong mixing are usually different from those of the surface (Jamet et al., 2007; Chierici et al., 2009; Signorini et al., 2013). In some studies, wind speed (Shadwick et al., 2010) and atmospheric $pCO_2$ (Leube and Taylor, 2002) were used to model the effect of air-sea $CO_2$ flux on surface $pCO_2$. Parad et al. (2014) and Murrell et al. (2014) estimated surface $pCO_2$ seasonal variations as a function of Julian day, and net primary production (Parad et al., 2014) was used to describe biological effects. Several other studies correlated surface $pCO_2$ with latitude and longitude (Olen et al., 2004; 2012; Marre et al., 2013). They showed that the accuracy of $pCO_2$ was associated with low c-660. It is reasonable and generally necessary to correlate surface $pCO_2$ to the parameters mentioned above (possibly excluding geo-locations) because it is difficult to directly describe $pCO_2$ in more mechanistic terms (physical, biological and chemical relationships).

In terms of methods and model uncertainties, both empirical regression and neural network approaches have been used to relate surface $pCO_2$ to SST, SSS, CHL and MLD in the open ocean (Ono et al., 2004; Barua et al., 2006; Jamet et al., 2007; Fixsen et al., 2009; Nakajima et al., 2013; Marre et al., 2015; Padhy et al., 2015; Meeza et al., 2016). Such parameterizations have provided $pCO_2$ with Root Mean Square Errors (RMSE) less than 17 $\mu$atm. In coastal margins, in addition to the empirical regression and neural network approaches, a mechanistic semi-analytical method (Bai et al., 2015) was also examined by modeling the ocean processes that control surface $pCO_2$. Unlike empirical models, mechanistic methods explicitly explain the physical and biogeochemical processes that control surface $pCO_2$ in the model. Although the mechanistic method was more meaningful than the empirical regression and neural network approaches, it has generally been effective only in regions where river discharge was the dominant influencing factor on $pCO_2$ (Bai et al., 2015). The $pCO_2$ RMSE uncertainties of those models for coastal oceans can reach 66.8 $\mu$atm (Hales et al., 2012), and the coefficient of determination ($R^2$) can be as low as 0.165 (Lorenz et al., 2010). Therefore, while remote estimation of surface $pCO_2$ for the open ocean is relatively mature due to less variable environmental conditions (mainly controlled by mesoscale ocean circulation), due to the complex dynamics of coastal regions (e.g., including river discharge, ocean sides, coastal upwelling, ground-water discharge and biological factors) (Richet et al., 2002; Banas et al., 2013; Cymek et al., 2014), remote estimation of surface $pCO_2$ is still challenging.

The monthly mean satellite products or climatology used as inputs in most published works can introduce significant uncertainties in nonlinear $pCO_2$ models. Likewise, the sensitivity of established models to individual input variables has rarely been studied. Satellite-derived SST and CHL have inherent uncertainties: 0.5–1.0 °C for SST (Jia et al., 2009) and 12–24% for CHL in waters of > 5 m bottom depth (Camilli et al., 2003). Error propagation in model-derived $pCO_2$ needs to be understood, especially for coastal waters. The developments in the present study are based on daily satellite data, and a sensitivity analysis was conducted to understand the principal factors that control $pCO_2$ and how errors in input parameters influence the final $pCO_2$ estimates.

2.2. Field data

The twenty five cruises used to obtain the underway surface water $pCO_2$ data used in this study are described in Table 2. These data, obtained between Sep. 2003 and Sep. 2012, are found at the Carbon Dioxide Information Analysis Center (CDIAC) (http://cdiac.ornl.gov/) and the U.S. Geological Survey (USGS). Seawater samples for measurements of $pCO_2$, SSS and SST were collected at a depth of 5 m using a shipboard flow-through seawater system (31,137 observations of each parameter). Full cruise tracks with color-coded surface $pCO_2$ values are shown in Fig. 1a. Surface $pCO_2$ data were measured with either a non-dispersive, infrared analyzer Li-COR™ (Frye et al., 1998; Pierson et al., 2009) or with a Multiparameter Inorganic Carbon Analyzer MICA (Wang et al., 2007). The Li-COR™ data had an accuracy of 2 $\mu$atm (or better) with a measurement interval near 2 min, and the MICA data had an accuracy of 2.5 $\mu$atm (or better) and a measurement interval around 2 min (Wang et al., 2007). The details of data collection, processing, and quality control can be found in Frye et al. (1998), Pierson et al. (2009) and Wang et al. (2007). Corresponding SSS and SST data were obtained using a CTD (SBE-21 or SBE-38, Seabird Inc., USA, YSI 6600) integrated in the underway $pCO_2$ system.

All cruise data obtained from CDIAC/SCUCAT has undergone quality control analysis. These data were converted into uniform format with an Interactive Data Language (IDL) program, and were visualized and quality controlled (i.e., by viewing data quality flags and metadata files) to discard apparent errors (e.g., individual spikes due to instrument malfunction or other factors). Surface $pCO_2$ that fluctuated greatly for consecutive measurements while other variables (SST, SSS) remained stable (e.g., part of the data collected over GU1005_Leg2 and WS1202) were assumed to be prone to measurement errors and were therefore discarded. Less than 0.1% of the available observations were discarded via this quality control protocol. A total of 31,137 $pCO_2$ observations were selected for model development and validation (see Section 2.4).
Hu, 2016).

2.4. Algorithm development and validation

Although the field measurements included several key properties (e.g., SST, SSH, and CHL) that can be used to model surface $pCO_2$, MODIS-derived data products for SST, CHL, $a_{CO_2}$, and $K_d$ Lee were preferred for use in multi-variate regression against field-measured $pCO_2$. One advantage of this choice is that uncertainties in the MODIS-derived data products will be implicitly included in the regression coefficients. When the same data products are used with these coefficients for $pCO_2$ predictions, such uncertainties cannot be canceled to a large extent.

To obtain concurrent field data and MODIS data, a time window of ±6 h was used. In order to assure satellite data quality as an image pixel was discarded if it was associated with any of the following quality control flags (Burton and Hu, 2015): atmospheric correction failure, land, sun glint, high radiance, large sensor viewing angle (>60°), stay light, cloud/ice, high solar zenith angle, low water-leaving radiance (low nLW_555), questionable navigation, CHL > 64 or <0.01 mg/m$^3$ suspicious atmospheric correction, dark pixel (scan line error) and navigation failure. Although SST is more tolerant than ocean color data to non-optimal observing conditions as defined in the quality flags (Feng and Hu, 2016), for consistency these criteria were applied to SST as well. Because the pixel size of the MODIS data used in this work is about 1 km, the $pCO_2$ field within the pixel was averaged to match the satellite data.

After the strict quality control and field data binning, for the period between Apr. 2008 and Sep. 2012 1516 conjugate observations of field-measured $pCO_2$ and MODIS data products were available for algorithm development and validation (Fig. 1b). In this dataset, field-measured $pCO_2$ ranged between 305.7 and 522.4 µatm; field-measured SSH ranged between 31.75 and 36.56; satellite SST ranged between 15.1 and 31.4°C; satellite CHL ranged between 0.076 and 3.624 mg/m$^3$; satellite $a_{CO_2}$ ranged between 0.009 and 0.185 m$^{-1}$; and satellite $K_d$ Lee ranged between 0.030 and 0.590 m$^{-1}$. Most of the variables in this dataset showed normal distributions with equal variance except for a few outliers. This dataset was divided randomly into two groups, with one group used for model development and coefficient tuning, and the other for model validation.

To determine the appropriate forms to relate the dependent variable (surface $pCO_2$) and the independent variables, two exercises were conducted. Following the principle of parsimony, a stepwise multiple linear regression (MLR) was first conducted to examine which independent variables (SST, SSH, CHL, $a_{CO_2}$, $K_d$ Lee) should be used to predict surface $pCO_2$. Although Julliard was not a real biochemical variable (more of a "tuning" parameter), it was selected and normalized sinusoidally to emphasize the seasonal cycle of surface $pCO_2$ (Friedrich and Oxelius, 2009; Leuwer et al., 2005; Signorini et al., 2013). Because CHL, $K_d$ Lee and $a_{CO_2}$ tend to be log-normal in their large-scale distributions (Campbell, 1995), these three variables were scaled logarithmically in the regression model. The results are presented in Table 3. All independent variables except CHL and $K_d$ Lee could be selected with 95% confidence (p<0.05) in the final stepwise MLR model, with RMSE of 14.83 µatm and R$^2$ of 0.75. However, the scatterplot between predicted $pCO_2$ and field-measured $pCO_2$ (not shown here, but with statistics listed in Table 3) indicated that the predicted $pCO_2$ tended to plateau at high $pCO_2$: for $pCO_2 >$ 420 µatm, the mean bias (MB) and mean ratio (MR) between model-predicted and field-measured $pCO_2$ from the stepwise MLR were $-39.336$ µatm and 0.916, respectively, suggesting that $pCO_2$ was significantly underestimated for $pCO_2 >$ 420 µatm, thus the performance of the MLR approach was not satisfactory and further improvement was required.

Exclusion of CHL and $K_d$ Lee in the MLR model was consistent with the parsimony step-wise test, even though they were used in other studies to model surface $pCO_2$ (see Section 2.1). To further examine the reason and to investigate whether the independent variables are
orthogonal, correlations among the independent variables (SST, SSS, CHL, Kb_D, a_pCO2, Jday) and dependent variable (surface pCO2) were examined and listed in Table 4. With 95% confidence (p<0.05), most of the independent variables were inter-correlated, suggesting that a principal component analysis (PCA) may be needed to remove the redundant information from these variables (see below). Correlation analysis also showed high correlation between a_pCO2 and CHL (or Kb_D), and higher correlation between surface pCO2 and a_pCO2 than between surface pCO2 and CHL (or Kb_D). Therefore, once a_pCO2 was explicitly included in the MLR model, CHL and Kb_D were implicitly included.

Considering the non-satisfactory performance of the MLR and the high correlations among the independent variables, PCA was used to determine the dominant, orthogonal modes that could be used to construct the model. As shown in Table 5, the derived six principal components (PCs) are orthogonal, and the first three PCs can explain >98% of the variance in the independent variables. Thus, a principal component regression (PCR) model was developed to predict surface pCO2 using the six PCs. The RMSE and R² of the PCR were 14.69 µatm and 0.75, respectively. Similar to the MLR results, the predicted pCO2 tended to plateau at high pCO2 values: for pCO2 > 420 µatm, MB and MR of the PCR were ~38.69 µatm and 0.917, respectively, indicating model deficiency of the PCR and a necessity for further effort to improve the model.

The non-satisfactory performance of the MLR and PCR methods indicated that linear regressions through either the independent variables or the orthogonal PCs could not explain the entire variance of the dependent variable, and that some non-linear forms may be required. Therefore, following the model development and tuning were based on multi-variate nonlinear regression (MNK) between field-measured pCO2 and the independent variables. After extensive trial and error, it was found that the use of MODIS-derived SST, CHL, and Kb_D provided optimal results (Table 6). Other parameters, such as MODIS-derived a_pCO2 (often inversely related to SS) in coastal waters due to conservative mixing and field-measured SSS, did not improve the efficiency of the model because of the limited model predicative capability at high pCO2 (Table 6). The functional relationship between field-measured pCO2 and the satellite data was modeled by a multi-variate nonlinear (quadratic polynomial) regression, implemented in the Interactive Data Language (IDL). The regression equation was determined as:

$$pCO2 = k_0 + k_1 \cdot SST + k_2 \cdot CHL + k_3 \cdot Kb_D + k_4 \cdot SSS + k_5 \cdot a_pCO2 + k_6 \cdot \log(CHL) + k_7 \cdot \log(Kb_D)$$

where $k_0$ is SST, $k_1$ is CHL, $k_2$ is Kb_D, $k_3$ is SSS, $k_4$ is $a_pCO2$, and $k_5$ is $\log(CHL)$, $k_6$ is $\log(Kb_D)$. In the equation above, $\gamma$ was optimized by iteration (ranging from 0 to 365) until the minimum RMSE was obtained.

During the model tuning phase, several different forms of Eq. (1) were examined to determine the best form of the regression function. These included use of field-measured SSS or MODIS-derived a_pCO2 instead of satellite Kb_D, and use of original CHL or Kb_D instead of logarithmic CHL or Kb_D. The results from these alternative functional forms were slightly worse than those from Eq. (1) (Table 6) except for the combinations of SSS and CHL, a_pCO2 and CHL, and a_pCO2 and SSS (last three rows in Table 6). However, models with combinations of a_pCO2 and CHL, and a_pCO2 and SSS tended to plateau for high pCO2 values (>240 µatm), with MB of 18.503 µatm and MR of 0.962 and 0.960, respectively, indicating

### Table 5

<table>
<thead>
<tr>
<th>Variable added</th>
<th>Decision to the new added variable</th>
<th>p value</th>
<th>RMSE (µatm)</th>
<th>ME (µatm)</th>
<th>MR</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SST</td>
<td>In</td>
<td>0.000</td>
<td>16.06</td>
<td>-41.251</td>
<td>1.129</td>
<td>0.983</td>
</tr>
<tr>
<td>log(CHL)</td>
<td>In</td>
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<td>15.16</td>
<td>-37.029</td>
<td>0.916</td>
<td>0.921</td>
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<tr>
<td>log(Kb_D)</td>
<td>Out</td>
<td>0.042</td>
<td>14.83</td>
<td>-38.356</td>
<td>0.973</td>
<td>0.916</td>
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<tr>
<td>log(a_pCO2)</td>
<td>Out</td>
<td>0.044</td>
<td>14.78</td>
<td>-35.443</td>
<td>0.976</td>
<td>0.916</td>
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<tr>
<td>log(Chl)</td>
<td>Out</td>
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<td>14.75</td>
<td>-30.622</td>
<td>0.961</td>
<td>0.917</td>
</tr>
<tr>
<td>log(Kd)</td>
<td>Out</td>
<td>0.135</td>
<td>14.75</td>
<td>-30.622</td>
<td>0.961</td>
<td>0.917</td>
</tr>
</tbody>
</table>

### Table 6

<table>
<thead>
<tr>
<th>Variables</th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>PC4</th>
<th>PC5</th>
<th>PC6</th>
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<tbody>
<tr>
<td>SST</td>
<td>0.996</td>
<td>-0.066</td>
<td>0.024</td>
<td>0.033</td>
<td>0.014</td>
<td>-0.004</td>
</tr>
<tr>
<td>log(CHL)</td>
<td>-0.037</td>
<td>-0.063</td>
<td>-0.022</td>
<td>-0.702</td>
<td>-0.489</td>
<td>-0.070</td>
</tr>
<tr>
<td>log(Kb_D)</td>
<td>-0.023</td>
<td>-0.040</td>
<td>0.005</td>
<td>0.497</td>
<td>-0.642</td>
<td>-0.583</td>
</tr>
<tr>
<td>log(a_pCO2)</td>
<td>-0.044</td>
<td>-0.043</td>
<td>-0.012</td>
<td>-0.465</td>
<td>0.765</td>
<td>-0.409</td>
</tr>
<tr>
<td>SSS</td>
<td>0.063</td>
<td>0.972</td>
<td>-0.198</td>
<td>0.104</td>
<td>0.029</td>
<td>-0.015</td>
</tr>
<tr>
<td>cos(Jday)</td>
<td>-0.013</td>
<td>0.196</td>
<td>0.980</td>
<td>0.028</td>
<td>0.016</td>
<td>0.011</td>
</tr>
</tbody>
</table>

### Variance explained (%)

| SST       | 90.09 | 6.49 | 2.15 | 0.52 | 0.22 | 0.01 |
| log(CHL)  | 84.49 |    |    |    |    | 0.01 |
| log(Kb_D) | 77.64 |    |    |    |    | 0.01 |
| log(a_pCO2) | 50.86 |    |    |    |    | 0.01 |
| SSS       | 49.10 |    |    |    |    | 0.01 |
| cos(Jday) | 29.51 |    |    |    |    | 0.01 |
| pCO2      | 10.00 |    |    |    |    | 0.01 |
underestimation at high pCO2 values. Although the model with a combination of SSS and CHL showed a slightly lower MB for pCO2 > 420 µatm as compared to the model in Eq. (1), this model had a slightly higher RMSE and lower R2, and its pCO2 prediction was significantly biased for pCO2 > 480 µatm (MB = 23.844 µatm, MR = 0.92). Furthermore, it is currently difficult to estimate SSS from satellite measurements over coastal waters. Therefore, Eq. (1) was preferred as the potential pCO2 model for this study. For reference and to follow the principle of model parsimony, a stepwise MRN against all terms in Eq. (1) was conducted. The model formula did become concise as shown in Eq. (2) compared to the formula in Eq. (1). However, the statistics in Table 6 showed that the stepwise MRN had a RMSE of 19.98 µatm (5.0%) and a R2 of 0.62, and its ability in estimating pCO2 for pCO2 > 420 µatm was also limited (MB = 37.922 µatm, MR = 0.916). Therefore, this stepwise MRN did not show improvement over the stepwise MLR or PCR or MRN above, and was not selected in this study to model surface pCO2.

\[ pCO2 = 2.0103x_1 + 339.2493x_2 + 0.5330x_3 + 0.1784x_4 - 0.0035x_5^2 + 234.268x_6^2 - 86.815x_7^2 \quad (2) \]

where \( x_1 = SSS, \ x_2 = \log_{10}(Kd)_{Kd,Lee}, \ x_3 = \log_{10}(CHL) \).

Table 7 is a summary of the model performance with the stepwise MLR, PCR, stepwise MRN, and MRN. Clearly, the MRN model with Eq. (1) showed the best performance in terms of RMSE, R2, MB, MR, the relationship between modeled and measured pCO2, and the range of modeled values measured pCO2. Thus, the final empirical pCO2 model was determined as:

\[ pCO2 = -7.2607x_1 + 790.20x_2 + 753.92x_3 + 704.22x_4 + 35.217x_5 + 7.044x_6 + 34.73x_7 + 1079.63x_8 + 108.24x_9 + 10.991x_{10} + 3.522x_{11} + 947.62x_{12} + 285.96x_{13} + 105.66x_{14} \quad (3) \]

where \( x_1 = SSS, \ x_2 = \log_{10}(Kd)_{Kd,Lee}, \ x_3 = \log_{10}(CHL), \ x_4 = \cos(2*\pi * \text{Julday} - 2553/365) \).

The MRN model in Eq. (3) was subsequently applied to the half of the dataset that was not used in the model development. The model-predicted pCO2 was compared with the field-measured pCO2, where R2, RMSE, MR and MB were used to gauge model performance. A histogram of the difference between field-measured pCO2 and model-predicted pCO2 was generated to examine the error distributions.

To examine which independent variable is mostly responsible for the predictive capacity of the pCO2 model, the variance that is explained by each variable was investigated by comparing the full model (Eq. (3), with all four variables selected) to a reduced model (i.e., after removal of a certain variable). Using the same regression format (quadratic polynomial), a total of 4 reduced models were developed with the exclusion of SSS, CHL, Kd_Lee, and Julday, respectively. In each case, variance in the surface pCO2 explained by the selected variables was calculated and compared with that of the full model, with the difference regarded as the variance explained by the excluded variable.

2.5 Spatial-temporal pCO2 distributions derived from MOBIS

The model in Eq. (3) was applied to the daily Level-2 MOBIS data for the period of July 2002–December 2014 to generate daily surface pCO2 maps. The daily maps were used to compose monthly mean pCO2 maps for each year, and these monthly mean maps were then used to compose monthly pCO2 climatology. All parameters, including monthly pCO2, CHL, Kd_Lee, and SSS, were averaged over the WFS to examine long-term trends and inter-annual changes.
3. Results

3.1. Model performance

Fig. 2a shows the MNR model for pCO₂ prediction. The RMSE during model training was 10.51 µatm, with a coefficient of variation (CV) of 2.8% and R² of 0.89. Fig. 2b shows the model validation obtained with the data that were not used in the model training. Statistical results for the validation data are similar to those for the model training, with an RMSE of 11.79 µatm, CV of 3.1% and R² of 0.88. The validation showed that model-predicted pCO₂ was almost non-biased, as MB (which was 1.0006) was close to 1 and MB (which was 0.003 µatm) was close to 0 µatm. A histogram of residuals (measured pCO₂ minus predicted pCO₂) for the combined datasets (both model training and validation data) is shown in Fig. 2c. The histogram shows that 97.6% of the residuals were smaller than the observed 82.45 µatm pCO₂ standard deviation (+/−σ).

The results shown in Table 8 indicated that variables used in our model (the full model) could explain 88.92% of the pCO₂ variance. When SST was excluded in the model, the remaining variables could only explain 68.62% of the pCO₂ variance. When Julian day was excluded, the model, 74.45% pCO₂ variance could be explained. Similarly, exclusion of CHL or Kd_Lee would reduce the explained variance to 82.06% and 79.63%, respectively. Clearly, SST was the most responsible variable in our model (exclusion of SST would reduce the explained variance by 20.3%), followed by Julian day. This is consistent with those reported in previous studies (Friedrich and Oschlies, 2009; Lefèvre et al., 2005; Signoret et al., 2012). CHL and Kd_Lee were the two most important variables in explaining the pCO₂ variance, consistent with later sensitivity analysis (see Section 4.1). Note that although Julian day is not a real biochemical variable, its use improved the model performance more than the use of CHL or Kd_Lee.

3.2. Temporal and spatial variation of surface pCO₂

Fig. 3 shows mean monthly pCO₂, CHL, Kd_Lee and SST over the entire WFS where pCO₂ is within the model range. Monthly climatologic maps of surface pCO₂ are presented in Fig. 4, with the model range outlined by red dashes. Distinct seasonal pCO₂ patterns can be seen in both Figs. 3 and 4, corresponding to the seasonal variation of CHL, Kd_Lee and SST.

On a seasonal scale the seasonal variation of pCO₂ was positively correlated with SST (r=0.72), and negatively correlated with CHL and Kd_Lee. In summer, surface pCO₂ can reach a maximum around 450 µatm. During this period, primary production is inhibited mainly by a deficiency of nutrients caused by ocean stratification. Thus CO₂ removal through photosynthesis is reduced in the summer, and the balance between respiration and photosynthesis is strongly shifted toward the former by increasing SST. In winter, surface pCO₂ attains a minimum of around 350 µatm. During this time, with the breakdown of the thermocline and increase of MLD (>50 m; Liu and Weisberg, 2007), phytoplankton blooms can occur as nutrients are brought to the surface by upwelling. Combined with the decrease of SST, which would by itself strongly decrease pCO₂ (see Section 4), surface pCO₂ would be expected to significantly decrease. However, another factor needs to be considered because deep water brought to the surface by wintertime vertical mixing is rich in dissolved inorganic carbon as a result of decomposition of organics in deep waters and also submerging groundwater discharge (Hu et al., 2006; Cyrnak et al., 2014). Thus the combined effect of enhanced vertical mixing and decreased SST is that pCO₂ reaches a minimum during winter but is not severely diminished. Although the interannual patterns of pCO₂, SST, CHL and Kd_Lee are generally similar throughout our study period, certain exceptions can be noted. In September of 2005, due to an intense red tide bloom that was triggered on the west-central Florida Shelf by two hurricanes combined with other influencing parameters (Hu et al., 2006), CHL peaked at 2.27 mg/n−3 (Fig. 3e). Coincidently, surface pCO₂ estimates decreased by 38 µatm relative to pCO₂ estimates in the previous month, but did not reach a minimum. The highest value of surface pCO₂ was attained in 2010 June (Fig. 3a) and was about 58 µatm higher than the previous month. Considering that there was almost no change in CHL and Kd_Lee, and Julian day was only a small adjusting factor, this increase was likely caused by the observed 3.4 °C increase of SST. Combined with the sensitivity analysis demonstrating that an increase of 1 °C in SST by itself can lead to an increase of about 15.7 µatm in surface pCO₂, the appearance of the pCO₂ maximum in June was reasonable. Comparing this interannual variability of spatially averaged pCO₂ on the WFS to modeled pCO₂ results for the whole

Table 8

Statistics of the full model and reduced models for explaining variance in the estimated surface pCO₂. The first row represents the full model (Eq. (3)) used in this study, while other rows represent models with one variable excluded. The last column shows the reduced variance (compared to the full model) when a variable was excluded.

<table>
<thead>
<tr>
<th>Model inputs</th>
<th>Excluded variable</th>
<th>Variance explained (%)</th>
<th>Variance explained by the excluded variable (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SST</td>
<td>NaN</td>
<td>88.92</td>
<td>NaN</td>
</tr>
<tr>
<td>logKd_Lee, logCHL</td>
<td>SST</td>
<td>68.62</td>
<td>20.3</td>
</tr>
<tr>
<td>Julian day</td>
<td>Kd_Lee</td>
<td>79.63</td>
<td>9.29</td>
</tr>
<tr>
<td>CHL</td>
<td>SST</td>
<td>82.06</td>
<td>6.86</td>
</tr>
<tr>
<td>Julian day</td>
<td>CHL</td>
<td>74.45</td>
<td>14.47</td>
</tr>
</tbody>
</table>

17
GOM (Xue et al., 2014), a similar pattern of seasonal variations with highs in summer and lows in winter was detected. However, the model sensitivity analysis and uncertainty and accuracy assessment that is described below (Section 4.2) indicates that the results obtained in the present work exhibit improved accuracy and less uncertainty.

In terms of observations on spatial scales (Fig. 3), although there were distinct gradients in CHL and Kd_Lee climatologic maps (not explicitly shown here), pCO₂ climatologic maps showed small gradients from inshore to offshore during winter and early spring (November to March) when SST was low. Other interesting features of Fig. 4 included two regions with elevated pCO₂ relative to their surroundings (red solid circles in Fig. 4). Among other possible influences, because there are large springs in this region (Bruneau et al., 1977) with low temperature and high pCO₂, this could be due to upwelling of submarine groundwater discharge, as pCO₂ is usually higher in fresh groundwater than surroundings (Murphy et al., 2009). From early spring to late fall (April to October), obvious pCO₂ gradients were observed, changing from high to low in the offshore direction. High pCO₂ in near shore regions can be related to tidal mixing and river runoff, carrying elevated DIC to coastal surface waters. Although DIC in coastal areas can be diminished by photosynthesis, high nearshore pCO₂ values are commonly observed. However, the extremely high pCO₂ values (> 550 µatm) in the nearshore regions of South Florida may not be reliable, as there was little pCO₂ data in this region and the pCO₂ model developed here was only valid for pCO₂ ranging from 300 to 550 µatm. On the other hand, such extremely high pCO₂ values could be realistic as pCO₂ had a positive response to SST changes and SST in this region was higher than in offshore waters. In the offshore region during our observation period, due to the combined effects of thermocline development and decreases in SST, surface pCO₂ was lower than for inshore waters. Nevertheless, in temporal terms, offshore surface pCO₂ values during the summer are higher than inshore pCO₂ values in the winter and early spring. In the area around the Florida Keys, pCO₂ values were high relative to other regions year round. This can be attributed to the influence of the LC in the Florida Strait (clearly shown in the SST climatologic map) and potentially submarine groundwater discharge in this very shallow region.

Compared with the modeled multi-year pCO₂ maps in Xue et al. (2014), the results shown here exhibit distinctive spatial distribution patterns across nearshore and offshore waters.

4. Discussion

4.1. Model sensitivity to environmental forcing and model uncertainty

The distribution of surface ocean pCO₂ is mainly controlled by ocean thermodynamics, physical processes, biological processes, and air-sea exchange (Takahashi et al., 2002; Inoue et al., 2003; Riebesell et al., 2001; Bai et al., 2013). Ocean thermodynamic effects are dependent on SST, and the relationship between surface pCO₂ and SST can be estimated using a simple exponential relationship: pCO₂ = pCO₂ていましたexp(0.0423(Tᵣ - Tₛ)) (Takahashi et al., 2002, 2009). Physical processes such as advection, upwelling and water mixing affect pCO₂ mainly by transport and mixing of different water masses with distinctive chemical and physical properties such as total alkalinity (TA), dissolved inorganic carbon (DIC), SST and SSS. Biological processes, including consumption of CO₂ by photosynthetic production of CO₂ by respiration, and utilisation of carbonate during calcification also have important direct effects on the pCO₂ of seawater (Bai et al., 2003). Air/sea CO₂ exchange can exert especially strong controls on surface pCO₂ under strong wind conditions (Bates et al., 1998; Bates and Merlivat, 2001; Turk et al., 2013). Nevertheless, in a limited case study, only one or two processes were observed to dominate the pattern of surface pCO₂ (Bai et al., 2015).

In order to better understand how surface pCO₂ responds to input variables, a sensitivity analysis was conducted. For each analysis, one input variable was varied while the others remained constant. Surface pCO₂ predictions were compared to examine the magnitudes of change with variations in SST, CHL and Kd_Lee. Considering the uncertainties observed during retrieval of satellite products, we varied CHL and Kd_Lee by ± 20% and SST by ± 1 °C. These are the upper bounds of the MODIS data product uncertainties over the WFS. The model response results are shown in Figs. 5 and 6, and additional statistics...
such as RMSE, MR, and MB are listed in Table 9.

A visual interpretation of Figs. 5 and 6 indicates that the model is more sensitive to input changes in CHL when CHL is $> 1.5$ mg m$^{-3}$. For CHL greater than $1.5$ mg m$^{-3}$, a 20% increase in CHL (Figs. 5a and 6a) produced $p$CO$_2$ predictions that were lower than the original $p$CO$_2$, while for CHL less than $1.5$ mg m$^{-3}$ the same 20% increase in CHL caused a substantially smaller change in the predicted $p$CO$_2$. For the entire data range in this analysis (Table 9), the RMSE, MR, and MB were 0.34 μatm, 1.022, and 8.86 μatm, indicating that a 20% increase in CHL resulted in an 8.06 μatm $p$CO$_2$ overestimate. For data with CHL $> 1.5$ mg m$^{-3}$, the RMSE, MR, and MB were 16.44 μatm, 0.968, and −12.44 μatm. In contrast, for data with CHL $< 1.5$ mg m$^{-3}$, the RMSE, MR, and MB were 10.07 μatm, 1.024, and 8.79 μatm, respectively. A similar disparity in model sensitivity was observed for a 20% decrease in CHL when CHL $> 1.5$ mg m$^{-3}$ and CHL $< 1.5$ mg m$^{-3}$ (Figs. 5b and 6b). For the entire data range, RMSE, MR, and MB were 9.26 μatm, 0.986, and −4.90 μatm. For data with CHL $> 1.5$ mg m$^{-3}$, $p$CO$_2$ was overestimated, with RMSE, MR, and MB being 24.09 μatm, 1.03 and 26.11 μatm. Consistent with the observations described above, for data with CHL $< 1.5$ mg m$^{-3}$ the model showed much reduced sensitivity to a 20% decrease in CHL, with an RMSE of 8.40 μatm, an MR of 0.984, and an MB of −5.87 μatm. Based on the characteristics shown in Figs. 5a, 5a, 6a, and 6b, the $p$CO$_2$ algorithm is especially sensitive to CHL at high concentrations. To
some extent, this reflects the complex role of CHL in controlling surface pCO₂.

As Kd_Lee is not entirely independent from CHL, it is also clearly seen that the pCO₂ algorithm is more sensitive to Kd_Lee as this variable becomes larger (> 0.2 m⁻¹). For Kd_Lee values greater than 0.2 m⁻¹, a 20% increase in Kd_Lee (Figs. 5c and 5e) resulted in substantial increases in predicted pCO₂, while for Kd_Lee values less than 0.2 m⁻¹, a 20% increase in Kd_Lee produced pCO₂ values close to the original pCO₂ prediction. When all data were used in the analysis the RMSE, MR and MB values for this experiment were 10.02 μatm, 0.997, and −0.68 μatm. For data with Kd_Lee > 0.2 m⁻¹, they were 29.43 μatm, 1.066, and 24.51 μatm, while for data with Kd_Lee ≤0.2 m⁻¹ the RMSE, MR and MB were 81.5 μatm, 0.994, and −1.83 μatm. Likewise, with a 20% decrease in Kd_Lee (Figs. 5d and 6d), pCO₂ was predicted to be lower than the original pCO₂ if Kd_Lee values were greater than 0.2 m⁻¹ (RMSE=24.04 μatm, MR=0.966, MB=−13.81 μatm) but higher if Kd_Lee values were less than 0.2 m⁻¹ (RMSE=20.81 μatm, MR=1.050, MB=18.41 μatm). When all data were used in the calculation, RMSE, MR and MB were 26.95 μatm, 1.047, and 17.01 μatm. The differences in model sensitivity for Kd_Lee > 0.2 m⁻¹ and Kd_Lee ≤0.2 m⁻¹ are consistent with those for CHL changes, as coastal waters typically have higher CHL and Kd_Lee than offshore waters.

The sensitivity of the pCO₂ model to SST varied over the modeled range of SST. For SST greater than 16°C (Figs. 5e and 5e), a 1°C increase in SST produced pCO₂ predictions higher than the original
pCO₂, while for SST less than 16 °C, the predicted pCO₂ was much closer to the original prediction. As would be expected from the above analyses, a 1 °C decrease in SST (Fig. 6d and e) for SST greater than 16 °C resulted in predicted pCO₂ values that were lower than the original pCO₂ while for SST less than 16 °C pCO₂ predictions were closer to the original pCO₂. The RMSE values for these two experiments (1 °C increase and 1 °C decrease in SST) were 16.03 and 11.98 μatm, with MR values of 1.039 and 0.989 and MB values of 11.57 and -4.52 μatm.

In summary, pCO₂ variations created by a 1 °C change in SST, 20% variations in CHL, and 20% variations in Kd/Lee were all within or close to the RMSE of the model although, notably, the model sensitivity varies with the model input range. Only in the case of Kd/Lee did 20% variations produce pCO₂ variations somewhat higher than the RMSE of the model. However, considering the range of SST in this region (minimum around 15 °C, maximum around 35 °C), a 1 °C temperature variation corresponds to a 6% variation in SST, whereby it is seen that the model is far more sensitive to SST than to CHL and Kd/Lee. Indeed, although coastal waters may occasionally have SST < 16 °C, CHL > 1.5 mg m⁻³, and Kd/Lee > 0.2 m⁻¹, when the entire WFS is considered as a whole at monthly intervals, these conditions are rarely met (Fig. 3), suggesting that the model uncertainties are within those specified in the model evaluation.

Because we chose to use satellite data products directly as the
Table 9: Model sensitivity to CHL, Kd,Lee and SST. For each case, the variable was set to artificially increase or decrease by 20% or 1°C while other variables were kept the same. RMSE, MAE (mean absolute error) between model-predicted CO2 and field-measured CO2 and MB (mean bias between model-predicted and field-measured CO2) were calculated by comparing the observed-predicted CO2 with the observed-predicted CO2. The model was more sensitive to changes in the input variables when CHL was > 1.5 mg m⁻³, Kd,Lee was > 0.2 m⁻¹ m⁻¹ or SST was > 16°C.

<table>
<thead>
<tr>
<th>Cases</th>
<th>RMSE (µatm)</th>
<th>MAE (µatm)</th>
<th>MB (µatm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% increase in CHL</td>
<td>10.34</td>
<td>0.92</td>
<td>8.06</td>
</tr>
<tr>
<td>20% increase in SST</td>
<td>20.36</td>
<td>0.96</td>
<td>18.48</td>
</tr>
<tr>
<td>1°C increase in CHL</td>
<td>10.02</td>
<td>0.97</td>
<td>8.05</td>
</tr>
<tr>
<td>1°C increase in SST</td>
<td>16.03</td>
<td>0.98</td>
<td>15.05</td>
</tr>
</tbody>
</table>

model input during model development, systematic errors (e.g., bias) other than random noise in the satellite data products are implicitly accounted for in the model coefficients. Thus, considering the combined effects of uncertainties in the satellite data products and the sensitivity test results, the uncertainties of the CO2 model should be between 10.5 and 21.0 µatm for typical data ranges. However, these uncertainties represent RMSE values for each data point. When the data are averaged over large scales in either space or time, the uncertainties in the mean products should be much smaller.

The empirical model developed for the WFS here shows improvement over published works (Table 1) in terms of RMSE and R², but not necessarily for other regions in the GOM (see below). Furthermore, the model is applicable all year round because data collected from different months were used in tuning the model coefficients. Therefore, with daily measurements from satellites, the model may be used study the impacts of extreme events on surface CO2 distributions (e.g., 2005 algal blooms and storms), although no such events were considered in the model tuning or validation. In addition, air-sea CO2 flux (P CO2 = k_d CO2sat - P CO2air), where k_d is the gas transfer velocity of CO2, and K_d is the solubility coefficient of CO2, can be calculated with auxiliary wind speed and atmospheric pCO2 data, allowing broad-scale assessments of the extent to which the WFS serves as a CO2 source or sink. Similarly, pH (pH = log[H₃O⁺]), where [H₃O⁺] is the total concentration of hydrogen ions or carbonate ion concentrations ([CO3²⁻]), and carbonate saturation states ([Ca²⁺][CO3²⁻]¹/[Ksp]) can be observed from modeled pCO2 and regional assessments of salinity-normalized TA on the WFS.

However, one shortcoming of the model, as is the case for any other empirical models, is that the model is good only at the data range within which it was tuned. Specifically, all data used in the tuning had pCO2 values between 300 and 550 µatm as the lower and upper bounds of the model's applicability. Field data showed that pCO2 could occasionally be > 600 µatm or even > 1000 µatm in nearshore waters. As these data had no concurrent satellite data, they were not used in the model tuning. Nevertheless, in the derived maps most values are indeed within the range of applicability except for some very nearshore waters (e.g., in Florida Bay). Thus, the pCO2 model should be appropriate to most of the data over the WFS.

4.2. Model testing in other regions of GOM

With the auxiliary underway pCO2 measurements in other regions of GOM, the model was also tested how the algorithm (Eq. (3)) performed in other GOM waters. Based on the distributions of cruise data after matching with satellite products, the validation was examined mainly in three regions (see Fig. 7): around the Mississippi delta, the southeastern GOM, and LC affected regions (open GOM, northern Caribbean and the Florida Strait). For region around the Mississippi River delta (Figs. 7a, b and 5a), predictions for the offshore region were better than the inshore. For the inshore region, predicted pCO2 deviated substantially from the in situ pCO2. This result was not unexpected since water
residence times are much shorter inshore, and dynamic salinity variations caused by extensive large river discharge create large variations in surface pCO2. Compared with the satellite-derived pCO2 map for Mississippi delta generated by Lohrenz and Cal (2006) for June 2003, the offshore patterns show general consistency but the results obtained in the present work reveal temporal and spatial variations in greater detail. For predictions in the northwestern GOM (Figs. 7a, b and 8b), the modeled pCO2 generally followed the in situ pCO2 variations, but with an RMSE of 44.1 μatm. For prediction in the LC affected region, pCO2 was well estimated (RMSE of 13.7 μatm) between July and December (Figs. 7c, d and 8d), while between January and June (Figs. 7e, f and 8e), the estimation was poor with an RMSE of 79.8 μatm. For the January to June period of high uncertainty, we propose that dominant influences on pCO2 influencing mechanisms may be different from the mechanisms that are dominant between July and December. Accordingly, pCO2 variations are not well represented by the parameters used in our model. To some extent, this hypothesis is demonstrated by examining the monthly distribution of the LC (http://www.7320.nrl.navy.mil/GL8hycom1-12_nord/www/arc_list_glimex1004MN.html). The extent of the LC shows different distribution patterns during these two periods. Because the controlling mechanisms for surface pCO2 can vary across geographic regions, region-specific algorithms need to be developed. For the Mississippi delta, river and ocean mixing are likely to strongly affect surface pCO2 distributions, and SSS is a good tracer for mixing effects. Due to the complexity of this region, much further research needs to be done. For the LC affected region, parameters that reflect the characteristics of LC need to be found in order to better estimate surface pCO2. For both the western and southern GOM, additional in situ data are needed for algorithm development.

5. Conclusion

With extensive field and satellite observations and after testing several algorithm approaches, an empirical algorithm for predicting the surface pCO2 on the West Florida Shelf was developed and validated. The algorithm took Julian day and MODIS-derived CHL, Kd, Lee, and SST as inputs, and determined algorithm coefficients through multivariate nonlinear regression against concurrent in situ pCO2 measurements. The algorithm showed reasonably good performance and was used to derive spatial distribution maps of surface pCO2 distributions on the WFS as well as their seasonality and interannual changes. Observed distributions and temporal changes can be well explained based on a sensitivity analysis for the input parameters. Application of the algorithm to other GOM waters showed variable performance, indicating that different pCO2 controlling mechanisms exist in different regions.

Acknowledgments

This work was supported by a USGS (G14PD000647) fellowship and a University South Florida fellowship-Gulf Oceanographic Charitable Trust Endowed Fellowship in College of Marine Science. We thank Dr. Xinping Hu (Texas A&M University) for sharing one cruise data in western GOM. LLR thanks the U.S. Geological Survey Coastal and Marine Geology Program and NASA grant NNH13ZDA001N for funding data collection and the compilation of GOM data which the authors used. The pCO2 data can be found at the Surface Ocean CO2 Atlas v6 (SOCAT), which is an international effort, supported by the International Ocean Carbon Coordination Project (IODCP), the Surface Ocean Lower Atmosphere Study (SOLAS), and the Integrated Marine Biogeochemistry and Ecosystem Research Program (IMBER), to deliver a uniformly quality-controlled surface ocean CO2 database. The many researchers and funding agencies responsible for the collection of data and quality control are thanked for their contributions to SOCAT. We also thank NASA for providing MODIS satellite data and processing software. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. The efforts of two anonymous reviewers, who provided extensive comments and suggestions to improve the manuscript, is greatly appreciated.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.csr.2016.09.004.
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APPENDIX B:

ESTIMATING SURFACE $pCO_2$ IN THE NORTHERN GULF OF MEXICO: WHICH REMOTE SENSING MODEL TO USE?

Estimating surface pCO₂ in the northern Gulf of Mexico: Which remote sensing model to use?

