Remote estimation of surface $p\text{CO}_2$ on the West Florida Shelf

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Abstract

Surface $p\text{CO}_2$ data from the West Florida Shelf (WFS) have been collected during 25 cruise surveys between 2003 and 2012. The data were scaled up using remote sensing measurements of surface water properties in order to provide a more nearly synoptic map of $p\text{CO}_2$ 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 $p\text{CO}_2$ model based on concurrent MODIS (Moderate Resolution Imaging Spectroradiometer) estimates of surface chlorophyll *a* concentrations (CHL, mg m^{-3}), diffuse light attenuation at 490 nm ($K_d\text{_{Lee}}$, m^{-1}), and sea surface temperature (SST, $^{\circ}\text{C}$). Validation using an independent dataset showed a $p\text{CO}_2$ Root Mean Square Error (RMSE) of $< 12 \mu\text{atm}$ and a 0.88 coefficient of determination (R^2) for measured and model-predicted $p\text{CO}_2$ ranging from 300 to 550 μatm . The model was more sensitive to SST than to CHL and $K_d\text{_{Lee}}$, with a 1°C change in SST leading to a $\sim 16 \mu\text{atm}$ change in the predicted $p\text{CO}_2$. Application of the model to the entire WFS MODIS time series between 2002 and 2014 showed clear seasonality, with maxima ($\sim 450 \mu\text{atm}$) in summer and minima ($\sim 350 \mu\text{atm}$) in winter. The seasonality was positively correlated to SST (high in summer and low in winter) and negatively correlated to CHL and $K_d\text{_{Lee}}$ (high in winter and low in summer). Inter-annual variations of $p\text{CO}_2$ were consistent with inter-annual variations of SST, CHL, and $K_d\text{_{Lee}}$. These results suggest that surface water $p\text{CO}_2$ of the WFS can be estimated, with known uncertainties, from

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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.

Keywords: surface $p\text{CO}_2$, satellite remote sensing, MODIS, chlorophyll, SST, Kd, WFS

1. Introduction

Atmospheric CO_2 has increased by 40% since the industrialization era (Sabine et al., 2004; Solomon et al., 2007). Correspondingly, oceanic uptake of CO_2 has resulted in ocean acidification and decreased surface water pH (by ~ 0.1 units) (Sun et al., 2012; Pachauri and Meyer 2014), leading to ecological degradation and a decrease of marine biodiversity (Widdicombe and Spicer 2008; Orr et al., 2005; Feely et al., 2012). Due to large spatial and temporal variations in surface water CO_2 partial pressure ($p\text{CO}_2$), the magnitude and even the sign of air/sea CO_2 fluxes can be highly variable (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., 2013). Accurate knowledge of surface $p