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ARTICLE INFO

Various approaches and models have been proposed to remotely estimate surface pCO₂ in the ocean, with variable performance as they were designed for different environments. Among these, a recently developed mechanistic and data analytical approach (MeSAA) has shown its advantages for its explicit inclusion of physical and biological forcing in the model, yet its general applicability is unknown. Here, with extensive in situ measurements of surface pCO₂, the MeSAA, originally developed for the summertime East China Sea, was tested in the northern Gulf of Mexico (GOM) where river plumes dominate water’s biochemical properties during summer. Specifically, the MeSAA-predicted surface pCO₂ was estimated by combining the dominating effects of thermodynamics, river-ocean mixing and biological activities on surface pCO₂. Firstly, effects of thermodynamics and river-ocean mixing (pCO₂(relev)) were estimated with a two-endmember mixing model, assuming conservative mixing. Secondly, pCO₂ variations caused by biological activities (ΔpCO₂_bio) were determined through an empirical relationship between sea surface temperature (SST)-normalized pCO₂ and MODIS (Moderate Resolution Imaging Spectroradiometer) 8-day composite chlorophyll concentration (chl). The MeSAA-modeled pCO₂ (sum of pCO₂(relev) and ΔpCO₂_bio) was compared with the field-measured pCO₂. The Root Mean Square Error (RMSE) was 22.94 µatm (5.41%), with coefficient of determination (R²) of 0.25, mean bias (MB) of −0.23 µatm and mean ratio (MR) of 1.001, for pCO₂ ranging between 316 and 512 µatm. To improve the model performance, a locally tuned MeSAA was developed through the use of a locally tuned ΔpCO₂_bio term. A multivariate empirical regression model was also developed using the same dataset. Both the locally tuned MeSAA and the regression models showed improved performance compared to the original MeSAA, with R² of 0.78 and 0.84, RMSE of 12.36 µatm (3.14%) and 10.66 µatm (2.68%), MB of 0.00 µatm and −0.10 µatm, and MR of 1.001 and 1.000, respectively. A sensitivity analysis was conducted to study the uncertainties in the predicted pCO₂, as a result of the uncertainties in the input variables of each model. Although the MeSAA was more sensitive to variations in SST and chl than in sea surface salinity (SSS), and the locally tuned MeSAA and the empirical regression models were more sensitive to changes in SST and SSS than in chl, generally for these three models the bias induced by the uncertainties in the empirically derived parameters (river endmember total alkalinity (TA) and dissolved inorganic carbon (DIC), biological coefficient of the MeSAA and locally tuned MeSAA models) and environmental variables (SST, SSS, chl) was within or close to the uncertainty of each model. While all these three models showed that surface pCO₂ was positively correlated to SST, the MeSAA showed negative correlation between surface pCO₂ and SSS and Chl, but the locally tuned MeSAA and the empirical regression showed the opposite. These results suggest that the locally tuned MeSAA worked better in the river-dominated northern GOM than the original MeSAA, with slightly worse statistics but more meaningful physical and biochemical interpretation than the empirical regression model. Because data from abnormal upwelling were not used to train the models, they are not applicable for waters with strong upwelling, yet the empirical regression approach showed ability to be further tuned to adapt to such cases.

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https://doi.org/10.1016/j.csr.2017.10.015
Received 14 March 2017; Received in revised form 6 September 2017; Accepted 30 October 2017
Available online 00 November 2017
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1. Introduction

Coastal air-sea CO₂ flux plays an important role in the global carbon budget (Borges et al., 2005; Cai et al., 2006; Cai, 2011; Chen et al., 2007). Due to the complexity of biogeochemical and physical processes in coastal margins (Jeffrey et al., 2005; Fontoul et al., 2008; Bai et al., 2009; Zhai et al., 2009; Atkins et al., 2013; Baier et al., 2013; Iwara et al., 2013; Maretta et al., 2010; Norman et al., 2013), large uncertainties still exist in coastal air-sea CO₂ flux estimation (Baier et al., 2013; Cai et al., 2013). On the other hand, oceanic uptake of CO₂ has resulted in ocean acidification or decreased surface water pH (by ~0.1 units) (Colesca and Wickett, 2005; Ver et al., 2005; Donn et al., 2009; Sun et al., 2012; Fuchanru and Meyer, 2014), leading to a decrease in marine biodiversity and decline in ecosystems and environments (Wildes et al., 2008; Donn, 2010; Fuchanru and Meyer, 2014). Surface pCO₂ is a critical term in understanding coastal ocean acidification and air-sea CO₂ flux calculation (Bai et al., 2013; Fedr et al., 2010; Cai et al., 2013). Thus, it is important to quantify surface pCO₂ with high accuracy.

In principle, surface water pCO₂ is controlled by four processes: physical mixing, thermodynamic effect, biological activities, and air-sea CO₂ exchange (Pimentel et al., 2008; Iwara et al., 2013; Ver et al., 2012). Different water masses have specific carbonate characteristics such as total alkalinity (TA, μmol kg⁻¹) and dissolved inorganic carbon (DIC, μmol kg⁻¹). The horizontal and vertical mixing among these water masses can affect the surface pCO₂ distribution in a dynamic way in a carbonate system, once sea surface temperature (SST, °C), sea surface salinity (SSS, practical salinity unit) and pressure are known. Any two parameters of TA, DIC, pCO₂ and pH can be combined to calculate the others and CO₂ speciation (e.g., [CO₃]⁻) and thus carbonate mineral saturation state using the CO₂ system program (CO2SYS) (Pierrard and Wallace, 2004). Ocean thermodynamic effect is dependent on SST, and the relationship between surface pCO₂ and SST can be estimated with an exponential function (pCO₂_EXP = e^(ΔCO₂-PICO₂) · (1 + ΔSST/SST)) (Takahashi et al., 2002, 2009) although the exact parameter can deviate slightly from 0.0423 in coastal waters (Bai et al., 2015; Joerden et al., 2015). Biological activities such as photosynthesis, respiration, and calcification have direct effects on surface pCO₂ (Reynaud et al., 2003) because photosynthesis consumes CO₂, respiration produces CO₂, and calcification depletes both TA and DIC in a 2 to 1 ratio. The air-sea CO₂ exchange can also impact surface pCO₂ values during extreme events (e.g., hurricane, storms) (Bates et al., 1998; Bates and Merlivat, 2001; Turk et al., 2013). However, it is difficult and challenging to quantify all these complicated processes separately.

Closely linked to the above processes, several environmental variables can affect surface water pCO₂ such as SST, SSS, mixed layer depth (MLD, m), and chlorophyll-a concentration (CHL, mg m⁻³). With these variables as model inputs, various approaches such as empirical regression (Golden and Cai, 2006; Libenba et al., 2010; Maree et al., 2015; Chen et al., 2016) and feedforward neural network (Jo et al., 2012) have been developed to model surface pCO₂ in coastal oceans. In addition, surface pCO₂ models have been developed for different oceanic regions through the use of self-organizing maps (SOMs), either pattern recognition neural network based (Jeffrey et al., 2005; Friedrich and Oschlies, 2009, 2009; Telizerskis et al., 2009; Nakaoka et al., 2013) or linear regression based (Signorini et al., 2013; Parard et al., 2013, 2019). Generally, these empirical approaches can predict surface pCO₂ with relatively low uncertainties (<40 μatm) and can be applied to different kinds of coastal margins (e.g., river-dominated, upwelling-dominated, and current-dominated) when the model coefficients are tuned locally. However, as with any other empirical approaches, the disadvantage of these models is that each model is only applicable to the modeled data range and environment, and the predicted result is hard to interpret physically, biologically, or chemically.

With the aim to overcome the problems inherited in empirical models, recently, a nonisentropic semi-mechanistic model together with SOMs has been developed and used in the upwelling dominated US western margins (Hales et al., 2012). In this model, temperature is used as a main parameter to measure vertical mixing which varies in different upwelling subregions; changes in DIC and TA caused by mixing and thermal forcing are modeled with changes in SST and CHL; and then surface pCO₂ is calculated from DIC and TA using CO2SYS. This method overcomes the nonlinearity of the marine carbonate system, but errors in the modeled DIC and TA could propagate through the calculation of surface pCO₂. Also recently, a mechanistic semi-analytical algorithm (MeSAA) was developed to model summertime surface pCO₂ in a river-dominated coastal ocean, namely the East China Sea (ECS) (Bai et al., 2015), to study pCO₂ variations in response to various controlling mechanisms during summertime. The main idea is to quantify the effects of dominant processes (horizontal river-ocean mixing, thermodynamic effect, and biological activities) on surface pCO₂ in summer when river discharge plays a significant role in affecting ocean properties. In the work of Bai et al. (2015), the effects of river-ocean mixing and thermodynamic were estimated by assuming conservative mixing between river and ocean end members, and the biological effect was parameterized by an empirical relationship between SST-normalized surface pCO₂ and CHL developed in the adjacent open ocean. Song et al. (2016) applied the MeSAA model to the Bering Sea in summertime, when it is dominated by oceanic waters. They modified the MeSAA by removing the river-ocean mixing term and adding a reference term that has relatively stable temperature with minimal influence from mixing and biological processes. Although both results showed relatively high uncertainties, such approach may still provide a new way in quantifying surface pCO₂ variations, especially for river-dominated regions. However, the applicability of this type of mechanistic approach to other river-dominated regions is unknown.

Compared with the ECS which is affected by only one big river
the northern Gulf of Mexico (GOM) (Fig. 1) receives river inputs from the Mississippi-Archafalaya River System (MARS) as well as several smaller rivers, resulting in a more complicated environment. Massively input of organic and inorganic terrestrial carbon and large amounts of nutrients enhance the biological activities in this area, which may lead to very low surface pCO$_2$ levels and a corresponding large uptake of atmospheric CO$_2$ (Cai, 2008; Lubchenco and Cai, 2006; Cai and Lubchenco, 2010; Huang et al., 2015a). In summertime, the northern GOM exhibits maximum stratification where thermodynamics, strong biological activities and horizontal mixing along salinity gradient are dominant factors in influencing surface pCO$_2$ (Rebollar et al., 2002; Moore et al., 2003; Huang et al., 2015a, 2015b). The MARS plume is not constrained on the continental shelf in summertime (Hu et al., 2003), instead, the plume can reach the slope areas and to the Florida Straits (Ortner et al., 1995; Hu et al., 2005). Therefore, river-ocean mixing may play a major role in influencing surface pCO$_2$ distributions in the northern GOM.

The primary objective of this paper is thus to test the applicability of the MESS model to another river-dominated margin, the northern GOM where river discharge plays an important role in affecting the ocean's biogeochemical properties. However, different from that of the East China Sea, the northern GOM is also a warmer, more closed marginal sea with more complex river end member conditions. Therefore, another objective is to compare the MESS model results with results from a locally tuned MESS model and a conventional empirical regression model, both specifically tuned for the same region. Although some work has been done in modeling surface pCO$_2$ in this area (Lubchenco and Cai, 2006; Lubchenco et al., 2010), due to lack of long-term in situ data, more work is required to develop improved models for synoptic mapping of surface pCO$_2$ with high accuracy via satellite remote sensing. In this study, the original MESS, the locally tuned MESS, and the empirical regression approaches are applied using an extensive dataset collected from the northern GOM to test the applicability of the MESS approach in the northern GOM, 2) understand the effects of river-ocean mixing and biological processes on surface pCO$_2$, 3) develop a locally tuned MESS model for the northern GOM, and 4) compare the performance of the MESS, locally tuned MESS, and a locally tuned empirical regression model. The ultimate goal is to make recommendations on model development for this complex region, where the findings may also be extended to other river dominated margins.

The manuscript is structured as follows. The background and motivation of this work are introduced above. Section 2 presents the data and data processing methods; Section 3 describes the methods used in developing each model (original MESS, locally tuned MESS, and empirical regression); Section 4 presents the performance evaluation of each model; Section 5 discusses the model sensitivity (to uncertainties of the input variables) and strengths/weaknesses of each model; Finally, Section 6 summarizes the main findings with conclusions.

2. Data sources and data processing

2.1. Field data

Several cruise surveys collected underway surface water pCO$_2$ data from the northern GOM waters and the GOM open waters. These are described in Tables 1 and 2, respectively. None of these data were used in a recent effort to estimate surface pCO$_2$ on the West Florida Shelf (WFS) (Chen et al., 2015a). Data from the northern GOM was collected between 2003 and 2013 in July–September, and data from the GOM open waters was collected between 2006 and 2012 in February–April and December. These data were obtained from the Carbon Dioxide Information Analysis Center (CDIAC) (http://cdiac.esd.ornl.gov/) (Wanninkhof et al., 2013a, 2013b; Sabine et al., 2014; Cai et al., 2012a, 2012b, 2014), the NOAA's Atlantic Oceanographic and Meteorological Laboratory (AOML) (http://www.aoml.noaa.gov/oco/co2web/co2data.html) (Wanninkhof et al., 2009, 2010, 2011a, 2011b, 2012a, 2013a), and the Lamont-Doherty Earth Observatory (LDEO) of Columbia University (http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/pages/pCO2data.html) (Sutherland et al., 2013). For pCO$_2$ data collected in the northern GOM, due to abnormal upwelling in July 2009 (Zheng et al., 2012; Huang et al., 2015a), pCO$_2$ data collected around the Mississippi River mouth and adjacent offshore region (red boxes in Figs. 1b and 1c) showed much lower pCO$_2$ values than those collected

![Surface pCO2](image)

Fig. 1. Spatial distributions of the field measured pCO$_2$ along the transects in the northern GOM (Table 1). (a) All cruises; (b) and (c) are for July 2006, 2007 and 2010, and July 2009, respectively. Note that around the Mississippi River delta and offshore region (red boxes in b and c), due to abnormal upwelling in July 2009 (Huang et al., 2015a), pCO$_2$ data collected in July 2009 in this area were not used in this study. (d) Same field data as shown in (a) where high quality MESS L3 8 day CHL data encompassed the field measurement data.
Table 1
Underway pCO2 measurements in the northern GOM during summer (July-September) at a depth of 5 m, with a measurement interval of ~2 or 3 min. For each cruise survey, the number of observations was greatly reduced when concurrent MODIS standard Level-3 daily Chl composite data was found. Corresponding cruise tracks are shown in Fig. 1. Note that pCO2 data collected in July 2009 around the Mississippi River delta and offshore region (red boxes in Figs. 1b and c) was not used in this study, due to abnormally upwelling in July 2009 (Huang et al., 2012) in this area, but data collected outside this region in July 2009 were still used. Also note that data listed in this table were not used in Chen et al. (2014) to develop a pCO2 model for the WPS.

<table>
<thead>
<tr>
<th>Cruise ID</th>
<th>Ship name</th>
<th>Date range</th>
<th># of observations</th>
<th># of observations with matching MODIS data</th>
</tr>
</thead>
<tbody>
<tr>
<td>GL0903, Leg1</td>
<td>R/V Gordon Gunter</td>
<td>2/16/2009</td>
<td>233</td>
<td>0</td>
</tr>
<tr>
<td>GL0902, Leg1</td>
<td>R/V Gordon Gunter</td>
<td>4/7/2009-4/13/2009</td>
<td>3104</td>
<td>118</td>
</tr>
<tr>
<td>GL0904, Leg1</td>
<td>R/V Gordon Gunter</td>
<td>9/14/2009-9/15/2009</td>
<td>362</td>
<td>19</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>67,669</td>
<td>676</td>
</tr>
</tbody>
</table>

Table 2
Underway pCO2 measurements in the GOM open waters during spring (Feb-Apr) and winter (Dec), which were used to model the biological effect on surface pCO2. These data were measured at a depth of 5 m, with a measurement interval of ~2 or 3 min. Data collected in summer was not used, due to the oligotrophic characteristics of the GOM open waters in summertime. For each cruise survey, the number of observations was greatly reduced when concurrent MODIS standard Level-3 daily Chl composite data was found. Corresponding cruise tracks are shown in Figs. 2a & 2b. Note that those data were not used in Chen et al. (2014) to develop a pCO2 model for the WPS.

<table>
<thead>
<tr>
<th>Cruise ID</th>
<th>Ship name</th>
<th>Date range</th>
<th># of observations</th>
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<td>362</td>
<td>19</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>67,669</td>
<td>676</td>
</tr>
</tbody>
</table>

In July of 2006, 2007 and 2010, as shown in Figs. 1b and 1c. Because of the abnormally upwelling condition did not meet the conditions in the original MeSAA approach (horizontal river-ocean mixing, thermodynamic effects, and biological activities dominate the variations of surface pCO2 in the summertime northern GOM) and abnormal upwelling may change the direction of air-sea CO2 flux (Huang et al., 2012). These low pCO2 values were not selected in this study. Data from the GOM open waters were selected in order to model the biological effect on surface pCO2. Note that due to the weak biological activities in the GOM open waters during summertime (CHL < 0.15 mg/m3), data in July-September were not selected in modeling the biological effect. Seawater samples for measurements of pCO2, SS and SST in both the northern GOM and the GOM open waters were collected at a depth of 5 m using a shipboard flow-through seawater system. The full cruise tracks in the northern GOM and GOM open waters with color-coded in situ pCO2 are shown in Figs. 1a and 2a, respectively. Surface pCO2 was measured with a combination of a gas equilibrator and a non-dispersive, infrared analyzer LI-COR™ (model 6251 or 6202 or 7000 or 840A or 823) (Feely et al., 1998; Pierrot et al., 2009) with an accuracy of 2 ppm (or lower) and a measurement interval of 2 or 3 min. The details of data collection, processing, and quality control can be found in Feely et al. (1998) and Pierrot et al. (2009) and Huang et al. (2013). In addition to pCO2, SS and SST data were collected using a CTD (SBE-19 or SBE-21 or SBE-820 or SBE-45, SeaBird Inc., USA, YSI 6600) integrated in the underway pCO2 system.

All cruise data obtained from CDAIC, AOML, and LIOHO have undergone quality control analysis. These data were converted into the same format with an Interactive Data Language (IDL) program, and were visualized and quality controlled (i.e., by examining data quality flags and metadata files) to discard apparent errors (e.g., individual spikes due to instrument malfunction or other factors). A total of 67,669 pCO2 observations were selected for the northern GOM to develop and validate the MeSAA and empirical models, and a total of 15,215 observations were selected for the GOM open waters to model the biological effect on surface pCO2 for the MeSAA.

The MeSAA has two explicit components on modeling physical and
biological effects, respectively. To model the physical effect, namely the effect of horizontal river and ocean mixing on surface $pCO_2$, through a two-endmember mixing model, TA and DIC data of the river and ocean endmembers were carefully selected. Specifically, river endmember $TA_{0}$ of 2420 μmol/kg and $DIC_{0}$ of 2040 μmol/kg at $SSS_{0} = 0.1$, and ocean endmember $TA_{ocean}$ of 2399.3 μmol/kg and $DIC_{ocean}$ of 2082.8 μmol/kg at $SSS_{ocean} = 36.04$ from Huang et al. (2015a) were applied in this study. $DIC_{0}$ was assumed to be 39 μmol/kg higher than $TA_{0}$ (Lee et al., 2012; Cat et al., 2013), and oceanic TA and DIC were linearly normalized to salinity of 35 using Eqs. (1) and (2) (marked as $TA_{35}$ and $DIC_{35}$, e.g., Yang et al., 2010) with the river endmember $TA_{0}$ and $DIC_{0}$ at $SSS_{0} = 0.1$ as the intercepts, respectively. To quantify the variations of riverine TA of the Mississippi and Atchafalaya Rivers, TA data of both rivers between May 2006 and Feb 2015, were obtained from the U.S. Geological Survey (USGS) water quality database (https://waterdata.usgs.gov/usa/wv/query?cb). TA data for Atchafalaya River was the average of two stations (USGS Station 07374525 in Wax Lake Outlet at Calunet, LA, 29°41'52"N, 91°22'22"W, and Station 07381600 in Lower Atchafalaya River at Morgan City, LA, 29°43'33.4"N, 91°12'42.6"W), and TA data for the Mississippi River was from USGS Station 07374525 in Mississippi River at Belle Chase, LA, (29°51'25"N, 89°58'40"W). As shown in Fig. 3, between May 2006 and Feb 2015, the TA ranges of Mississippi river and Atchafalaya River were 1204.0–2940.0 μmol/kg and 1014.0–3170.0 μmol/kg, respectively.

Fig. 3. Variation of TA of the Mississippi and Atchafalaya rivers between May 2006 and Feb 2015. Data for Atchafalaya River was the average of two stations (USGS Station 07381590 in Wax Lake Outlet at Calunet, LA, 29°41’52”N, 91°22’22”W, and Station 07381600 in Lower Atchafalaya River at Morgan City, LA, 29°43’33.4”N, 91°12’42.6”W), and TA data for Mississippi River was from the USGS Station 07374525 in Mississippi River at Belle Chase, LA, (29°51’25”N, 89°58’40”W).
summertime during this period, the TA range of Mississippi river was 2040–2850 μmol/kg, and the TA range of Arctofalaya River was 1460–2850 μmol/kg. According to the river flow rates of both rivers in summertime between May 2006 and Feb 2015, the Mississippi river contributed around 82% to the total river discharge to the northern GOM (data not shown here), thus the variation of river endmember TA0 was 1935.6–2094.8 μmol/kg. The uncertainty of the parameters of TA0 and DICc caused by the variations in riverine TA and DIC in summertime were analyzed and quantified in Section 5.1.

\[
\text{TA}_{\text{sum}} = (\text{TA}_{\text{sum}} - \text{TA}_0) 	imes (15 - \text{SSS}) + \text{TA}_0 \\
\text{DIC}_{\text{sum}} = (\text{DIC}_{\text{sum}} - \text{DIC}_c) \times (15 - \text{SSS}) + \text{DIC}_c
\]

(1)

2.2. MODIS data

To quantify the effect of biological activities on surface pCO2, standard NASA Level-3 CHL data (version RE2011.0) between 2003 and 2013 were obtained from the NASA Goddard Space Flight Center (https://oceancolor.gsfc.nasa.gov/). The use of satellite CHL was not only because there was no field CHL data available, but more importantly, the pCO2 models were developed in the satellite era. Therefore, if satellite-derived CHL was used to train the models (see Sections 5.1–5.3) the errors in satellite-derived CHL would be implicitly included in the model coefficients. The 8-day composite Level-3 CHL data at 9-km resolution were generated from measurements by the Moderate Resolution Imaging Spectroradiometer (MODIS) on the Aqua satellite using community-accepted standard algorithms. Specifically, the Gordon and Wang (1994) algorithm was used to remove the atmospheric effects, after which a combination of band-ratio algorithm (O’Reilly et al., 2000) and band-subtraction algorithm (Hsu et al., 2012) was used to estimate CHL. Various data quality flags (e.g., straylight, sun glint, etc.) were used to screen low-quality data when generating the global composite data (Part et al., 2003). In general, comparison between satellite-derived CHL and field measured CHL showed uncertainties ranging from 5% to 33% (Giglio and Casey, 2004; Bailey and Werdell, 2006; Mein et al., 2007; Camizzaro et al., 2013a).

3. Methods in model development

Concurrent and collocated MODIS and field data were used to develop and test all three models: the original MeSAA with its parameterization as presented in Bai et al. (2015), a modified MeSAA with locally-tuned parameterization, and an empirical regression model. Here “concurrent” means that the time of the field data collection is within the MODIS 8-day period, and “collocated” means that the field pCO2 data within a 9-km MODIS pixel was averaged to match the satellite data.

After the strict quality control and field data binning, for the period between 2003 and 2013, 676 conjugate observations of field-measured pCO2 and MODIS CHL data were available for the northern GOM (Fig. 1d), and 589 conjugate observations of field-measured pCO2 and MODIS CHL data for the period between 2006 and 2013 were available for the GOM open waters (Fig. 2b). In the matched dataset for the northern GOM, field-measured pCO2 ranged between 316.13 and 451.70 μatm, field-measured SST ranged between 27.95 and 31.51°C, field-measured SSS ranged between 26.85 and 36.67, and satellite CHL ranged between 0.043 and 1.609 mg/m². In the matched dataset for the GOM open waters, the range of field-measured pCO2, field-measured SST, field-measured SSS, and satellite measured CHL were 338.22–394.04 μatm, 22.30–26.35°C, 35.06–36.57, and 0.058–0.650 mg/m², respectively. These matched datasets were used to develop and validate the following pCO2 models.

For both the original and locally tuned MeSAA models, pCO2 was derived from the estimation of the influence from thermodynamics, river-ocean mixing, and biological activities. Field-measured pCO2 was not used in the model development but used for model evaluation only. For the empirical regression model, the 2003–2013 pCO2 dataset was divided randomly into two groups with one for model training and the other for model validation.

3.1. A brief description of the MeSAA

The details of this satellite remote sensing pCO2 model – MeSAA – can be found in Bai et al. (2015), but for completeness a brief description is provided here.

For the physical aspect of river-ocean mixing (pCO2rivermixing), conservative mixing of TA and DIC was assumed (Cai et al., 2010; Wang et al., 2013; Yang et al., 2015), and TA and DIC at certain salinity level were estimated with a linear river-ocean mixing model as shown in Eq. (3) (Jiang et al., 2006; Bai et al., 2015; Yang et al., 2015). Each pair of TA and DIC with ancillary SST, SSS and pressure was used to calculate a pCO2 value with Eq. (4) using the CO2SYS (Pierrot and Wallace, 2006).

\[
P_{\text{CO2rivermixing}} = \text{CO2SYS}(\text{TA}, \text{DIC}, \text{SST}, \text{SSS})
\]

(4)

As shown in Fig. 2c, there is a clear trend showing the relationship between SST and surface pCO2. To model the effect of biological activities on surface pCO2, this thermodynamic effect needs to be removed first. To do so, pCO2 data in the GOM open waters was restricted to within ± 1°C of the monthly averaged SST of each month, and normalized to the monthly averaged SST using Eq. (5) (Takahashi et al., 2002, 2009).

\[
P_{\text{CO2biomix}} = P_{\text{CO2rivermix}} \times e^{\frac{282.03}{299.0}-T_{\text{SST}}}
\]

(5)

where T is SST in °C, and subscripts ‘nor’ and ‘obs’ symbolize the normalized and observed values.

The variation of SST-normalized surface pCO2 (P_{CO2biomix}) was supposed to be caused by the biological activities, which were related to changes in CHL. Thus pCO2biomix was regressed against log10(CHL) by linear regression as shown in Eq. (6) and Fig. 2d. CHL was scaled logarithmically because CHL tends to be log-normal in large scale distributions (Campbell, 1995).

\[
P_{\text{CO2biomix}} = -38.57 \times \log_{10}(\text{CHL}) + 328.84
\]

(6)

The integration of the changing rates in pCO2biomix over changes in CHL was regarded as the effect of biological activities on surface pCO2. Therefore, to model the changing rates of surface pCO2 corresponding to CHL changes, partial derivatives (over CHL) on both sides of Eq. (6) were calculated, and then the variation of surface pCO2 caused by biological activities (Δp_CO2biomix) was obtained using Eq. (7) (CHL was empirically set to 0.01 mg/m²) by integrating the derived partial derivatives over the range of CHL. However, the final modeled pCO2 via such integration alone showed large difference from the field-measured pCO2. Therefore, different from Bai et al. (2015), two empirical coefficients (a and b) were added in Eq. (7) to account for the different pCO2 response to biological activities between the northern GOM and GOM open waters through empirical regression, thus the final biological coefficient (8), which was the coefficient of log_10(CHL) in the biological term Δp_CO2biomix was 36.04.
where $a = 2.49$, $b = 2.57$, and $CHL_c = 0.01$ ng/m$^3$.

For model evaluation, the sum of river-ocean mixing and biological activities was used to represent the MeSAA-predicted surface $pCO_2$, as specified in Eq. (8) even though the biological component was based on empirical data fitting (Bai et al., 2015). The model-predicted $pCO_2$ was compared with the field-measured $pCO_2$, where coefficient of determination ($R^2$), root mean square error (RMSE), mean ratio (MR), and mean bias (MB) were used to gauge model performance. A histogram of the difference between field-measured $pCO_2$ and model-predicted $pCO_2$ was also generated to examine the error distributions.

$pCO_2 = pCO_2_{observed} + \Delta pCO_2_{gain}$

3.2. Locally tuned MeSAA

The original MeSAA used an empirical relationship trained in the adjacent open ocean, where river-ocean mixing is minimum, to model the effects of biological activities on surface $pCO_2$ in the ECS (Bai et al., 2015). The extrapolation from open-ocean to the river-dominated northern GOM is problematic. Therefore, in the locally tuned MeSAA, the open-ocean-based modeling component for the biological effects was replaced with a locally-trained empirical relationship between $\Delta pCO_2_{gain}$ and SS (SST, SST, and CHL), while the modeling of the river-ocean horizontal mixing ($pCO_{2,river-ocean}$) was kept the same as in the original MeSAA. Specifically, the residuals between the field-measured $pCO_2$ and $pCO_{2,river-ocean}$ were expressed as $\Delta pCO_2$, which was calculated first using Eq. (9). Then, the relationships between $\Delta pCO_2$ and environmental parameters such as SST, SST, and CHL were examined. Finally, $\Delta pCO_2$ was regressed against SST, SST, and CHL by an empirical linear regression, and the calculated $pCO_2$ by Eq. (10) was regarded as the effect of biological activities on surface $pCO_2$, namely $\Delta pCO_2_{gain}$:

$\Delta pCO_2 = pCO_{2,observed} - pCO_{2,measured}$

where $\Delta pCO_2_{gain} = 19.54 \times SST + 8.31 \times log_{10}{CHL} - 777.40$.

Similar to the original MeSAA, for model evaluation, the sum of $pCO_{2,river-ocean}$ and $\Delta pCO_2_{gain}$ was used to represent the surface $pCO_2$ estimated from the locally tuned MeSAA. RMSE, $R^2$, MB and MR were calculated to gauge the model performance. A histogram of the difference between field-measured $pCO_2$ and modeled $pCO_2$ was generated to examine the error distributions.

3.3. Empirical regression

Chen et al. (2016) showed a multi-variate statistical approach to model surface $pCO_2$ on the WFS. The same approach was used to develop the relationship between surface $pCO_2$ and environmental variables (SST, SST, CHL) as well as day of the year (Julday) for the northern GOM. The dataset was divided randomly into two groups, with one group used for model training and coefficient tunning, and the other for model validation. The relationships between surface $pCO_2$ and environmental variables were examined.

After extensive trial and error tests using various functional forms and model inputs, the regression equation was determined as:

$pCO_2 = l_0 + l_1 \times SST + l_2 \times SST + l_3 \times CHL + l_4 \times SST \times CHL + l_5 \times SST \times SST + l_6 \times SST \times CHL + l_7 \times SST \times CHL \times CHL + l_8 \times CHL \times CHL + l_9 \times CHL \times CHL \times CHL + \text{Context}$

where $l_0 = \text{SST}$, $l_1 = \text{SST}$, $l_2 = \text{log}_{10}{CHL}$, $l_3 = \cos(2\pi(Julday - 71)/365)$.

In this equation, Julday was sinusoidally normalized to reflect the seasonal feature (Friedrich and Ochtheim, 2006; Lejeune et al., 2006; Signorini et al., 2013), and $\gamma$ was a tuning parameter ranging from 0 to 365 days and was determined to be 330 by iteration until the minimum root mean square error (RMSE) between modeled and measured $pCO_2$ was reached. The final empirical $pCO_2$ model was thus determined as:

$pCO_2 = -220.75 + 112.24 \times SST + 426.12 \times CHL + 1.53 \times SST + 3.05 \times SST + 2.88 \times CHL + 12.50 \times SST + 0.85 l_1 + 7.67 l_2 + 2.75 l_3 - 0.99 l_4 - 72.33 l_5 + 1.96 l_6 + 281.11 l_7$

where $l_0 = \text{SST}$, $l_1 = \text{SST}$, $l_2 = \text{log}_{10}{CHL}$, $l_3 = \cos(2\pi(Julday - 71)/365)$.

The model was subsequently applied to the other half of the dataset that was not used in the model development. RMSE, $R^2$, MB and MR were calculated to quantify the model performance in both model development and model validation. A histogram of the difference between field-measured $pCO_2$ and modeled $pCO_2$ was generated to examine the error distributions.

Note that although the model form in Eq. (12) is the same as in Chen et al. (2016), the model coefficients are specifically tuned for this dataset, thus different from those in Chen et al. (2016) for the WFS.

4. Results

In this section, the performance of each of the three models (original MeSAA, locally tuned MeSAA, and empirical regression) is examined and compared, in terms of statistical measures and spatial distribution patterns of modeled $pCO_2$.

4.1. Original MeSAA

Fig. 4a shows the comparison between $pCO_{2,river-ocean}$ calculated with the river-ocean mixing model and field-measured surface $pCO_2$. Clearly, the values of $pCO_{2,river-ocean}$ was higher than the field-measured surface $pCO_2$ across the SSS range (26.65–26.67) used in this study, but such a discrepancy was reduced at high SSS. This is because that the effect of biological uptake of CO2 is strong and has not been taken into account yet, and at high SSS the TA and DIC values were getting close to those of the ocean endmember, thus $pCO_{2,river-ocean}$ values were getting close to the field-measured $pCO_2$.

The variation of the biological term ($\Delta pCO_{2,biog}$) along with SSS in Fig. 4b demonstrated that the biological CO2 removal at low SSS was more intense than at high SSS as $\Delta pCO_{2,biog}$ could reach $-209$ ppm at low SSS. This is consistent with the high $pCO_{2,river-ocean}$ values at low salinity as shown in Fig. 4a and reported in the literature (Huang et al., 2013, 2015).

The MeSAA-modeled $pCO_2$ (sum of $pCO_{2,river-ocean}$ and $\Delta pCO_{2,biog}$) was compared with the field-measured $pCO_2$ in Fig. 4c. Generally, the modeled $pCO_2$ followed the in situ $pCO_2$ variations quite well at SSS $\geq 30$ with RMSE of 22.02 ppm (5.59%), MB of $-1.32$ ppm and MR of 0.999 (Table 3). For SSS $\leq 30$, surface $pCO_2$ was strongly overestimated with RMSE of 47.48 ppm (13.72%), MR of 42.08 ppm and MR of 1.121 (Table 3). Statistics for the whole SSS range used in this study showed a $R^2$ of 0.25, RMSE of 22.94 ppm (5.91%), MB of $-0.33$ ppm and MR of 1.001 (Table 3). The strong overestimation in surface $pCO_2$ at SSS $\leq 30$ ($\sim 7\%$ of the northern GOM has such low salinity, the statistics was derived based on a salinity study that has not been published) was assumed to be caused either by the variations in the river endmember $TA_{river}$ and $DIC_{river}$, which could have a larger influence in the modeling of $pCO_{2,river-ocean}$ at low SSS, or by the insufficient modeling of the biological removal of CO2. Quantification of the effect of the variations in $TA_{river}$ and $DIC_{river}$ in Section 5.1 demonstrated that the overestimation in surface $pCO_2$ at SSS $\leq 30$ was mainly due to the variations in $TA_{river}$ and $DIC_{river}$.

In Fig. 5c, the histogram of the modeled $pCO_2$ residuals in Section 5.1 shows that 75.7% of the residuals were smaller than the standard deviation of the observed $pCO_2$ ($\pm 26.43$ ppm).

Comparing with the results of previously published works (Lohrenz and Cair, 2006; Lohrenz et al., 2010), the results from the MeSAA showed significant improvement, where the same $pCO_2$ ranges
RMSE reduced from 50.2 µatm in Lohrenz and Col (2006) to 22.94 µatm in this study. Even though R² from the MeSAA was lower than in Lohrenz et al. (2010), the results here are still encouraging as the study region in Lohrenz et al. (2010) was much smaller and pCO₂ variation was much larger than the study here.

The spatial distribution of the MeSAA-predicted pCO₂ is shown in Fig. 5a. Compared with the in situ pCO₂ distribution (Fig. 1d), the MeSAA model appeared to be able to regenerate the spatial pCO₂ patterns, especially for the inshore-offshore pCO₂ gradient. The relatively low pCO₂ values (120–150 µatm) near the Mississippi River mouth and in the east of the MARS as well as the relatively high pCO₂ values in the west of the northern GOM were all predicted well. On the other hand, the distribution of the pCO₂ residuals shown in Fig. 5b revealed that in some locations (e.g., east of the northern GOM or to the east of 90°W) surface pCO₂ was either underestimated or overestimated. Such a discrepancy could be due to the rapid changes of the river plumes in response to wind and coastal currents, which in turn influenced the biological activities and therefore surface pCO₂. Clearly, the river-ocean mixing model or the biological effect model did not capture such changes very well, and in such a complex environment it is challenging to model the surface pCO₂ with very high accuracy (e.g., RMSE < 10 µatm).

To further examine the possible causes of the relatively large uncertainties in the MeSAA-modeled surface pCO₂, the relationships between the pCO₂ residuals and the environmental parameters (SST, SSS, and CHL) were investigated. As shown in Fig. 6d, there was a general

<table>
<thead>
<tr>
<th>Methods</th>
<th>R²</th>
<th>RMSE (µatm)</th>
<th>RMSE (%)</th>
<th>ME (µatm)</th>
<th>RR</th>
<th>Relationship between modeled and measured pCO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>MetSAA</td>
<td>0.25</td>
<td>22.94</td>
<td>5.81</td>
<td>-0.23</td>
<td>1.001</td>
<td>( Y = 0.578X + 167.32 )</td>
</tr>
<tr>
<td>SSS &gt; 30</td>
<td>0.25</td>
<td>22.93</td>
<td>5.90</td>
<td>-0.22</td>
<td>1.001</td>
<td>( Y = 0.578X + 167.32 )</td>
</tr>
<tr>
<td>SSS ≤ 30</td>
<td>0.25</td>
<td>22.95</td>
<td>5.82</td>
<td>-0.23</td>
<td>1.001</td>
<td>( Y = 0.578X + 167.32 )</td>
</tr>
<tr>
<td>Locally tuned</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeSAA</td>
<td>0.76</td>
<td>11.44</td>
<td>3.16</td>
<td>-0.15</td>
<td>1.001</td>
<td>( Y = 0.873X + 91.07 )</td>
</tr>
<tr>
<td>SSS &gt; 30</td>
<td>0.76</td>
<td>11.44</td>
<td>3.16</td>
<td>-0.15</td>
<td>1.001</td>
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<tr>
<td>Empirical Regression</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Whole SSS range</td>
<td>0.84</td>
<td>11.25</td>
<td>3.62</td>
<td>-0.06</td>
<td>1.001</td>
<td>( Y = 0.962X + 62.83 )</td>
</tr>
<tr>
<td>SSS &gt; 30</td>
<td>0.84</td>
<td>11.25</td>
<td>3.62</td>
<td>-0.06</td>
<td>1.001</td>
<td>( Y = 0.962X + 62.83 )</td>
</tr>
<tr>
<td>SSS ≤ 30</td>
<td>0.84</td>
<td>11.25</td>
<td>3.62</td>
<td>-0.06</td>
<td>1.001</td>
<td>( Y = 0.962X + 62.83 )</td>
</tr>
<tr>
<td>Model validation</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Whole SSS range</td>
<td>0.83</td>
<td>10.98</td>
<td>2.73</td>
<td>-0.21</td>
<td>1.000</td>
<td>( Y = 0.803X + 73.21 )</td>
</tr>
<tr>
<td>SSS &gt; 30</td>
<td>0.83</td>
<td>10.98</td>
<td>2.73</td>
<td>-0.21</td>
<td>1.000</td>
<td>( Y = 0.803X + 73.21 )</td>
</tr>
<tr>
<td>SSS ≤ 30</td>
<td>0.83</td>
<td>10.98</td>
<td>2.73</td>
<td>-0.21</td>
<td>1.000</td>
<td>( Y = 0.803X + 73.21 )</td>
</tr>
<tr>
<td>Both model and validation</td>
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<tr>
<td>Whole SSS range</td>
<td>0.83</td>
<td>10.94</td>
<td>2.71</td>
<td>-0.20</td>
<td>1.000</td>
<td>( Y = 0.884X + 68.15 )</td>
</tr>
<tr>
<td>SSS &gt; 30</td>
<td>0.83</td>
<td>10.94</td>
<td>2.71</td>
<td>-0.20</td>
<td>1.000</td>
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<td>( Y = 0.884X + 68.15 )</td>
</tr>
</tbody>
</table>
linear relationship between the pCO2 residuals and SSS. This indicated that, although SSS could modulate the biological term \( \Delta pCO2_{biom} \) (Fig. 4b) and SSS was also used in the parameterization of \( pCO2_{biom} \), the effect of SSS in the MeSAAS-modeled pCO2 was still not sufficiently expressed. The relationship between \( pCO2_{biom} \) and CHL in Eq. (6) assumed that variations in the normalized pCO2 were dominated by the biological effects. However, in reality other possible factors such as the dynamic effects of mesoscale eddies, Loop Current, and vertical mixing of surface pCO2 could also play a role, as shown in the data scattering in Fig. 3d. Furthermore, the effects of the biological activities may work differently in the northerly GOM coastal waters from the GOM open waters, thus direct application of the biological relationship developed from the latter to the former may be questionable, requiring modification of the MeSAAS.

4.2. Locally tuned MeSAAS

Fig. 4c shows the comparison between modeled \( \Delta pCO2_{biom} \) using the locally tuned MeSAAS and the residuals (\( \Delta pCO2_{model} \)) in the field-measured pCO2 after subtracting the horizontal mixing term \( pCO2_{biom} \). At SSS ≤ 35, the model performed reasonably well, but at SSS > 35 the biological removal of surface CO2 appeared to be too strong. The comparison between the modeled pCO2 (from the locally tuned MeSAAS) and field-measured pCO2 in Fig. 4d also showed similar patterns for data with SSS ≤ 35 and SSS > 35.

Statistically (Table 3), the locally tuned MeSAAS showed better performance than the original MeSAAS in estimating surface pCO2 regardless of the SSS range considered. At SSS ≤ 30, the mean bias in the estimated pCO2 was 5.70 µatm, possibly due to variations in the TA0 and DIC parameters, yet such a positive bias was much smaller than that of the original MeSAAS (MB = 42.08 µatm) due to differences in modeling the biological term \( \Delta pCO2_{biom} \). Such a greatly reduced underestimation in surface pCO2 at SSS ≤ 30 indicated that, although the modeled result of Eq. (10) (based on Figs. 3a and 3b) was regarded as the biological term \( \Delta pCO2_{biom} \), it may also include some pCO2 residuals in the mixing term that was not fully accounted for in the parameterization of \( pCO2_{biom} \), or in other weak but non-ignorable processes (e.g., vertical mixing), all of which were included implicitly in the empirical coefficients of Eq. (10). The histogram of the pCO2 residuals (Fig. 5) shows that 97.3% of the residuals were smaller than the standard deviation of the observed pCO2 (± 36.43 µatm), which also indicated that the locally tuned MeSAAS had improved performance comparing to the original MeSAAS.

Figs. 4e and 5e show the spatial distributions of surface pCO2 and pCO2 residuals derived from the locally tuned MeSAAS model. Compared with the field-measured pCO2 distributions, the spatial distributions along the inshore-offshore gradient showed similar patterns, which also showed more detailed features and higher accuracies than from the original MeSAAS model. In addition, the relative low pCO2 values near the river mouth and in the east of the northern GOM as well as the relatively high pCO2 values in the west of the northern GOM were all revealed clearly. Compared with the pCO2 residual distributions from the original MeSAAS, the residual distributions from the locally tuned MeSAAS in Fig. 5e showed lower uncertainties, suggesting improved model performance.

4.3. Empirical regression

Figs. 7a–7e show the relationships between surface pCO2 and environmental variables (CHL, SSS and SST), and Figs. 7f–7l show the multi-variate regression model (Eq. (11)) for the pCO2 prediction. For the model development (Fig. 7f), RMSE was 10.35 µatm (2.63%), with a \( R^2 = 0.84 \), MB of −0.00 µatm and MR = 1.001. There was negligible overestimation at SSS > 30 (RMSE = 9.40 µatm (2.03%), MB = −0.97 µatm, and MR = 1.001) and slight underestimation at SSS ≤ 30 (RMSE = 8.80 µatm (2.51%), MB = −5.58 µatm, and MB = 0.996). Fig. 7e shows the model validation with data not used in the model training. Performance measures are similar to those for the model
training, with an RMSE of 10.98 µatm (2.73%), R² of 0.83, MB of −0.21 µatm and MR of 1.00. RMSE for the combined datasets (both model development and model validation) was 10.66 µatm (2.68%), with an R² of 0.84, MB of −0.10 µatm, and MR of 1.00 (Table 3). The histogram of residuals for the combined datasets (Fig. S5) shows that 97.9% of the residuals were smaller than the standard deviation of the observed pCO₂ (± 26.43 µatm).

Figs. 5g and 5h show the spatial distribution of empirically-modeled surface pCO₂ and the pCO₂ residuals. Similar to those from the locally tuned MeSAA, the spatial patterns along the inshore-offshore gradient agree with those determined from in situ measurements, and they also showed more detailed features than those provided by the original MeSAA.

In summary, the empirical regression method showed slightly better performance than the locally tuned MeSAA, and both models showed improvements over the original MeSAA.

5. Discussion

In this section, the sensitivities of the mechanistic models (original MeSAA and locally tuned MeSAA) and the empirical model (empirical regression) to the empirical coefficients and uncertainties in the model inputs are analyzed, and strengths and weaknesses of each model as well as the controls of surface pCO₂ in summertime northern GOM are discussed.

5.1. Sensitivity analysis of the MeSAA

5.1.1. Model sensitivity to empirical coefficients

The parameterization of the MeSAA included two types of empirically derived coefficients: the first included the TA and DIC values of the river and ocean endmembers, which affected the horizontal mixing term pCO₂mixing, and the second included the biological coefficient of biological activities to surface pCO₂, which influenced the biological term pCO₂bio.

As described in Section 2.1, the variation of the river endmember TA was 193.6–2894.4 µmol/kg, about 2.5% lower or higher than the TA₀ value (2420 µmol/kg) used in this study. Therefore, in order to evaluate the model sensitivity to changes in TA₀ and DIC₀, river endmember TA₀ was varied by ±20% with the assumption that DIC₀ was about 30 µmol/kg higher than TA₀, while all other parameters remained unchanged. In addition, TA and DIC values for the ocean endmember were fixed because the Loop Current water was stable.

Visual inspection of Figs. 8a and 8b indicate that the MeSAA was more sensitive to changes in TA₀ and DIC₀ at lower SSS. For SSS < 30, a 20% increase in TA₀ (Fig. 8a) produced about 47.60 µatm higher pCO₂, while for SSS > 30 the same 20% increase in TA₀ and DIC₀ caused a much smaller change (MB = 8.15 µatm) in the predicted pCO₂. A similar disparity in the model sensitivity was observed for a 20% decrease in TA₀ when data were partitioned to SSS ≤ 30 and SSS > 30 (Fig. 8b). The detailed statistics in Table 4 also suggested that the MeSAA was more sensitive to TA₀ and DIC₀ for low-SSS (SSS ≤ 30) waters than for high-SSS (SSS > 30) waters. Therefore, the overestimation in the MeSAA-modeled pCO₂ at SSS ≤ 30 in Section 4.1 could be attributed to the variations in river end member TA₀ and DIC₀. However, on the other hand, based on the statistics over the whole SSS range used in this study, the uncertainties in the MeSAA-predicted pCO₂ due to changes in TA₀ and DIC₀ were within the RMSE uncertainties of the MeSAA.

Similar to the sensitivity analysis of the MeSAA to TA₀ and DIC₀, we examined the effect of the variations in the biological coefficient (B = 96.04) on the MeSAA-modeled pCO₂. B was varied by ±20%. As shown in Figs. 8c and 8d and Table 4, a 20% increase (decrease) in B produced about −22.51 µatm (22.51 µatm) lower (higher) pCO₂, with higher changes in modeled pCO₂ at lower SSS (≤ 30). Either with a 20% increase or decrease in B, in each case, the RMSE at the whole SSS range, SSS > 30, and SSS ≤ 30 were 23.38 µatm, 22.91 µatm and 38.25 µatm, respectively. Compared with the statistics of the MeSAA model itself, these results indicate that the MeSAA was sensitive to the biological coefficient B, and the sensitivity decreased with increasing SSS.

5.1.2. Model sensitivity to environmental parameters

Field SST, SSS, and satellite CHL were used during the development of the MeSAA. In order to better understand how the MeSAA model responds to these input variables, a sensitivity analysis was conducted. For each test, one input variable was varied while the others remained constant.
unchanged. Considering the typical uncertainties of satellite-derived SST and CHL, SST was varied by ± 1°C, SSS by ± 1, and CHL by ± 35%. Note that although field-measured SSS was used in the model due to the lack of satellite-derived high-resolution SSS, in the future such SSS could be derived from ocean color data with a possible uncertainty of ± 1. The model response results are shown in Figs. 8e–g, with statistics such as RMSE, MB, and MB listed in Table 4.

Variations in SST and SSS would only affect the horizontal mixing term pCO₂ mixing of the MeSAA. As shown in Figs. 8e–g, the sensitivities of the MeSAA to SST and SSS changes are similar. A 1°C increase produced higher pCO₂ (MB = 19.65 μatm, Fig. 8e), and a 1°C decrease produced lower pCO₂ (MB = −19.01 μatm, Fig. 8f). Likewise, a 1 increase (decrease) in SSS produced lower (higher) pCO₂ (MB = −10.00 μatm or 10.54 μatm, Figs. 8g and h), with slightly higher pCO₂ decrease (increase) for SSS = 30 than for SSS = 20. These results suggest that the MeSAA is more sensitive to SST changes than to SSS changes.

Variations in CHL would only influence the biological term ∆pCO₂biol of the MeSAA. Figs. 8i and j demonstrate that the MeSAA had the same sensitivity to CHL changes at different SSS values, with MB of −12.52 μatm and 17.97 μatm for 35% increase and decrease in CHL, respectively.

In short, the sensitivity analysis showed that pCO₂ variations caused by the assumed changes in both the model coefficients and input environmental variables were all within or close to the RMSE uncertainty of the MeSAA model itself, although the model showed relatively higher sensitivity to the biological coefficient B and SST. Thus, unless the uncertainties in these model inputs are systematic biases instead of random noise – which is unlikely according to the validation result of satellite data products – these uncertainties would not have a significant influence on the MeSAA-predicted pCO₂ when large regions are considered as a whole.

5.2. Sensitivity analysis of the locally tuned MeSAA

Based on the parameterizations of the locally tuned MeSAA in Section 4.2, the sensitivities of the locally tuned MeSAA to T_A, and DIC, and SST were the same as the MeSAA. Therefore, only sensitivities of the locally tuned MeSAA to SST and CHL were analyzed.

Figs. 9a and b show the sensitivity of the locally tuned MeSAA to SST, with statistics shown in Table 4. Note that since SSS was included in both the physical mixing term pCO₂ mixing and the biological term ∆pCO₂biol of the locally tuned MeSAA, the variation in SSS would influence both terms. As a result, the locally tuned MeSAA showed the
Fig. 8. Sensitivity of the MeSAA to the parameterizations of river endmember $T_A$ (a and b), the biological coefficient (B) (c and d), SST (e and f), SSS (g and h), and CHL (i and j). Data used here are from the dataset of the northern GIN (Table 1 and Fig. 1b). In each panel, only one parameter was varied while all others were kept unchanged, and the newly-modeled $pCO_2$ corresponding to each set of parameterization variation is compared with the originally-modeled $pCO_2$. Note that the statistics of each analysis were shown in each panel, as listed in Table 4.
Opposite sensitivity effect to SSS, comparing to the original MeSAA. Specifically, an increase (decrease) of 1.0 in SSS produced higher (lower) pCO2 (MB = 9.55 μm or = 8.90 μm), with slightly higher pCO2 increases (decreases) for SSS > 30 than for SSS ≤ 30.

As shown in Figs. 4c and 4d and Table 4, the locally tuned MeSAA showed little sensitivity to changes in CHL. With a 25% increase (decrease) in CHL, pCO2 was modeled to be 1.09 μm (−1.55 μm) higher (lower) than the originally-modeled pCO2.

5.3. Sensitivity analysis of the empirical regression

Similar to the sensitivity analysis of the MeSAA, the performance of the empirical models was also evaluated against changes in the input parameters, with SST, SSS, and CHL varied by +1°C, ±1, and ±35%, respectively. The results are presented in Fig. 10 and Table 4.

Figs. 10a and 10b indicate that the empirical model was more sensitive to changes in SST at high SSS (> 30) than at low SSS (≤ 30). A 1°C increase in SST resulted in MB of 21.26 μm for SSS > 30 but only led to MB of 6.84 μm for SSS ≤ 30. Similarly, a 1°C decrease in SST resulted in MB of −15.75 μm for SSS > 30 but only −1.30 μm for SSS ≤ 30. The sensitivity to SSS changes is the opposite, with slightly higher sensitivity for the data group with SSS ≤ 30. A 1 increase in SSS resulted in MB of 8.01 μm in the predicted pCO2 for SSS > 30 but MB of 9.38 μm for SSS ≤ 30 (Fig. 10c). A1 decrease in SSS resulted in MB of −10.00 μm for SSS > 30 but MB of −11.37 μm for SSS ≤ 30 (Fig. 10d).

The empirical model is not sensitive to CHL changes over the modeled data range. With either 35% increase or 35% decrease in CHL, the predicted pCO2 did not show much difference from the original predictions (Figs. 10e and 10f), where the MB of these two experiments were 0.95 μm and −5.67 μm, respectively.

In summary, the predicted pCO2 variations induced by a 1°C change in SST and a 35% change in CHL were all within or close to the RMSE of the empirical model. Only in the case of SST changes of 1°C did the modeled pCO2 variations exceed the RMSE of the model. In general, the empirical model was more sensitive to SST and SSS than to CHL. Considering the combined effects of uncertainties in the satellite data products and the sensitivity test results, uncertainties in the empirically modeled pCO2 should be between 10.66 and 21.86 μm for typical data ranges. However, these uncertainties represent RMSE values for individual data points instead of systematic biases. When the data are averaged over large scales in either space or time, the uncertainties in the mean products should be much smaller.

5.4. Mechanistic or empirical approach

Statistically, the locally tuned MeSAA (R² = 0.78, RMSE = 12.36 μm, MB = 0.05 μm, and MR = 1.00) and the empirical regression model (R² = 0.84, RMSE = 10.06 μm, MB = −0.10 μm, and MR = 1.00) showed similar but better performance than the original MeSAA model (R² = 0.25, RMSE = 22.94 μm, MB = −0.23 μm, and MR = 1.00). This is also revealed in the scatterplots for these three models (Figs. 4e, 4d, and 4f). Similarly, although all these three models reproduced the spatial distribution patterns of pCO2 well, the locally tuned MeSAA and the empirical regression models showed more details and improved accuracy (Fig. 5).

The sensitivity analyses showed that the MeSAA model was sensitive to both the empirical coefficients (river endmember TAn and δ13Cm, and biological coefficient B) and the three environmental variables.
Fig. 9. Sensitivity of the locally tuned MeSSA changes in SSS (a and b) and CHL (c and d). Note that the sensitivity of the locally tuned MeSSA in TA0 and SST are the same as that of the original MeSSA. In each panel, only one parameter was varied while all others were kept unchanged, and the newly-modeled pCO2 corresponding to each set of parameterization variation is compared with the originally-modeled pCO2. Note that the statistics of each analysis were shown in each panel, as listed in Table 4.

(SST, SSS, CHL), and the locally tuned MeSSA was sensitive to the river endmember TA0 and DIC0, and sensitive to SST and SSS but not to CHL. The MeSSA was more sensitive to the biological coefficients B while the locally tuned MeSSA and the empirical regression models were more sensitive to SST. All three models showed positive correlations between surface pCO2 and SST, but the MeSSA showed negative correlation with SSS and CHL while the locally tuned MeSSA and the empirical regression models showed the opposite signs in the same correlations. However, all these uncertainties in the predicted surface pCO2 are within the model uncertainties except for the case of SST in the empirical model.

Overall, while the empirical regression model resulted in slightly better performance than the locally tuned MeSSA in predicting surface pCO2, interpretation of the model drivers is more straightforward with the latter, as both physical and biological forcing in the latter are explicitly expressed. Indeed, both the original MeSSA and the locally tuned MeSSA showed encouraging results in terms of model accuracy and physical interpretation over the northern GOM. However, currently only an empirical relationship was used to quantify the biological term in both models, this requiring further improvement in quantifying the biological effect in a more meaningful way. In addition, when extending the MeSSA approach to other seasons (the current study was only conducted for summertime) in the northern GOM or to other similar systems, the locally-tuned MeSSA may be more practical than the original MeSSA because of local tuning in determining the biological effect. However, a major limitation in both the original MeSSA and the locally tuned MeSSA that implemented in this study is that one of the model inputs, namely SSS, is from the field measurements due to lack of community-accepted algorithms to estimate SSS from high-resolution (1-km) satellite measurements. This deficiency in remote sensing algorithm makes it difficult to generate synoptic maps using satellite data alone. Clearly, an immediate need is to develop and validate a remote sensing SSS algorithm in order to derive surface pCO2 maps using the established model here. The changing relationship between SSS and the absorption coefficient of colored dissolved organic matter (CDOM) in the northern GOM in recent studies (Hu et al., 2003; Del Castillo and Miller, 2008; Lohrenz et al., 2010; Canziani et al., 2013b) indicated that empirical regression modeling may not be sufficient to derive a general relationship applicable to the whole northern GOM. More advanced empirical techniques such as neural network or support vector machine may be tried instead (e.g., Chen and Hu, 2017). In the end, because data from upwelling cases were excluded in all three models in order to satisfy the conditions in the original MeSSA approach (summiertime East China Sea where river-ocean mixing dominates the processes), the models are not expected to work in regions with strong upwelling. Indeed, if all three models were to be applied to the upwelling case shown in Fig. 1c (July 2009 around the Mississippi River delta), the predicted pCO2 would show large deviations from the field-measured pCO2, with RMSE of 103.6–166.33 μatm. However, if data from this event were used together with all other data during training of the empirical regression model, the result would show significant improvement in the predicted pCO2, with RMSE of 14.75 μatm and R2 of 0.79 for the entire dataset, and RMSE of 53.17 μatm for the upwelling data (N = 13). Clearly, the applicability of the empirical regression model strongly depends on the data used in the model training, and more field data collected under upwelling cases are required to further tune the empirical regression model for general application with high confidence.

5.5. Controls of surface pCO2 in the summertime northern GOM

While the focus of the paper is on comparison of models in estimating surface pCO2 in order to provide guidance on future model selection when applying to remote sensing data, understanding of model uncertainties requires knowledge of the various controlling mechanisms in affecting surface pCO2. As described in Section 1, surface pCO2 can be affected by ocean mixing (both horizontal and vertical), biological activities, thermodynamics, and air-sea exchange. In summertime northern GOM, horizontal river-ocean mixing, biological activities and thermodynamics are the dominant factors in influencing surface pCO2.
Fig. 10. Sensitivity of the empirical regression model to changes in SST (a and b), SSS (c and d), and CHL (e and f). In each panel, only one parameter was varied while all others were kept unchanged, and the newly modeled $p$CO$_2$ corresponding to each set of parameterization variation is compared with the originally modeled $p$CO$_2$. Note that the statistics of each analysis were shown in each panel, as listed in Table 4.

and all these three factors were included in the parameterization of the original and locally tuned MeSAA. However, vertical mixing and air-sea exchange are also likely to cause some variations in surface $p$CO$_2$, especially during and after extreme events (e.g., hurricanes, storms). Such processes were not considered in the parameterization of the MeSAA. On the other hand, in the parameterization of the MeSAA, conservative river-ocean mixing was assumed first, and the biological effect was then removed from the mixing term to derive the modeled surface $p$CO$_2$. These two processes may not occur on the same time scale and/or spatial scale, causing large uncertainties in the modeled surface $p$CO$_2$.

6. Conclusion

Using extensive field and satellite data, several models to predict surface $p$CO$_2$ using SST, SSS, and CHL were thoroughly tested over the northern GOM, with the ultimate goal of understanding model performance and sensitivity to uncertainties in the input variables. These include a recently established mechanistic model (i.e., MeSAA) originally developed for the East China Sea, a locally tuned MeSAA with local tuning to determine the biological effect, and a statistical empirical model. While the empirical model led to slightly better performance than the locally tuned MeSAA because the unknown factors driving the model uncertainties may be accounted for in the empirical coefficients, the physical and biological effect on the surface $p$CO$_2$ can only be explicitly interpreted by the mechanistic model. Additionally, the empirical regression approach could be further tuned for regions with upwelling. The study also suggests future directions in model development as well as in satellite-based SSS algorithms in order to derive accurate surface $p$CO$_2$ maps for river-dominated coastal regions. For example, instead of using a biological term determined from open-ocean waten a locally tuned biological term ($\Delta$CO$_2$) may be used in the MeSAA to account for $p$CO$_2$ residuals in the horizontal mixing and biological processes as well as other processes (e.g., vertical mixing).

Acknowledgements

This work was supported by a USGS fellowship, a University of South Florida fellowship, and the U.S. NASA (NNX14AM37G and NNX17AC40G to C. Han, NNH13ZDA001H and NNH16AM770 to W.J. Gil). We also thank GHAC, NOAA AOML, and LIOO for providing all the available cruise data, and thank NASA for providing MODIS satellite data. Two anonymous reviewers provided comments and suggestions to help improve this manuscript, whose efforts are appreciated.


APPENDIX C:

ESTIMATING SEA SURFACE SALINITY IN THE NORTHERN GULF OF MEXICO
FROM SATELLITE OCEAN COLOR MEASUREMENTS

Estimating sea surface salinity in the northern Gulf of Mexico from satellite ocean color measurements

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ARTICLE INFO
Keywords:
Sea surface salinity
MODIS
SeaWiFS
Gulf of Mexico
Remote sensing reflectance
Neural network

ABSTRACT
Sea surface salinity (SSS) is an important parameter to characterize physical and biogeochemical processes, yet its remote estimation in coastal waters has been difficult because satellite sensors designed to “measure” SSS lack sufficient resolution and coverage. The challenge of estimating SSS in the northern Gulf of Mexico (GOM) is addressed through modeling, validation, and extensive tests in contrasting environments. Specifically, using extensive SSS datasets collected by many groups spanning > 10 years and MODIS (Moderate Resolution Imaging Spectroradiometer) and SeaWiFS (Sea-Viewing Wide Field-of-View Sensor) estimated remote sensing reflectance in the 412, 443, 488 (480), 555, and 667 (676) nm and sea surface temperature (SST) at a multilayer perceptron neural network-based (MPNN) SSS model has been developed and validated with a spatial resolution of ~1 km. The MPNN was selected over many other empirical approaches such as principal component analysis (PCA), multi-nonlinear regression (MNR), decision tree, random forest, and support vector machines (SVMs) after extensive evaluations. The MPNN was trained by a back-propagation learning technique with Levenberg-Marquardt optimization and Bayesian regularization. The model showed an overall performance of root mean square error (RMSE) = 1.2, with coefficient of determination (R²) = 0.86, mean bias (MB) = 0.0, and mean ratio (MR) = 1.0 for SSS ranging between -1.0 and 37.0 (N=3646). Validation using an independent dataset showed a RMSE of 1.1, MB of 0.0, and MR of 1.0 for SSS ranging between -27.0 and 37.0 (N=412). The model with its original parameterization has been tested in the Mississippi-Archafalaya coastal region, Florida’s Big Bend region, and in the offshore Mississippi River plume, with satisfactory performance obtained in each case. Comparison with concurrent Aquarius-derived SSS maps (110-km resolution) showed similar agreement in offshore waters as indicated above, but the near 1-km resolution SSS maps revealed more fine-scale features as well as salinity gradients in coastal waters. The sensitivity of the model to realistic model inputs errors in satellite-derived SST and RR was also thoroughly examined, with uncertainties in the model-derived SSS being always <1 for SSS >30. The extensive validation, evaluation, and sensitivity test all indicated the robustness of the MPNN model in estimating SSS in most, if not all, coastal waters and offshore plumes in the northern GOM. Thus, the model provided a basis for generating near real-time 1-km resolution SSS maps from satellite measurements. Moreover, the model showed limitations when applied to regions with known algal blooms or upwelling as they both led to low RR in the blue bands that may be falsely recognized as caused by low SSS.

1. Introduction

1.1. Challenge in mapping sea surface salinity of coastal waters

Sea surface salinity (SSS) is an important parameter in understanding many physical and biogeochemical processes in coastal waters (Fennel et al., 2011; Xue et al., 2013). SSS data is used as support of studies examining the mixing between riverine freshwater and offshore oceanic water and changes in other water properties (Hu et al., 2004; Palacios et al., 2009; Devlin et al., 2013; Houssen-Delvigne et al., 2015; Ying et al., 2015). Further, SSS is an important parameter in tracing the pathway of the riverine-delivered terrestrial substance (e.g. organic and inorganic carbon, nutrients) into the ocean, as well as examining the intensity of stratification and studying variations in water’s optical properties, hypoxia, and algal blooms in coastal margins (Rahalais et al., 1996, 2002; Cannizzaro et al., 2013; Weisberg et al., 2014; O’Connor et al., 2016; Le et al., 2016).

However, obtaining SSS at synoptic scales with frequent coverage in
coastal waters has proved difficult due to inadequate ship-based measurements (that lack of appropriate resolutions) or failures in satellite SSS measurement algorithms. The two existing satellite sensors, based on microwave remote sensing and designed to "measure" SSS from space, are the ESA SMOS (the Soil Moisture and Ocean Salinity) and NASA Aquarius/SAC-D. Yet the coarse spatial resolution (30–100 km) and low revisit frequency (3 days or more), along with the issues of land contamination, limit their use in observing the dynamic variations in SSS in coastal waters (Koblinsky et al., 2003; Lagerloef et al., 2008; Font et al., 2012; Kere et al., 2014).

Recent advances in ocean color remote sensing have shown potentials in synoptic and frequent mapping of SSS (Wong et al., 2007; Qin et al., 2008; Palacios et al., 2006; Marghany and Hashim, 2011; Urgun and Ilhan, 2012; Bai et al., 2013; Geiger et al., 2013; Qing et al., 2013; Vandermeulen et al., 2014; Zhu et al., 2017). In these studies, SSS was modeled from apparent optical properties (AOPs) such as spectral remote sensing reflectance (Rs, m−1), inherent optical properties (IOPs) such as absorption coefficient, or other satellite parameters such as Sea Surface Temperature (SST, °C) and chlorophyll-a concentration (CHL, mg m−3). Regardless of the method, the underlying principle is that colored dissolved organic matter (CDOM) is a good tracer of SSS in coastal oceans (Voda et al., 1997; Hu et al., 2003; Coble et al., 2004; Del Vecchio and Bough, 2004), and CDOM absorption coefficient (adcDMM) at 440 nm can be, at least in theory, estimated from ocean color measurements and then used to estimate SSS assuming conservative mixing for both (e.g., Siddorn et al., 2001; Johnson et al., 2005; Chen and Gardner, 2004; Hong et al., 2005; Guo et al., 2007; Bowers and Begg, 2009). Indeed, in river-dominated coastal regions, CDOM mainly comes from terrestrial inputs through river discharges and non-point source land runoff (Chen, 1996; Nelson et al., 2007). This plays a key role in determining the optical properties (especially Rs) of coastal ocean waters. However, due to the distinct CDOM characteristics of each local river endmember and its seasonality, the relationship between adcDMM and SSS may vary in space and time (Chen, 1999; Hu et al., 2003; Del Vecchio and Bough, 2004; Bowers and Begg, 2006; Bai et al., 2013; Geiger et al., 2013), making it impossible to apply a locally designed SSS algorithm to other regions. Adding to this difficulty are the uncertainties in the satellite-retrieved Rs and adcDMM; these uncertainties can cause a well-established, ship-based SSS relationship to become unreliable. Such difficulties can be clearly seen from Fig. 2 in the supplemental materials for the northern Gulf of Mexico when satellite-derived adcDMM was used to estimate SSS. Thus, in general, mapping SSS in coastal waters from space still represents a major challenge for the ocean color research community.

1.2. Study region and objectives

The study region is the northern Gulf of Mexico (GOM) that receives discharge from numerous rivers. The Mississippi River provides the largest river discharge into northern GOM. Rounding as the world's 8th largest river in freshwater discharge and sediment delivery, the Mississippi River system drains 41% of the land in the United States (Milliman and Meade, 1983). About 70% of the river's flow drains through the lower Mississippi River into the GOM, with the remaining 30% delivered to the Atchafalaya basin, and finally into the GOM (U.S. Army Corps of Engineers, 2008) forming the Mississippi/Atchafalaya River system (MARS). In addition to the MARS, there are some smaller rivers along the coast of the northern GOM, such as Sonoran, Pescoc, and Apalachicola Rivers; these also play significant roles in affecting the coastal water properties (Matraw and Elder, 1984; Averett et al., 1994; Murrell et al., 2002). With large seasonal loadings of freshwater, inorganic and organic matters, and nutrients, from the MARS and other rivers, the northern GOM maintains an active ecosystem with dynamic physical and biogeochemical processes. Here, SSS plays an important role in the physical mixing between the MARS and GOM open waters (Xue et al., 2013), the hypoxia phenomena induced by intensified biological activities and vertical stratification (Wissman et al., 1997; Rabalais et al., 2002), and the distribution and variation of the carbonate properties such as total alkalinity (TA) and surface partial pressure of CO2 (pCO2) (Yang et al., 2015; Chen et al., 2016).

Synoptic SSS estimation in the northern GOM has been attempted in several published studies. Using data from SMOS and Aquarius, Fourrier et al. (2016) examined the seasonal and intrannual variations of SSS in the GOM. However, the study was limited by the coarse spatial resolution (30–100 km) and lack of coverage in coastal waters as a result of sensor limitations. Based on total absorption coefficients at 446 and 553 nm derived from the SNPP-VIIRS (Suomi National Polar-orbital Partnership satellite with the Visible Infrared Imaging Radiometer Suite) measurements and SSS measurements from several nearshore stations, Vandermeulen et al. (2014) developed a simple SSS model using linear regression between SSS and absorption difference. Due to the dynamics and complexity of the northern GOM, only 65% of the data tested with the model showed a SSS uncertainty of ±2; one possibility for this result is that the relationship between absorption difference and SSS may change in space and time. Indeed, although linear relationships between SSS and adcDMM have been developed on a regional basis (Bough et al., 1993; Ahn et al., 2008; Palacios et al., 2009; Bai et al., 2013), in the northern GOM the SSS-adcDMM relationship appears to be different is several studies (Hu et al., 2003; Del Castillo and Miller, 2006; Lobon et al., 2010). Such discrepancies indicate that unlike SSS, CDOM may not follow conservative mixing, and both CDOM production from phytoplankton degradation (Nelson et al., 1998, 2010; Twardowski and Donguy, 2001; Street and Markager, 2005) and CDOM photochemical bleaching (Chen and Gardner, 2004) may contribute to the variations in the SSS-adcDMM relationship (Del Vecchio and Bough, 2004). Consequently, to date there has been no reliable model to estimate SSS from ocean color measurements in this region.

Extensive SSS data have been collected from the northern GOM by numerous groups and agencies. Acknowledging the limitation of SMOS and Aquarius, lack of reliable ocean color-based SSS models, the unstable SSS-adcDMM relationship in the northern GOM, and high uncertainties in satellite-derived adcDMM (Hu et al., 2003; Le and Hu, 2013; Munnino et al., 2014), the goal of the present study is to address the challenge of mapping SSS from ocean color measurements over the optically complex northern GOM, with the following specific objectives:

1. Develop a relatively robust model to estimate SSS at 1-km resolution from ocean color measurements;
2. Quantify uncertainties in the estimated SSS through extensive evaluations under various oceanographic conditions (e.g., Mississippi/Atchafalaya coastal region, Florida's Big Bend, and Mississippi River plume) and through sensitivity studies;
3. Understand the limitations of this approach in order to determine its applicability to time-series data.

The paper is structured as follows. Field and satellite data are presented first, and optical characteristics of the waters with different SSS ranges are analyzed. Secondly, methods in developing SSS models are briefly reviewed. Finally, in the Results and Discussion sections, the trained SSS model is statistically validated and evaluated under different conditions, with model sensitivities to the model inputs analyzed and model limitations investigated.

2. Data and methods

2.1. Dataset

2.1.1. Field data

To assure enough spatial and temporal coverage under all possible oceanographic conditions and measurement scenarios, we compiled all publicly available SSS data collected over the past 20 years in the
northern GOM. These include two data types: those collected from nautical cruise surveys, and these from fixed-location buoys. Tables 1 and 2 present a general description of the data source, data volume, time span, and data range for each dataset. These data cover all seasons. The data in Table 1 were used to develop the SSS model, while the data in Table 2 (independent from those in Table 1) were used to evaluate the SSS model. Collectively these data represent the most complete dataset for the northern GOM.

In Table 1 (model development), the SSS data (collected between 1997 and 2015) ranged between 0.0 and 39.8. Ship-based underway SSS data were obtained from the databases of Carbon Dioxide Information Analysis Center (CDIAC), NOAA Atlantic Oceanographic & Meteorological Laboratory (AOML), Texas A&M University (TAMU), Lamont-Boothby Earth Observatory (LEDO), and University of South Florida (USF). The data were collected by numerous research groups funded by different agencies. For example, between 1997 and 2000, SSS was collected by the Northeastern GOM (NEGOM) program funded by the Bureau of Ocean Energy Management (BOEM, formerly known as Minerals Management Service) and archived at TAMU. Between 2011 and 2013, SSS was collected by the C-SAGE consortium funded by the GOM Research Initiative, with data archived at USF.

Typically, ship-based SSS data were collected at a depth of ≤5 m using a CTD (SRB-21 or SBE-38 or SBE-45, SeaBird Inc., USA, YSI 6600) integrated in the shipboard flow-through seawater system, with a measurement interval near 2 min and an accuracy of 0.05. SSS time-series from CDIAC and NOAA National Data Buoy Center (NDBC) were collected at a depth of ≥3 m using a CTD (SRB MicroCAT C/T Recorder, or SBE 37-MW MicroCAT), with a measurement interval of ~3 h or ≤1 h and an accuracy of 0.02. It is difficult to present each dataset in a detailed graphical format, but the full cruise tracks with color-coded SSS values are shown in Fig. 1a, with over 11,000 SSS measurements in each month.

Similar to Table 1, Table 2 lists the various data sources of field SSS measurements that were used for independent model evaluation under differing conditions. Specifically, for a general evaluation of the developed SSS model, SSS data collected at discrete stations were obtained from the NOAA National Centers for Environmental Information (NCEI) and Florida Fish and Wildlife Conservation Commission (FWC) and Florida Fish and Wildlife Research Institute (FWRI). These SSS data were collected in 2010 and 2014, ranging between 3.8 and 37.5. To test the model performance is the Mississippi-Achelafaya coastal region, undersea SSS measurements from two cruises (GIM06 and GIM10533) were obtained from CDIAC; these SSS data were collected in June 2006 and March 2010 and ranged between 0.02 and 36.62. To examine the model performance in the Florida’s Big Bend region, SSS data collected at discrete stations were obtained from NOAA NGU and FWC; these data were collected in 2010, 2011 and 2014, ranging between 11.4 and 36.4. To evaluate the model performance in quantifying SSS in the Mississippi river plumes, discrete SSS measurements from USF, and underway SSS cruise WSL2234 from CDIAC, were compiled; these SSS data were collected in Aug. and Sep. 2015, ranging between 29.1 and 36.4. To test the model performance in deriving SSS time-series at fixed locations, SSS time-series data from three buoys (“crtl1”, “40022”, and “CoastM”) were obtained from NDBC and CDIAC. SSS from buoy “crtl1” was collected between 2011 and 2015, ranging between 1.0 and 30.1; SSS from buoy “40022” were collected between
Table 2
SSS measurements used to evaluate the MPNN model under different conditions. Three SSS were collected at a depth of < 5 m from all seasons. The specific purpose of each dataset is annotated in bold italic font. Only a small proportion of these measurements were found to have co-located and concurrent (± 24 h) MODIS SST and Rrs data (last column). Corresponding cruise tracks in each case are shown in Figs. 1–12. Note that the time-series SSS data from buoys “Coastal” “402022” and “CoastalS” shown in italics below were not used in model development.

<table>
<thead>
<tr>
<th>Project/cruise_ID</th>
<th>Data source</th>
<th>Date</th>
<th>Data type</th>
<th>Range of SSS</th>
<th>Range of SSS with matching satellite data</th>
<th># of observations</th>
<th># of observations with matching satellite data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purpose Deepwater Horizon</td>
<td>To conduct a general validation of the MNPNN model</td>
<td>NCEI</td>
<td>Sept–Oct, 2010</td>
<td>Discrete</td>
<td>10.8–10.7</td>
<td>7.2–7.6</td>
<td>209</td>
</tr>
<tr>
<td>Support SKEMAP</td>
<td>FWC</td>
<td>Oct, 2014</td>
<td>Discrete</td>
<td>29.1–36.1</td>
<td>34.4–36.1</td>
<td>158</td>
<td>79</td>
</tr>
<tr>
<td>SEAMAP</td>
<td>FWC</td>
<td>Jan, 2014</td>
<td>Discrete</td>
<td>24.3–37.5</td>
<td>26.8–37.1</td>
<td>178</td>
<td>80</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>3.8–37.5</td>
<td>26.8–37.1</td>
<td>1,615</td>
<td>1,126</td>
</tr>
<tr>
<td>Purpose GM0006</td>
<td>To test the model performance in the MORGAS region</td>
<td>CIORD</td>
<td>Jan, 2006</td>
<td>Continuous</td>
<td>0.7–36.1</td>
<td>22.6–36.1</td>
<td>5,938</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>0.6–36.6</td>
<td>3.0–36.6</td>
<td>7,711</td>
<td>3,345</td>
</tr>
<tr>
<td>Purpose DEEPEND</td>
<td>To test the model performance in the Mississippi River plume</td>
<td>USF</td>
<td>Aug, 2015</td>
<td>Discrete</td>
<td>29.1–36.4</td>
<td>31.3–36.3</td>
<td>27</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>0.1–36.4</td>
<td>3.0–36.6</td>
<td>15,741</td>
<td>1,243</td>
</tr>
<tr>
<td>Purpose SS15234</td>
<td>To test the model performance in the Big Bend region</td>
<td>CIORD</td>
<td>Sep, 2015</td>
<td>Continuous</td>
<td>32.3–36.0</td>
<td>32.4–35.6</td>
<td>1,009</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>32.1–36.1</td>
<td>31.3–36.3</td>
<td>1,636</td>
<td>491</td>
</tr>
<tr>
<td>Purpose Buoy 42322</td>
<td>To test the model performance at fixed locations</td>
<td>NDBC</td>
<td>2013–2015</td>
<td>Continuous</td>
<td>31.7–36.3</td>
<td>33.5–36.5</td>
<td>493</td>
</tr>
<tr>
<td>(25°26'N, 83°47’W)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buoy 3250</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buoy 3252</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buoy central</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIORD</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NDBC</td>
<td>2015–2016</td>
<td>Continuous</td>
<td>1.0–38.1</td>
<td>2.7–27.6</td>
<td>1,861</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
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<tr>
<td>Purpose Buoy 3252</td>
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<tr>
<td>(25°26'N, 83°47’W)</td>
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<tr>
<td>Buoy coastal</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIORD</td>
<td>2015–2016</td>
<td>Continuous</td>
<td>1.0–38.1</td>
<td>2.7–27.6</td>
<td>1,861</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Total</td>
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<tr>
<td>Purpose Buoy 3252</td>
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<td>(25°26'N, 83°47’W)</td>
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<td></td>
</tr>
<tr>
<td>Buoy coastal</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIORD</td>
<td>2015–2016</td>
<td>Continuous</td>
<td>1.0–38.1</td>
<td>2.7–27.6</td>
<td>1,861</td>
<td>65</td>
<td></td>
</tr>
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<td>Total</td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

* DEEPEND: Deep-Plume Nekton Dynamics of the Gulf of Mexico; SEAMAP: Southeast Area Monitoring and Assessment Program.
* NCEI: National Centers for Environmental Information.

Fig. 1. Spatial distributions of the field-measured SSS in the GOM along the cruise tracks. (a) Cruise tracks from all data described in Table 1; (b) Cruise tracks from the same data but with co-located and concurrent (± 24 h) satellite Rrs and SST (for interpretation of color in this figure, the reader is referred to the web version of this article.)

2014 and 2015, ranging between 31.7 and 36.5; SSS from buoy “Coastal” were collected in 2009, 2011, and 2013–2014, ranging between 15.7 and 35.6. These buoy-measured SSS data represent independent data to evaluate the algorithm performance, as 99.9% of them were excluded in the model development. Furthermore, daily means of these continuous SSS data were used for statistical analysis (see Section 3.5 and Table 2). The spatial distributions of these SSS data are shown in each case in Section 3.

Z.1.2. Satellite data
The satellite data used in this study were downloaded from the NASA Goddard Space Flight Center (GSFC) [http://oceancolor.gsfc.nasa.gov/]. Daily standard NASA Level-1 ocean color data products (reprocessing version R2014.0) with spatial resolution of ~1 km were derived from the Moderate resolution Imaging Spectroradiometer (MODIS) on the Aqua satellite and Sea-Viewing Wide Field-of-View Sensor (SeaWiFS) on the SeaStar satellite. MODIS data included SST and Rrs in 5 spectral bands (412, 443, 488, 547, 667 nm) between July 2002 and December 2015, and SeaWiFS data included Rrs in 5 spectral bands (412, 443, 490, 555, 670 nm) between November 1997 and July 2002. Both SST and Rrs data were used as inputs of the SSS model. SST was used to capture the possible contrast in temperature between river...
and oceanic waters, particularly the upwelling water masses which are
represented by lower temperatures (Palacios et al., 2009). The 5 visible
spectral bands were selected mainly considering the exponential decay
of CDOM absorption from the blue to the red. Rs(667) from MODIS or
Rs(670) from SeaWiFS has been used as a surrogate for sediment
concentration in the water column (Stampf and Pennock, 1985; Wynne
et al., 2006; Barron et al., 2005), therefore the use of Rs(667) was to help
minimize the turbidity effects in SS-CDOM retrievals through em-
pirical techniques. Note that although MODIS does have a 531-nm band
and SeaWiFS has a 510-nm band, for cross-sensor consistency they were not
used in this study. For the same reason, to ensure consistency between
MODIS Rs(547) and SeaWiFS Rs(555), MODIS Rs(547) was con-
verted to Rs(555) nm based on the standard SeaDAS7.0.2 processing
procedure using Eqs. (1) and (2). In addition, to test the published
regression model, daily standard MODIS Level-1A data (version R2014.0)
in Sep. 2014 were downloaded from NASA GSFC and processed to Level
3 using SeaDAS7.0.2 to derive the total absorption coefficients at 488,
547 and 555 nm.

\[
\text{Rs}(555) = 10^{4(a_3 \times \log_{10}(\text{Rs}(547)) - b_3)}, \quad \text{Rs}(547) < \text{sw}
\]

\[
\text{Rs}(555) = a_2 \times \text{Rs}(547) + b_2, \quad \text{Rs}(547) \geq \text{sw}
\]

where \(a_1 = 0.01723, a_2 = 0.986, b_1 = 0.81495, b_2 = 1.03, \) and \(b_3 = 0.000216.\)

In addition to the satellite ocean color data products, standard NASA
Level-3 monthly SS composites, derived from Aquarius measure-
ments, were also downloaded from the NASA GSFC. These data were
used to compare with the corresponding SS composites estimated
from MODIS measurements with the SS model developed in this study.

2.2 Method

2.2.1. Model selection, and principle of structure of MPNN

Our first attempt to estimate SS from satellite-derived Rs was
through the SS-QCDM relationship where CDOM was estimated from
satellite-derived Rs using the Quasi-Analytical Algorithm (Lee et al.,
2002). However, the results were unsatisfactory, with virtually no re-
lationship observed between field-measured SS and satellite-derived
CDOM for SS between 27 and 37 (Supplemental Fig. S1). Therefore,
the approach of deriving SS through explicit use of CDOM was aban-
donned, but other empirical methods were tested.

In the published literature, statistical approaches such as multi-
variate linear regression (MLR) and artificial neural network (ANN)
were used to develop satellite-based SS models (Wong et al., 2007;
Ahn et al., 2008; Palacios et al., 2009; Marginny et al., 2011; Ucarhurt
et al., 2012; Bai et al., 2013; Griger et al., 2013; Qi et al., 2013;
Vandermeulen et al., 2014). In this study, the commonly used tradi-
tional empirical methods (i.e., MLR, multi-variate nonlinear regression
(MNR), and principle component analysis (PCA) regression) and ma-
nchine learning based approaches (i.e., decision tree, random forest,
and Support Vector Machine (SVM) regression) were all tested, but all
yielded unsatisfactory results (see below). Among the tested approaches
was artificial neural network (ANN), which showed better performance
than all other approaches. ANN was then selected for the SS remote
sensing model in this study; one distinct advantage of ANN is that it can
approximate the nonlinear relationship between observations and tar-
tioned variable (SS), without explicitly knowing their functional de-
pendence (Thiria et al., 1993).

In the past, ANN techniques have been widely used in retrieving
AOPs, IOPs, and other parameters such as CHl and total suspended
matter (Tanaka et al., 2004; Chauhan et al., 2005; Vilas et al., 2011;
Ioursou et al., 2011, 2013; Jamer et al., 2012; Chen et al., 2014, 2015).
The type of ANN used in this study is a multilayer perceptron neural
network (MPNN) (Bishop, 1995; Gross et al., 1999), which is a feed-
forward neural network that consists of one input layer, one or more
hidden layers, and one output layer. As shown in Fig. 2, neurons of each
layer are forward connected to the neurons in the adjacent layer, but
without any connections to neurons in the preceding layers. Inputs are
distributed into the MPNN by the first layer. In the hidden and output
layers, each neuron is randomly initialized with two parameters: weight
and bias, which are used to transform the input signals by an activation
function. Once the number of hidden layers and the number of neurons
in each layer are determined, the structure of the MPNN is fixed, and
the weights and biases associated with each connection are also fixed.
The values of weights and biases are adjusted through iteration to
minimize the sum of the squared errors between the modeled outputs
and the real outputs (i.e., the parameters to be retrieved) by a su-
ervised learning technique.

For the MPNN presented in this work, a back-propagation learning
technique with a Levenberg-Marquardt optimization and a Bayesian
regularization algorithm was implemented in Matlab (R2013a). To
transform the input signals in each layer, the classic hyperbolic tangent
sigmoid (a = tanh(x)) and linear activation functions (a = purely
linear) were applied to the hidden and output layers, respectively. The
back-propagation learning technique is a backward iterative learning
algorithm; it starts at the output layer and ends at the input layer,
where the weight and bias of each neuron are updated based on the
errors between the current outputs and the actual output values (Dejter
Nelson, 1989; Goil, 1995). The Levenberg-Marquardt optimization
algorithm, also known as the damped least-squares method, is a com-


Fig. 2. Architecture of the MPNN, consisting of one input layer, one hidden layer, and one
output layer. The cross-layer connections are marked with different colors, indicating
different weights and biases. The number of neurons in the input and output layers of the
SSMS are fixed as specified in the rectangular boxes, and the number of neurons in the
hidden layer was varied to derive the best MPNN format.
2.2.2. Data preprocessing of MPNN

Based on the data range of the first SS measurements in Table 1, both MODIS-derived data products – SST and Rs (412, 443, 488, 555, 667 nm) and SeaWiFS-derived data products – Rs (412, 443, 490, 555, 670 nm) were used in the MPNN SS model development. To obtain high quality data, concurrent field-measured SSS and satellite-measured SST and Rs (Table 1) were selected using the following criteria. Considering the diurnal tidal cycle in most regions of the northern GOM, a time window of ± 6 h between field and satellite measurements was used. Various data quality flags (e.g., atmospheric correction failure, stray light, sun glint, etc.) (Chen and Hu, 2017) were applied to discard all low-quality satellite data, and valid data within a 3 × 3 box centered at the location of each field SS measurement were extracted and averaged (Byrne and Woerdeman, 2000) if the number of valid pixels was ≥ 5 and the variance of these valid pixels was ≤ 15%. Such averaged data was used to represent satellite observations over the location. After applying these strict quality controls, field data binning to match satellite pixel resolution, 3640 conjugate observations of field-measured SSS and satellite data products were determined valid between 1997 and 2015, and available for the MPNN SS model development (Fig 1b). Note that for SS measurement, both between 1997 and 2002, field-measured SST data was used as surrogate of satellite-measured SST due to the lack of SST measurements by SeaWiFS. As demonstrated in the sensitivity analysis in Section 3.6, the MPNN SS model is insensitive to SST, and this replacement should have little influence in the modeled SSS. In the conjugate dataset, field- measured SSS ranged between 1.4 and 38.0, satellite-measured SST ranged between 9.7 and 33.3 °C, and satellite-measured Rs covered a wide dynamic range. Detailed statistics of each parameter are described in Table 3.

One advantage of using concurrent satellite SST and Rs measurements directly to train the MPNN is that uncertainties in these satellite-derived data products will be implicitly included in the empirically-derived weights and biases of the MPNN. When the same data products are used for SST predictions as those which were used in model development, such uncertainties, to a large extent, should be self-cancelling.

Before the MPNN training, to avoid conditioning problems and to make the MPNN equally sensitive to all inputs and output (Joumou et al., 2011), both the MPNN inputs (SST and Rs) and output (SSS) in the conjugate dataset were normalized by subtracting the mean and dividing by the standard deviation (σ) of each parameter using the following equations (Lawrence, 1991):

$$nSST = \frac{(SST - \text{mean}(SST))}{\sigma(SST)}$$  

$$nRs(λ) = \frac{(Rs(λ) - \text{mean}(Rs(λ)))}{\sigma(Rs(λ))}$$  

$$nSSS = \frac{(SSS - \text{mean}(SSS))}{\sigma(SSS)}$$  

Therefore, the output of the MPNN needs to be denormalized with the mean and standard deviation of SS using the inversion of Eq. (3).

The normalized conjugate dataset was randomly divided into two parts, with 70% (2548 points) used to train the MPNN, and 30% (1012 points) to test the trained MPNN to confirm the predictive power of the model.

2.2.3. Training of MPNN

Several studies showed that any continuous function can be represented by a MPNN with one hidden layer (Hornik et al., 1989, Aires et al., 2001). Therefore, to train the SS model using the normalized dataset in Table 1, based on the principle that the number of weights should not be greater than the number of training equations, a group of MPNNs with one hidden layer (Fig 2) were tested by varying the number of hidden neurons between 1 and 60. In each test, the weights and biases were randomly initialized 10 times to avoid the unfortunate set of initial weights and bias (the case where the MPNN can be trained well but cannot be generalized well when applied to a new dataset or a satellite image). Once the number of hidden neurons was determined, the optimal network structure with finalized coefficients of weights and bias was determined.

In the training phase of the MPNN, different formulas and different combinations of the input variables were thoroughly tested. For example, according to commonly used Rs formats in CDOM and chlorophyll algorithms (Carde et al., 1999; Hu et al., 2012), Rs in log-linear scale, Rs base ratios (i.e., Rs(412)/Rs(555), Rs(443)/Rs(555), and relative band differences were all used as model inputs and tuned following the steps described above. According to Geiger et al. (2013), in the model tuning phase, geological latitude and longitude data were also chosen as the inputs to train the model.

2.2.4. Accuracy assessment

The empirical nature of the MPNN makes it extremely important to understand the model applicability under various oceanographic conditions from different coastal and offshore regions. In this study the model accuracy was evaluated using independent datasets that were not used in model development. These datasets are described in Table 2, representing different scenarios ranging from river plumes and coastal runoff in different regions of the northern GOM. To increase the data volume, the time difference between satellite and field measurements was relaxed to 24 h. In addition, to evaluate model performance, the model-derived SSS was compared with those estimated from the satellite microwave measurements as well as time-series data obtained from marine buoys.

To compare the model-derived SSS and field-measured SSS, and to gauge the performance of the MPNN in the training and various evaluation phases, coefficient of determination (R²), root mean square error (RMSE), mean bias (MB) and mean ratio (MR) were used, and the same statistics were also applied in the sensitivity analysis below.

2.2.5. Sensitivity to errors in the input variables (SST and Rs)

The inputs to the MPNN model, namely MODIS-derived SST and Rs, are not error free. In order to understand the model sensitivity to such input errors, SST and Rs errors were first simulated using uncertainty values reposted in the literature, and then fed to the MPNN model. SSS derived from the same MPNN using error-free inputs and error-added inputs were then compared to determine the model's sensitivity to input errors.

For evaluation of model sensitivity to SST errors, because MODIS SST uncertainties in the GOM are around 0.5-1 °C (Hu et al., 2009), SST

<table>
<thead>
<tr>
<th>Variables</th>
<th>Field-measured SSS</th>
<th>Satellite-measured SST (°C)</th>
<th>Rs(412) (w-1)</th>
<th>Rs(443) (w-1)</th>
<th>Rs(488) (w-1)</th>
<th>Rs(555) (w-1)</th>
<th>Rs(677) (w-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>38.8</td>
<td>35.6</td>
<td>0.023056</td>
<td>0.028241</td>
<td>0.037942</td>
<td>0.044670</td>
<td>0.052600</td>
</tr>
<tr>
<td>Minimum</td>
<td>1.4</td>
<td>9.7</td>
<td>0.000237</td>
<td>0.000683</td>
<td>0.001256</td>
<td>0.002843</td>
<td>0.003002</td>
</tr>
<tr>
<td>Median</td>
<td>35.5</td>
<td>26.4</td>
<td>0.005194</td>
<td>0.005790</td>
<td>0.005183</td>
<td>0.001869</td>
<td>0.002020</td>
</tr>
<tr>
<td>Mean</td>
<td>34.4</td>
<td>25.9</td>
<td>0.000003</td>
<td>0.000522</td>
<td>0.005488</td>
<td>0.002942</td>
<td>0.002553</td>
</tr>
</tbody>
</table>

Table 3: Statistics of the conjugate dataset in Table 1 after matching with concurrent satellite SST and Rs measurements with a time window of ± 6 h (41440). This dataset was used to develop the MPNN SS model, with 70% used to train the MPNN and the remaining 30% used to test the trained model. Corresponding cruise tracks of this dataset are shown in Fig 1b.
errors of ± 1 °C were added to the SST data in the MPNN model, where the corresponding Rs values were kept the same.

For evaluation of model sensitivity to Rs errors, MODIS Rs errors were simulated using reported MODIS Rs uncertainty values and spectral dependence of MODIS Rs errors [Hu et al., 2013]. In other words, MODIS Rs errors are not spectrally independent, but errors in one band, to a large degree, are related to errors in another band, with additional random errors (Fig. 10 of Hu et al., 2013).

The spectrally-dependent and independent Rs errors were simulated in the following way, following the same approach of Qi et al. (2017):

1) Simulate 5000 Rs_{467} errors following a Gaussian distribution with a zero mean and a standard deviation of 5 × 10^{-4} sr^{-1} (Hu et al., 2013). This is basically the error distribution determined from MODIS measurements in ocean gyres;

2) Calculate the corresponding spectrally-dependent Rs errors at 412, 443, 488, and 555 nm using Eqs. (6)-(10) (Hu et al., 2013);

3) Add 5000 spectrally-independent Rs errors in each band; these errors also follow a Gaussian distribution with zero mean and an assumed standard deviation (S). The addition of these errors to those in Step 2 lead to partially spectrally-dependent errors, representing realistic cases from ocean color measurements;

4) Select one Rs spectrum from the training dataset described in Table 1 (corresponding field-measured SSS = S1), estimate SSS using the MPNN model. Then, add the 5000 erroneous Rs spectra to the selected Rs spectrum, one by one, and calculate the corresponding SSS using the same MPNN model (marked as S2 for each of the 5000 input spectra). The SSS errors would be S2-S1 where S2 has 5000 values and S1 is a single value. The standard deviation of the 5000 SSS errors represents the SSS uncertainty due to input Rs errors;

5) Repeat step 4 for the whole data set for different S1 values, leading to SSS uncertainties for each S1 due to the same input Rs errors; and

6) Bin the S1 values with an interval of 1 in SSS, SSS uncertainties (from the MPNN model) for each bin are calculated as the mean and standard deviation from all standard deviation values within each bin.

\[ \text{Rss457error} = 3.330 \times \text{Rs467error} - 0.000041 \]  
\[ \text{Rss555error} = \text{Rss457error} \]  
\[ \text{Rss488error} = 3.6615 \times \text{Rss555error} - 0.00002 \]  
\[ \text{Rss443error} = 0.7322 \times \text{Rss488error} + 0.0001 \]  
\[ \text{Rss412error} = 0.0154 \times \text{Rss467error} + 0.0003 \]  

Note that Eq. (6) was from Hu et al., 2013, Eq. (7) was one assumption made in this study, and Eqs. (8)-(10) were calculated based on Table 1 in Hu et al., 2013, with R² of 0.994, 0.996, and 0.241, respectively.

In total, four experiments (Experiments 1, 2, 3, and 4) were conducted based on the steps above. In these experiments, the spectrally-dependent Rs errors were kept the same, but the spectrally-independent Rs errors were varied to have their standard deviations (i.e., the \( \Delta \) term in Step 3 above) of 1.2 × 10^{-3} sr^{-1}, 2.3 × 10^{-3} sr^{-1}, and 3.6 × 10^{-3} sr^{-1}, respectively, in each experiment.

3. Results

3.1. Optical characteristics of the training dataset

Fig. 3 shows the Rs spectra of the dataset used for model development (Table 1), which covered a high dynamic range. The Rs peaks occurred in different bands for different SSS ranges. Specifically, for SSS ≤ 36 (Fig. 3a), Rs peaks were found in all bands except 412 nm, suggesting significant influence by phytoplankton pigments and/or CDOM as they both strongly absorb light in the blue. For higher SSS (Fig. 3b-d), most spectra showed higher Rs in the blue than in other wavelengths, indicating clearer waters than the lower-SSS waters. There are some exceptions where the magnitudes of Rs are high in the green and red wavelengths, indicating waters rich in suspended sediments. From Fig. 3, it is clear that similar spectra shapes may correspond to different SSS values. Such characteristic indicated the complex relationships between SSS and Rs spectra (or water types), suggesting difficulties in retrieving SSS via traditional inversion algorithms (either empirical or semi-analytical). However, the subtle differences between these spectra formed the basis of using an MPNN approach to address the technical challenge. Furthermore, the full dynamic range in both magnitudes and spectral shapes indicated the comprehensiveness of the dataset, which is important for the MPNN empirical model to work under most, if not all, scenarios because there is no explicit functional relationship between the spectral Rs and SSS in the model.

3.2. MPNN model training and validation

3.2.1. MPNN model training

Following the procedure described in Section 2.2.3, different formulas and different groups of the input variables were tested. It was found that when SST and spectral Rs data were used as the model inputs and the number of neurons in the hidden layer was set to 3, the MPNN showed the best performance in terms of RMSE, R², MB, and MR when field-measured SSS was used to gauge the model performance. Therefore, this model setting was regarded as the optimal structure of the MPNN. As a reference, Table 4 shows the performance of all tested empirical approaches, including MLR, MNN, PCA, decision tree, random forest, and SVM regression, along with the MPNN. Clearly, the MPNN showed the best performance, and therefore was selected in this study.

As shown in Fig. 4 and Table 5, 79% of the dataset used in the training of the MPNN (Fig. 4a) showed a RMSE of 1.2 (6.9%) and R² of 0.86, with MB of 0.0 and MR of 1.0. The remaining 30% of the dataset used in the testing of the trained MPNN (Fig. 4b) showed a RMSE of 1.2 (5.9%) and R² of 0.86, with MB of 0.1 and MR of 1.0. For the entire dataset (Fig. 4c), the testing showed a RMSE of 1.2 (1.0%) and R² of 0.86, with MB of 0.0 and MR of 1.0. In addition, the model showed better performance at SSS > 30 than with SSS ≤ 30 in both model training and testing, with RMSE of 1.0 and 3.0, MB of −0.1 and 1.4, and MR of 1.0 and 1.1 for SSS > 30 and SSS ≤ 30, respectively, in model training, and RMSE of 1.0 and 2.8, MB of −0.0 and 1.3, and MR of 1.0 and 1.1, respectively, in model testing. The histogram of the residuals in SSS estimation in both model training and testing (Fig. 4d) showed that 78.3% of the residuals were within the RMSE based on the whole dataset (which was 1.2) and 96% of the residuals were within RMSE of 2, indicating great improvement over the published work (Vandermergeen et al., 201-9). The near symmetrical distribution around 0.0 indicated minimal mean bias in the modeled SSS. However, the relatively large and positive MB with SSS ≤ 30 indicate overestimation, as the MPNN model is more sensitive to Rs uncertainties in this salinity range (see Section 3.0).

3.2.2. MPNN model validation

To further validate the developed MPNN SSS model, an independent dataset as described in Table 2 and Fig. 5a was used. Note that this dataset was not used in either the MPNN model training or testing above. The comparison between MODIS-estimated SSS and field-measured SSS in Fig. 5b showed a RMSE of 1.1 (3.4%), MB of 0.0 and MR of 1.0, again with better performance with SSS > 30 (RMSE = 1.0, MB = −0.1, and MR = 1.0) than with SSS ≤ 30 (RMSE = 3.0, MB = 2.8, and MR = 1.1). Again, similar to the results shown in the model training, relatively large uncertainties occurred for SSS ≤ 30, which was mainly attributed to the relatively high sensitivity of the
MPNN model to its uncertainties in this salinity range (see Section 3.6). The spatial distribution and histogram of the residuals in Fig. 5c & d showed that 78.4% of the residuals were within the RMSE of the developed model and 92.5% were within RMSE of 2. Most of the large residuals (> 2.0 or < -2.0) were found in the Mississippi river delta where SSS was < 30, and where the positive MB and MR values indicated overestimation.

3.3. Model evaluation for various cases

The scatter plots and statistics of model validation provided overall statistical measures and uncertainties of the MPNN model. To further evaluate the model performance in different regions under different scenarios in the GOM (e.g., Mississippi-Achafalaya coastal waters, Mississippi River plume, Florida's Big Bend area, etc.), the model was further evaluated with different dataset groups for each case (Table 2, Section 2.1.1). Note that in each case, the field-measured SSS dataset was independent from other cases, and none of these datasets was used in the MPNN training, testing, or validation above.

3.3.1. Mississippi-Achafalaya coastal waters

Underwater SSS measurements from two cruises (GM0606 and GI41003) described in Table 2 were used to evaluate the MPNN model performance in coastal waters off the Mississippi-Achafalaya region. The results for cruise GM0606 are shown in Fig. 6. For the whole dataset, the RMSE was 2.4, with MB of 0.4 and MR of 1.0. At SSS > 30, the variation of MODIS-estimated SSS along the cruise track agreed well with the field-measured SSS with RMSE of 1.5, MB of 0.3, and MR of 1.0. At SSS < 30, the model showed higher uncertainties (RMSE = 4.0, MB = -2.1, and MR = 1.1) especially in three locations (marked as A, B, C in Fig. 6a-c). These locations are in close proximity of the coastline, where the Mississippi-Achafalaya river flows change fast (e.g., hours) following tidal mixing. The spatial distribution of the MODIS-estimated SSS along the cruise track in Fig. 6b showed agreement with field-measured SSS (overlaid in Fig. 6d), with low SSS values nearshore and higher SSS values offshore. Furthermore, a 6-day MODIS SSS

<table>
<thead>
<tr>
<th>Model</th>
<th>Kernel function</th>
<th>Model Inputs</th>
<th>RMSE</th>
<th>R²</th>
<th>MB</th>
<th>MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLR</td>
<td>-</td>
<td>Rs Band ratio</td>
<td>1.8/1.7</td>
<td>0.73/0.73</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td>MNR</td>
<td>-</td>
<td>Rs Band ratio and SST</td>
<td>1.5/1.5</td>
<td>0.61/0.61</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td>PCA Regression</td>
<td>-</td>
<td>Rs3 (x) and SST</td>
<td>2.2/2.2</td>
<td>0.50/0.50</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td>Decision Tree</td>
<td>Simple Tree</td>
<td>Rs3 (x) and SST</td>
<td>1.5/1.9</td>
<td>0.79/0.79</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td></td>
<td>Medium Tree</td>
<td>Rs3 (x) and SST</td>
<td>1.1/1.1</td>
<td>0.89/0.89</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td></td>
<td>Complex Tree</td>
<td>Rs3 (x) and SST</td>
<td>0.8/0.8</td>
<td>0.93/0.93</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td>Random Forest</td>
<td>Boosted Trees</td>
<td>Rs3 (x) and SST</td>
<td>1.8/2.0</td>
<td>0.71/0.71</td>
<td>-1.5/-1.5</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td></td>
<td>Bagged Trees</td>
<td>Rs3 (x) and SST</td>
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<td>0.91/0.91</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td>SVM</td>
<td>Linear</td>
<td>Rs3 (x) and SST</td>
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<td>0.49/0.49</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td></td>
<td>Quadratic</td>
<td>Rs3 (x) and SST</td>
<td>1.8/2.0</td>
<td>0.72/0.72</td>
<td>0.2/0.2</td>
<td>1.0/1.0</td>
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<tr>
<td></td>
<td>Cubic</td>
<td>Rs3 (x) and SST</td>
<td>6.5/7.3</td>
<td>-2.7/-2.7</td>
<td>-2.1/-2.1</td>
<td>1.0/1.0</td>
</tr>
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<td></td>
<td>Fine Gaussian</td>
<td>Rs3 (x) and SST</td>
<td>2.3/2.3</td>
<td>0.54/0.54</td>
<td>0.3/0.3</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td></td>
<td>Medium Gaussian</td>
<td>Rs3 (x) and SST</td>
<td>1.7/1.7</td>
<td>0.74/0.74</td>
<td>0.2/0.2</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td></td>
<td>Coarse Gaussian</td>
<td>Rs3 (x) and SST</td>
<td>2.1/2.1</td>
<td>0.61/0.61</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
<tr>
<td>MPNN</td>
<td>Leave-one-Mouriri-out optimization and a Bayesian linear</td>
<td>Rs3 (x) and SST</td>
<td>1.2/1.2</td>
<td>0.86/0.86</td>
<td>0.0/0.0</td>
<td>1.0/1.0</td>
</tr>
</tbody>
</table>

* Rs Band ratios = ([Rss(667)/Rss(555), Rss(671)/Rss(488), [Rss(667)/Rss(443)]].
composite map (Fig. 6d) covering the cruise period also showed agreement with field-measured SSS (Fig. 6c) although the statistics are slightly worse due to the larger time difference (RMSE = 36, MB = –0.3, and NR = 1.0).

Results for the GM0003 cruise are shown in Fig. 7. Similar to those found from the GM0606 cruise, MODIS-estimated SSS mimicked the variation patterns of field-measured SSS, with RMSE of 3.4, MB of 0.6 and NR of 1.0 (Fig. 7a), and the spatial distributions in MODIS-estimated SSS showed lower SSS values in nearshore waters than in offshore waters (Fig. 7b), a result of river discharge and other terrestrial runoff. Also similar to GM0606, better model performance was found for SSS > 30 (RMSE = 1.6, MB = –0.3, and NR = 1.0) than for SSS ≤ 30 (RMSE = 4.7, MB = 0.3, and NR = 1.0). The agreement between MODIS-estimated SSS and field-measured SSS along the cruise track can also be visualized in Fig. 7c. Such an agreement appeared even better when MODIS data along the cruise track was extracted from a 12-day composite map covering the cruise period (Fig. 7c) (RMSE = 3.7, MB = 0.5, and NR = 1.1). Indeed, when the field-measured SSS was color coded in the same way as with the MODIS composite SSS map (Fig. 7d), their agreement in spatial distribution patterns is clearly revealed, both showing lower SSS in nearshore waters than in offshore waters.

In short, in Mississippi-Atchafalaya coastal waters the MPNN SSS model could capture the SSS variations with a reasonable accuracy and quantified uncertainties.

3.3.2. Mississippi River plume

To test the model performance in quantifying SSS of river plumes, both discrete and continuous SSS measurements from two experiments were used (Table 2).

The first experiment was in the northern GOM where the Mississippi River plume was found on 14 August 2015 from field measurements. SSS measurements collected between 9 and 21 August 2015 (DEEPEX cruise in Table 2) with cruise track overlaid in Fig. 8a & b) were used to examine the performance of the SSS model, with results shown in Fig. 8a & c). Within a 24-h time window, MODIS-estimated SSS showed agreement with field-measured SSS across the river plume (Fig. 8a), with RMSE of 0.2, MB of 0.2, and NR of 1.0. The corresponding MODIS

### Table 5

<table>
<thead>
<tr>
<th>Statistics</th>
<th>RMSE</th>
<th>MB</th>
<th>NR</th>
<th>$R^2$</th>
<th># of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model training (≤ 6 h)</td>
<td>3.0</td>
<td>1.0</td>
<td>1.2</td>
<td>1.4</td>
<td>0.86</td>
</tr>
<tr>
<td>Model testing</td>
<td>2.8</td>
<td>1.0</td>
<td>1.2</td>
<td>1.3</td>
<td>0.86</td>
</tr>
<tr>
<td>RMSS model validation (≤ 24 h)</td>
<td>3.0</td>
<td>1.0</td>
<td>1.1</td>
<td>2.8</td>
<td>0.86</td>
</tr>
<tr>
<td>Northern GOM (A general validation)</td>
<td>3.0</td>
<td>1.0</td>
<td>1.1</td>
<td>2.8</td>
<td>0.86</td>
</tr>
<tr>
<td>River plume</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.86</td>
</tr>
<tr>
<td>Big Bend region</td>
<td>2.7</td>
<td>1.7</td>
<td>1.9</td>
<td>0.7</td>
<td>0.86</td>
</tr>
<tr>
<td>Comparison with Aquarius</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.86</td>
</tr>
<tr>
<td>Comparison with buoy SSS</td>
<td>4.1</td>
<td>1.2</td>
<td>2.7</td>
<td>2.1</td>
<td>0.86</td>
</tr>
</tbody>
</table>

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Fig. 5. Performance of the MPNN SSS model from evaluation using an independent dataset in Table 2. Note that this dataset was not used in either model training or model testing as described in Fig. 6. (a) Spatial distributions of the field-measured SSS; (b) comparison between satellite-estimated SSS and field-measured SSS; (c–d) spatial distributions and histogram of the SSS residuals, respectively.

3.3.3. Florida’s Big Bend region

Fig. 6a shows the field-measured SSS in the Big Bend region and in the offshore NEOM, where the data are described in Table 2. Comparison between concurrent (±24 h) MODIS-derived SSS and field-measured SSS is shown in Fig. 6b, with a RMSE of 1.9, MB of 0.4 and MR of 1.0. In terms of absolute uncertainties the SSS model showed better performance with SSS > 30 (RMSE = 1.7, MB = 0.6, and MR = 1.0) than with SSS ≤ 30 (RMSE = 2.7, MB = -0.7, and MR = 1.0). As shown in the enhanced RGB image on 6 June 2014 (Fig. 10c), a wide band of dark feature (near parallel to the coastline) is evident. The comparison between MODIS SSS along the cruise track (Fig. 10d) with field-measured SSS excellent and colored along the cruise track (streaks). Note that the red dots on Fig. 10a and (c) indicate that there are no concurrent MODIS-derived SSS.
facilitate comparison, field-measured SSS between 6 and 13 June 2014 was color coded and annotated on this image; the corresponding comparison with MODIS is marked as solid circles in Fig. 10b. The comparison showed a RMSE of 1.4, MB of 0.6, and MR of 1.0. The MODIS SSS composite map for this period in Fig. 10d showed low SSS values in the plume region and higher SSS offshore, suggesting that the SSS model worked well in Florida’s Big Bend area in revealing not only SSS spatial patterns, but also absolute SSS values.

3.4. Comparison with Aquarius SSS

Aquarius was designed to measure SSS through microwave sensing, with a known uncertainty of < 0.3 (Abe and Elachi, 2014). To evaluate the performance of the SSS model developed in this study on a monthly scale, MODIS-estimated SSS along the cruise track from August 2014 were compared. Fig. 11a & b showed the spatial distributions of MODIS-estimated SSS and Aquarius-estimated SSS. Both captured the offshore river plume, and their spatial patterns appeared to be similar in offshore waters. The striking differences are in their spatial resolutions, and coverage. MODIS showed more details in SSS spatial variations because of its much finer resolution (1-km) than Aquarius (1’). Also, due to the coarse resolution, Aquarius simply has no coverage in nearshore waters. In contrast, MODIS showed large near-shore SSS gradients, especially around the Mississippi Delta and Florida’s Big Bend. Fig. 11c & d further quantified the comparison between MODIS and Aquarius SSS along two artificial transects (transects 1 and 2 shown in Fig. 8).
in Fig. 1a & b). Clearly, while the SSS magnitudes are similar between the two measurements, MODIS provided more detailed SSS variations along the two offshore transects. When MODIS-estimated SSS along those two transects were averaged over the corresponding Aquarius pixels, the results in Fig. 1c shows agreement between MODIS and Aquarius with RMSE of 0.8, MB of 0.3 and MR of 1.0.

3.5. Comparison with Buoy-measured SSS

The above evaluations are focused on spatial changes in SSS. To test the model performance in deriving SSS time-series at fixed locations in both nearshore and offshore waters, SSS data collected by several marine buoys (Section 2.1.1, Table 2) were used. The three buoy stations were selected according to their data availability.

During model development, < 0.1% of these buoy data were found to have concurrent (± 6 h) satellite data due to cloud cover, sun glint, and other factors which prevented valid MODIS retrievals. For validation purpose, these 0.1% of data were excluded, but daily means of the buoy data were used to compare with MODIS-derived SSS within ± 1 day. Considering the daily standard deviation of < 1.0 from ~97% of the buoy data, there should be little bias in the derived SSS daily means.

Fig. 10 shows the locations of two nearshore buoys and one offshore buoy, and comparison between MODIS-derived SSS and buoy-measured SSS from 2009 to 2015. Clearly, even for nearshore waters where SSS may approach zero, MODIS-derived SSS showed good agreement with buoy-measured SSS. For the entire range, RMSE in MODIS SSS is 2.7 with a mean ratio of 1.0 (B = 367). However, the errors are not evenly distributed, and tend to show higher uncertainties in the intermediate SSS range (between 12 and 25) than in other SSS ranges. This may be explained by the model sensitivity to input IRS errors (see section below).

A striking finding is the scarce data from MODIS over the two nearshore locations. Even though the odds of cloud-free conditions are about 30% for the GOM (Hu et al., 2005), valid MODIS data are far < 30% due to sun glint and stray light. This points to the need for correcting these artifacts to recover the low-quality data to make them.
usable for the SSS model.

3.6. Model sensitivity to input SST and Rrs errors

Fig. 13 shows the model sensitivity to input SST errors. Statistically, with +1°C errors added, the MPNN model showed slight SSS underestimation, with RMSE of 0.5, MB of −0.2, and MR of 1.0. With −1°C errors added, the MPNN model showed slight overestimation in SSS, with RMSE of 0.3, MB of 0.2 and MR of 1.0. These results suggest that the MNPN SSS model responded to SST errors in a negative way, but in both cases the model was insensitive to SST errors.

Fig. 14 shows the simulated Rrs errors in each experiment. The red lines represent those spectrally-dependent errors (Eqs. (6), (8)–(10)). From Experiment 1 to Experiment 4, with increased spectrally-independent errors, points become more scattered around the red line, representing unrealistic scenarios.

Fig. 15 shows the SSS uncertainties from the MPNN model at each SSS interval (from 1 to 37), corresponding to the input Rrs errors in each experiment. It is interesting to see that the MPNN SSS model was less sensitive to the same input Rrs errors at SSS < 10 and SSS > 23 than at 10 ≤ SSS ≤ 23. The increased uncertainties with decreasing SSS for SSS > 23 are less easy to understand because a decrease in SSS is often accompanied by an increase in CDOM and a decrease in Rrs442 and Rrs443 (e.g., Fig. 3), leading to increased relative Rrs412 and Rrs443 errors. However, the low SSS uncertainties at SSS < 10 are counterintuitive as the same argument no longer holds true. To investigate the reason, the Rrs spectra for SSS < 10 and 10 ≤ SSS ≤ 23 were compared. Although the values of Rrs412 and Rrs443 at SSS < 10 were lower than those at 10 ≤ SSS ≤ 23, the Rrs spectral shapes at SSS < 10 were much closer to the spectral shapes of the simulated Rrs errors, thus leading to lower SSS uncertainties at SSS < 10.

In general, SSS uncertainties increased with increasing Rrs errors, especially for SSS > 23 (Fig. 15). Because the simulated Rrs errors in Fig. 14 were all larger than those estimated from MODIS measurements (Hu et al., 2013) except for Experiment 1, the SSS uncertainties in Fig. 15 should be regarded as the higher bound of the model sensitivity to input Rrs errors. In Experiment 2 where the spectrally-independent Rrs errors were simulated with a standard deviation of 1.2 × 10^{-4}sr^{-1}, the resulting SSS uncertainties were < 1.0 at SSS > 30. As SSS of most coastal waters is the GOM is > 30, such Rrs error-induced SSS uncertainties should have limited effect on the modeled SSS in most regions. Furthermore, because MODIS and SeaWiFS Rrs spectra instead of field-measured Rrs spectra were used in the model development, the uncertainties in MODIS and SeaWiFS Rrs were already taken care of implicitly by the MPNN.

4. Discussion

4.1. Which approach to use?

Regardless of the various approaches published in the literature, because SSS does not have an apparent optical signature in the visible domain, estimating SSS from ocean color measurements is all based on the principle of CDOM-SSS relationship, either explicitly or implicitly. For the former, Hu et al. (2013) clearly showed that CDOM-SSS relationship in the northern GOM varied across different coastal regions, and the test of the CDOM-based approach did not yield any reliable retrievals for the SSS range of 20°–36° (see Supplemental Fig. S1). Then, why did the MPNN empirical approach could lead to relatively accurate SSS retrievals without the need of re-tuning of the model across the various sub-regions?

Indeed, although semi-analytical models together with the use of explicit CDOM-SSS relationship have the advantage of better understanding of the various model terms in their physical meanings, in
practice they often suffer from uncertainties in the model inputs and from unknown factors (i.e., variable CDOM-salinity relationship across subregions) not accounted for in the models. In contrast, empirical models may deal with all these uncertainties and unknown factors through model tuning of the model forms and empirical coefficients. For example, the impact of turbidity on SSS retrievals is implicitly accounted for through the use of RMSE(667), and the variable CDOM-salinity relationships may be reflected in the Rrs spectral shapes that are also implicitly accounted for through the use of the Rrs in all bands. This has been demonstrated by all empirical models tested in the initial data diagnosis (Table 4). They all showed better performance than the model based on explicit CDOM-salinity relationship. Some of these models (e.g., Random Forest – bagged tree; Decision Tree – complex tree) actually showed only slightly worse performance than the selected MPNN model, suggesting the general feasibility of using empirical models to address complex questions. However, for the same reason why empirical models may work, without explicit understanding of why they work, their application must be restricted only to the environments in which they were trained, and this is exactly why the model was evaluated extensively in different environments.

4.2. Model applicability and limitations

The extensive evaluation results suggest that for the salinity range of $-1$ to $-37$, the empirical MPNN can estimate SSS with an overall uncertainty of $\pm 1.2$. While the uncertainty is higher for intermediate SSS range ($10-25$) than for other ranges, the relatively small uncertainty for SSS $> 30$ is particularly useful for monitoring and

![MPNN response to noise in SST](image)

![MPNN response to noise in SST](image)
quantifying offshore river plumes and non-point freshwater runoff as SSS in the offshore plumes rarely dropped to < 30 (Hu et al., 2004, 2005). Such ability is particularly useful for studying biogeochemical processes and validating numerical circulation models. For regions with SSS < 30, the uncertainty of SSS estimated by the MPNN model was ~3.0. These regions are mostly inshore areas where riverine freshwater mixes with oceanic waters with a high dynamic SSS range. An uncertainty of 3.0 for such highly dynamic low-salinity water may be acceptable, especially when large salinity anomaly is expected after flooding events. Such ability may help decision-making in aquaculture.

Fig. 14. Simulated Res errors in the 4 experiments to test the sensitivity of the MPNN model to input Res errors. From Experiment 1 to Experiment 4, Res6/07 errors were assumed to have a normal distribution with standard deviation of 5 × 10^{-2} m^{-1} (Hu et al., 2013), and Res errors in other bands were calculated using Eq. (6) (red line in each panel) superimposed by normally distributed random noise. The standard deviation of the added noise are 2 × 10^{-1} m^{-1}, 1.2 × 10^{-1} m^{-1}, 2.3 × 10^{-1} m^{-1}, and 3.6 × 10^{-1} m^{-1}, respectively, in the 4 experiments. In each experiment, the Res noise added in each band are completely independent of each other, but with the same standard deviation.

Fig. 15. Sensitivity of the MPNN SSS model to input Res errors, based on the simulated Res errors in Experiment 1–4 in Fig. 14. In each experiment, each of the 3640 SSS points showed an uncertainty value from the sensitivity experiment, defined as the standard deviation of the 2000 simulated SSS residual errors. These uncertainty values were binned to 1 SSS increment, resulting in mean and standard deviation shown in the y-axis.
management (i.e., oyster farming). Indeed, although empirical in nature, the MPNN model appears to be applicable to most, if not all, coastal waters in northern GOM. This may seem surprising because the CDOM – SS relationship does vary with region and season (Hu et al., 2003) and therefore, even if error-free CDOM can be derived from MODIS, regional and seasonal CDOM – SS relationships should still be required for different regions and seasons if a CDOM-SS explicit model were to be used. One explanation of the robust MPNN performance is that because CDOM is not used explicitly in the MPNN, rather spectral Rrs data with their corresponding SS were used to train the MPNN, the variable CDOM – SS relationship was implicitly included in the neurons and empirical coefficients. This is clearly shown in the model evaluation results for the Big Bend region. The region has different CDOM – SS relationship than from the Mississippi River plume (Hu et al., 2003), yet the same MPNN model worked reasonably well in this region (Fig. 10). One additional advantage of using the MPNN model is that there is no need to assume CDOM is a conservative parameter (Chen and Gardner, 2004), and the complex CDOM-SS relationship for turbid coastal waters of the northern GOM was addressed implicitly by the MPNN model through the use of the spectral Rrs data overall. The evaluation results using ship surveys for nearshore and offshore waters as well as buoy time-series data for nearshore stations suggest the robustness of the model in estimating SSS in coastal waters of the northern GOM.

However, because of its empirical nature, the MPNN model is only applicable to waters that are encompassed by the training datasets. Although we believe that nearly all field-collected SSS data from major cruise surveys in the past 18 years have been used in model training and validation, there is no guarantee that these data covered all possible oceanographic conditions. One such exceptional condition is upwelling, which may bring CDOM-rich high-salinity water to the surface, and/or bring nutrients to surface waters which stimulate phytoplankton blooms. Both will result in false overestimation of SSS. However, strong coastal upwelling is rare in the northern GOM (Müller-Karger, 2000), and coastal upwelling on the WFS (Weisberg et al., 2016) only caused slight overestimation in SSS (5.5% in the upwelling zone versus 36.4% in surrounding waters, with underestimation within the model uncertainty). These coastal upwelling events can be identified through the use of SST anomaly imagery. Likewise, offshore upwelling due to deep-water intrusion and/or wind mixing can also be easily recognized and ruled out by examining SST anomalies (Hu et al., 2013). Therefore, these cases are unlikely to cause major problems in model applications. However, to create the best outcomes for the MPNN model, the SST anomaly and bloom data should be used as a selection criterion to mask the MODIS imagery prior to their inclusion in the model. In the future, a scheme to combine the MPNN model results and upwelling index (through either numerical models or SST anomalies) may be implemented for operational use of the model in generating daily SSS imagery from MODIS in near-real time. Such applications may enhance the capacity of the existing Virtual Buoy System (VBS, Hu et al., 2014) in monitoring coastal water quality.

The MPNN model has been thoroughly tested for the northern GOM. One question is whether it can be applied to other coastal regions. While each region may have its unique Rrs – SSS relationship, we believe that the general approach may be applicable as long as sufficient local data have been collected to retrain the model. Indeed, even without such a local tuning, the application of the MPNN model (with its default coefficients) to the East China Sea showed reasonable spatial patterns of low-SSS nearshore waters and higher-SSS offshore waters (see figures in Supplemental material), which are consistent to those reported in Bai et al. (2013).

Although the MPNN model has been shown applicable to the northern GOM waters with known uncertainties, when applying it to satellite data to derive SSS maps and time series, the limitation is not in the model itself but in scarce MODIS data for nearshore waters. This is clearly shown in Fig. 12d. The scarce MODIS data is due to not only cloud cover but also sun glint, cloud-adjacent stray light, and other factors such as large solar or view angles (Fan and Hu, 2016). Clearly, future effort should also be dedicated to “recover” these low-quality data in order to increase data quantity without sacrificing too much data quality.

Finally, because all empirical ANN models work like a “black-box” and researchers other than the model developer have no way to test them for other regions or other datasets, in this study the MPNN program has been packaged as one executable file for others to test, where a detailed description is also provided in the supplemental materials. It should be straightforward to run the model under a MATLAB environment. Furthermore, although the present MPNN model was developed for MODIS data, it can also be applied to other satellite data with careful attention to the slight difference between their band settings.

5. Conclusion

Accurate estimation of SSS is coastal waters and river plumes of the northern GOM from optical remote sensing has been a challenging task due to non-conservative mixing of CDOM and SSS, variable CDOM-SS relationship in different regions, and due to high uncertainties in the satellite-derived Rrs and CDOM in turbid and dynamic coastal waters (e.g. Mississippi River delta). In this study, with satellite-estimated Rrs at 412, 443, 488, 555, and 667 nm and SST as inputs, a neural network-based model (MPNN) has been developed and thoroughly evaluated for coastal waters of the northern GOM and for the offshore Mississippi River plume. The model showed reasonably good performance in the Mississippi-Atchafalaya Coastal region and Florida’s Big Bend region and was capable of detecting and quantifying the offshore Mississippi River plume. However, the operational use of this model in generating daily MODIS SSS maps still requires efforts to rule out some rare cases of coastal upwelling.

Notations

AOML Atlantic Oceanographic & Meteorological Laboratory
AOPs Apparent Optical Properties
AON Artificial Neural Network
BOEM Bureau of Ocean Energy Management
CDIAC Carbon Dioxide Information Analysis Center
CDOM Colored Dissolved Organic Matter
CIIL Chlorophyll a Concentration
DEEPEND/Deep-Pelagic: Nekton Dynamics of the Gulf of Mexico
FWC Florida Fish and Wildlife Conservation Commission
FWRI Fish and Wildlife Research Institute
GOM Gulf of Mexico
GSC Goddard Space Flight Center
IOPs Inherent Optical Properties
LED National Oceanic and Atmospheric Administration
NOAA National Environmental Satellite, Data, and Information Service
NOAA National Data Buoy Center
NGOM Northeastern Gulf of Mexico
PCAD Principle Component Analysis
pCO2 Partial Pressure of CO2
PSS Potential Temperature
R2 Determination coefficient
RMSE Root Mean Square Error
RS Remote Sensing Reflectance
SEAMAP Southeast Area Monitoring and Assessment Program

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SeaWiFS Sea-Viewing Wide-Field-of-View Sensor
SMOS Soil Moisture and Ocean Salinity
SNPP Suomi National Polar-orbiting Partnership
SST Sea Surface Temperature
SSH Sea Surface Salinity
TA Total Alkalinity
TAMU Texas A&M University
USF University of South Florida
VIIRS Visual Infrared Imaging Radiometer Suite

Acknowledgements

This research was supported by the U.S. NASA Ocean Biology and Biogeochemistry program (NNX13AD08G, NNX14AI69G, NNX15AI33A) and by a University of South Florida fellowship. The research was also supported by grants from the BP-Gulf of Mexico Research Initiative through the DEEPEND consortium and through a project on river plumes and hydrocarbon transport, with data available in the Gulf of Mexico Research Initiative Information & Data Cooperators (GdI) at https://data.gulfresearchinitiative.org/data/R4/0x8257:3200:00109. The authors are indebted to all researchers, including those of AOML, CDIAC, PWC, LDGO, NODC, TAMU, and USF, who have collected, quality controlled, and shared all cruise survey data. The authors also thank NASA for providing MODIS, SeaWiFS, and Aquarius ocean data. Three anonymous reviewers provided extensive comments to help improve the presentation of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.rse.2017.09.004.

Reference

In summary, the method provides a powerful tool for detecting ocean color changes in coastal and open ocean environments using SENTINEL-3A data. The approach is validated through comparisons with in situ measurements and MODIS satellite data. The results demonstrate the potential of the method for monitoring coastal water quality and detecting anthropogenic impacts.

References:


APPENDIX D:

A MACHINE LEARNING APPROACH TO ESTIMATE SURFACE OCEAN $pCO_2$
FROM SATELLITE MEASUREMENTS

A machine learning approach to estimate surface ocean \(p\text{CO}_2\) from satellite measurements

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Abstract

Surface partial pressure of CO\(_2\) (\(p\text{CO}_2\)) is a critical parameter in the quantification of air-sea \(CO_2\) flux, which farther plays an important role in quantifying the global carbon budget and understanding ocean acidification. Yet, the remote estimation of \(p\text{CO}_2\) in coastal waters (under influences of multiple processes) has been difficult due to complex relationships between environmental variables and surface \(p\text{CO}_2\). To date there is no unified model to remotely estimate surface \(p\text{CO}_2\) in oceanic regions that are dominate by different oceanic processes. In our study area, the Gulf of Mexico (GOM), this challenge is addressed through the evaluation of different approaches, including multi-linear regression (MLR), multi-nonlinear regression (MNR), principle component regression (PCR), decision tree, supporting vector machines (SVMs), multilayer perceptron neural network (MPNN), and random forest based regression ensemble.

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(RFRE). After modeling, validation, and extensive tests under different scenarios, the RFRE model proved to be the best approach. The RFRE model was trained using data comprised of extensive $p$CO$_2$ datasets (collected over 16 years by many groups) and MODIS (Moderate Resolution Imaging Spectroradiometer) estimated sea surface temperature (SST), sea surface salinity (SSS), surface chlorophyll concentration (Chl), and diffuse attenuation of downwelling irradiance (Kd). This RFRE-based $p$CO$_2$ model allows for the estimation of surface $p$CO$_2$ from satellites with a spatial resolution of ~1 km. It showed an overall performance of a root mean square error (RMSE) of 9.1 μatm, with a coefficient of determination ($R^2$) of 0.95, a mean bias (MB) of -0.03 μatm, a mean ratio (MR) of 1.00, an unbiased percentage difference (UPD) of 0.07%, and a mean ratio difference (MRD) of 0.12% for $p$CO$_2$ ranging between 145 and 550 μatm. The model, with its original parameterization, has been tested with independent datasets collected over the entire GOM, with satisfactory performance in each case. The sensitivity of the RFRE-based $p$CO$_2$ model to input errors of each environmental variable was also thoroughly examined. The results showed that all induced uncertainties were close to, or within, the uncertainty of the model itself with slightly higher sensitivity to SST and SSS than to Chl and Kd. The extensive validation, evaluation, and sensitivity analysis indicate the robustness of the RFRE model in estimating surface $p$CO$_2$ in most, if not all, GOM waters. The RFRE model approach was applied to the Gulf of Maine (a contrasting oceanic region to GOM), with local model training. The results showed significant improvement over other models suggesting that the RFRE may serve as a robust approach for other regions once sufficient field-measured $p$CO$_2$ data are available for model training.

**Keywords:** surface $p$CO$_2$, SST, SSS, Chlorophyll, Kd, satellite remote sensing, Gulf of Mexico

1. **Introduction**
Since the industrial revolution, the continuous consumption of fossil fuels has increased atmospheric CO₂ by ~40% (Sabine et al., 2004; Solomon et al., 2007). Correspondingly, the oceanic uptake of CO₂ has resulted in a ~30% increase in ocean acidity and ~0.1 (pH units) decrease of pH (Orr et al., 2005; Doney et al., 2009; Sun et al., 2012; Pachauri and Meyer 2014). These changes in the ocean have led to a decrease in marine biota and a degradation of marine ecosystems (Widdicombe and Spicer 2008; Doney, 2010; Dickinson et al., 2012). Therefore, understanding oceanic uptake of anthropogenic CO₂ and its changing rate are pressing concerns of the research community. However, due to the dynamics of the partial pressure of surface water CO₂ (pCO₂), large uncertainties still exist in the quantification of regional air-sea CO₂ flux (Takahashi et al., 2002, 2009, 2014; Sarma, 2003; Borges et al., 2005; Hofmann et al., 2011; Sarma et al., 2012; Chen et al., 2013; Wanninkhof et al., 2013a). Therefore, accurate and synoptic knowledge of surface oceanic pCO₂ is critical to studying the ocean’s role in global carbon cycling within a changing world.

Satellite remote sensing, with its advantages of spatial and temporal resolution and coverage, has become an important tool for synoptic estimation of oceanic surface pCO₂. In principle, surface pCO₂ is mainly controlled by four interrelated processes – a thermodynamic process, biological activities, physical mixing, and the air-sea CO₂ exchange (Fennel et al., 2008; Ikawa et al., 2013; Xue et al. 2016). These four processes are closely related to satellite-derived environmental variables such as sea surface temperature (SST, °C), sea surface salinity (SSS, dimensionless), surface chlorophyll-a concentration (Chl, mg m⁻³), diffuse attenuation of downwelling irradiance (Kd, m⁻¹), as well as other variables such as wind speed (m s⁻¹) and mixed layer depth (MLD, m) (i.e., Bai et al., 2015; Marrec et al., 2015; Moussa et al., 2016; Chen et al., 2016 & 2017; Lohrenz et al., 2018, etc.). Specifically, the thermodynamic quantities, solubility of CO₂ and the
dissociation constants of the carbonate system are mainly controlled by SST and SSS (Weiss, 1974; Millero et al., 2006). SST and SSS can also be good tracers of water masses (i.e., freshwater inputs, upwelled waters) that have distinct carbonate characteristics such as total alkalinity (TA) and dissolved inorganic carbon (DIC) (Lee et al., 2006; Yang et al., 2015). Because of the consumption and production of CO₂ in the biological processes of photosynthesis and respiration, and the depletion of TA and DIC in a 2 to 1 ratio in biological calcification (i.e., Reynaud et al., 2003; Salisbury et al., 2008; Fay & McKinley, 2017), the biological effects on surface pCO₂ can be implicitly interpreted from optical parameters such as Chl and Kd. Ocean mixing (both horizontal and vertical) is closely related to MLD as well as SST and SSS; and, the influence of air-sea CO₂ exchange on surface pCO₂ can be deduced from wind speed (Bates et al., 1998; Bates and Merlivat, 2001; Turk et al., 2013). However, in a specific oceanic system, only one or two processes (and thus their corresponding environmental variables), may dominantly control the changes of surface pCO₂ (Bai et al., 2015).

Using the environmental variables mentioned above, several satellite-based surface pCO₂ models have been proposed and developed in the published literature for different oceanic regions (both open and coastal ocean waters). Of these, remote estimation of surface pCO₂ in the open ocean is relative mature due to less variability in the open ocean’s environmental conditions than those in coastal oceans. Both traditional empirical regressions (i.e., multi-linear regression (MLR), multi-nonlinear regression (MNR)) (e.g., Stephens et al., 1995; Sarma, 2003; Ono et al., 2004; Olsen et al., 2004; Rangama et al., 2005; Sarmi et al., 2006; Jamet et al., 2007; Chen et al., 2011) and machine-learning based regressions (i.e., multilayer perceptron neural network (MPNN), self-organizing maps (SOMs)) (e.g., Telszewski et al., 2009; Friedrich and Oschlies, 2009; Nakaoka et al., 2013; Moussa et al., 2016; Landshützer et al. 2014) have been used to model surface pCO₂ for
open-ocean waters, with a root mean square error (RMSE) of $< 17 \mu\text{atm}$ in most cases. For coastal oceans, due to their complexity and dynamics in the biogeochemical and physical processes, satellite mapping of surface $pCO_2$ is still a challenging task. Specifically, in addition to MLR, MNR, and SOMs (e.g., Lefèvre et al., 2002; Chierici et al., 2009; Zhu et al., 2009; Shadwick et al., 2010; Borges et al., 2010; Jo et al., 2012; Tao et al., 2012; Signorini et al., 2013; Marrec et al., 2014; Parard et al., 2014; Marrec et al., 2015; Chen et al., 2016), other empirical approaches such as principle component regression (PCR) (Lohrenz & Cai, 2006; Lohrenz et al., 2010) and regression tree (Lohrenz et al., 2018), and semi-analytical approaches (Hale et al., 2012; Bai et al., 2015; Chen et al., 2017) have been proposed for different coastal regions dominated by a single oceanic process (river-dominated, upwelling-dominated, or ocean current-dominated). For these complex regions, RMSE in the satellite-derived $pCO_2$ from these approaches is generally much higher than for open-ocean waters, and it can reach 88.6 $\mu\text{atm}$.

Despite these extensive efforts in establishing the various approaches or models, several problems still exist in the current satellite mapping of surface $pCO_2$. First, most approaches mentioned above are investigated in only one oceanic region, often dominated by a single major oceanic process. Although Signorini et al. (2013) proposed a MLR approach for the entire U. S. East Coast, in which the East Coast was actually divided into different sub-regions through SOMs and the MLR $pCO_2$ model was parameterized for each sub-region with RMSE of 22.4 - 36.9 $\mu\text{atm}$. Similarly, Hales et al. (2012) developed a semi-analytical approach for the entire U. S. West Coast, but the West Coast was divided into different sub-regions through SOMs, each with a unique $pCO_2$ model parameterization for each sub-region. The resulted RMSE varied between 6.6 and 65.0 $\mu\text{atm}$. Because such models are developed and parameterized for specific regions, any proposed models to estimate $pCO_2$ for a certain ocean region may have poor applicability in other regions even after
local parameterization. In other words, at present there is no unified approach, let alone unified model to remotely estimate surface $p$CO$_2$ for large ocean regions dependent on differing oceanic processes such as Gulf of Mexico (GOM). The semi-analytical approach proposed by Bai et al. (2015) showed potential to work for any oceanic waters, yet in practice it is difficult or even impossible to separate and quantify the effects of each oceanic process (i.e., horizontal mixing, vertical mixing, biological activities, air-sea CO$_2$ exchange) on surface $p$CO$_2$ with high accuracy (i.e., RMSE $<$ 10 μatm). Further, in Bai’s study, the semi-analytical approach was implemented for the East China Sea, but tested solely with summertime data. Chen et al. (2017) adopted Bai’s approach to the northern GOM with localized parameterization, and similarly, using summertime data. Chen et al. (2017) found that the semi-analytical approach was not as good as an empirical approach in terms of model uncertainties and the model’s capability in estimating $p$CO$_2$ under different oceanic conditions (i.e., coastal upwelling).

Therefore, the objective of this work was to develop an empirical approach with general applicability to estimate surface $p$CO$_2$ from satellites for large oceanic regions encompassing multiple processes, with improved model performance over those published in the literature. The ultimate goal is to extend this approach to all regional oceans around the globe. Below we present such a machine-learning based approach, namely a random forest based regression ensemble (RFRE). The RFRE approach was selected over many other approaches after extensive testing (see Section 2.3.1 for details about performance of each tested approach). Using this approach, a $p$CO$_2$ model with low uncertainties was developed for the entire GOM, a semi-enclosed subtropical sea that encompasses many different oceanic processes (see Section 2.1 for details about the selection of this study region). To show the general applicability of this approach, the RFRE was also tested over high-latitude waters in the Gulf of Maine (G. Maine), which showed improved performance
over other published approaches and therefore great potential for general applications in other oceanic regions.

This paper is arranged as follows. First, the study region is briefly introduced to justify the selection, followed by description of the satellite and field data used. Then, methods in data preprocessing, model development, accuracy assessment, model sensitivities to the errors of satellite variables are described. Results of the monthly $p\text{CO}_2$ climatologic maps and time series of surface $p\text{CO}_2$ are presented. Finally, the environmental variables used to model surface $p\text{CO}_2$ and to trace its interannual variabilities, the general application of the approach to other oceanic regions, as well as its advantages and limitations, are discussed.

2. Data and methods

2.1. Study region

The region of GOM, bounded by 18°–31° N and 98°–79° W, was selected to test the RFRE approach for three reasons. First, neither regional satellite-based $p\text{CO}_2$ models, nor a unified $p\text{CO}_2$ approach or model, is available for the entire GOM. Most of the sub-regional studies (Lohrenz & Cai, 2006; Lohrenz et al., 2010; Chen at al., 2016 & 2017; Lohrenz et al., 2018) are focused on the West Florida Shelf (WFS) and the northern GOM waters, where large uncertainties exist in the satellite-derived $p\text{CO}_2$ (i.e., variable RMSE of 12.0–50.2 μatm). Second, due to lack of synoptic and frequent mapping of surface $p\text{CO}_2$ over the entire GOM, it is still unclear whether the GOM serves as a CO$_2$ source or sink, as shown by the discrepancies in the published studies (Takahashi et al., 2009; Coble et al., 2010; Robbins et al., 2014; Xue et al., 2014). Third, as a semi-enclosed subtropical ocean, the GOM covers multiple regions with different dominating processes (i.e., freshwater inputs from Mississippi and Atchafalaya River System (MARS), Loop Current, oceanic
currents, mesoscale ocean circulation, occasional coastal upwelling) which control surface \( p\text{CO}_2 \). Therefore, if a RFRE-based unified \( p\text{CO}_2 \) model can be developed in this challenging environment, it may suggest that the application of the RFRE approach to other oceanic regions may deliver good results.

2.2. Data source

2.2.1. Field data

Over the past 16 years, there have been more than 220 cruise surveys that collected underway \( p\text{CO}_2 \) data from the GOM waters during different seasons. We compiled all the publicly available flow-through \( p\text{CO}_2 \) data measured in the GOM, as well as \( p\text{CO}_2 \) data collected from a fixed-location buoy in the Mississippi River delta. The data used for model development and independent validation are presented in Tables 1 and 2, respectively, with a general description of the data source, data volume, time span and data range for each dataset. Collectively these data represent the most complete \( p\text{CO}_2 \) dataset for the GOM.

**Table 1.** Underway and buoy \( p\text{CO}_2 \) measurements from different platforms in the GOM. These surface \( p\text{CO}_2 \) data were collected at a depth of \( \leq 5 \) m over all seasons. Only a small portion of these measurements were found to have co-located and contemporaneous (\( \pm 6 \) h) satellite derived Chl, Kd, SSS and SST data (last column). These surface \( p\text{CO}_2 \) data encompass typical variation range in surface \( p\text{CO}_2 \) in most of the GOM waters, and these data were used to develop an optimal satellite \( p\text{CO}_2 \) model for the GOM through thorough tests of different empirical approaches. The corresponding spatial distributions of the surface \( p\text{CO}_2 \) data are shown in Fig. 1.

<table>
<thead>
<tr>
<th>Platform (Vessel/Buoy)</th>
<th>Data Source</th>
<th>Year covered</th>
<th>( p\text{CO}_2 ) range (( \mu \text{atm} ))</th>
<th>( p\text{CO}_2 ) range (( \mu \text{atm} ))</th>
<th># of data</th>
<th># of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buoy CoastMS (39°N, 88.6°W)</td>
<td>NCEI/NODC</td>
<td>2009-2014</td>
<td>72.10-464.50</td>
<td>251.20-468.73</td>
<td>5,132</td>
<td>47</td>
</tr>
<tr>
<td>R/V Cape Hatteras</td>
<td>NCEI/NODC</td>
<td>2009-2010</td>
<td>102.73-1708.85</td>
<td>145.32-437.27</td>
<td>26,794</td>
<td>748</td>
</tr>
<tr>
<td>C/S Explorer of the Seas</td>
<td>NCEI/NODC</td>
<td>2002-2015</td>
<td>332.76-432.64</td>
<td>338.68-410.96</td>
<td>46,833</td>
<td>5,066</td>
</tr>
<tr>
<td>--------------------------</td>
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</tr>
<tr>
<td>R/V Pelican</td>
<td>NCEI/NODC</td>
<td>2013</td>
<td>223.05-1836.05</td>
<td>382.19-387.84</td>
<td>47,275</td>
<td>9</td>
</tr>
<tr>
<td>R/V Gordon Gunter</td>
<td>AOML</td>
<td>2008-2016</td>
<td>68.66-1484.22</td>
<td>195.29-538.39</td>
<td>202,718</td>
<td>7,679</td>
</tr>
<tr>
<td>M/V Las Cuevas</td>
<td>AOML</td>
<td>2009-2012</td>
<td>199.08-528.60</td>
<td>273.87-486.89</td>
<td>30,859</td>
<td>1,238</td>
</tr>
<tr>
<td>R/V Marcus G. Langseth</td>
<td>NCEI/NODC</td>
<td>2013</td>
<td>304.55-536.31</td>
<td>350.93-370.05</td>
<td>2,014</td>
<td>98</td>
</tr>
<tr>
<td>R/V Brown</td>
<td>NCEI/NODC</td>
<td>2003-2012</td>
<td>192.74-502.34</td>
<td>299.01-443.71</td>
<td>35,622</td>
<td>828</td>
</tr>
<tr>
<td>R/V Falkor</td>
<td>TAMU</td>
<td>2012</td>
<td>370.00-452.20</td>
<td>371.4-1419.2</td>
<td>6,938</td>
<td>207</td>
</tr>
<tr>
<td>R/V Bald</td>
<td>NCEI/NODC</td>
<td>2006-2007</td>
<td>84.64-2083.60</td>
<td>198.90-448.55</td>
<td>36,045</td>
<td>295</td>
</tr>
<tr>
<td>F. G. Walton Smith</td>
<td>NCEI/NODC</td>
<td>2011-2015</td>
<td>85.83-2773.92</td>
<td>280.13-552.42</td>
<td>100,007</td>
<td>1,309</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>2002-2016</td>
<td>72.10-2773.92</td>
<td>145.32-552.42</td>
<td>550,235</td>
<td>17,551</td>
</tr>
</tbody>
</table>

* Data statistics after matching with contemporaneous (±6h) satellite data.

In Table 1 (data used for model development), the $pCO_2$ data (collected between 2002 and 2016) ranged between 72.10 and 2773.92 μatm. These *in situ* $pCO_2$ field data were obtained from the databases of NOAA National Centers for Environmental Information (NCEI) (formerly the National Oceanographic Data Center (NODC) [https://www.nodc.noaa.gov/ocads](https://www.nodc.noaa.gov/ocads)) (Sutton et al., 2012; Wang & Huang, 2014(a-c); Millero et al., 2016(a-d); Salisbury et al., 2016; Takahashi et al., 2016(a); Wanninkhof et al., 2011(a-f), 2013(b-g), & 2016(d)). NOAA Atlantic Oceanographic and Meteorological Laboratory (AOML) [http://www.aoml.noaa.gov/oed/oedweb/oce.html](http://www.aoml.noaa.gov/oed/oedweb/oce.html) (Wanninkhof et al., 2014(a-b), 2016(a-c, e-g)), University of Delaware (UD), and Texas A&M University (TAMU). The corresponding spatial distribution of these $pCO_2$ data is shown in Fig. 1a, with over 550,000 $pCO_2$ measurements in total.
Fig. 1. Spatial distributions of the surface $pCO_2$ measurements in the GOM along the cruise tracks. (a) Cruise tracks from all data described in Table 1 (N=550,235); (b) Cruise tracks from the same data but with co-located and contemporaneous ($\pm$ 6h) satellite Chl, Kd, SSS and SST (N=17,551) data. Five sub-regions, each about 220 km by 110 km, are selected to examine the interannual monthly time series of surface $pCO_2$. Box 1 is near the Mississippi River delta, Box 2 is on the West Florida Shelf, Box 3 is near the Loop Current, Box 4 is in the western GOM open waters, and Box 5 presents the “dead zone” along the Louisiana coast.

Typically, the ship-based surface $pCO_2$ data were collected at a depth of 5 m using a combination of a gas equilibrator and a non-dispersive, infrared analyzer Li-COR™ (model 6251, or 6262, or 7000 or 840A) integrated in the shipboard flow-through seawater system, with a measurement interval of 2 or 3 min and an accuracy of 2 $\mu$atm (or better). The buoy-based $pCO_2$ data were collected at a depth of $< 1$ m using a Li-COR™ model 820 with a sampling frequency of every 3 h and an accuracy of 2 $\mu$atm. The details of data collection, processing, and quality control can be found in Feely et al. (1998), Sabine (2005), Fierrot et al. (2009), and Huang et al. (2015).

Table 2. Underway $pCO_2$ measurements used for independent validation of the developed $pCO_2$ model. These surface $pCO_2$ measurements were collected from different cruises (N=10) by the
research vessel of R/V Gordon Gunter. None of these datasets was used in the pCO₂ model training and they were not included in Table 1. See section 3.2 and supplemental file for the spatial distribution of each cruise dataset.

<table>
<thead>
<tr>
<th>Cruise ID</th>
<th>Data Source</th>
<th>Date</th>
<th>pCO₂ range (μatm)</th>
<th>pCO₂ range (μatm)²</th>
<th># of data</th>
<th># of data²</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU0902_leg1</td>
<td>AOML</td>
<td>Apr. 2009</td>
<td>354.33 - 412.10</td>
<td>383.33 - 393.64</td>
<td>4,027</td>
<td>976</td>
</tr>
<tr>
<td>GU0902_leg2</td>
<td>AOML</td>
<td>Apr. and May 2009</td>
<td>359.38 - 391.76</td>
<td>373.57 - 388.30</td>
<td>7,234</td>
<td>771</td>
</tr>
<tr>
<td>GU1606_Leg1</td>
<td>AOML</td>
<td>Sep. 2016</td>
<td>157.42 - 484.47</td>
<td>247.10 - 448.21</td>
<td>5,626</td>
<td>1,051</td>
</tr>
<tr>
<td>GU1609_Leg2</td>
<td>AOML</td>
<td>Nov. 2016</td>
<td>330.39 - 412.19</td>
<td>330.39 - 390.02</td>
<td>5,000</td>
<td>723</td>
</tr>
<tr>
<td>GU1701_Transit_Leg</td>
<td>AOML</td>
<td>May, 2017</td>
<td>326.46 - 396.13</td>
<td>326.46 - 396.70</td>
<td>1,231</td>
<td>429</td>
</tr>
<tr>
<td>GU1703_Leg2</td>
<td>AOML</td>
<td>Jul 23 - Aug 05, 2017</td>
<td>129.73 - 453.17</td>
<td>253.46 - 437.58</td>
<td>7,288</td>
<td>725</td>
</tr>
<tr>
<td>GU1704_Leg2</td>
<td>AOML</td>
<td>Sep. 2017</td>
<td>283.31 - 511.31</td>
<td>311.02 - 423.80</td>
<td>6,308</td>
<td>1,548</td>
</tr>
<tr>
<td>GU1705_Transit_Leg</td>
<td>AOML</td>
<td>Oct. 2017</td>
<td>383.59 - 408.43</td>
<td>384.26 - 406.31</td>
<td>1,232</td>
<td>253</td>
</tr>
<tr>
<td>GU1706_Transit_Leg</td>
<td>AOML</td>
<td>Nov. 2017</td>
<td>327.26 - 403.66</td>
<td>227.26 - 384.01</td>
<td>1,352</td>
<td>639</td>
</tr>
</tbody>
</table>

^Data statistics after matching with contemporaneous (≤24h) satellite data.

Similar to Table 1, Table 2 lists data from ten flow-through pCO₂ cruise surveys that were used for independent model evaluation under different conditions. These cruises were conducted on the NOAA research vessel – R/V Gordon Gunter, and the pCO₂ data were obtained from the NOAA AOML databases (Wanninkhof et al., 2014b & 2016f; Sullivan et al., 2017). Specifically, pCO₂ data collected in Apr. and May 2009 (GU0902_leg1 and GU0902_leg2) were from the southern and western GOM waters, ranging between 354.33 and 412.10 μatm; data collected in Sep. and Nov. 2016 (GU1606_Leg1 and GU1609_Leg2) and Sep. 2017 (GU1704_Leg2) were from the northern and western GOM waters, ranging between 157.42 and 511.31 μatm; data collected in Jul. and Aug. 2017 (GU1703_Leg2) focused on the northern GOM waters, ranging between 129.73 and 453.17 μatm; and, data collected in May, Jul., Oct., and Nov. 2017 (GU1701_Transit_Leg, GU1703_Leg1, GU1705_Transit_Leg, and GU1706_Transit_Leg) focused on the northern and eastern GOM, with a pCO₂ range of 253.30 – 443.21 μatm. Note that all these cruise data in Table 2 represent independent datasets for evaluating the pCO₂ model performance as 99% of them were
excluded in the model development. The spatial distributions of these $pCO_2$ datasets are shown in Section 3.2 and in the supplemental materials.

2.2.2. Satellite data

NASA standard daily Level-2 data products (version R2014.0) covering the GOM for the period of Jul. 2002 – Dec. 2017 with a spatial resolution of ~1 km were downloaded from the NASA Goddard Space Flight Center (GSFC) (https://oceancolor.gsfc.nasa.gov). These Level-2 data products were derived from measurements by the Moderate Resolution Imaging Spectroradiometer (MODIS) on the Aqua satellite, and they included Chl, SST, and spectral remote sensing reflectance ($Rrs$, sr$^{-1}$) in 7 bands between 412 and 678 nm. The spectral $Rrs$ data were used to calculate the diffuse attenuation coefficient at 488 nm (Kd, m$^{-1}$) using the semi-analytical algorithm developed by Lee et al. (2005), and to calculate SSS using an empirical approach recently developed by Chen & Hu (2017). The Kd product is often called Kd_Lee but for brevity it is simply called Kd in this study. The MODIS-derived environmental variables including Chl, Kd, SST, and SSS were used as inputs of the surface $pCO_2$ model. Specifically, SST was used to capture the thermodynamic effects, SSS was used to monitor the freshwater characteristics of multiple river inputs, and Chl and Kd were used to quantify (implicitly) the effects of biological activities on surface $pCO_2$.

2.3. Methods

2.3.1. Data preprocessing

Time and location data from the in situ $pCO_2$ measurements were used to identify the co-located and contemporaneous MODIS-derived data products (Chl, Kd, SST, and SSS) between July 2002 and December 2017. These data were used in the RFRE $pCO_2$ model development.
To obtain high-quality data, co-located and contemporaneous field-measured $p$CO$_2$ and MODIS-derived Chl, Kd, SST and SSS were selected using the following criteria. Considering the tidal cycle characteristics (i.e., diurnal) in most regions of the GOM, a time window of ± 6h between field and MODIS measurements was used. Low-quality satellite data under various non-optimal conditions (e.g., atmospheric correction failure, cloud, stray light, sun glint, etc.) were excluded using the NASA standard quality control criteria (Patt et al., 2003; Barnes and Hu, 2015). Valid satellite data within a 3×3 km box centered on the location of each in situ field $p$CO$_2$ measurement were extracted and averaged (Bailey and Wendell, 2006). Only if the number of valid pixels in the 3×3 km box was ≥ 5 and its variance was ≤ 10% the extracted data were used together with the field measurement in the model development. After applying these quality control screenings, 17,551 conjugate observations of field-measured $p$CO$_2$ and satellite data products between 2002 and 2016 were determined to be valid and available for the RFRE $p$CO$_2$ model development (Fig. 1b). In this conjugated dataset, both the responsive variable (surface $p$CO$_2$) and predictive variables (SST, SSS, Chl, and Kd) show a typical variation of each, although some extremely low and high field $p$CO$_2$ measurements in the nearshore waters (Fig. 1a) were excluded due to lack of valid contemporaneous satellite observations. Specifically, in the model development, field-measured $p$CO$_2$ ranged between 145.32 and 552.42 μatm, MODIS Chl ranged between 0.03 and 53.96 mg m$^{-3}$, MODIS Kd ranged between 0.019 and 1.373 m$^{-1}$, MODIS SST ranged between 13.48 and 33.28 ºC, and MODIS SSS ranged between 10.96 and 38.34.

The selection of the predictive variables (i.e., SST, SSS, Chl and Kd) was based on our previous studies in the northern GOM and eastern GOM (Chen et al., 2016 & 2017). In Chen et al. (2016), various experiments were conducted to examine the relationship between surface $p$CO$_2$ and different environmental variables (i.e., SST, SSS, Chl, Kd, colored dissolved organic matter
(CDOM)) in different forms (i.e., linear scale or log_{10} scale). From these experiments, log_{10}(Chl), log_{10}(Kd), and SST were proven to be the most effective variables in estimating surface pCO\textsubscript{2} in WFS waters. The study in Chen et al. (2017) found that in addition to SST, log_{10}(Chl), and log_{10}(Kd), SSS was also a critical parameter in estimating surface pCO\textsubscript{2} in the northern GOM. This is because of the large freshwater inputs with distinct carbonate characteristics from the MARS. In addition, in both studies (and in many other studies), Julian day (Jday, or day of year) normalized sinusoidally was used as a “tuning” parameter to emphasize the seasonal cycle of surface pCO\textsubscript{2} (Friedrich and Oschlies, 2009; Lefèvre et al., 2005; Signorini et al., 2013; Chen et al., 2016 & 2017). Therefore, to estimate the surface pCO\textsubscript{2} for the entire GOM, all the four environmental variables (SST, SSS, Chl, and Kd) as well as Jday should be included in the RFRE pCO\textsubscript{2} model.

One advantage of using contemporaneous satellite-derived data (SST, SSS, Chl, Kd, and Jday) instead of in situ data to train the RFRE pCO\textsubscript{2} model, is that uncertainties in the satellite-derived data will be implicitly included in the empirically-derived weights of the RFRE (i.e., model coefficients). Then, when the same data products are used for surface pCO\textsubscript{2} predictions, such uncertainties in the satellite-derived data, to a large extent, should be cancelled.

2.3.2. Model selection, and principle and training of RFRE

In the published literature, both empirical and semi-analytical approaches were used to develop satellite-based surface pCO\textsubscript{2} models (see Section 1). The study in Chen et al. (2017) showed that although semi-analytical approaches had the advantages of explaining oceanic processes explicitly, their performance for northern GOM were not as good as those of empirical approaches. Therefore, in this study, the commonly used traditional empirical approaches (i.e., MLR, MNR, and PCR) and machine-learning based empirical approaches (i.e., MPNN, regression tree, regression ensembles, and SVMs) were all tested using the same training dataset (Table 1 & Fig. 1b) and the
same input variables. Among these trialed approaches, RFRE showed the best performance over all others (Eq. 1), and thus, RFRE was selected to develop the satellite-based $pCO_2$ model in this study (see Section 3.1 for detailed model comparison results). One distinct advantage of the machine-learning based RFRE approach is that it can approximate the nonlinear relationship between predictive variables and targeted variable (i.e., surface $pCO_2$) without explicitly knowing their functional dependence.

$$pCO_2 = f(\text{input variables}) = f_{\text{RFRE}}(\text{SST}, \text{SSS}, \log_{10}(\text{Chl}), \log_{10}(K_d), \cos(J_{\text{day}}/365)) \quad (1)$$

RFRE is one type of ensemble learning which combines many weighted regression trees to implement the random forest algorithm (Breiman, 2001) in Matlab (R2017a). Individual regression trees tend to overfit, and the RFRE takes the advantage of each regression tree via bootstrap aggregation (or bagging) to reduce model overfitting and to improve model generalization (Breiman, 1996; James et al., 2013). In model training, regression trees in the ensemble grow independently on a drawn bootstrap replica of the training dataset. In other words, each regression tree can select a random subset of predictors to use at each decision split and can involve many splits in the random forest algorithm. This way, correlations among the developed regression trees are greatly reduced, resulting in improved independency among the regression trees. In addition, this subsampling allows an out-of-bag estimate of the predictive performance by evaluating the predictions on those observations which were not used in the bootstrap sample. In this study, the regression ensemble function “fitensemble” in Matlab (R2017a) was used to develop the relationship between surface $pCO_2$ and environmental variables. There are two important parameters to define this RFRE model structure: the minimum leaf size and number of learning cycles (i.e., the number of regression trees). Leaf size refers to the number of data samples used in each node of a regression tree, and the minimum leaf size, thus determines the splits and depth of
a regression tree. The number of regression learning cycles determines the number of regression
trees to be included in the RFRE. By trial and error, the minimum leaf size and the number of
learning cycles of the RFRE were optimized to 8 and 30, respectively. With these settings, the
prediction accuracy of the RFRE model became stable, and the RFRE model were developed to
predict surface $pCO_2$.

2.3.3. Accuracy assessment

Two types of model evaluation were used to quantify the performance of the RFRE model in
estimating surface $pCO_2$ in the GOM.

First, in the model development phase, the modeled $pCO_2$ were compared with the in situ field
$pCO_2$ in both model training and cross-validation. A 10-fold cross validation was used during this
phase, where the training dataset was randomly partitioned into 10 equal-size subsamples. Of these
10 subsamples, 9 subsamples were used to train the model, and the remaining subsample was
retained to test the model. The cross-validation process was repeated 10 times, with each of the 10
subsamples used exactly once as the validation dataset. The advantage of such a validation method
is that all observations are used in both model training and model validation to include all the
scenarios in the training dataset, and each observation is used for validation only once. Standard
statistical measures, including root mean square error (RMSE, both absolute and relative),
coefficient of determination ($R^2$), mean bias (MB), mean ratio (MR), unbiased percent difference
(UPD), and mean relative difference (MRD) (Barnes & Hu, 2015), were used to quantify the
accuracy of the RFRE-estimated $pCO_2$.

Second, for the developed RFRE $pCO_2$ model, extensive independent validation was conducted
using the ten cruise datasets listed in Table 2. In each cruise-based independent validation,
satellite-derived surface $p$CO$_2$ along the cruise track from contemporaneous (± 24h) daily $p$CO$_2$ maps and from the $p$CO$_2$ composites of the cruise period were compared with the field-measured $p$CO$_2$, respectively. The 24h criteria was set based on the assumption that surface $p$CO$_2$ would not show significant variation (i.e., < 5 μatm) within 24h. In each comparison, statistics of RMSE, R$^2$, MB, MR, UPD, and MRD were calculated. Also, the field-measured surface $p$CO$_2$ data along the cruise track were color-coded (in the same way as the satellite $p$CO$_2$ map) and overlaid onto the $p$CO$_2$ composite to visually examine the consistency between the field-measured $p$CO$_2$ and the satellite-derived $p$CO$_2$.

2.3.4. Model sensitivity to errors in the input variables

The satellite input variables to the RFRE $p$CO$_2$ model (SST, SSS, Chl, and Kd) have inherent uncertainties. In order to understand the sensitivity of the RFRE model to such input errors, the uncertainties of each MODIS-derived variable were fed into the RFRE model. Surface $p$CO$_2$ derived from the same RFRE using error-free inputs and error-added inputs were then compared to determine the model’s sensitivity to input errors of each variable.

Errors in each of the satellite-derived environmental variables were quantified based on the published literature. Specifically, satellite SST has an uncertainty of ± 1 °C (Hu et al., 2009), SSS has an uncertainty of ± 1 for SSS > 30 (Chen & Hu, 2017), Chl shows an uncertainty of 5%–30% (Gregg and Casey, 2004; Bailey and Werdell, 2006; Melin et al., 2007) and 12–24% in waters of > 5m bottom depth (Cannizzaro et al., 2013), and Kd has an uncertainty of ~13% (Zhao et al., 2013). To be consistent with the published studies (i.e., Chen et al., 2016; Lohrenz et al., 2018), errors of ± 1 °C, ± 1, ± 20%, ± 20% were added in the MODIS-derived SST, SSS, Chl, and Kd, respectively, to understand the error propagation to the satellite-derived $p$CO$_2$. 

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3. Results

3.1. Model performance

Using the same training dataset (Table 1 and Fig. 1b), all the empirical approaches described in Section 2.3.2, including MLR, MNR, PCR, regression tree, regression ensembles, SVMs, and MPNN were trialed with the same model inputs of SST, SSS, Chl, and Kd (Eq. 1) (see Section 2.3.1 for the selection of these variables). Table 3 shows the model results of each approach. Clearly the RFRE showed the best performance. However, the three regression trees (simple tree, medium tree, and complex tree) and the MPNN (red in Table 3) also tended to be good models with only slightly worse performance (i.e., RMSE < 20 μatm), thus these models together with the RFRE were selected as potentially good models. To confirm whether the RFRE model is indeed the best one, based on the cruise dataset of GU1703_Leg2, independent validation was done for each of the potentially good models selected in Table 3. The cruise GU1703_Leg2 was used mainly because the $pCO_2$ data were collected around the Mississippi River delta, which was the most dynamic region in the GOM. Table 4 shows the comparison of these potentially good models. The RFRE did show the best performance over others. Validation using several other cruise datasets in Table 2 also showed that the RFRE had better performance than others, and the RFRE was therefore selected in this study.

Table 3. Model comparison of different empirical approaches including traditional empirical approaches (MLR, MNR, and PCR) and machine-learning based empirical approaches (regression tree, regression ensemble, SVMs, and MPNN). The non-shaded statistics were derived from model training, and the shaded statistics were derived from model validation. Models with an RMSE < 20 μatm are shown in red and these models were further compared through an independent validation (see text). The random forest based regression ensemble (RFRE) model is highlighted
in bold to contrast it as the best-performance model. All these models were developed using the same dataset (see Table 1) and the same input variables. Each of them was optimized in the tests, with the best results shown here. For models trained with regression tree, ensemble of regression trees, SVMs, a 10-fold cross validation was implemented.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Algorithm/Kernel function</th>
<th>RMSE (μatm)</th>
<th>R²</th>
<th>MB (μatm)</th>
<th>MR</th>
<th>UFD (%)</th>
<th>MRD (%)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLR</td>
<td></td>
<td>26.55 (3.59%)</td>
<td>0.53</td>
<td>0.00</td>
<td>1.00</td>
<td>4.23</td>
<td>6.63</td>
<td>8,776</td>
</tr>
<tr>
<td>MNB</td>
<td></td>
<td>25.10 (7.66%)</td>
<td>0.58</td>
<td>0.00</td>
<td>1.01</td>
<td>4.12</td>
<td>6.54</td>
<td>8,776</td>
</tr>
<tr>
<td>PCR</td>
<td></td>
<td>24.30 (7.25%)</td>
<td>0.66</td>
<td>0.00</td>
<td>1.01</td>
<td>4.20</td>
<td>6.53</td>
<td>8,776</td>
</tr>
<tr>
<td>Regression tree</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simple tree</td>
<td></td>
<td>14.70 (4.55%)</td>
<td>0.86</td>
<td>-0.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.70</td>
<td>17,551</td>
</tr>
<tr>
<td>Medium tree</td>
<td></td>
<td>16.14 (4.94%)</td>
<td>0.83</td>
<td>-0.05</td>
<td>1.00</td>
<td>0.09</td>
<td>0.21</td>
<td>17,551</td>
</tr>
<tr>
<td>Complex tree</td>
<td></td>
<td>11.70 (3.57%)</td>
<td>0.91</td>
<td>0.00</td>
<td>1.00</td>
<td>0.05</td>
<td>0.11</td>
<td>17,551</td>
</tr>
<tr>
<td>Ensemble of regression trees</td>
<td></td>
<td>24.37 (7.31%)</td>
<td>0.61</td>
<td>-0.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.39</td>
<td>17,551</td>
</tr>
<tr>
<td>Boosted tree</td>
<td></td>
<td>24.68 (8.42%)</td>
<td>0.60</td>
<td>-0.00</td>
<td>1.00</td>
<td>0.00</td>
<td>1.18</td>
<td>17,551</td>
</tr>
<tr>
<td>Random forest (bagged trees)</td>
<td></td>
<td>6.68 (2.84%)</td>
<td>0.87</td>
<td>-0.03</td>
<td>1.00</td>
<td>0.06</td>
<td>0.05</td>
<td>17,551</td>
</tr>
<tr>
<td>SVM</td>
<td>Linear</td>
<td>27.94 (9.73%)</td>
<td>0.48</td>
<td>0.41</td>
<td>1.01</td>
<td>0.45</td>
<td>0.85</td>
<td>17,551</td>
</tr>
<tr>
<td>SVM</td>
<td>Quadratic</td>
<td>24.46 (7.20%)</td>
<td>0.60</td>
<td>-1.18</td>
<td>1.00</td>
<td>-0.20</td>
<td>0.10</td>
<td>17,551</td>
</tr>
<tr>
<td>SVM</td>
<td>Cubic</td>
<td>24.57 (7.23%)</td>
<td>0.60</td>
<td>-1.18</td>
<td>1.00</td>
<td>-0.20</td>
<td>0.10</td>
<td>17,551</td>
</tr>
<tr>
<td>SVM</td>
<td>Fine Gaussian</td>
<td>27.38 (8.20%)</td>
<td>0.50</td>
<td>-1.34</td>
<td>0.97</td>
<td>-2.65</td>
<td>-2.54</td>
<td>17,551</td>
</tr>
<tr>
<td>SVM</td>
<td>Medium Gaussian</td>
<td>32.30 (9.73%)</td>
<td>0.61</td>
<td>-3.26</td>
<td>0.99</td>
<td>-1.48</td>
<td>-1.04</td>
<td>17,551</td>
</tr>
<tr>
<td>SVM</td>
<td>Coarse Gaussian</td>
<td>9.06 (2.91%)</td>
<td>0.95</td>
<td>-0.02</td>
<td>1.00</td>
<td>0.07</td>
<td>0.11</td>
<td>17,551</td>
</tr>
<tr>
<td>SVM</td>
<td>Levenberg-Marquardt and Bayesian</td>
<td>11.98 (3.50%)</td>
<td>0.90</td>
<td>0.13</td>
<td>1.00</td>
<td>0.08</td>
<td>0.14</td>
<td>5,850</td>
</tr>
</tbody>
</table>

Table 4. Model results comparison with RMSE < 20 μatm in Table 3 (red font) based on independent validation using the underway pCO₂ data collected on cruise “GU1703 Leg2” (see Table 2). This cruise data was used primary because it was collected around the Mississippi River delta, the most dynamic region in the GOM. The random forest based regression ensemble (RFRE) model is highlighted in red to contrast it as the best model performance. The RFRE model also showed better performance than others when evaluated using other datasets listed in Table 2. Note
that the difference in the number of data matchups (N) of each approach is due to the requirement of the spatial homogeneity in the matchup selection criteria (see Section 2.3.1).

<table>
<thead>
<tr>
<th>Approach</th>
<th>Algorithm/Kernel function</th>
<th>RMSE (µatm)</th>
<th>MB (µatm)</th>
<th>MR</th>
<th>UPD (%)</th>
<th>MRD (%)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression tree</td>
<td>Simple tree</td>
<td>51.80</td>
<td>-28.15</td>
<td>0.92</td>
<td>-8.79</td>
<td>-7.57</td>
<td>706</td>
</tr>
<tr>
<td></td>
<td>Medium tree</td>
<td>56.51 (15.42%)</td>
<td>-33.89</td>
<td>0.91</td>
<td>-10.50</td>
<td>-9.12</td>
<td>718</td>
</tr>
<tr>
<td></td>
<td>Complex tree</td>
<td>51.24 (14.72%)</td>
<td>-33.10</td>
<td>0.91</td>
<td>-10.04</td>
<td>-8.80</td>
<td>717</td>
</tr>
<tr>
<td>Ensemble of regression trees</td>
<td>Random forest (bagged trees)</td>
<td>11.88 (5.33%)</td>
<td>-1.22</td>
<td>1.00</td>
<td>-0.16</td>
<td>-0.01</td>
<td>725</td>
</tr>
<tr>
<td>SVM</td>
<td>Fine Gaussian</td>
<td>39.29 (8.77%)</td>
<td>-10.45</td>
<td>0.98</td>
<td>-2.28</td>
<td>-1.95</td>
<td>726</td>
</tr>
<tr>
<td>MPNN</td>
<td>Levenberg-Marquardt and Bayesian</td>
<td>37.07 (11.99%)</td>
<td>7.12</td>
<td>1.03</td>
<td>2.10</td>
<td>2.67</td>
<td>717</td>
</tr>
</tbody>
</table>

Fig. 2 shows the performance of the RFRE model in both model training and cross-validation, color coded by data density (the number of data points in each pCO₂ interval of 2 µatm). Clearly, most of the data pairs of field pCO₂ and modeled pCO₂ follow closely along the 1:1 line without apparent outliers (see the red and green color). Statistically, during the model training, the RFRE-modeled pCO₂ showed good agreement with the field-measured pCO₂ with a RMSE of 6.68 µatm (2.04%), R² of 0.97, MB of -0.03 µatm, MR of 1.00, UPD of 0.06%, and MRD of 0.08%. Similar statistics were also found in the 10-fold cross validation (RMSE = 9.09 µatm (2.79%), R² = 0.95, MB = -0.03 µatm, MR = 1.00, UPD = 0.07%, MRD = 0.12%).
Fig. 2. RFRE model performance in estimating surface \( pCO_2 \) in the GOM in both (a) model training, and (b) model validation, using the conjugate dataset described in Table 1 and Fig. 1b. The data pairs are color coded by data density, which represents the number of data points at each \( pCO_2 \) interval of 2 \( \mu atm \).

3.2. Independent validation under different scenarios

To conduct independent model validation, in addition to the cross-validation in the model development, the developed RFRE \( pCO_2 \) model was further examined to quantify its predictability in estimating surface \( pCO_2 \) from satellites under different scenarios in the GOM, using 10 cruise datasets collected over the GOM in different months (Table 2). For each cruise, the field-measured surface \( pCO_2 \) dataset was independent from other cruises, and none of these 10 cruise datasets were used in the model training above.

Fig. 3 shows the results based on the underway \( pCO_2 \) data collected from cruise GU1703_Leg2 between July 22 and August 05, 2017. This cruise mainly covered the Mississippi Delta and its offshore area (Fig.3a). The field-measured \( pCO_2 \) showed dynamic variation with very low \( pCO_2 \) values around the Mississippi river mouth and in the river plume, and relatively high \( pCO_2 \) in the
offshore waters. Fig. 3b shows the comparison between field-measured $p$CO$_2$ and contemporaneous satellite-derived $p$CO$_2$. Clearly, the spatial and temporal variations of the field-measured $p$CO$_2$ along the cruise track were well captured in the contemporaneous satellite-derived $p$CO$_2$, with a RMSE of 18.88 μatm (5.53%), MB of -1.22 μatm, MR of 1.00, UPD of -0.16%, and MRD of -0.01%. Furthermore, a 15-day MODIS $p$CO$_2$ composite map (Fig. 3a) covering the cruise period also showed agreement with the field-measured $p$CO$_2$ with low $p$CO$_2$ values nearshore and high $p$CO$_2$ values offshore, although the statistics is a bit worse due to the larger time difference (RMSE = 37.65 μatm (16.13%), MB = -1.22 μatm, MR = 1.01, UPD = 0.31%, and MRD = 1.31%, N = 5,331).

**Fig. 3.** RFRE surface $p$CO$_2$ model performance in the Mississippi River delta and offshore regions, evaluated with underway $p$CO$_2$ data collected from cruise GU1703_Leg2 (Table 2). The underway data was not used in the model training. (a) MODIS surface $p$CO$_2$ composite map for the cruise period (Jul. 22–Aug. 05, 2017), with field-measured $p$CO$_2$ along the cruise track overlaid and color coded in the same way as the MODIS image; (b) Comparison between field-measured $p$CO$_2$ and contemporaneous (± 24h) MODIS-derived $p$CO$_2$; (c) Comparison between field-measured $p$CO$_2$ and MODIS-derived $p$CO$_2$ extracted from the MODIS composite map for the cruise period (a).
The red dots with values of 0 on the X-axis in (b) and (c) indicate that there are no contemporaneous MODIS-derived $\rho$CO$_2$ due to various non-optimal satellite observing conditions, and ‘P1’ and ‘P2’ in each panel represent the start and end of the cruise, respectively.

Fig. 4 is the validation result based on one cruise dataset (GU1606_Leg1) collected in the northwestern GOM as well as the Mississippi delta between September 03 and 15, 2016. Although there were no strong river discharges during this cruise period, low field-measured $\rho$CO$_2$ values were found in the nearshore region along the Louisiana and Texas coast with distinct increases towards offshore waters (Fig. 4a). Similar to those found from cruise GU1703_Leg2 in Fig. 3, MODIS-estimated surface $\rho$CO$_2$ mimicked the variation patterns of the field-measured $\rho$CO$_2$ (Fig. 4b), with RMSE of 26.10 μatm (7.57%), MB of -6.44 μatm, MR of 0.99, UPD of 1.36% and MRD of -1.10%. This agreement was also evident in the comparison between field-measured $\rho$CO$_2$ and satellite-derived $\rho$CO$_2$ extracted from a 13-day composite map covering the cruise period (Fig. 4a & 4c), with lower $\rho$CO$_2$ in nearshore waters than in offshore waters.

Fig. 4. Same as Fig. 3, but the RFRE surface $\rho$CO$_2$ model performance was evaluated along the Louisiana and Texas coast with underway $\rho$CO$_2$ data collected from cruise GU1606_Leg1 (Table

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2). The underway data was not used in the model training. (a) MODIS surface $pCO_2$ composite map for the cruise period (Sep. 03–15, 2016), with field-measured $pCO_2$ overlaid and color coded along the cruise track; (b) Comparison between field-measured $pCO_2$ and contemporaneous ($\pm$ 24h) MODIS-derived $pCO_2$; (c) Comparison between field-measured $pCO_2$ and MODIS-derived $pCO_2$ extracted from the MODIS composite map for the cruise period (a). The red dots with values of 0 on the X-axis in (b) and (c) indicate that there are no contemporaneous MODIS-derived $pCO_2$ due to various non-optimal satellite observing conditions, and 'P1' and 'P2' in each panel represent the start and end of the cruise, respectively.

In addition to cruise GU1606_Leg1, two other cruises (GU1704_Leg2 and GU1609_Leg2, see supplemental file) also covered a similar region (i.e., northwestern GOM and the Mississippi delta). In Fig. S1a, surface $pCO_2$ was measured on cruise GU1704_Leg2 in late September (17-31) 2017, with cruise track almost exactly the same as cruise GU1606_Leg1 (Fig. 4). Similar to cruise GU1606_Leg1, the spatial variation in surface $pCO_2$ showed the same pattern with low $pCO_2$ values inshore and high values offshore, but with less spatial contrast in surface $pCO_2$ possibly due to reduced river discharge and land runoff. Again, agreement with similar statistics were found between the field-measured $pCO_2$ and the satellite-derived $pCO_2$ extracted either from the contemporaneous ($\pm$ 24h) $pCO_2$ maps or from the 14-day $pCO_2$ composite covering the cruise period. Different from cruise GU1606_Leg1 and GU1704_Leg2, results in Fig. S2 were based on a winter cruise (GU1609_Leg2) between November 03 and 14, 2016, which collected surface $pCO_2$ from the Mississippi delta and offshore waters in the northwestern GOM. The surface $pCO_2$ in winter showed lower values than in summer, with much reduced spatial variation along the cruise track. The comparison along the cruise track also showed agreement between MODIS retrievals and field measurements with similar statistics.
Fig. 5 is the results based on flow-through $p$CO$_2$ data collected from cruise GU1703_Lecl in the eastern GOM waters between July 02 and 17, 2017. Field-measured $p$CO$_2$ from this cruise showed large difference between the southern and northern GOM waters (Fig. 5a). In the southern waters, surface $p$CO$_2$ was around 420 μatm with little spatial variation, while in the northern part, under the influence of the Mississippi River discharge, low surface $p$CO$_2$ with dynamic variation (250-380 μatm) was found. Additionally, this cruise also captured the low $p$CO$_2$ (~380 μatm) characteristics of the Mississippi river plume relative to the surrounding waters. Statistically, the contemporaneous (+24h) satellite-derived $p$CO$_2$ agreed with the field-measured $p$CO$_2$ with RMSE of 21.90 μatm (5.40%), MB of -12.96 μatm, MR of 0.97, UPD of -3.31%, and MRD of -3.15% (Fig. 5b). Similar model performance was also found in the comparison between field-measured $p$CO$_2$ and satellite-derived $p$CO$_2$ from the 16-day $p$CO$_2$ composite map of the cruise period (RMSE = 20.62 μatm (5.13%), MB = -12.66 μatm, MR = 0.97, UPD = -3.06%, and MRD = -2.92%, Fig. 5c). Specifically, the low $p$CO$_2$ values and their dynamic variation in the northern coastal waters of the GOM and the low $p$CO$_2$ features in the river plume (which were not captured (or not captured completely) in Fig. 5b due to the lack of contemporaneous (+24h) satellite measurements, were well revealed in Fig. 5a & 5c. Satellite-derived surface $p$CO$_2$ in both Figs. 5b & 5c showed underestimation as compared to the field-measured $p$CO$_2$, and this could be caused by the time difference between field and satellite measurements. As mentioned in Section 2.3.3, the 24h time window was selected by assuming insignificant surface $p$CO$_2$ variations within the time window. However, in reality, waters in the river-dominated coastal region and along the edge of the river plume could vary in finer timescale (i.e., < 24h), in which case the satellite-derived $p$CO$_2$ did not correspond to the same water masses as measured in the field.
**Fig. 5.** RFRE surface $p$CO$_2$ model performance in the eastern GOM, evaluated with underway $p$CO$_2$ data collected from cruise GU1703_Leg1 (Table 2). The underway data was not used in the model training. (a) MODIS surface $p$CO$_2$ composite map for the cruise period (Jul. 02–17, 2017), with field-measured $p$CO$_2$ overlaid and color coded along the cruise track; (b) Comparison between field-measured $p$CO$_2$ and contemporaneous (± 24h) MODIS-derived $p$CO$_2$; (c) Comparison between field-measured $p$CO$_2$ and MODIS-derived $p$CO$_2$ extracted from the MODIS composite map for the cruise period (a). The red dots with values of 0 on the X-axis in (b) and (c) indicate that there are no contemporaneous MODIS-derived $p$CO$_2$ due to various non-optimal satellite observing conditions, and ‘P1’ and ‘P2’ in each panel represent the start and end of the cruise, respectively.

In addition to cruise GU1703_Leg1, three other cruises (GU1701_Transit_Leg, GU1705_Transit_Leg, and GU1706_Transit_Leg) in Table 2 also collected flow-through $p$CO$_2$ from the eastern GOM. These data were collected in different months which represented different seasonal characteristics of surface $p$CO$_2$ in the GOM. The results, based on each of these three cruise datasets, are shown in Figs. S3-S5, respectively. In Fig. S3, cruise GU1701_Transit_Leg was conducted between May 05 and 08, 2017. In contrast to cruise GU1703_Leg1 data in Fig. 5,
there was no obvious Mississippi River plume during this cruise. Surface $p$CO$_2$ showed lower but similar spatial variation from the southern to northern GOM waters, and such spatial variations were well captured in both the contemporaneous satellite-derived $p$CO$_2$ (RMSE = 10.78 μatm (3.04%), MB = 4.97 μatm, MR = 1.01, UPD = 1.39%, and MRD = 1.43%) and the satellite $p$CO$_2$ composite map covering the cruise period along the cruise track (RMSE = 10.20 μatm (2.81%), MB = 2.91 μatm, MR = 1.01, UPD = 0.81%, and MRD = 0.85%). The cruise surveys used in Figs. S4 & S5 followed almost the same cruise tracks as shown in Fig. S3; one collected $p$CO$_2$ in October 2017 (Fig. S4) and the other in November 2017 (Fig. S5). Again, there was no significant Mississippi River plume and little spatial variation in the field-measured $p$CO$_2$ during these two cruise periods. In both cases, the satellite-derived $p$CO$_2$ (both contemporaneous, (± 24h) satellite $p$CO$_2$, and $p$CO$_2$ from satellite composite of the cruise period) showed high consistency with the field-measured $p$CO$_2$, with similar statistics as shown in Fig. S3.

Results in Fig. 6 are based on flow-through $p$CO$_2$ data collected from cruise GU0902_leg2 between April 21 and May 06, 2009. This cruise covered the western GOM, mainly the southwestern and the northern offshore waters. From the spatial distribution of surface $p$CO$_2$ along the cruise track (Fig. 6a) and its time series distribution (black dots in Figs. 6b & 6c), surface $p$CO$_2$ did not show much spatial variation (360–400 μatm). For the contemporaneous (± 24h) satellite-derived $p$CO$_2$, it showed almost perfect agreement with the field-measured $p$CO$_2$ with a RMSE of 4.39 μatm (1.14%), MB of -0.80 μatm and MR of 1.00, UPD of -0.21% and MRD of -0.21%. Similar statistics were also derived for $p$CO$_2$ extracted from satellite $p$CO$_2$ composite map covering the cruise period.
Fig. 6. RFRE $p$CO$_2$ model performance in quantifying surface $p$CO$_2$ in the southern GOM, evaluated with underway $p$CO$_2$ data collected from cruise GU0902_leg2 (Table 2). The underway data was not used for model training. (a) MODIS surface $p$CO$_2$ composite map for the cruise period (Apr. 21–May 06, 2009), with field-measured $p$CO$_2$ overlaid and color coded along the cruise track; (b) Comparison between field-measured $p$CO$_2$ and contemporaneous ($\pm$ 24h) MODIS-derived $p$CO$_2$; (c) Comparison between field-measured $p$CO$_2$ and MODIS-derived $p$CO$_2$ extracted from the MODIS composite map for the cruise period (a). The red dots with values of 0 on the X-axis in (b) and (c) indicate that there are no contemporaneous MODIS-derived $p$CO$_2$ due to various non-optimal satellite observing conditions, and ‘P1’ and ‘P2’ in each panel represent the start and end of the cruise, respectively.

Similar to GU0902_leg2 in Fig. 6, cruise GU0902_leg1 covered the other part of the western GOM between Apr. 7 and 16, 2009, with surface $p$CO$_2$ between ~350 µatm and ~410 µatm. The validation results from cruise GU0902_leg1 are shown in Fig. S6. The spatial and temporal variations in surface $p$CO$_2$ were well captured in both the contemporaneous satellite-derived $p$CO$_2$ (RMSE = 8.89 µatm (2.31%), MB = -4.42 µatm, MR = 0.99, UPD = -1.17%, and MRD = -1.15%)
and the satellite-derived $p$CO$_2$ composite covering the cruise period (RMSE = 13.31 μatm (3.39%), MB = -6.63 μatm, MR = 0.98, UPD = -1.74%, and MRD = -1.68%).

3.3. Model sensitivity

Fig. 7 shows the sensitivity of the RFRE $p$CO$_2$ model to the input errors of each satellite variable (SST, SSS, Chl, and Kd). A visual interpretation of Fig. 7 indicates that the model is more sensitive to input errors in SST and SSS than in Chl and Kd, and the errors introduced in each case were close to or within the uncertainties of the model itself.

**Fig. 7.** RFRE $p$CO$_2$ model sensitivity to changes in the input SST, SSS, Chl, and Kd, based on the dataset used to develop the $p$CO$_2$ model in Table 1 and Fig. 1b. The data pairs are color coded by data density, which represents the number of data points at each $p$CO$_2$ interval of 2 μatm. Results show that the $p$CO$_2$ model is tolerant to at least ±1 °C noise in the input SST, ±1 noise in the input SSS, ±20% noise in the input Chl, and ±20% noise in the input Kd, and the $p$CO$_2$ model is more tolerant to noise in Chl and Kd than in SST and SSS.

Statistically, with +1 °C errors added (Fig. 7a), the RFRE model showed slight overestimation, with RMSE of 10.80 μatm (3.46%), $R^2$ of 0.91, MB of 2.17 μatm, MR of 1.01, UPD of 1.22% and
MRD of 1.27%. With -1 °C errors added (Fig. 7a), the RFRE model showed slight underestimation in surface $pCO_2$, with RMSE of 10.13 µatm (2.68%), $R^2$ of 0.92, MB of 0.99, UPD of 0.81%, and MRD of 0.77%. These results suggest that the RFRE $pCO_2$ model responded to SST errors in a positive way (an increase in SST would lead to an increase in surface $pCO_2$ and vice versa), but in both cases the model was insensitive to SST errors considering the model uncertainties described in Section 3.1.

The sensitivity of the RFRE model to SSS was similar to SST, and in both cases of +1 and -1 errors added into SSS, the response of the RFRE did not show great difference comparing to the originally-modeled surface $pCO_2$. Specifically, with +1 errors added in SSS, the RFRE model showed slight overestimation in surface $pCO_2$ (RMSE = 12.57 µatm (3.93%), $R^2 = 0.88$, MB = 2.40 µatm, MR = 1.01, UPD = 0.77%, MRD = 0.84%). With -1 errors added into SSS, the RFRE model still showed little overestimation (RMSE = 12.06 µatm (3.19%), $R^2 = 0.89$, MB = 0.18 µatm, MR = 1.00, UPD = 0.07%, MRD = 0.12%). However, clearly for $pCO_2 > 450$ µatm, the newly-predicted $pCO_2$ was obviously underestimated.

Unlike SST and SSS, the RFRE $pCO_2$ model showed little sensitivity to Chl, and the uncertainties introduced in the estimated $pCO_2$ by adding ± 20% errors in Chl was < 7 µatm (Figs. 7e & 7f). Specifically, with 20% errors added, the newly-predicted $pCO_2$ was slightly underestimated (RMSE = 5.28 µatm (1.46%), $R^2 = 0.98$, MB = -0.13 µatm, MR = 1.00, UPD = -0.02%, and MRD = -0.01 %). With -20% errors added, the newly-predicted $pCO_2$ was slightly overestimated (RMSE = 6.07 µatm (1.75%), $R^2 = 0.97$, MB = 0.51 µatm, MR = 1.00, UPD = 0.21%, and MRD = 0.23%).

Similar to Chl, the RFRE model also showed little sensitivity to Kd. In both cases of +20% and -20% errors added in Kd, the newly-predicted $pCO_2$ did not show much difference from the originally-predicted $pCO_2$. With +20% errors added in Kd, the model showed a RMSE of 6.27
μatm (1.95%), R^2 of 0.97, MB of 0.75 μatm, MR of 1.00, UPD of 0.26%, and MRD of 0.28%.

With ~20% errors added in Kd, the model showed similar statistics (RMSE = 7.70 μatm (2.07%), R^2 = 0.96, MB = 0.15 μatm, MR = 1.00, UPD = 0.12%, and MRD = 0.14%).

Overall, the RFRE pCO₂ model did not show high sensitivity to the errors in each input satellite variable including SST, SSS, Chl, and Kd. With errors added in each variable, the uncertainties induced in the new-predicted pCO₂ were all close to or within the uncertainties of the model itself. Since satellite data of each variable were used directly in the model development, such uncertainties were implicitly included in the developed model, and these uncertainties would be cancelled to a large extent when applying the RFRE model to the same satellite data products. The insensitivities of the RFRE pCO₂ model to Chl and Kd are further discussed in Section 4.1.

3.4. Seasonal and interannual variations of surface pCO₂

Fig. 8 shows the monthly climatological maps of surface pCO₂ of the GOM based on the MODIS data between July 2002 and December 2017. Fig. 9 shows the area-averaged monthly time series of surface pCO₂ in the GOM. Fig. 10 shows the interannual variations of surface pCO₂ monthly anomalies (i.e., monthly mean minus monthly climatology) in the study period. Generally, on seasonal timescale, distinct seasonal pCO₂ patterns can be seen in both Fig. 8 and Fig. 9, with high pCO₂ in summer and lower pCO₂ in winter; on decadal timescale, there is small interannual variability (e.g., within ±10 μatm) in surface pCO₂ over the GOM except in the northern coastal waters (e.g., Box 1, Box 5, where anomalies are within ±30 μatm).
**Fig. 8.** Monthly climatology of surface $p$CO$_2$ in the GOM, derived from MODIS using the RFRE $p$CO$_2$ model for the period between July 2002 and December 2017. These maps are valid only for the GOM waters as described in Fig. 1.

In terms of spatial distribution, surface $p$CO$_2$ (Fig. 8) was characterized by relatively low $p$CO$_2$ values (300-350 μatm) along the northern GOM coasts (especially the Louisiana coast) accompanied with low SSS in most months. This result is quite different from the results shown in Xue et al. (2013), which found relatively high $p$CO$_2$ values ($\geq 500$ μatm) in the Louisiana coastal waters. The difference between the findings of this study and those of Xue et al. (2013) is possibly
due to their overestimation in surface \( pCO_2 \) on the Louisiana shelf. In Lohrenz et al. (2018), similar low surface \( pCO_2 \) was also found in this area, but with relatively higher model uncertainties (RMSE > 30 \( \mu \)atm). Indeed, from the spatial distribution of field-measured \( pCO_2 \) data of the GOM shown in Fig. 1a, low surface \( pCO_2 \) values (< 350 \( \mu \)atm) were found along the Louisiana coast all the year round. There were some extremely high \( pCO_2 \) (> 1000 \( \mu \)atm) values collected in the very nearshore regions, but these high \( pCO_2 \) values were located in the estuaries. Due to the sharp changes in water properties (i.e., SST, SSS, TA, and DIC), there was a sharp decrease in surface \( pCO_2 \) from estuaries to the adjacent coastal waters. Additionally, fewer low \( pCO_2 \) waters were found between September and November due to the low river discharge (~5,000-10,000 m\(^3\)/sec) during this period. On the WFS, surface \( pCO_2 \) showed little spatial variation in each month, with low surface \( pCO_2 \) (~350 \( \mu \)atm) in winter and high \( pCO_2 \) (~400 \( \mu \)atm) in summer. This result agreed well with the results shown in Chen et al. (2016), except that relatively high \( pCO_2 \) (500-550 \( \mu \)atm) was estimated along the nearshore waters of Florida between May and August in Chen et al. (2016) but not here. In fact, water properties on the WFS are mainly controlled by oceanic currents and winds (e.g., wind-driven coastal currents, Loop Current) with winter conditions favoring upwelling (Liu & Weisberg, 2005 & 2012). The spatial distribution of field-measured \( pCO_2 \) on the WFS in Fig. 1a also showed little spatial gradient from inshore to offshore waters. Due to the high temperature of the Loop Current, relatively high \( pCO_2 \) was found in these waters during wintertime. In winter and early spring, the southern GOM showed relatively higher \( pCO_2 \) values than the northern GOM, mainly due to its lower latitude (thus relatively higher SST). Between May and October, the GOM waters become near isothermal with little spatial gradient in SST, and the surface \( pCO_2 \) in the GOM-wide regions (except the northern coastal regions) showed almost homogeneous distribution with slight spatial variation in each month.
Fig. 9. Monthly surface $p$CO$_2$ time series in the whole GOM and in the five sub-regions annotated in Fig. 1a. Errorbars in each time series plot represent the standard deviations of the monthly mean of surface $p$CO$_2$ in each region. Box 1 is near the Mississippi River delta, Box 2 is on the West Florida Shelf, Box 3 is near the Loop Current, Box 4 is in the western GOM open waters, and Box 5 presents the “dead zone” along the Louisiana coast.

In terms of seasonal variations, monthly time series of surface $p$CO$_2$ based on $p$CO$_2$ maps between July 2002 and December 2017 of the entire GOM (black line in Fig. 9) showed high $p$CO$_2$ values (~405 μatm) in summer and low $p$CO$_2$ (~355 μatm) in winter with a standard deviation of ~ ± 17 μatm on average. Xue et al. (2013) also found comparable seasonal variation in the Gulf-wide averaged $p$CO$_2$, but with a relatively higher standard deviation (≥ 50 μatm). Similarly, in Fig 9, $p$CO$_2$ in the selected sub-regions of Box 2, Box 3, and Box 4, representing the WFS, Loop Current and southwestern GOM, respectively, also showed similar temporal variation patterns although with some differences in magnitude. For example, $p$CO$_2$ in the sub-region of Loop Current waters (Box 3), was relatively higher than $p$CO$_2$ in the sub-regions of WFS and southwestern GOM in
winter. Such difference is mainly caused by the warmer characteristics (thus higher SST) of the Loop Current. The seasonal variation of the $p$CO$_2$ time series in the northern GOM was quite different from that of the regions mentioned above. In the Mississippi River delta represented by Box 1, $p$CO$_2$ showed lower values (−290-380 μatm, ± 23 μatm) than most GOM waters (Fig. 8) in all seasons. In addition to the general variation patterns of high to low from summer to winter, finer time scale variations were found in summertime, with a $p$CO$_2$ decrease in July or August in most of the years. This decrease in surface $p$CO$_2$ was mainly attributed to the phytoplankton blooms, induced by the nutrient-rich freshwater inputs through the MARS river discharge in the spring (April to June). The depletion of nutrients restricted the continuous biological uptake of surface water CO$_2$ and kept the surface $p$CO$_2$ from decreasing further (Huang et al., 2012 & 2015; Guo et al., 2012). The resulted richness in oxygen and organic matter promoted the growth of bacteria, which decomposed the organic matters (either from terrestrial river runoff or generated from biological activities) in the water column and released CO$_2$ back to seawater (Gardner et al., 1994; Cai et al., 2011; Cai, 2011). Therefore, surface $p$CO$_2$ tended to increase in late summer and fall, and then decreased as the water became colder. Similar to the case shown in the Mississippi delta, the representative sub-region of the Louisiana coast (Box 5) showed a similar variation pattern in surface $p$CO$_2$ but with larger seasonal magnitude (−280-420 μatm, ± 17 μatm). The region is the famous “dead zone” in the GOM (Keul et al., 2010). In summertime, the eutrophication and excessive utilization of oxygen cause hypoxia in this area (Rabalais et al., 2002; Laurent et al., 2017), thus more CO$_2$ is released back to the seawater and, therefore, surface $p$CO$_2$ tends to be higher as compared to the Mississippi delta. The finer time scale variation in surface $p$CO$_2$ on the Louisiana Shelf (demonstrated by the two sub-regions around the Mississippi river delta (Box 1) and the Hypoxia zone off the Louisiana coast (Box 5)), was also found by Lohrenz
et al. (2018) but with higher standard deviation and variation, but was not found by Xue et al. (2013).

![Graphs showing interannual variability of modeled pCO2](image)

**Fig. 10.** Interannual variability of the modeled pCO2 in the entire GOM (a) and the five sub-regions (b-f) over the study period of 2002-2017. Monthly pCO2 anomalies on the Y-axis in each panel were derived by subtracting the monthly climatology from the monthly mean. In panels b & f, a secondary Y-axis of SSS was added to show the corresponding interannual SSS anomalies in the sub-regions of Mississippi delta (Box 1) and “dead zone” (Box 5). Box 1 is near the Mississippi...
River delta, Box 2 is on the West Florida Shelf, Box 3 is near the Loop Current, Box 4 is in the western GOM open waters, and Box 5 presents the “dead zone” along the Louisiana coast.

In terms of interannual variation, overall, there is indistinguishable decadal trend in the monthly $pCO_2$ anomalies (Fig. 10). Over the river-dominated coastal region in the northern GOM, surface $pCO_2$ showed relatively larger interannual variability than in other GOM waters. Over the entire GOM (Fig. 10a), the interannual monthly $pCO_2$ anomalies showed little variation of within ±5 μatm, with negative (positive) values in most months before (after) the year of 2012. In the Mississippi delta (Box 1) and “dead zone” area (Box 5), due to the complexity and dynamics of the biogeochemical processes in these regions, $pCO_2$ showed larger anomalies between -30 and 30 μatm. For these two regions, it is found that the anomalies in SSS showed similar variation to surface $pCO_2$ variation, indicating that SSS may control the interannual variations of surface $pCO_2$ in these regions. Different from the northern coastal waters, $pCO_2$ in other GOM waters (WFS, Loop Current, Southwestern GOM waters) represented by Boxes 2 – 4 (Figs. 10c-10e) showed similar but slightly larger anomalies (within ±10 μatm) comparing to that of the entire GOM (Fig. 10a). Similar to the interannual variations of $pCO_2$ over the entire GOM in Fig. 10a, in these regions, the anomalies in surface $pCO_2$ tended to be positive (close and above zero) over the years since 2012, while the increasing trend is still indistinguishable considering the overall variations of the $pCO_2$ anomalies in the study period. Generally, surface $pCO_2$ in the GOM tended to increase but the increasing trend is not well captured in our data. In addition, the decadal variation here could be part of the long-term trend (≥30 years), or part of the decadal timescale fluctuation (Thomas et al., 2008; Gruber, 2009; Mckinley et al., 2011; Fay & Mckinley, 2013). Yet it is impossible to differentiate these two scenarios using our data. In the study of Landschützer et al. (2013), both positive and negative trends were found in surface $pCO_2$ of the GOM over the period
of 1998-2007, leading to no apparent overall trend over the entire GOM. We also examined the interannual variations of the four satellite-derived environmental variables (SST, SSS, Chl, and Kd), and found no decadal trend. Because these variables were used to model surface $pCO_2$, it is no surprise to see indistinguishable decadal trend in the modeled surface $pCO_2$ over the GOM.

4. Discussion

4.1. Which environmental variables to use in the RFRE

In this study, we used four environmental variables, including SST, SSS, Chl, and Kd, to model surface $pCO_2$ in the GOM. These variables were selected based on our previous studies and other studies in the published literature. In Chen et al. (2016 & 2017), all these variables were proven to be important and efficient in modeling surface $pCO_2$ in the GOM, although other empirical approaches other than the RFRE were used. Indeed, SST and SSS are commonly used to capture the effects of thermodynamics and ocean mixing, and Chl and Kd are used to implicitly quantify the biological effect on surface $pCO_2$. Because there is no known function between each predictive variable and surface $pCO_2$, a machine-learning based RFRE approach was used to model the unknown complex relationships between these predictive variables and surface $pCO_2$. The RFRE approach was selected after extensive comparison with other empirical approaches. The RFRE-based $pCO_2$ model, after modeling training using extensive datasets, showed excellent performance in estimating surface $pCO_2$ with little uncertainties (RMSE < 10 μatm) for a large dynamic range.

In section 3.3, a model sensitivity analysis showed that the response of the RFRE model to the added errors in each model input variable was close to or within the model uncertainties, with relatively higher sensitivity to SST and SSS than to Chl and Kd. These results suggest that the
model is insensitive to small errors (±20%) in the satellite data products. Such insensitivity may raise the question of whether true changes in surface $pCO_2$ can be captured by the model. For example, while an increasing rate of 1.5 μatm per year has been reported in atmospheric $pCO_2$ (Landschützer et al., 2013), the model did not show any long-term trend in surface $pCO_2$. Then two fundamental questions arise: 1) because the model showed little sensitivity to small errors in Chl and Kd, why are they still used in the RFRE model? 2) Can the model capture the long-term trend of surface $pCO_2$ in response to increased atmospheric $pCO_2$?

Indeed, although the RFRE model is insensitive to small errors in the input Chl and Kd, it does not mean that Chl and Kd are not important in modeling surface $pCO_2$ for two reasons. One, both Chl and Kd were scaled logarithmically before being used in the model in order to account for their log-normality in their large-scale distributions (Campbell, 1995). Then, their dynamic ranges were “dampened” after log transformation, and same occurred with the input errors. For example a 20% error is transformed to an error of 0.08 ($=\log(1.2)$). In comparison, the variations of Chl and Kd in $\log_{10}$ scale (and their errors) were much smaller than those in SST (13.48–33.28 °C, with 1 °C error) and SSS (10.90–38.34, with 1.0 error). This explains why the RFRE model was more sensitive to SST and SSS changes than to Chl and Kd changes. On the other hand, both Chl and Kd carry information (implicitly) of biological activities, thus cannot be ignored in the model. In fact, Chl and Kd showed strong negative correlations (Figs. 11a & 11b) to surface $pCO_2$ in the northern GOM. In coastal waters, surface $pCO_2$ showed strong correlation with Chl, Kd, and SSS (Fig. 10a, 10b, & 10d), indicating that the biological activities and freshwater inputs are the dominant factors in controlling surface $pCO_2$ in these waters. On the other hand, in the GOM oligotrophic waters and coastal areas with little freshwater inputs, SST appeared to be the dominant
factor in controlling surface $p$CO$_2$ (Fig. 10c). Therefore, it is necessary to include all four environmental variables in the RFRE $p$CO$_2$ model.

![Correlation Maps](image)

**Fig. 11.** Maps of correlation coefficients at 1-km resolution between Chl (a), Kd (b), SST (c), SSS (d), and surface $p$CO$_2$, respectively. These correlations were derived from the interannual monthly anomalies.

Then, because atmospheric $p$CO$_2$ was not used in the model explicitly, if changes in atmospheric $p$CO$_2$ cannot be captured implicitly in one or more of the four variables (SST, SSS, Chl, and Kd), it would be impossible for the RFRE $p$CO$_2$ model to capture the changes in the atmospheric $p$CO$_2$ (~1.5 µatm per year, Landschützer et al. 2013), mainly caused by the human activities (e.g., fossil
fuel burning). It is therefore desirable to include atmospheric \( p\text{CO}_2 \) in future modeling efforts in order to better detecting decadal trends in surface \( p\text{CO}_2 \) under anthropogenic forcing. Nevertheless, the work here introduces an empirical \( p\text{CO}_2 \) approach that is applicable to a large oceanic region (e.g., GOM) with different dominant oceanic processes, making it possible to better understand the spatial and seasonal variations in surface \( p\text{CO}_2 \) of the entire GOM, as compared to ship-based measurements.

4.2. Implication for general applications over other regions

The results shown in Section 3 demonstrate that the RFRE-based \( p\text{CO}_2 \) model developed for the entire GOM can be well applied to different regions of the GOM. This is true in both river-dominated and current-dominated regions, both with low uncertainties (RMSE < 10 \( \mu \text{atm} \)). One question is whether this RFRE approach (not the model itself) can be applied to other oceanic regions. To examine its general applicability to other oceanic waters, we tested this RFRE approach on the G. Maine which was selected for two main reasons: First, the G. Maine shows great contrast to GOM with relatively small riverine discharge (i.e., <1000 m\(^3\)/sec from the largest river – Saint John River) but strong semi-diurnal tidal mixing, as well as wide-open interactions with the North Atlantic waters (i.e., Gulf Stream, Labrador Current). Second, it is located at a relatively high latitude (41.7–46 °N, 71–64 °W), and rapid warming is found with an increasing rate of 0.23 °C per year in SST since 2004 (Pershing et al., 2015). In addition to the resulting ecological impact (i.e., decrease in fisheries), this warming would have direct impact on air-sea \( \text{CO}_2 \) flux and long-term carbon cycling. However, the published study of satellite mapping of surface \( p\text{CO}_2 \) over this region shows very large uncertainties (i.e. RMSE ~ 35 \( \mu \text{atm} \)) (Signorini et al., 2013). Therefore, it would be significant if the RFRE approach could work in the G. Maine with a much lower uncertainty.
Surface $p$CO$_2$ data collected in the G. Maine between 2002 and 2016 (Fig. 12a) were compiled from the global surface $p$CO$_2$ database (LDEO) (version 2015, Takahashi et al., 2016b) and matched with the MODIS data products (including SST, Chl, and Kd) using the criteria described in Section 2.2.1. Here a time window of $\pm$ 3h was used to account for the semi-diurnal tidal characteristics in the G. Maine. The conjugate $p$CO$_2$ dataset (Fig. 12b) showed dynamic variation range in each variable (field-measured $p$CO$_2$: 202–558 $\mu$atm; satellite SST: 1.6–25 $^\circ$C; field-measured SSS: 25–34 (note there is no satellite SSS available for the G. Maine at 1 km resolution); satellite Chl: 0.26–19.9 mg m$^{-3}$; and satellite Kd: 0.05–0.68 m$^{-1}$).

![Fig. 12. Spatial distributions of the surface $p$CO$_2$ measurements in the Gulf of Maine along the cruise tracks. (a) Cruise tracks from all data between 2002 and 2016 in all seasons (N=482,384); (b) Cruise tracks from the same data but with co-located and contemporaneous ($\pm$ 3h) satellite Chl, Kd and SST (N=4,559).](image)

Before locally tuning a RFRE $p$CO$_2$ model for the G. Maine, we first tested the locally parameterized MLR model proposed by Signorini et al. (2013) for the G. Maine. Similar to its original results, the model was found to yield a RMSE of $\sim$42 $\mu$atm. Then we tested the RFRE
model (Fig. 2), which was parameterized for the GOM, to the G. Maine. Poor model performance was obtained (RMSE = 89.6 μatm), suggesting that the effects of the input variables to surface $pCO_2$ may work differently in the G. Maine than from the GOM. Because the RFRE-based $pCO_2$ model is empirical and is locally-trained, it can only be applied to similar environments. Whereas the GOM-trained RFRE model uses satellite SSS as an input to account for the effect of freshwater mixing in the G. Maine, because there is no relevant satellite SSS available at 1 km spatial resolution, it is not practical to include SSS as a predictor. Furthermore, considering the relatively small river discharge in this area and the poor correlation (R=0.07) between SSS and surface $pCO_2$, SSS may not necessarily be an effective predictor in surface $pCO_2$ in the G. Maine. Therefore, in the G. Maine, the only satellite variables used as predictive variables to model surface $pCO_2$ were SST, Chl, and Kd as well as Julian day. Similar to the GOM, using the same training dataset (Fig. 10b) and same input variables (SST, Chl, Kd, and Julian day), all the empirical approaches described in Section 2.3.2 were also tested in the G. Maine. The RFRE approach proved to have the best model performance in the G. Maine as well.

![Graphs showing model performance](image)

**Fig. 13.** RFRE model performance in estimating surface $pCO_2$ in the Gulf of Maine in both model training (a) and model validation (b) using the conjugate dataset described in Fig. 10b.
Fig. 13 shows the performance of the locally tuned RFRE in the G. Maine. In the model training, satellite-derived $p\text{CO}_2$ showed good agreement with the field-measured $p\text{CO}_2$ with a RMSE of 8.93 μatm (2.54%), $R^2$ of 0.97, MB of 0.11 μatm, MR of 1.00, UPD of 0.13%, and MRD of 0.16%. In the 10-fold cross validation, similar statistics were also derived (see Fig. 13b). We further validated this locally parameterized RFRE model in the G. Maine using several independent datasets, and similar results were found as in the validation shown in Section 3.2. These results demonstrated the feasibility of the RFRE approach in the G. Maine once local parameterization was achieved. As an example, Fig. 14 shows the monthly $p\text{CO}_2$ maps in the G. Maine in 2013. Comparing to the GOM, distinct and opposite seasonality with high $p\text{CO}_2$ in winter and lower $p\text{CO}_2$ in summer is shown for the G. Maine, indicating different driving mechanisms of surface $p\text{CO}_2$ in these two contrasting oceanic regions. In the G. Maine, strong vertical mixing during wintertime brings large amounts of DIC to the surface. Although large amounts of nutrients are also brought to the surface, due to low SST and poor light availability, there is no strong biological uptake of CO$_2$. In the summertime, more light is available, with warming of surface waters, biological activities (i.e., algal blooms) become active and the corresponding uptake of CO$_2$ begins to draw the surface $p\text{CO}_2$ down.
Fig. 14. Monthly surface $p$CO$_2$ of 2013 in the Gulf of Maine (latitude: 41.7–46.0° N, longitude: 71.0–64° W), derived from MODIS using the RFRE $p$CO$_2$ model. Large data gaps in the $p$CO$_2$ map of Dec. 2013 were mainly caused by various non-optimal satellite observing conditions (i.e., cloud, stray light).

In short, although the RFRE-based model (with model parameterization developed for the GOM) could not be directly applied to the G. Maine, the RFRE approach can still be applied to the G. Maine with localized parametrization. The resulting model performance appears to exhibit significant improvement over those published in the literature. This result strongly suggests the potential of the RFRE approach in regional applications around the globe.
4.3. Advantages and limitations of the RFRE

The extensive evaluation results in Section 3.2 suggest that for surface $pCO_2$ of 145–550 µatm in the GOM, the empirical RFRE model can estimate surface $pCO_2$ with an overall uncertainty of < 10 µatm. Comparing to other empirical approaches (either traditional or machine-learning based) tested in this study, the RFRE approach shows great advantages in estimating surface $pCO_2$ in different environments of the GOM. Specifically, the northern GOM waters, with large amounts of freshwater inputs from the MARS, have distinct and different carbonate properties than other GOM waters. Most of the empirical approaches showed poor performance when applied to the entire GOM, possibly due to their poor local parameterization in dealing with disparate water masses. In contrast, the RFRE approach presented in this study appears to work well in all these different-processes-dominated regions of the GOM. Consequently, a GOM-wide RFRE $pCO_2$ model is generalized, with the variable relationships between predictors and response variables implicitly included in the empirical coefficients (i.e., weights of each regression tree). In addition, the weak response of the RFRE $pCO_2$ model to errors in each of the satellite variables (i.e., RMSE ≤ 12 µatm, see sensitivity analysis in Section 3.3) shows the model’s tolerance to input errors in the satellite variables. Furthermore, a test of the RFRE approach in the G. Maine (after local parameterization) also shows better performance and significant improvement over other empirical approaches, including the approaches tested in this study and those in the published literature. In contrast, the GOM-parameterized RFRE model performs poorly in the G. Maine without local parameterization; this indicates the intrinsic empirical nature of the RFRE approach. Overall, the RFRE approach shows great advantages over other empirical approaches in satellite mapping of surface $pCO_2$ in the two contrasting ocean regions of the GOM and the G. Maine. The flexibility of the RFRE model in dealing with these two different oceanic processes indicates its likely
potential to serve as a robust approach in estimating surface $pCO_2$ from satellites for other ocean regions.

Although the RFRE-based $pCO_2$ model has shown to be applicable to most GOM waters with relatively low uncertainties, due to its empirical nature, it is unknown whether it works for waters with surface $pCO_2$ outside the 145–550 μatm range. This limitation is caused by the scarcity of valid MODIS data outside this range, although this range should represent the surface $pCO_2$ levels of most GOM waters (Fig. 1a). Furthermore, even within this range, for empirical approaches the model’s satisfactory performance does not necessarily indicate that the model is applicable in all types of waters driven by different processes. However, because of the extensive dataset used to train the model and another extensive dataset used to validate the model, the typical concern of lack of data with empirical approaches may be eliminated. Indeed, the data used in training the model consisted of > 220 cruise surveys in the past 16 years covering all seasons and water types in the GOM, thus representing the most complete $pCO_2$ dataset for the GOM. Likewise, the validation results from another similar comprehensive dataset, under different scenarios in the GOM, suggest that the RFRE model should be able to estimate surface $pCO_2$ for most, if not all, GOM waters. Similar conclusions may be drawn for the G. Maine, where most of the $pCO_2$ collected between 2002 and 2016 were used to train and validate the RFRE model. Because only a small amount of data were available in winter, the model performance for the G. Maine requires further evaluation more wintertime field data become available. Likewise, $pCO_2$ in the GOM can certainly be > 550 μatm or < 145 μatm (Fig. 1a) along the northern coasts and in the Florida Bay, yet these data were not included in the model training due to the unavailability of contemporaneous satellite data after quality control and application of the matchup criteria (see Section 2.2.1). However, these extreme $pCO_2$ values only appeared in some of the very nearshore waters, and in
practice these waters should be masked to avoid misinterpretation of the model results. In fact, most of these waters have no satellite data retrievals due to various reasons (e.g., atmospheric correction failure, straylight, land contamination, etc.), thus having little effect on the model results.

In addition to the model applicability range, due to its empirical nature and its machine-learning based technique, the RFRE approach works like a “black box” without explicit understanding of the driving mechanisms between the input and output variables. Unlike the semi-analytical approaches (i.e., Bai et al., 2015; Chen et al., 2017) which separate and explicitly quantify the contributions of different processes to the overall surface $p\text{CO}_2$ (i.e., river-ocean mixing, biological activities, etc.), the RFRE approach quantifies all of them together. As a result, it is difficult to explain clearly how each process affects the variation of surface $p\text{CO}_2$. On the other hand, because different oceanic processes may not be independent from each other and they may collectively drive the surface $p\text{CO}_2$, it may be advantageous to treat all input variables as a whole in order to achieve a better model accuracy. Indeed, the comparison between empirical and semi-analytical approaches in Chen et al. (2017) did show that the empirical approach could produce better estimates of surface $p\text{CO}_2$ than the semi-analytical approach under different conditions.

Finally and most importantly, the satisfactory performance of the RFRE approach in the two contrasting regions, the GOM and the G. Maine, indicates that the RFRE approach could serve as a robust empirical approach for other ocean regions once local parameterization is obtained. Indeed, a preliminary test indicated that if the training datasets of the GOM and the G. Maine were merged together, an RFRE model with the same parameterization for both regions could yield similar model performance statistics as those from the two separate models (Figs. 2 & 11). This additional test strongly suggests that the RFRE approach offers great potential for estimating surface $p\text{CO}_2$ in different ocean regions.
5. Conclusion

Accurate estimation of surface ocean $pCO_2$ from satellite remote sensing has been a challenging task due to the different regional processes that dominate $pCO_2$. Such processes are difficult to model with mechanistic approaches, and also difficult to model with traditional empirical approaches because the predictor-response relationship can vary substantially across adjacent sub-regions and because high uncertainties may exist in the satellite-derived intermediate data products (SSS, Chl and Kd) in turbid and dynamic coastal waters. In this study, with satellite-derived SST, SSS, Chl, and Kd as inputs, a random forest based regression ensemble (RFRE) approach has been developed and thoroughly evaluated for a large, semi-enclosed sea - the Gulf of Mexico. The RFRE-based model showed good performance with an overall uncertainty of < 10 μatm and higher uncertainty in the northern GOM than in the southern GOM due to the complexity and dynamics of the Mississippi-Atchafalaya River system. This is the first time that a unified empirical $pCO_2$ model has been demonstrated to show consistent performance across many different water types in the entire GOM. The RFRE approach used to test the G. of Maine indicates great potential for the RFRE to be a robust approach for regional $pCO_2$ modeling in regional studies as long as sufficient in situ field data are available for model training. Finally, future research needs to be focused on improving the capability of the satellite-based RFRE $pCO_2$ model in tracing decadal and long-term scale variations in surface $pCO_2$ under anthropogenic forcing.

Acknowledgements

This research was supported by a University of South Florida student fellowship and the U.S. NASA Ocean Biology and Biogeochemistry program (NNX14AL98G, NNX17AH03G). The authors are indebted to all researchers, including those of NOAA AOML, NOAA NCEI, Weijun Cai (UD), and Xinping Hu (TAMU), who have collected, processed, quality controlled, and shared
all the cruise survey data. These data played an essential role in calibrating and validating the empirical $pCO_2$ algorithm in this work. The authors also thank NASA for providing MODIS satellite data.

**Notations**

<table>
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<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AOML</td>
<td>Atlantic Oceanographic and Meteorological Laboratory</td>
</tr>
<tr>
<td>CDOM</td>
<td>Colored dissolved organic matter</td>
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<tr>
<td>Chl</td>
<td>Surface water chlorophyll-a concentration, in mg m$^{-3}$</td>
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<tr>
<td>DIC</td>
<td>Dissolved inorganic carbon, in μmol kg$^{-1}$</td>
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<tr>
<td>Kd</td>
<td>Diffuse attenuation coefficient of downwelling irradiance, in m$^{-1}$</td>
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<tr>
<td>G. Maine</td>
<td>Gulf of Maine</td>
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<td>GOM</td>
<td>Gulf of Mexico</td>
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<td>GSFC</td>
<td>Goddard Space Flight Center</td>
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<td>Jday</td>
<td>Julian day</td>
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<tr>
<td>LDEO</td>
<td>Global surface $pCO_2$ database collated by T. Takahashi of the Lamont-Doherty Earth Observatory of Columbia University</td>
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<tr>
<td>MARS</td>
<td>Mississippi and Atchafalaya River system</td>
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<tr>
<td>MB</td>
<td>Mean bias</td>
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<td>MLD</td>
<td>Mixed layer depth</td>
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<td>MLR</td>
<td>Multi-linear regression</td>
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</table>
MNR  Multi-nonlinear regression

MODIS/Aqua  Moderate Resolution Imaging Spectroradiometer on Aqua satellite

MPNN  Multilayer Perceptron Neural Network

MR  Mean ratio

MRD  Mean relative difference

NCEI  National Centers for Environmental Information

NODC  National Oceanographic Data Center

$pCO_2$  Partial pressure of surface water CO$_2$ in μatm

PCR  Principle component regression

$R^2$  Coefficient of determination

RFRE  Random Forest based Regression Ensemble, a machine learning technique

RMSE  Root mean square error

SOMs  Self-organizing maps

SSS  Sea surface salinity

SST  Sea surface temperature, in °C

SVMs  Supporting vector machines

TA  Total alkalinity, unit: μmol kg$^{-1}$

TAMU  Texas A&M University
UD University of Delaware

UPD Unbiased percent difference

WFS West Florida Shelf

Reference


Millero, F.; R. Wanninkhof; R. Woosley (2016). Partial pressure (or fugacity) of carbon dioxide, salinity and other variables collected from Surface underway observations using Carbon dioxide (CO₂) gas analyzer, Shower head chamber equilibrator for autonomous carbon

Millero, F.; R. Wanninkhof; R. Woosley (2016a). Partial pressure (or fugacity) of carbon dioxide, salinity and other variables collected from Surface underway observations using Carbon dioxide (CO₂) gas analyzer, Shower head chamber equilibrator for autonomous carbon dioxide (CO₂) measurement and other instruments from F.G. Walton Smith in the Caribbean Sea, Coastal Waters of Florida and others from 2012-02-27 to 2012-09-25 (NCEI Accession 0157425). Version 1.1. NOAA National Centers for Environmental Information. Dataset. doi:10.3334/CDIAC/OTG.COAST_WALTON_SMITH_2012.

Millero, F.; R. Wanninkhof; R. Woosley (2016b). Partial pressure (or fugacity) of carbon dioxide, salinity and other variables collected from Surface underway observations using Carbon dioxide (CO₂) gas analyzer, Shower head chamber equilibrator for autonomous carbon dioxide (CO₂) measurement and other instruments from F.G. Walton Smith in the Coastal Waters of Florida, Coastal Waters of Louisiana and others from 2013-03-31 to 2013-12-21 (NCEI Accession 0157431). Version 1.1. NOAA National Centers for Environmental Information. Dataset. doi:10.3334/CDIAC/OTG.COAST_WALTON_SMITH_2013.

Millero, F.; R. Wanninkhof; R. Woosley (2016c). Partial pressure (or fugacity) of carbon dioxide, salinity and other variables collected from Surface underway observations using Carbon dioxide (CO₂) gas analyzer, Shower head chamber equilibrator for autonomous carbon dioxide (CO₂) measurement and other instruments from F.G. Walton Smith in the Coastal


Salisbury, J.; C. Hunt; A. Mannino (2016). Partial pressure (or fugacity) of carbon dioxide, dissolved inorganic carbon, pH, alkalinity, temperature, salinity and other variables collected from Surface underway, discrete sample and profile observations using Alkalinity titrator, CTD and other instruments from PELICAN in the Coastal Waters of Louisiana, Coastal Waters of Texas and Gulf of Mexico from 2013-09-09 to 2013-09-22 (NCEI Accession 0157461). Version 1.1. NOAA National Centers for Environmental Information. Dataset.


Wang, Y., Huang, J. (2014c). Partial pressure (or fugacity) of carbon dioxide, salinity and other variables collected from underway - surface observations using Carbon dioxide (CO2) gas
analyzer, Shower head chamber equilibrator for autonomous carbon dioxide (CO₂) measurement and other instruments from the CAPE HATTERAS in the Gulf of Mexico from 2009-01-09 to 2010-03-21 (NODC Accession 0115765). Version 1.1. National Oceanographic Data Center, NOAA. Dataset. doi:10.3334/CDIAC/OTG.CAPE_HATTERAS_GM.


Wanninkhof, R.; B. Huss; R. Castle (2013b). Partial pressure (or fugacity) of carbon dioxide, salinity and other variables collected from underway - surface observations using Carbon
dioxide (CO₂) gas analyzer, Shower head chamber equilibrator for autonomous carbon
dioxide (CO₂) measurement and other instruments from the EXPLORER OF THE SEAS
in the Caribbean Sea, Gulf of Mexico and North Atlantic Ocean from 2002-03-02 to 2002-
12-28 (NODC Accession 0108131). Version 1.1. National Oceanographic Data Center,

Wanninkhof, R.; B. Huss; R. Castle (2013c). Partial pressure (or fugacity) of carbon dioxide,
salinity and other variables collected from underway - surface observations using
Barometric pressure sensor, Carbon dioxide (CO₂) gas analyzer and other instruments from
the EXPLORER OF THE SEAS in the Caribbean Sea, Gulf of Mexico and North Atlantic

Wanninkhof, R.; B. Huss; R. Castle (2013d). Partial pressure (or fugacity) of carbon dioxide,
salinity and other variables collected from underway - surface observations using
Barometric pressure sensor, Carbon dioxide (CO₂) gas analyzer and other instruments from
the EXPLORER OF THE SEAS in the Caribbean Sea, Gulf of Mexico and others from

Wanninkhof, R.; R. D. Castle; J. Shanhahoff (2013e). Partial pressure (or fugacity) of carbon
dioxide, salinity and other variables collected from underway - surface observations using
Carbon dioxide (CO₂) gas analyzer, Shower head chamber equilibrator for autonomous
carbon dioxide (CO₂) measurement and other instruments from NOAA Ship RONALD H.
BROWN in the Caribbean Sea, Gulf of Mexico and others from 2009-04-17 to 2009-10-


APPENDIX E:

DOMINANT CONTROLS OF SURFACE OCEAN $p$CO$_2$ IN COASTAL OCEANS:
ANALYSIS OF IN SITU TIME SERIES DATA

Chen, S., and Hu, C. Dominant controls of surface water $p$CO$_2$ in different coastal environments

(prepared).
Dominant controls of surface water $pCO_2$ in different coastal environments

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Abstract

Atmospheric $pCO_2$ has been increasing significantly since global industrialization. Satellite observing systems and new algorithms allow for synoptic estimation of surface $pCO_2$, which has great advantages in quantifying the air-sea CO$_2$ flux and understanding ocean acidification. However, most published satellite $pCO_2$ remote sensing algorithms are quite limited in capturing the interannual variabilities in surface $pCO_2$ especially in the coastal ocean environments. To improve the capabilities of satellite remote sensing in monitoring surface $pCO_2$ in such environments, the driving mechanisms of surface $pCO_2$ over seasonal and interannual time scales need to be well understood. As such, a time series of in situ $pCO_2$ data, and other environmental variables from field or satellite measurements along the coasts of the United States of America and its territories at different latitudes were analyzed by separating the effects of temperature and non-temperature on surface $pCO_2$. On seasonal time scales, surface $pCO_2$ tended to be dominated by the temperature effect ($pCO_2$-T) through sea surface temperature (SST) and wind speed (with exceptions in special environments such as river-dominated) in tropical and subtropical oceanic waters, and tended to be driven by the non-temperature effect ($pCO_2$-nonT) in temperate zone. On interannual time scales, both atmospheric $pCO_2$ and surface $pCO_2$ showed significant increasing trends over short time scales (i.e., $< 10$ years). In contrast to the seasonal driving mechanisms in

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surface $p$CO$_2$, the interannual variabilities of surface $p$CO$_2$ was mainly controlled the non-temperature effect (through air-sea CO$_2$ exchange via atmospheric $p$CO$_2$) in tropical and subtropical waters but by the temperature effect (warming effect of SST) in temperate regions. It was the first time that the driving mechanisms of surface $p$CO$_2$ in various coastal ocean environments over both seasonal and interannual time scales were thoroughly examined. This study suggests that, to better capture the seasonal and interannual signals in surface $p$CO$_2$ from satellites, atmospheric $p$CO$_2$ needs to be considered in the surface $p$CO$_2$ remote sensing algorithms. The non-temperature effect on surface $p$CO$_2$ especially the biological effects (e.g., algal blooms) need to be further investigated in the future.

Keywords: surface $p$CO$_2$, sea surface temperature, Chlorophyll, driving mechanisms, remote sensing

1. Introduction

Since global industrialization, fossil fuel burning and land use change (e.g., deforestation) have projected large amounts of carbon into the atmosphere. Based on the most recent report, in the past decade (2007-2016), there were $\sim$10.7 ±1.2 Gg C yr$^{-1}$ anthropogenic carbon released into the atmosphere, with 4.7 ± 0.1 Gg C yr$^{-1}$ remaining in the atmosphere, 2.4 ± 0.5 Gg C yr$^{-1}$ absorbed by the ocean, and the rest being taken up by the terrestrial biosphere (Le Quéré et al., 2018). As a result, global warming, carbon cycling, and ocean acidification are rapidly becoming pressing concerns for the environmental research community. To better understand the carbon cycling and ocean acidification processes in the rapidly changing world, surface partial pressure of CO$_2$ ($p$CO$_2$) is one of the key parameters to measure and study. Studies show that surface $p$CO$_2$ has been increasing with an average rate of $\sim$1.5-1.9 μatm yr$^{-1}$ and variable rates between 1.2 ± 0.5 and 2.1 ± 0.5 μatm yr$^{-1}$ in different ocean basins (Takahashi et al., 2009; 2014). However, these rates are
for the open ocean waters, which is mainly controlled by the large-scale ocean circulations. Yet, little is known about the interannual variabilities of surface $p$CO$_2$ in coastal oceans, due to the scarcities of field data measurements and the dynamic and complex biogeochemical and physical processes in coastal regions.

Although the coastal ocean only represents ~7% of the global oceanic area, it accounts for ~50% of the world’s net primary production (Muller-Karger et al., 2005). However, due to the inadequate knowledge of CO$_2$ uptake or release from various ecosystems (i.e., estuaries, salt marshes, coral reefs, and upwelling shelves) in the coastal margins, coastal oceans are still the most controversial regions in balancing the global budget of CO$_2$ (Chen et al., 2003). For example, Borges (2005) found the coastal oceans behave as a CO$_2$ sink at high, subtropical, and tropical latitudes, and a CO$_2$ source at temperate latitudes, while Cai et al. (2006) suggested that the continental shelves serve as a CO$_2$ sink at middle and high latitudes, and a source of CO$_2$ at low latitudes. Most of the uncertainties in the quantification of air-sea CO$_2$ fluxes in the coastal oceans come from the large variations of surface $p$CO$_2$ and its lack of spatial and temporal coverages from field data measurements.

In contrast to field data measurements, several recent studies proved the capabilities and advantages of using ocean color satellite remote sensing in monitoring surface $p$CO$_2$ in coastal oceans (e.g., Lohrenz and Cai, 2006; Lohrenz et al., 2010 and 2018; Hales et al., 2012; Signorini et al., 2013; Bai et al., 2015). However, two major problems exist in these published $p$CO$_2$ remote sensing algorithms. First, large uncertainties exist in most of these satellite-derived surface $p$CO$_2$ (i.e., Root Mean Square Error (RMSE) $\geq$ 20 μatm). These large uncertainties are mainly caused by the insufficiency of the defined regression formula in modeling the complex and unknown relationships between surface $p$CO$_2$ and related environmental variables. Using multi-variate
second order polynomial regression fit, Chen et al. (2016 and 2017) improved the accuracy in the satellite-derived surface $p$CO$_2$ with reduced RMSE of $< 12 \mu$atm, but the algorithms were only locally tuned for the West Florida Shelf and northern Gulf of Mexico (GOM), respectively. Second, most of the published $p$CO$_2$ remote sensing algorithms were applied for the seasonal variations in surface $p$CO$_2$, while few of them were attempted to monitor the interannual changes in surface $p$CO$_2$. Recently, Chen et al. (under review) did such analysis for the entire GOM using an unified $p$CO$_2$ remote sensing algorithm and found that surface $p$CO$_2$ anomalies in the GOM tended to be positive (by $\sim 5 \mu$atm) after 2012. This increase in surface $p$CO$_2$ is quite smaller comparing to the increasing rate in atmospheric $p$CO$_2$. To further verify this result and to increase the capabilities of satellite remote sensing in monitoring surface $p$CO$_2$ under anthropogenic forcing, the driving mechanisms in surface $p$CO$_2$ over interannual time scales need to be investigated and well understood.

In the open ocean waters, the dominant controls of surface $p$CO$_2$ were attempted in several studies on seasonal time scales (Takahashi et al., 2002; Bennington et al., 2009; Fay and McKinley, 2013 and 2017). Specifically, Takahashi et al. (2002) proposed a computational method to decompose the seasonal variation of surface $p$CO$_2$ into two parts: one is caused by the temperature effect ($p$CO$_2$-T), and the other is caused by the non-temperature effect ($p$CO$_2$-nonT). The temperature effect on surface $p$CO$_2$ is computed by perturbing the mean annual surface $p$CO$_2$ with the difference between the mean and the observed sea surface temperature (SST, °C) using Eq. 1, based on the isothermal seawater experiments ($\frac{\partial npco_2}{\partial SST} = 0.0423$ °C$^{-1}$) in Takahashi et al. (1993).

That’s, a parcel of seawater with an annual mean $p$CO$_2$ value was subjected to seasonal temperature changes under isothermal conditions, to determine if changes in the seasonal SST (alone) would change the surface $p$CO$_2$. Eq. 2 is the quantification of the non-temperature effect
on surface $pCO_2$ ($pCO_{2\_nonT}$), in which the temperature effect is removed from the observed surface $pCO_2$ by normalizing the observed $pCO_2$ to a constant annual mean SST. Changes in $pCO_2$ from this component primarily come from change in total dissolved inorganic carbon (DIC, $\mu$mol/kg) and total alkalinity (TA, $\mu$mol/kg), and it includes the net consumption of CO$_2$ by phytoplankton, net TA change due to calcification and nitrate utilization, air-sea exchange of CO$_2$, and variation of DIC and TA by vertical mixing of subsurface waters or horizontal mixing of different water masses. In the open ocean, the non-temperature effect mainly refers to the net biological effect. Using this method, Takahashi et al. (2002) found that, the seasonal amplitude of surface $pCO_2$ in high latitudes ($\geq 40^\circ$ poleward) and equatorial zones was dominated by the biology effect (which refers to the non-temperature effect, more exactly), and dominated by the temperature effect in the subtropical regions. Similar findings were also shown in Fay & McKinley (2017).

In contrast to the open ocean, because of the dynamic and complex biogeochemical and physical processes in coastal oceans, the driving mechanisms of surface $pCO_2$ over seasonal time scales could be different from the open oceans even at similar latitudes. However, such knowledge is quite limited in current studies. This study will fill in this research gap towards a better understanding of the driving mechanisms in the seasonal and interannual variations of surface $pCO_2$, meanwhile it will also facilitate the future development of surface $pCO_2$ remote sensing algorithms.

$$pCO_{2\_T} = pCO_{2\_annual\_mean} \times \exp[0.0423(SST_{\text{obs}} - SST_{\text{mean}})] \quad (1)$$

$$pCO_{2\_nonT} = pCO_{2\_obs} \times \exp[0.0423(SST_{\text{mean}} - SST_{\text{obs}})] \quad (2)$$
Great efforts have been made to observe surface $p$CO$_2$ in the coastal ocean via the global time series observation system (NOAA Pacific Marine Environmental Laboratory (PMEL) moored $p$CO$_2$ systems) in the past decade to document the temporal changes in oceanic carbon, although the observing network is still in its infancy. To address the questions described above and to improve the quantification of surface $p$CO$_2$ from ocean color remote sensing, the objectives of this study include: 1) Investigate the seasonal and interannual variations of surface $p$CO$_2$ in the coastal ocean environments in tropical and subtropical and temperate zones; 2) Quantify the effects of temperature and non-temperature components ($p$CO$_2$$_T$ and $p$CO$_2$$_{nonT}$) on surface $p$CO$_2$ and analyze the dominant controls of surface $p$CO$_2$ at different latitudes over seasonal and interannual time scales; and 3) Examine the correlations between environmental variables and surface $p$CO$_2$ components.

2. Data and methods

2.1. Data

2.1.1. In situ data time series

Table 1 provides a summary of the time series observations from buoy systems compiled for this study. The corresponding geolocations of these buoys are shown in Fig. 1. These time series data were collected by the NOAA PMEL carbon program (https://www.pmel.noaa.gov/co2/story/Buoys+and+Autonomous+Systems), and obtained from the NOAA National Centers for Environmental information (NCEI) (https://www.nodc.noaa.gov/ocads/oceans/Moorings/) (Sabine et al., 2010; Cross et al., 2014(a-c); Sutton et al., 2010, 2011, 2013(a-d), 2014(a-b), and 2015). Basically, to assure sufficient temporal coverage, only those buoys that have at least two years’ data collection were selected. As a result,
ten buoys (C1-C10, where “C” represents Coastal Ocean) data collected along the coasts of the United States of America and its territories were firstly processed. These buoys covered various coastal ocean ecosystems different latitudes. Generally, buoys C1-C5 are located in the tropical and subtropical zones, and buoys C6-C10 are located in the temperate zone. Specifically, buoy C1 and C2 were in coral reef environments, with buoy C1 deployed on the southwestern coast of Puerto Rico and C2 positioned in the Cheeca Rocks, an inshore patch reef within the Florida Keys National Marine Sanctuary; buoy C3 was located in the nearshore region of the Louisiana Shelf, which was greatly affected by the Mississippi River discharge (river discharge rate of \(\sim 17,000 \text{ m}^3 \text{ s}^{-1}\)) and river plume with a sea surface salinity (SSS) range of 14.00-35.64, and buoy C6 was deployed in the southwestern coast of the Gulf of Maine at a higher latitude than buoy C3, and it was also affected by river discharge but at a greatly reduced magnitude (river discharge rate of \(\sim 0.27 \text{ m}^3 \text{ s}^{-1}\)) with a SSS range of 22.56-33.38 and by strong tidal currents (\(\sim 2 \text{ m s}^{-1}\)); buoy C4 was located in the Gray’s Reef National Marine Sanctuary in the subtropical coastal ocean waters at a slightly higher latitude of 31.399°N than buoy C3, and it represents a general coastal ocean environments (e.g., without coral reef and river discharges); Buoy C5 and C7 were placed in the coastal upwelling zones at different latitudes; and buoys of C8-C10 were located in the Gulf of Alaska ecosystem, which is seasonally affected by the ice-melt freshwater inputs. In addition, three open ocean buoys (O1-O3, where “O” represents Open Ocean) located in the oligotrophic waters of Atlantic and Pacific were also selected because of their sufficient temporal coverage. Buoy O1 and O2 are in the tropical and subtropical zones, and O3 is in the temperate zone. These three open ocean buoys were mainly used as references for the analysis of the buoy time series data (i.e., buoys C1-C10) in the coastal ocean.
For each of the buoys, both atmospheric and surface \( p\text{CO}_2 \) were measured with a non-dispersive, infrared analyzer Li-COR™ (model LI-820) (Sabine, 2005; Sutton et al., 2014c). The Li-COR™ data had an accuracy of 2 \( \mu \text{atm} \) (or better) and a sampling frequency of every 3 h. Surface \( p\text{CO}_2 \) data were collected at a water depth of < 1 m, and atmospheric \( p\text{CO}_2 \) data were collected at 1.2 m above the sea surface. The details of data collection, processing, and quality control can be found in Sabine (2005) and Sutton et al. (2014c). In addition, SST and sea surface salinity (SSS) data were obtained using a CTD (SBE37, MicroCAT C-T Recorder) integrated in the autonomous CO2 mooring system.

2.2. Satellite data

For each buoy listed in Table 1, a spatial area of 110 km (N to S) by 110 km (W to E) covering the buoy location was defined. Correspondingly, standard daily Level-2 ocean color data products at spatial resolution of 1-km (Version R2018.0) from Moderate Resolution Imaging Spectroradiometer (MODIS) Aqua covering the defined area for the time domain of the buoy data (Table 1) were downloaded from NASA Goddard Space Flight Center (http://oceancolor.gsfc.nasa.gov/). These Level-2 data products included ocean color data such as Chlorophyll-a concentration (Chl, mg m\(^{-3}\)) and spectral remote sensing reflectance (Rrs, \( \text{sr}^{-1} \)) at visible bands between 412 and 678 nm. The spectral Rrs data were used to calculate the diffuse attenuation coefficient of downwelling irradiance at 488 nm (\( K_a \), m\(^{-1}\)) using the semi-analytical algorithm developed by Lee et al. (2005).

In addition to ocean color data products, global daily wind data products at 10 m above the sea surface between 2005 and 2017 were obtained from the NOAA National Centers for Environmental Prediction (NCEP) reanalysis dataset. This reanalysis dataset is a joint product from the NCEP and the National Center for Atmospheric Research (NCAR) with a spatial
resolution of 2.5 degree. These wind data products are wind vectors (in $u$ (W to E) and $v$ (S to N) directions), and daily wind speed were calculated from the $u$ and $v$ vectors and then interpolated to the same spatial resolution (i.e., 1-km) as the ocean color data.

2.2. Methods

2.2.1. Data preprocessing

Time and location data from the in situ $pCO_2$ measurements were used to identify the co-located and contemporaneous Chl, $K_d$, and wind speed data for each of the buoys listed in Table 1. These data, together with the in situ time series of SST, SSS, and atmospheric $pCO_2$, were used as ancillary data for the investigation of the seasonal and interannual variation of surface $pCO_2$.

To obtain high-quality data, contemporaneous field-measured $pCO_2$ and MODIS-derived Chl and $K_d$ for each buoy were selected using the following criteria. A time window of ±6 h between field and MODIS measurements was used. Low-quality MODIS data under various non-optimal observing conditions (e.g., atmospheric correction failure, cloud, stray light, sun glint, etc.) were excluded using the NASA standard quality control criteria (Patt et al., 2003; Barnes and Hu, 2015). Valid satellite data within a $3 \times 3$ km box centered on the location of each buoy were extracted and averaged (Bailey and Werdell, 2006). To assure the satellite data quality, only if the number of valid pixels in the $3 \times 3$ km box was ≥ 5 and its variance was ≤ 10%, the extracted data were used.

Similar to the extraction of Chl and $K_d$, the wind speed data were also matched for each buoy. Since there was no detailed hour and minute stamps of the daily wind speed data products, valid wind speed data within a $3 \times 3$ km box centered on the location of each buoy were extracted and averaged for any daily wind speed data, as long as there was in situ $pCO_2$ measurements on that
day. Again, to assure the matchup data quality, the extracted data were used only if the number of valid pixels in the 3×3 km box was ≥ 5 and its variance was ≤ 10%.

2.2.2. Decomposition of surface $pCO_2$

Basically, Eqs. 1 and 2 were used to decompose the temperature effect ($pCO_2_T$) and non-temperature effect ($pCO_2_nonT$) on surface $pCO_2$. The $pCO_2_T$ component is derived by disturbing the annual mean of surface $pCO_2$ with seasonal SST relative to the annual mean SST. The $pCO_2_nonT$ component is calculated by normalizing the observed $pCO_2$ to a constant annual mean SST, in which the temperature effect was removed from the observed $pCO_2$.

Therefore, to apply these two equations (Eqs. 1 and 2), two terms are needed: the annual mean of surface $pCO_2$ and SST. To calculate these two terms for each of the buoys listed in Table 1, all the available in situ data in the time domain (from multiple years) of each buoy were used. Specifically, for each buoy, first, the monthly means of surface $pCO_2$ and SST in each year were calculated from the in situ daily measurements; second, the derived monthly means of each year were used to calculate the monthly climatology (i.e., the average of the multi-year monthly means) of surface $pCO_2$ and SST; and finally, based on the monthly climatology of surface $pCO_2$ and SST, the annual mean surface $pCO_2$ and SST were derived. Here, it should be clarified that, the monthly climatology of surface $pCO_2$ and SST does not mean the real monthly climatology (i.e., over ≥ 30 years), in fact, they are the multi-year average of the monthly means in each year.

With the derived annual mean of surface $pCO_2$ and SST for each buoy, Eqs. 1 and 2 were applied to the in situ data to derive the two components of surface $pCO_2$: $pCO_2_T$ and $pCO_2_nonT$. Following the steps described above, the monthly mean of these $pCO_2$ components in each year,
and their monthly climatology (i.e., multi-year based monthly averages) were also derived for subsequent data analyses.

2.2.3. Statistical analyses

To quantify the seasonal magnitudes of surface $pCO_2$ and its $pCO_2$ components, their seasonal maximum and minimum were derived first. Then the seasonal magnitude of surface $pCO_2$ was computed using Eq. 3, and this seasonal magnitude represents the net seasonal variation of *in situ* surface $pCO_2$. The seasonal magnitudes of the $pCO_2_T$ and $pCO_2_{nonT}$ components were also computed similarly using Eqs. 4 and 5, respectively.

$$\Delta pCO_2 = \max(pCO_2) - \min(pCO_2)$$ \hspace{1cm} (3)

$$\Delta pCO_2_T = \max(pCO_2_T) - \min(pCO_2_T)$$ \hspace{1cm} (4)

$$\Delta pCO_2_{nonT} = \max(pCO_2_{nonT}) - \min(pCO_2_{nonT})$$ \hspace{1cm} (5)

The relative importance ($RI$) of the temperature and non-temperature effects was quantified by normalizing the difference of seasonal magnitudes between $pCO_2_T$ and $pCO_2_{nonT}$ with the seasonal magnitude of surface $pCO_2$ based on Eq. 6.

$$RI = (\Delta pCO_2_T - \Delta pCO_2_{nonT}) / \Delta pCO_2$$ \hspace{1cm} (6)

$RI$ is an indicator to tell briefly about which effect dominates the seasonal variations of surface $pCO_2$. Generally, if $RI$ is positive, it means the effect of temperature changes on surface $pCO_2$ exceeds the effect of the non-temperature (i.e., changes in TA and DIC), suggesting that the temperature effect is a dominant driver of seasonal surface $pCO_2$, and vice versa. Besides, if $RI$ is more close to 1 (-1) at one station comparing to other stations, it means the temperature (non-temperature) effect plays a more important role in modulating the seasonal changes of surface $pCO_2$. 

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\( pCO_2 \) at that station. In contrast, if \( RI \) is close to 0, it would suggest that these two compete processes (temperature and non-temperature effects) plays comparable but opposite roles in varying seasonal surface \( pCO_2 \), thus they cancel with each other to a large extent.

To further understand the seasonal variations of surface \( pCO_2 \) and its driving environmental factors, the correlations between surface \( pCO_2 \) (as well as \( pCO_2 \_T \) and \( pCO_2 \_nonT \)) and the environmental variables (i.e., SST, SSS, Chl, \( K_a \), and wind speed) were investigated. The correlations were quantified by Pearson correlation coefficient (\( R \)) based on the time series data of the monthly anomalies, which were derived by removing the climatological seasonality from the interannual monthly mean. Only if the \( p \) value was \( < 0.05 \), the correlation \( R \) was considered as a significant correlation.

In addition to the analysis of dominant drivers (i.e., temperature or non-temperature effect) and the corresponding dominant environmental variables in the seasonal variations of surface \( pCO_2 \) in different coastal ocean systems, to further understand the driving mechanisms in surface \( pCO_2 \) on interannual time scales, the interannual trends (if there is any) over short term time scales (i.e., \( < 10 \) years) in surface \( pCO_2 \), as well as atmospheric \( pCO_2 \) and environmental variables (i.e., SST, SSS, Chl, \( K_a \), and wind speed) in these coastal ocean environments were also examined at a confidence level of \( \geq 95\% \), based on their time series data of interannual monthly anomalies.

3. Results

3.1. Seasonal variations of surface \( pCO_2 \) and its components

Following the steps described in Section 2.2, the seasonal variations of surface \( pCO_2 \) and its components (\( pCO_2 \_T \) and \( pCO_2 \_nonT \)) for each buoy (Table 1) were derived (Figs. 2 and 3), and their seasonal amplitudes were quantified (Table 2). Generally, it was found that, the temperature
effect and non-temperature effect are in opposite phases with 6 months difference. Surface $p$CO$_2$ was dominated by the temperature effect in the tropical and subtropical zones, and was dominated by the non-temperature effect in the temperate zone. There are a few exceptions in some special ocean environments (e.g., coral reefs, river-dominated, upwelling-dominated), where surface $p$CO$_2$ showed irregular seasonality and both temperature and non-temperature effects play comparable roles in modulating seasonal changes of surface $p$CO$_2$.

3.1.1. Tropical and subtropical zones

Fig. 2 shows the seasonal variations of surface $p$CO$_2$ and its components ($p$CO$_2$ T and $p$CO$_2$ nonT) of the buoys located in tropical and subtropical zones. From tropical to subtropical regions, surface $p$CO$_2$ showed stronger seasonal signals with high values in summer and low in winter. The seasonality of surface $p$CO$_2$ showed variable patterns in coastal oceans because of the particular biogeochemical and physical processes at each station.

In open ocean waters (Fig. 2 and Table 2), surface $p$CO$_2$ in the tropical zone (represented by buoy O1 at 22.670 °N) showed very small seasonal variation with an amplitude of 22.22 μatm, corresponding to small changes in seasonal SST (23.7 – 26.5 °C). Similarly, both the temperature and non-temperature components also showed very small seasonal changes with an amplitude of 44.48 μatm and 23.29 μatm, respectively. The seasonal variations of surface $p$CO$_2$ mainly follows with the temperature effect ($p$CO$_2$ T) with a relative importance factor $RI$ of 0.95, suggesting the dominant controls of temperature effect on seasonal surface $p$CO$_2$. In the subtropical zone (represented by buoy O2 at 31.780 °N), surface $p$CO$_2$ also showed similar but stronger seasonality (seasonal amplitude = 90.68 μatm) comparing to buoy O1, with a $RI$ factor of 0.78. That’s, the seasonal warming effect also dominates the seasonal variations of surface $p$CO$_2$ in the subtropical open ocean waters. At both stations, the non-temperature effect ($p$CO$_2$ nonT) is about 6 months
out of phase relative to temperature effect ($pCO_2$,$T$). Although this competing non-temperature effect is not a dominant control of the seasonal $pCO_2$, clearly it does play a role in modulating the overall seasonal changes in surface $pCO_2$ with a reduced seasonal amplitude than without this effect. These results are consistent with the findings in previous studies (Takahashi et al., 2002; Ullman et al., 2009; Fay and McKinley, 2017).

Comparing to open ocean waters, surface $pCO_2$ in coastal oceans varied quite differently even at similar latitudes or in the same kind of coastal ecosystems (Fig. 2 and Table 2). But generally, similar to those found in the open ocean waters, $pCO_2$,$T$ and $pCO_2$,$nonT$ are ~6 months out of phase, and surface $pCO_2$ is also primarily dominated by $pCO_2$,$T$ in coastal regions except for special coastal environments (e.g., coral reefs, river-dominated, upwelling-dominated). For example, station C4 is located in a common coastal environment (i.e., with little river inputs, without upwelling, no coral reefs). As a result, surface $pCO_2$ at station C4 followed closely with $pCO_2$,$T$ in phase with high $pCO_2$ in winter and low in summer, indicating that surface $pCO_2$ is mainly controlled by SST over seasonal time scales. In fact, the overall seasonal variations of surface $pCO_2$ and its components at buoy C4 is quite similar to those of buoy O2 in the subtropical open ocean waters with the same relative importance factor $RI$ of 0.78. The major difference between the two is that, surface $pCO_2$ at buoy C4 had a larger seasonal amplitude (154.37 µatm at C4 vs. 90.68 µatm at O2) because of the active oceanic process in coastal oceans.

In the coral reef coastal environments (represented by buoy C1 and C2), surface $pCO_2$ could show quite different seasonal variations from that in tropical and subtropical oceanic waters. It is found that, surface $pCO_2$ was mainly dominated by $pCO_2$,$T$ at site C1 (in tropical zone), while it was mainly dominated by $pCO_2$,$nonT$ at site C2 (in subtropical zone). Specifically, at site C1, surface $pCO_2$ had a seasonal amplitude of 60.26 µatm, and a relative importance factor $RI$ of 0.63. The
overall seasonal changes of surface $pCO_2$ was closely in phase with the $pCO_2\_T$, suggesting the dominant controls of the temperature effect in affecting seasonal surface $pCO_2$. This result is consistent with the published studies for the same coral reef environment (Gray et al., 2012). In contrast, at site C2, the seasonal variation of surface $pCO_2$ follows the change of $pCO_2\_nonT$ closely, with a larger seasonal amplitude of 227.94 μatm than that at buoy C1 and a negative relative importance factor $RI$ of -0.53. That’s, instead of being dominated by $pCO_2\_T$, the seasonal variation of surface $pCO_2$ at site C2 is mainly controlled by the non-temperature effect.

In the river-dominated coastal environment (represented by buoy C3), Surface $pCO_2$ showed irregular and complex seasonal variations as expected. From January to September, surface $pCO_2$ tended to be dominated by $pCO_2\_nonT$, and October and December, it tended to be mainly affected by $pCO_2\_T$. The two competing effects of $pCO_2\_T$ and $pCO_2\_nonT$ resulted in a seasonal amplitude of surface $pCO_2$ of 114.88 μatm in this coastal environment. The relative importance factor $RI$ was -0.05, suggesting that the temperature and non-temperature effects played comparable roles in affecting the overall seasonality of surface $pCO_2$.

In the coastal upwelling ecosystem (represented by buoy C5), Surface $pCO_2$ varies from high to low from spring to fall, and this variation was coupled in phase with the $pCO_2\_nonT$ with the relative importance factor $RI$ of -0.90, suggesting the non-temperature effect was the major control of the seasonal surface $pCO_2$.

3.1.2. Temperate zone

Fig. 3 is the seasonal variations of surface $pCO_2$ and its components ($pCO_2\_T$ and $pCO_2\_nonT$) of the buoys in temperate zones. Similar to the findings in tropical and subtropical zones, the temperature effect and non-temperature were also ~6 months out of phase with each other,
suggesting their competing roles in varying seasonal surface $pCO_2$. However, in contrast to the results in tropical and subtropical zones, the seasonality of surface $pCO_2$ was found to be dominated by the non-temperature effect in the temperate zone with a few exceptions in special ocean environments where surface $pCO_2$ showed irregular seasonal patterns.

In the open ocean waters (represented by buoy O3, Fig. 3 and Table 2), surface $pCO_2$ did not show clear seasonality from winter to summer (e.g., no obvious sinusoidal variation patterns). As to its $pCO_2$ components, both $pCO_2_{-T}$ and $pCO_2_{-nonT}$ showed strong and comparable seasonal amplitudes (seasonal amplitude of $pCO_2_{-T} = 127.21 \mu$atm, and seasonal amplitude of $pCO_2_{-nonT} = 125.71 \mu$atm) but in the opposite phase. Most likely, the two competing effects partially cancel with each other to a large extent on seasonal scales, thus leading to little seasonal changes in surface $pCO_2$. In this oceanic environment, both the temperature and non-temperature effects play important roles in affecting surface $pCO_2$, with a relative importance factor $R_I$ of 0.07. Based on the $pCO_2$ data collected from the Weather Station “P” (50° N, 145° W, which is ~23 km from buoy O3) in 1972-1975 by Wong and Chaa (1991), Takahashi et al. (2002) also found similar seasonal variation patterns in surface $pCO_2$ and its components, but with some difference in the seasonal amplitude of surface $pCO_2$ (i.e., surface $pCO_2$ amplitude = 20 \mu atm in this study, and surface $pCO_2$ amplitude = 50 \mu atm in Takahashi et al. (2002)). Since the statistics in Takahashi et al. (2002) was based on data collected in 1972-1975, and the present study is based on data collected in 2007-2015, the ocean environment could have changed within > 30 years with the increase of anthropogenic atmospheric $pCO_2$.

In the coastal ocean waters (Fig. 3 and Table 2), surface $pCO_2$ showed low values in spring and summer and high values in winter time at most stations, with some difference in the seasonal patterns from station to station. Specifically, in the river-dominated region at buoy C6, although
surface $p\text{CO}_2$ reached a minimum in spring and a maximum in winter, similar to the surface $p\text{CO}_2$ at buoy C3 (around the Mississippi delta), it showed some finer irregular seasonal patterns (e.g., a sub-maximum in August). In details, surface $p\text{CO}_2$ was in phase with $p\text{CO}_2\_T$ between April and August, while it was in couple with the variation of $p\text{CO}_2\_\text{nonT}$ in other months. These two competing effects of $p\text{CO}_2\_T$ and $p\text{CO}_2\_\text{nonT}$ resulted in a seasonal amplitude of surface $p\text{CO}_2$ of 138.22 $\mu$atm and a relative importance factor $RI$ of 0.29, suggesting that the temperature effect plays a relatively more dominant role in controlling the seasonal variation of surface $p\text{CO}_2$ than at station C3 (where $RI = -0.05$). This is reasonable because the river discharge at this station was way-less than that at station C3 (i.e., 17,000 m$^3$/s vs. 0.27 m$^3$/s).

In the coastal upwelling ecosystem, similar to the $p\text{CO}_2$ in the subtropical upwelling system at site C5, surface $p\text{CO}_2$ at site C7 also followed closely with the $p\text{CO}_2\_\text{nonT}$ in phase, with a relative important factor $RI$ of 0.76, suggesting the non-temperature effect is the major control of the seasonal surface $p\text{CO}_2$. However, the seasonal variation patterns of surface $p\text{CO}_2$ is quite different from that at C5. Here at C7, surface $p\text{CO}_2$ reached a minimum in summer and maximum in winter. The different seasonal variation patterns of surface $p\text{CO}_2$ in these two upwelling systems were mainly attributed to the difference of the balance between the biological uptake of CO$_2$ and upwelling enrichment of CO$_2$, and was discussed in Section 4.1.

In the coastal regions with seasonal ice melting, represented by buoy C8-C10 in the Gulf of Alaska ecosystems, it was found that surface $p\text{CO}_2$ showed strong seasonal amplitude of 309.81 $\mu$atm, 279.42 $\mu$atm, and 168.28 $\mu$atm, at station C8, C9, and C10, respectively. The seasonal $p\text{CO}_2$ varies in couple with $p\text{CO}_2\_\text{nonT}$ closely in phase, which suggests the dominant control of the non-temperature effect over the temperature effect in surface $p\text{CO}_2$ over seasonal time scales in these coastal environments. This result is quite different from the findings in the temperate open ocean.
waters (represented by buoy 03), where the two competing effects both dominated the seasonal variations of surface $p\text{CO}_2$, leading to little seasonality in surface $p\text{CO}_2$. With the increase of latitude from buoy C8 to buoy C10, the relative importance of the non-temperature effect seems to increase with the relative important factor $R_I$ of -0.77, -0.80, and -0.84, for buoy C8, C9, and C10, respectively.

3.2. Interannual variations of surface $p\text{CO}_2$

In addition to the seasonal variabilities, we also examined the interannual variabilities of surface $p\text{CO}_2$ as well as atmospheric $p\text{CO}_2$ for each buoy in Table 1, with results shown in Figs. 4 and 5, and Table 3. The interannual variabilities of the surface $p\text{CO}_2$ components ($p\text{CO}_2$ _T and $p\text{CO}_2$ _nonT) were also quantified to help find the dominant controls of the interannual changes in surface $p\text{CO}_2$. Due to the data limitation, the interannual trends analyzed here mainly refers to the short-term (3-10 years) trend, which may differ from the long-term (i.e., > 30 years) trend signals. In general, both atmospheric $p\text{CO}_2$ and surface $p\text{CO}_2$ and its components showed interannual variation trends in most sites (with exceptions in some special environments) selected in this study. It was found that, the interannual variabilities in surface $p\text{CO}_2$ was mainly dominated by the non-temperature effect in tropical and subtropical zones, and was mainly controlled by the temperature effect in the temperate zone.

3.2.1. Tropical and subtropical zones

Fig. 4 is the interannual variations of surface $p\text{CO}_2$ and atmospheric $p\text{CO}_2$ of the buoys located in tropical and subtropical zones. Generally, atmospheric $p\text{CO}_2$ showed significant increasing rates (i.e., 1.20~3.60 μatm yr$^{-1}$ at $p < 0.05$) in all buoy stations. However, the corresponding surface $p\text{CO}_2$ showed variable interannual signals in different ocean environments.
In the open ocean waters from tropical (represented by buoy O1) to subtropical zone (represented by buoy O2) (Fig. 4 and Table 3), atmospheric $p$CO$_2$ showed clear interannual increase with a rate of $1.20 \mu$atm yr$^{-1}$ and $1.94 \mu$atm yr$^{-1}$ (at $p < 0.05$) over a short-term time scale of 2007-2015 and 2005-2007 at buoy O1 and O2, respectively. Correspondingly, surface $p$CO$_2$ also showed significant interannual increase with a rate of $2.77 \mu$atm yr$^{-1}$ and $5.76 \mu$atm yr$^{-1}$ (at $p < 0.05$). It is found that, the increase in surface $p$CO$_2$ was mainly resulted from the increase of the $p$CO$_2$ nonT (i.e., the interannual trend of $p$CO$_2$ nonT is greater than that of $p$CO$_2$ T, see Table 3). However, we did not find any strong and significant interannual trend in SST, SSS, and wind speed. While considering the significance of the stable increase of the interannual atmospheric $p$CO$_2$, we believe that the dominant control of the non-temperature effect in the interannual trend of surface $p$CO$_2$ is most likely attributed to continuous sink of CO$_2$ from air to the surface ocean waters over interannual time scales under anthropogenic forcing. On the other hand, although the increase rate of surface $p$CO$_2$ in subtropical zone is statistically over doubled than that in tropical zone, the interannual trend of surface $p$CO$_2$ in subtropical zone was only based on 3 years’ data (i.e., 2005-2007). More data over longer time series are needed to verify this finding (see discussion in Section 4.2).

In the coastal ocean waters at different latitudes (buoy C1-C5 in Fig. 4 and Table 3), atmospheric $p$CO$_2$ all showed clear interannual trend at an increasing rate of $1.69-3.60 \mu$atm yr$^{-1}$ (at $p < 0.05$) over a short-term scale (3-10 years). However, the interannual surface $p$CO$_2$ varied from region to region. Nevertheless, In the coastal environment without coral reefs and river discharges (represented by site C4), surface $p$CO$_2$ did show significant interannual trend at an increasing rate of $2.97 \mu$atm yr$^{-1}$ (at $p < 0.05$), and most of this interannual variability came from the $p$CO$_2$ nonT component (i.e., the interannual trend of $p$CO$_2$ nonT = $3.44 \mu$atm yr$^{-1}$, and the interannual trend
of $pCO_2_T = -0.97 \mu atm yr^{-1}$, see Table 3), suggesting that the non-temperature effect is the dominant control of surface $pCO_2$ over interannual time scale. Interestingly, the surface $pCO_2$ actually showed two interannual signals with a clear increase before 2012 (i.e., 2006-2012) and a clear decrease after 2012 (2012-2015). Yet more data are needed to further verify this phenomenon (See discussion in Section 4.2).

In the coral reef environments (represented by buoy C1 in tropical zone and C2 in subtropical zone), surface $pCO_2$ and its components did not show any significant trend over years of 2009-2015 in the tropical zone. While in the subtropical zone, surface $pCO_2$ showed a significant increasing trend of 11.44 $\mu atm yr^{-1}$ (at $p < 0.05$) over the period of 2010-2015. This interannual variabilities were found to be mainly dominated by the non-temperature effect $pCO_2_{nonT}$ (see Table 3).

In the river-dominated coastal environment (represented by buoy C3), no significant trend were found in surface $pCO_2$ as well as its temperature and non-temperature components (i.e., $pCO_2_T$ and $pCO_2_{nonT}$). In fact, there is only a few months’ data available over the period of 2009-2014. Therefore, the results derived here may not be representative for the real situation, and more data are needed for further examination (see discussion in Section 4.2).

In the coastal upwelling environment (represented by buoy C5), surface $pCO_2$ showed large interannual variability mostly within $\pm 50 \mu atm$ but without clear interannual trend over the period of 2010-2015. However, significant and comparable interannual trends were found in both $pCO_2_T$ (rate = 8.17 $\mu atm yr^{-1}$) and $pCO_2_{nonT}$ (rate = -8.13 $\mu atm yr^{-1}$) in opposite directions. Thus it seems these two competing effects canceled with each other to a large extent over interannual time scales, resulting in little interannual variabilities in surface $pCO_2$. It is noticed that surface $pCO_2$ seems to show an increase in the period of 201-2012 and a decrease over the years
of 2012-2013, but the data was very noisy and more data over longer time series are required to further analysis (see discussion in Section 4.2).

3.2.2. Temperate zone

Fig. 5 is the interannual variations of surface $p$CO$_2$ and atmospheric $p$CO$_2$ of the buoys located in temperate zone. Again, atmospheric $p$CO$_2$ were found to be increasing with significant increasing rates (i.e., 1.20–3.60 μatm yr$^{-1}$ at $p < 0.05$) in all buoy stations, and the corresponding surface $p$CO$_2$ also showed significant increase except a few special ocean environments.

In the open ocean waters (represented by buoy O3, Fig. 5 and Table 3), surface $p$CO$_2$ showed slight but insignificant increasing trend (0.57 μatm yr$^{-1}$). However, the two competing components of $p$CO$_2$ _T and $p$CO$_2$ _nonT did show significant but opposite trends with a rate of 5.38 μatm yr$^{-1}$ and ~4.60 μatm yr$^{-1}$, respectively. Thus it seems that these two competing components canceled with each other to a large extent, leading to little interannual trend in surface $p$CO$_2$, and statistically the slight interannual increase was mainly attributed to the temperature effect.

In the river-dominated coastal environment (represented by buoy C6, Fig. 5 and Table 3), similar to the results found in subtropical zone (i.e., C3), there was no significant trends shown in surface $p$CO$_2$ as well as its temperature and non-temperature components ($p$CO$_2$ _T and $p$CO$_2$ _nonT). However, different from buoy C3, here the statistics were based on data collected from each month over 9 years (i.e., 2006-2014), so there should not be large uncertainties in the derived surface $p$CO$_2$ anomalies. Considering the dynamics of river discharges to such coastal ocean environment, it seems that, the interannual variabilities of surface $p$CO$_2$ in this coastal environment was mainly driven by the river discharges, despite of the anthropogenic forcing of the $p$CO$_2$ increase in the atmosphere.
In the coastal upwelling environment (represented by buoy C7, Fig. 5 and Table 3), in contrast to the phenomenon at buoy C5, surface pCO$_2$ here showed a significant decrease with a rate of -5.69 µatm yr$^{-1}$ over the years of 2006-2015, despite of the interannual increase in atmospheric pCO$_2$. Meanwhile, both pCO$_2$ T and pCO$_2$ nonT showed significant trends with an increase rate of 2.32 µatm yr$^{-1}$ and a decrease rate of -7.98 µatm yr$^{-1}$, respectively, suggesting that the non-temperature effect is the dominant control of surface pCO$_2$ on interannual time scales.

In the coastal regions with seasonal ice melting (represented by buoy C8-C10, Fig. 5 and Table 3), surface pCO$_2$ all showed significant increasing trends at variable rates of 24.97 µatm yr$^{-1}$, 10.68 µatm yr$^{-1}$, and 5.37 µatm yr$^{-1}$, at sites C8, C9, and C10, respectively. At site C8, the statistics was based on data in 2013-2016, it is found that, both pCO$_2$ T and pCO$_2$ nonT showed positive interannual increase with a rate of 6.54 µatm yr$^{-1}$, and 15.56 µatm yr$^{-1}$, respectively, but the increase of pCO$_2$ nonT was insignificant (i.e., p > 0.05). Therefore, the extremely high increasing trend in surface pCO$_2$ at site C8 is skeptical. Considering the significance of the interannual increase of pCO$_2$ T, we believe the increase in surface pCO$_2$ was mainly controlled by the temperature effect (see discussion in Section 4.2). Similarly, it was found that the significant interannual increases of surface pCO$_2$ at sites C9 and C10 were mainly attributed to the significant increase in pCO$_2$ T, suggesting the dominant control of the temperature effect in the interannual surface pCO$_2$ in these coastal ocean environments (see discussion in Section 4.2).

4. Discussion

4.1. Driving mechanisms in seasonal surface pCO$_2$

As shown in Section 3.1, over seasonal time scales, surface pCO$_2$ was found to be mainly driven by the temperature effect in tropical and subtropical zones and was mainly controlled by the non-
temperature effect in the temperate zone with exceptions in a few special environments (e.g., coral reefs, river-dominated, upwelling-dominated). It was easy to understand the temperature effect was mainly related to SST and environmental variables that are closely related to SST such as wind speed. While for the non-temperature effect, it is not clear that which environmental variable is important in modulating this effect.

In fact, the non-temperature effect is the overall effect of biological activities (e.g., net CO\textsubscript{2} utilization, net TA change due to carbonate production and nitrate utilization), ocean mixing between different water masses that are characterized by different carbonate properties (i.e., changes in DIC and TA), and air-sea CO\textsubscript{2} fluxes. Yet it is very difficult to separate and quantify each of these non-temperature effect because of the interactions among them. Therefore, to help better understand the dominant environmental variables in affecting the non-temperature effect on surface pCO\textsubscript{2} over seasonal time scales and to improve the accuracy of satellite remote sensing of surface pCO\textsubscript{2}, various environmental variables were used as proxies of different biogeochemical and physical processes in affecting surface pCO\textsubscript{2}. Specifically, optical parameters such as Chl and K\textsubscript{d} are used as proxies of the biological productivities, atmospheric pCO\textsubscript{2} and wind speed are used to approximate the effect of the air-sea CO\textsubscript{2} exchange, SST, SSS, and wind speed are used as to indicate the effect of ocean mixing. The correlations between these environmental variables and surface pCO\textsubscript{2} as well as its components (pCO\textsubscript{2} T and pCO\textsubscript{2} nonT) were analyzed in details (Table 4).

In the tropical and subtropical ocean waters, surface pCO\textsubscript{2} was mainly dominated by the temperature component pCO\textsubscript{2} T (i.e., buoy O1-O2, C1, and C4, see Section 3.1.1), and strong correlations (i.e., R > 0.9) between pCO\textsubscript{2} T and SST were found with consistence (Table 4). Correspondingly, wind speed also showed significant negative correlations with pCO\textsubscript{2} T in these
ocean environments, suggesting wind-driven ocean mixing plays a role in modulating $pCO_2$ and thus surface $pCO_2$. It should be clarified that, the dominant control of temperature effect does mean the unimportance of the non-temperature effect. In fact, both effects are important in modulating the overall seasonal variation of surface $pCO_2$. In these ocean environments, significant correlations were found between $pCO_2$ nonT and atmospheric $pCO_2$, suggesting the contribution of the air-sea CO$_2$ fluxes to the seasonal variations of $pCO_2$ nonT, and thus surface $pCO_2$.

In the temperate ocean waters, surface $pCO_2$ was mainly driven by the non-temperature effect $pCO_2$ nonT (i.e., buoy C7-C10, see Section 3.1.2). However, the non-temperature effect refers to different oceanic processes in different ocean environments. For example, the non-temperature effect mainly refers to upwelling at station C7, while it mainly refers to the seasonal ice-melting and mixing between the freshwater and oceanic waters at stations C8-C10. Specifically, for the buoys (i.e., C8-C10) located in the Gulf of Alaska which is affected by seasonal ice-melting, SSS can be $<20$ (see Table 1). However, we did not find any significant correlations between $pCO_2$ nonT and SSS except at station C9 ($R = -0.43$). Because of the cold water characteristic of the ice-melting freshwater, we did find significant negative correlations found between $pCO_2$ nonT and SST. In the open ocean waters (represented by buoy O3), both $pCO_2$ T and $pCO_2$ nonT play comparable but competing roles in modulating seasonal surface $pCO_2$ (see Section 3.1.2). For this ocean environment, $pCO_2$ nonT showed strong correlations with SST, SSS, and wind speed, with $R$ of -0.88, 0.66, and 0.31, respectively, suggesting the effect of ocean mixing on the non-temperature effect of surface $pCO_2$. In addition, $pCO_2$ nonT also showed significant correlations with atmospheric $pCO_2$, thus the air-sea CO$_2$ fluxes also contributed to the seasonal variations of $pCO_2$ nonT and thus surface $pCO_2$. On the other hand, SST, SSS and wind speed also showed strong correlations with $pCO_2$ T but in the opposite directions as with $pCO_2$ nonT.
with $R$ of 0.99, -0.67, and -0.28, indicating the effect of ocean mixing as well as thermodynamics on the temperature effect of surface $pCO_2$.

However, as shown in Section 3.1.1, there are a few special coastal ocean environments are found to have irregular seasonal signals in surface $pCO_2$. In the coral reef environment at buoy C2, the non-temperature effect ($pCO_2$ nonT) dominated the seasonal surface $pCO_2$ ($R = -0.53$). As a result, $pCO_2$ nonT showed a significant negative correlation ($R = -0.31$) with SSS and significant positive correlation ($R = 0.16$) with wind speed (Table 4), suggesting that the effect of ocean mixing on the carbonate properties (e.g., TA and DIC). Meanwhile, atmospheric $pCO_2$ also showed a significant positive correlation ($R = 0.37$) with $pCO_2$ nonT, indicating the contribution of air-sea CO$_2$ fluxes to the non-temperature $pCO_2$ component ($pCO_2$ nonT). In fact, this effect is also visible in Fig. 2 for station C2, where the seasonal $pCO_2$ nonT co-varies with the seasonal atmospheric $pCO_2$ to some extent.

In the river-dominated regions in both subtropical zone (C3) and temperate zone (C6), surface $pCO_2$ was found to be dominant by the temperature effect in summertime and by the non-temperature effect in other seasons. However, there is some difference between the two, as C3 is affected by large river discharges (i.e., 17,000 m$^3$ s$^{-1}$) while C6 is affected by small river discharge (i.e., ~0.27 m$^3$ s$^{-1}$) but strong tidal mixing (i.e., ~2 m s$^{-1}$). Both freshwater inputs and strong ocean mixing would affect the non-temperature $pCO_2$ component ($pCO_2$ nonT), as these two processes would bring DIC and nutrient enriched waters to the ocean surface. Indeed, as a good indicator of these processes, SSS showed significant positive correlations ($R = 0.42$ at C3, and $R = 0.23$ at C6) with $pCO_2$ nonT at both stations. Meanwhile, significant correlations were also found between the biological proxies (i.e., Chl and $K_a$) and $pCO_2$ nonT at site C6 (Table 4), suggesting the biological uptake of CO$_2$ also has an effect on the non-temperature $pCO_2$ component. However,
negative but insignificant correlations were found between biological proxies and \( p\text{CO}_2\_\text{nonT} \) at site C3. Considering the data quantity (\( N = 19 \)) used in the correlation statistics, more data are needed for further verification. On the other hand, the mixing between freshwater and open ocean waters and the tidal mixing typically would bring colder waters to the ocean surface, and this would also affect the surface ocean temperature. As a result, strong negative correlations (\( R = -0.92 \) at C3, and \( R = -0.61 \) at C6) were found between \( p\text{CO}_2\_\text{nonT} \) and SST at both river-dominated regions.

In the upwelling-dominated regions in both subtropical zone (i.e., C5) and temperate zone (i.e., C7), surface \( p\text{CO}_2 \) was found to be dominant by the non-temperature effect (see Section 3.1). However, the seasonal patterns are quite different between the two regions, as surface \( p\text{CO}_2 \) varied from high to low from spring to fall at C5, but from high to low from winter to summer at C7 (see Figs. 2 and 3). Upwelling along the U.S. western coast in spring and summer brings lots of \( \text{CO}_2 \) and nutrient enriched waters to the surface of these oceanic systems (e.g., Renault et al., 2016), which would enhance the growth of phytoplankton. It’s found that the intensities of the biological uptake of nutrient and \( \text{CO}_2 \) is much stronger at station C7 (i.e., peak Chl > 5 mg m\(^{-3}\)) than at station C5 (i.e., peak Chl < 2.5 mg m\(^{-3}\)) especially in spring. Thus, the competing processes of addition of \( \text{CO}_2 \) through upwelling and the biological drawdown of \( \text{CO}_2 \) via phytoplankton uptake finally leads to a net \( p\text{CO}_2 \) increase in spring at station C5. However, we did not find any significant correlations between the biological proxies (i.e., Chl and \( K_d \)) and \( p\text{CO}_2\_\text{nonT} \). Considering the large uncertainties (~30%) in the satellite derived Chl and \( K_d \), the signal to noise ratio could be very low after removing the seasonality in these parameters, making it difficult to detect the correlations between these parameters with \( p\text{CO}_2\_\text{nonT} \). On the other hand, the upwelling waters
are typically characterized as cold water, correspondingly, strong negative correlations were found between $pCO_2$ non T and SST ($R = -0.70$ at C5 and $R = -0.57$ at C7, at $p < 0.05$).

4.2. Driving mechanisms in interannual surface $pCO_2$

To further examine the dominant controls of surface $pCO_2$ over interannual time scales, the interannual variations of the environmental variables (e.g., SST, SSS, and wind speed, atmospheric $pCO_2$) for each buoy in Table 1 were also processes and analyzed (Table 3). Specifically, SST is used as a proxy of the temperature effect ($pCO_2$ T), and SSS, wind speed, and atmospheric $pCO_2$ were used as proxies of the non-temperature effect ($pCO_2$ non T). It should be clarified that Chl and $K_0$ were not used in this analysis mainly because of the data scarcities and large uncertainties of these data in the study period of each buoy.

In the tropical and subtropical zones, the interannual surface $pCO_2$ was found to be mainly dominated by the non-temperature effect with exceptions in special ocean environments (e.g., river-dominated, upwelling-dominated) (see Section 3.2). However, the interannual anomalies of SSS and Wind speed did not show clear signals in most stations, suggesting that there was little change in the physical ocean environments (e.g., ocean mixing). In contrast, the atmospheric $pCO_2$ all showed clear interannual increase for all the buoys located in the tropical and subtropical zones. Therefore, it is most likely that, the dominant control of non-temperature effect on the interannual increase of surface $pCO_2$ was mainly caused by the interannual changes in the air-sea $CO_2$ flux. The air-sea $CO_2$ flux mainly depends on the $CO_2$ gas solubility which is related to SST, the gas transfer velocity which is related to wind speed, and the relative difference between the atmospheric $pCO_2$ and surface $pCO_2$ (e.g., Burges et al., 2005; Takahashi et al., 2009; Wanninkhof et al., 2013). Since there is little changes in both SST and wind speed (buoys O1-O2 and C1-C5, see Table 3), it is most likely that the interannual increase in surface $pCO_2$ was mainly driven by
the atmospheric $p$CO$_2$. Yet, it still could be possible that Chl and $K_d$ may have some interannual signals that dominates the non-temperature effect on surface $p$CO$_2$. However, a recent study by Chen et al. (prepared) did not find any interannual trend in both Chl and $K_d$ in the different regions of the Gulf of Mexico. Further studies need to be conducted for a clear interpretation of this non-temperature effect.

In the temperate zone, surface $p$CO$_2$ was found to be mainly controlled by the temperature effect over interannual time scales with some exceptions in special ocean environments (e.g., river-dominated, upwelling-dominated) (see Section 3.2). Interestingly, although SST did not show clear interannual patterns in tropical and subtropical zones, it did show significant interannual trends with variable increasing rates between 0.17 and 0.65 °C yr$^{-1}$ in the temperate zone. This finding confirmed the dominant warming effects on surface $p$CO$_2$ over short-term interannual time scales in the temperate zone, despite of the leading control of the non-temperature effect on the seasonal changes of surface $p$CO$_2$ in this region.

In the river-dominated regions (represented by buoy C3 and C6), surface $p$CO$_2$ did not show clear and significant interannual trends as presented in Figs. 4 and 5. At station C3, SSS showed a significant decrease with a rate of -0.46 yr$^{-1}$ over the period of 2009-2014, while at station C6, SSS showed a significant but slight increase with a rate of 0.09 yr$^{-1}$ over the period of 2006-2014. Therefore, it seems the insignificant increase (decrease) trend in surface $p$CO$_2$ at station C3 (C6) was mainly caused by interannual decrease (increase) in SSS. Still, further investigation is needed with more in situ time series data available.

In the upwelling-dominated regions (represented by buoy C5 and C7), surface $p$CO$_2$ showed decrease over interannual time scales at both C5 (-0.28 μatm yr$^{-1}$, at $p > 0.05$) and C7 (-5.69 28 μatm yr$^{-1}$, at $p < 0.05$). At both stations, SST and SSS showed significant interannual trends, while
no significant interannual signal was found in the wind speed. It is suspected that, the strong biological uptake of CO$_2$ with the sufficient supply of nutrients from upwelling may exceed the enrichment of CO$_2$ from subsurface over interannual time scales, and the difference between the two is getting stronger over years. Still, more ancillary data over long time series are required to further investigation.

4.3. Implication and future improvements

Based on the buoy data time series located in various oceanic ecosystems, the seasonal and interannual variations of surface $p$CO$_2$ were investigated in this study. We found that, over seasonal time scales, surface $p$CO$_2$ was mostly driven by the temperature effect in tropical and subtropical zones and was mainly dominated by the non-temperature effect in temperate zones; and over interannual time scales, surface $p$CO$_2$ was mainly controlled by the non-temperature effect in the tropical and subtropical zones and was mainly driven by the temperature effect in the temperate zone. Specifically, for the non-temperature effect either over seasonal or interannual time scales, the effects of ocean mixing and air-sea CO$_2$ fluxes are expressed well by the environmental proxies (e.g., SST, SSS, and wind speed). It is found that, atmospheric $p$CO$_2$ is an important parameter in driving both seasonal and interannual surface $p$CO$_2$ at most buoy stations in this study. However, this factor was not included in most of the published surface $p$CO$_2$ satellite remote sensing algorithms. Thus it should be why these developed $p$CO$_2$ remote sensing algorithms are most limited in capturing the interannual variabilities in surface $p$CO$_2$.

Although the general seasonal and interannual variations patterns in surface $p$CO$_2$ and its dominant controls of the temperature or non-temperature effects as well as the dominant environmental variables were found, future improvements are still needed to increase the accuracy of satellite mapping of surface $p$CO$_2$. 
Specifically, in the coastal oceans, the biological activities are known to be active and it is thought to be an important process in modulating surface $p$CO$_2$ (Norman et al., 2013; Ikawa et al., 2013; Huang et al., 2015). However, due to the data insufficiencies of both the field and concurrent satellite measurements, no significant correlations were found between surface $p$CO$_2$ and the satellite-based optical parameters (i.e., Chl, Kd) for most coastal ocean buoys. It is possible that the biological proxies may vary on different time scales from that of the surface $p$CO$_2$. This is not an unreasonable possibility, considering the complexities of the biological processes (i.e., photosynthesis, respiration, and calcification) in modulating surface $p$CO$_2$. In the future, instead of using limited satellite-based Chl and Kd data, in situ time series of the biological proxies (i.e., dissolved oxygen, apparent oxygen utilization, nutrients, Chl fluorescence, and Kd) should be measured together with surface $p$CO$_2$ for a better understanding of the biological role in changing surface $p$CO$_2$. More importantly, the algal bloom effect on surface $p$CO$_2$ needs to be thoroughly investigated by examining the $p$CO$_2$ variations before, during, and after an algal bloom.

In terms of interannual variations of surface $p$CO$_2$, the current analyses were based on 3-10 years of time series data, therefore, the derived short-term interannual variabilities may not be representative of a long-term (i.e., > 30 years) trend. Besides, the analyses were based on data collected over different time periods. From Figs. 4 and 5, it seems the interannual variation rate of surface $p$CO$_2$ changes over different study periods. For example, at station C4, the surface $p$CO$_2$ seems to be increasing between 2006 and 2012 but seems to be decreasing between 2012 and 2015. Therefore, to better quantify the interannual variabilities in surface $p$CO$_2$, more time series data are needed. Furthermore, it is found that non-temperature effect ($p$CO$_2$ nonT) dominates the interannual changes of surface $p$CO$_2$ in most cases, with a much higher rate than the increase of atmospheric $p$CO$_2$. To further differentiate the effects of air-sea CO$_2$ change, biological effects,
and vertical mixing, and quantify the role of each process in the interannual variations of surface $p$CO$_2$, long term field-measured biological data (i.e., oxygen, nutrients, Chl, and K$_d$) and physical data (i.e., mixed layer depth, and wind speed) are needed.

Last, but not least, for similar types of coastal environments (i.e., coral reef, river-dominated, and upwelling) the dominant control of surface $p$CO$_2$ varies, due to the different environmental characteristics (e.g., the strength of river discharges and tidal mixing) in each system at different latitudes. To further interpret the difference in surface $p$CO$_2$ in the same type of coastal environment, more ancillary data are also needed to better characterize the carbonate process in each coastal ecosystem.

5. Conclusion

Using both in situ time series data and satellite data at different latitudes along the coasts of the U.S. and its territories, the dominant controls and driving mechanisms of surface $p$CO$_2$ on seasonal and short-term interannual time scales were quantified and analyzed. The temperature (non-temperature) effect was found to be dominant in modulating the seasonal $p$CO$_2$ variations in the tropical and subtropical zones (temperate zone) and the interannual $p$CO$_2$ variations in the temperate zone (tropical and subtropical zones), with exceptions in a few special coastal ocean environments (e.g., coral reefs, river-dominated, upwelling-dominated). The study also suggests future directions in the development of surface $p$CO$_2$ satellite remote sensing algorithms. For example, atmospheric $p$CO$_2$ should be used in the surface $p$CO$_2$ remote sensing algorithms to better capture the interannual variabilities in surface $p$CO$_2$. Meanwhile, to further examine the driving mechanisms of surface $p$CO$_2$ on different time scales, more data (e.g., Chl) collected over longer time series are required for future investigation.
Acknowledgements

This research was supported by a University of South Florida student fellowship. The authors are indebted to all researchers, including those of NOAA NCEI, who have collected, processed, quality controlled, and shared all the cruise survey data. These data played an essential role in this work. The authors also thank NASA for providing MODIS ocean color data, NCEP for providing the wind speed data.

Reference


Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/OTG.TSM_GRAYSRF_81W_31N.


Table 1. Summary of in situ time series data compiled for this study (from low latitude to high latitudes in sequence). Buoys of O1-O2 and C1-C5 are located in the tropical and subtropical zones (i.e., latitude within 0–35°N, shaded in blue), and buoys of O3 and C6-C10 are located in the temperate zone (i.e., latitude within 35–66.5°N, shaded in green). Note that “O” represents Open Ocean, and “C” represents Coastal Ocean. See Fig. 1 for the location of each buoy.

<table>
<thead>
<tr>
<th>Buoy</th>
<th>Geolocation</th>
<th>Period</th>
<th>SST</th>
<th>SSS</th>
<th>Atmospheric pCO₂</th>
<th>Surface pCO₂</th>
<th>Number of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>17.954°N, 67.051°W</td>
<td>2009-2015</td>
<td>23.92-31.71</td>
<td>31.73-36.37</td>
<td>387.4-427.4</td>
<td>317.9-538.4</td>
<td>16,454</td>
</tr>
<tr>
<td>C2</td>
<td>22.870°N, 157.970°W</td>
<td>2007-2015</td>
<td>22.90-32.20</td>
<td>36.02-33.37</td>
<td>396.9-399.1</td>
<td>349.1-496.7</td>
<td>17,201</td>
</tr>
<tr>
<td>C3</td>
<td>24.898°N, 86.618°W</td>
<td>2010-2015</td>
<td>16.75-33.13</td>
<td>32.42-38.92</td>
<td>364.6-413.3</td>
<td>182.4-736.8</td>
<td>10,760</td>
</tr>
<tr>
<td>C4</td>
<td>30.000°N, 88.600°W</td>
<td>2009-2014</td>
<td>12.66-32.42</td>
<td>14.00-35.64</td>
<td>350.7-430.0</td>
<td>71.1-607.5</td>
<td>5,022</td>
</tr>
<tr>
<td>C5</td>
<td>31.399°N, 80.368°W</td>
<td>2006-2015</td>
<td>9.84-30.99</td>
<td>79.20-56.40</td>
<td>352.6-436.3</td>
<td>268.2-619.6</td>
<td>15,663</td>
</tr>
<tr>
<td>O1</td>
<td>31.780°N, 64.200°W</td>
<td>2002-2007</td>
<td>18.61-26.74</td>
<td>35.44-36.08</td>
<td>357.1-387.4</td>
<td>317.6-447.3</td>
<td>5,116</td>
</tr>
<tr>
<td>O2</td>
<td>34.320°N, 120.810°W</td>
<td>2010-2016</td>
<td>9.03-20.00</td>
<td>31.09-33.92</td>
<td>366.3-433.2</td>
<td>220.4-806.3</td>
<td>13,223</td>
</tr>
<tr>
<td>O3</td>
<td>43.024°N, 70.543°W</td>
<td>2006-2014</td>
<td>0.85-22.32</td>
<td>22.56-33.18</td>
<td>253.0-462.6</td>
<td>194.4-696.2</td>
<td>17,011</td>
</tr>
<tr>
<td>O4</td>
<td>50.120°N, 144.830°W</td>
<td>2007-2015</td>
<td>4.35-16.23</td>
<td>32.12-32.76</td>
<td>357.1-406.6</td>
<td>340.1-466.6</td>
<td>16,826</td>
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<tr>
<td>C8</td>
<td>57.697°N, 132.315°W</td>
<td>2013-2015</td>
<td>2.70-14.71</td>
<td>17.52-32.42</td>
<td>367.3-437.5</td>
<td>188.5-586.4</td>
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</tr>
<tr>
<td>C9</td>
<td>59.911°N, 189.348°W</td>
<td>2011-2017</td>
<td>3.09-18.78</td>
<td>17.25-33.33</td>
<td>399.3-449.6</td>
<td>124.6-487.4</td>
<td>12,291</td>
</tr>
</tbody>
</table>
Table 2. Seasonal amplitudes of atmospheric \textit{pCO}_2, surface \textit{pCO}_2 and its components (\textit{pCO}_2\_T and \textit{pCO}_2\_nonT), and the relative importance (Eq. 6) of the temperature and non-temperature effects in affecting surface \textit{pCO}_2 at each buoy location (Table 1, from low latitude to high latitudes in sequence). Note that statistics of the buoys located in the tropical and subtropical zones and temperate zone are shaded in blue and green, respectively.

<table>
<thead>
<tr>
<th>Buoy</th>
<th>Seasonal amplitude (μatm)</th>
<th>Relative importance (R) of \textit{pCO}_2_T and \textit{pCO}_2_nonT (Eq. 6)</th>
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<td>Surface \textit{pCO}_2</td>
<td>Atmospheric \textit{pCO}_2</td>
</tr>
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<td>60.26</td>
<td>9.67</td>
</tr>
<tr>
<td>O1</td>
<td>22.32</td>
<td>12.61</td>
</tr>
<tr>
<td>C2</td>
<td>227.94</td>
<td>15.00</td>
</tr>
<tr>
<td>C3</td>
<td>114.88</td>
<td>30.33</td>
</tr>
<tr>
<td>C4</td>
<td>154.37</td>
<td>23.19</td>
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<tr>
<td>O2</td>
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<td>C5</td>
<td>95.82</td>
<td>16.58</td>
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<tr>
<td>O6</td>
<td>138.22</td>
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<td>C7</td>
<td>123.22</td>
<td>19.75</td>
</tr>
<tr>
<td>O3</td>
<td>20.81</td>
<td>16.18</td>
</tr>
<tr>
<td>C8</td>
<td>309.81</td>
<td>17.96</td>
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<tr>
<td>C9</td>
<td>279.42</td>
<td>17.24</td>
</tr>
<tr>
<td>C10</td>
<td>168.28</td>
<td>18.21</td>
</tr>
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</table>
Table 3. Interannual variabilities (i.e., interannual trend) of the atmospheric pCO₂, surface pCO₂ and its components ($\rho$CO₂ T and $\rho$CO₂ nonT), and the corresponding environmental variables based on the buoy time series data in Table 1 and Fig. 1 (from low latitude to high latitudes in sequence). Statistics of the buoys located in the tropical and subtropical zones and temperate zone are shaded in blue and green, respectively. Note that values in brackets are the corresponding R² of each statistic of the interannual trend, and statistics are highlighted in blue if the corresponding p value is < 0.05.

<table>
<thead>
<tr>
<th>Buoy</th>
<th>Surface pCO₂ (µatm/µyr)</th>
<th>Atmospheric pCO₂ (µatm/µyr)</th>
<th>$\rho$CO₂ T (µatm/µyr)</th>
<th>$\rho$CO₂ nonT (µatm/µyr)</th>
<th>SST (°C/µyr)</th>
<th>SSS</th>
<th>Wind speed (m s⁻¹/µyr)</th>
<th>Period</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>-0.02 (0.00)</td>
<td>1.69 (0.74)</td>
<td>-0.32 (0.01)</td>
<td>0.29 (0.01)</td>
<td>-0.02 (0.01)</td>
<td>0.03 (0.01)</td>
<td>0.08 (0.06)</td>
<td>2009-2015</td>
<td>79</td>
</tr>
<tr>
<td>O1</td>
<td>2.77 (0.07)</td>
<td>1.20 (0.76)</td>
<td>0.87 (0.11)</td>
<td>1.93 (0.42)</td>
<td>0.05 (0.12)</td>
<td>0.03 (0.07)</td>
<td>-0.10 (0.00)</td>
<td>2007-2015</td>
<td>76</td>
</tr>
<tr>
<td>C2</td>
<td>11.44 (0.26)</td>
<td>2.40 (0.67)</td>
<td>2.57 (0.21)</td>
<td>9.91 (0.05)</td>
<td>0.14 (0.05)</td>
<td>-0.00 (0.00)</td>
<td>-4.02 (0.00)</td>
<td>2010-2015</td>
<td>48</td>
</tr>
<tr>
<td>C3</td>
<td>-2.03 (0.01)</td>
<td>2.19 (0.72)</td>
<td>-3.66 (0.16)</td>
<td>7.19 (0.07)</td>
<td>-0.32 (0.19)</td>
<td>-0.46 (0.27)</td>
<td>0.02 (0.00)</td>
<td>2009-2014</td>
<td>24</td>
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<tr>
<td>C4</td>
<td>-2.97 (0.09)</td>
<td>1.99 (0.86)</td>
<td>-0.97 (0.04)</td>
<td>3.44 (0.11)</td>
<td>0.03 (0.03)</td>
<td>-0.04 (0.00)</td>
<td>0.01 (0.00)</td>
<td>2006-2015</td>
<td>75</td>
</tr>
<tr>
<td>O2</td>
<td>5.36 (0.43)</td>
<td>1.94 (0.59)</td>
<td>1.34 (0.02)</td>
<td>4.56 (0.25)</td>
<td>0.09 (0.02)</td>
<td>-0.06 (0.18)</td>
<td>-4.06 (0.27)</td>
<td>2002-2007</td>
<td>22</td>
</tr>
<tr>
<td>C5</td>
<td>-2.62 (0.09)</td>
<td>3.60 (0.72)</td>
<td>8.17 (0.47)</td>
<td>-8.13 (0.11)</td>
<td>0.48 (0.47)</td>
<td>0.09 (0.40)</td>
<td>-4.07 (0.07)</td>
<td>2010-2015</td>
<td>62</td>
</tr>
<tr>
<td>C6</td>
<td>-0.33 (0.00)</td>
<td>2.55 (0.86)</td>
<td>0.87 (0.01)</td>
<td>-9.98 (0.01)</td>
<td>0.03 (0.02)</td>
<td>0.00 (0.02)</td>
<td>0.02 (0.00)</td>
<td>2006-2014</td>
<td>87</td>
</tr>
<tr>
<td>C7</td>
<td>-5.69 (0.32)</td>
<td>1.75 (0.80)</td>
<td>2.32 (0.22)</td>
<td>-7.98 (0.44)</td>
<td>0.17 (0.25)</td>
<td>-0.06 (0.14)</td>
<td>-4.03 (0.05)</td>
<td>2006-2015</td>
<td>70</td>
</tr>
<tr>
<td>C8</td>
<td>0.57 (0.02)</td>
<td>2.16 (0.83)</td>
<td>5.98 (0.38)</td>
<td>-4.60 (0.27)</td>
<td>0.33 (0.51)</td>
<td>-0.01 (0.09)</td>
<td>-4.06 (0.02)</td>
<td>2007-2015</td>
<td>76</td>
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<tr>
<td>C9</td>
<td>10.68 (0.22)</td>
<td>1.42 (0.28)</td>
<td>10.05 (0.09)</td>
<td>1.00 (0.72)</td>
<td>0.65 (0.15)</td>
<td>-0.14 (0.07)</td>
<td>0.20 (0.07)</td>
<td>2013-2015</td>
<td>38</td>
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<tr>
<td>C10</td>
<td>2.57 (0.23)</td>
<td>2.55 (0.72)</td>
<td>4.55 (0.57)</td>
<td>0.67 (0.00)</td>
<td>0.34 (0.55)</td>
<td>-0.09 (0.04)</td>
<td>-4.04 (0.01)</td>
<td>2011-2017</td>
<td>55</td>
</tr>
</tbody>
</table>
Table 4. Correlations (Pearson correlation coefficient – $R$) between surface $p_{CO_2}$ as well as its components ($pCO_2_T$ and $pCO_2_{nonT}$) and different environmental variables (i.e., SST, SSS, atmospheric $pCO_2$, Chl and $K_a$ in log$_{10}$ scale, and wind speed) for all the buoys listed in Table 1 from low latitude to high latitude in sequence. Statistics of the buoys located in the tropical and subtropical zones and temperate zone are shaded in blue and green, respectively. Note that the value of $R$ is highlighted in blue if the corresponding $p$ value is < 0.05.

<table>
<thead>
<tr>
<th>Buoy</th>
<th>Variables</th>
<th>SST</th>
<th>SSS</th>
<th>Atmospheric $pCO_2$</th>
<th>Chl</th>
<th>$K_a$</th>
<th>Wind speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Surface $pCO_2$</td>
<td>0.44</td>
<td>0.50</td>
<td>-0.10</td>
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<td>NaN</td>
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<td>$pCO_2_T$</td>
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<td>-0.10</td>
<td>-0.39</td>
<td>-0.12</td>
<td>NaN</td>
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<tr>
<td></td>
<td>$pCO_2_{nonT}$</td>
<td>-0.32</td>
<td>0.38</td>
<td>0.12</td>
<td>NaN</td>
<td>NaN</td>
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<tr>
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<td>$N$</td>
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<td>79</td>
<td>79</td>
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</tr>
<tr>
<td>O1</td>
<td>Surface $pCO_2$</td>
<td>0.54</td>
<td>0.10</td>
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<td>-0.08</td>
<td>-0.35</td>
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<tr>
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<td>-0.03</td>
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<tr>
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<td>0.17</td>
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<tr>
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<td>76</td>
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</tr>
<tr>
<td>C2</td>
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<td>$pCO_2_T$</td>
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<td>48</td>
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</tr>
<tr>
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<td>Surface $pCO_2$</td>
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<td>$pCO_2_{nonT}$</td>
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<td>0.42</td>
<td>0.41</td>
<td>-0.29</td>
<td>-0.44</td>
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<td>$N$</td>
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<td>24</td>
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<td>19</td>
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<td>C4</td>
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Fig. 1. Spatial distributions of the buoys listed in Table 1. Buoys of O1-O2 and C1-C5 are located in the tropical and subtropical zones (i.e., latitude within 0–35° N), and buoys of O3 and C6-C10 are located in the temperate zone (i.e., latitude within 35–66.5° N). Note that “O” represents Open Ocean, and “C” represents Coastal Ocean. See Table 1 for detailed description of the data collected from each buoy.
Fig. 2. Seasonal variations of atmospheric $p$CO$_2$, surface $p$CO$_2$ and its components ($p$CO$_2$$_T$ and $p$CO$_2$$_{nonT}$) of the buoys located in the tropical and subtropical zones (see Table 1 and Fig. 1) from low latitude to high latitude in sequence. See Table 2 for detailed statistics.
Fig. 3. Same as Fig. 2, here are the seasonal variations of atmospheric $pCO_2$, surface $pCO_2$ and its components ($pCO_2\_T$ and $pCO_2\_noT$) of the buoys located in the temperate zone (see Table 1 and Fig. 1) from low latitude to high latitude in sequence. See Table 2 for detailed statistics.
Fig. 4. Interannual variabilities of atmospheric $p$CO$_2$ and surface $p$CO$_2$ of the buoys located in the tropical and subtropical zones (see Table 1 and Fig. 1) from low latitude to high latitude in sequence. The overlaid dashed red line is the interannual variation trend. See Table 3 for detailed statistics.
Fig. 5. Same as Fig. 4, here are the interannual variabilities of the atmospheric $p$CO$_2$ and surface $p$CO$_2$ of the buoys located in the temperate zone (see Table 1 and Fig. 1) from low latitude to high latitude in sequence. The overlaid dashed red line is the interannual variation trend. See Table 3 for detailed statistics.
APPENDIX F:

AUTHOR CONTRIBUTIONS AND COPYRIGHT CLEARANCES

1. Author Contributions

Appendix A: Remote estimation of surface $p$CO$_2$ on the West Florida Shelf

S. Chen developed the research approach, processed the data, conducted the analyses, and wrote the manuscript.

C. Hu assisted in developing the research approach, acquired funding for the research, and reviewed drafts of the manuscript.

R. H. Byrne analyzed data and reviewed drafts of the manuscript.

L. L. Robbins provided and analyzed data, and reviewed drafts of the manuscript.

B. Yang analyzed data and reviewed the manuscript.

Appendix B: Estimating surface $p$CO$_2$ in the northern Gulf of Mexico: Which remote sensing model to use?

S. Chen developed the research approach, processed the data, conducted the analyses, and wrote the manuscript.

C. Hu assisted in developing the approach, acquired funding for the research, and reviewed drafts of the manuscript.

W. J. Cai analyzed the data and reviewed drafts of the manuscript.
B. Yang reviewed drafts of the manuscript.

Appendix C: Estimating sea surface salinity in the northern Gulf of Mexico from satellite ocean color measurements

S. Chen developed approach, processed data, conducted analyses and wrote manuscript

C. Hu developed approach, acquired funding, and reviewed manuscript

Appendix D: A machine learning approach to estimate surface ocean $pCO_2$ from satellite measurements

S. Chen developed approach, processed data, conducted analyses and wrote manuscript

C. Hu developed approach, acquired funding, and reviewed manuscript

R. Wanninkhof provided data and reviewed manuscript

W. J. Cai provided data and reviewed manuscript

L. Barbero provided data and reviewed manuscript

2. Copyright Clearances

Appendix A:
Appendix B:

Remote estimation of surface pCO₂ on the West Florida Shelf
Shuangling Chen, Chuannin Hu, Robert H. Byrne, Lisa L. Robbins, Bo Yang
Continental Shelf Research

Estimating surface pCO₂ in the northern Gulf of Mexico: Which remote sensing model to use?
Shuangling Chen, Chuannin Hu, Wei-Jun Cal, Bo Yang
Continental Shelf Research

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APPENDIX G:

PUBLICATIONS (PUBLISHED AND SUBMITTED)


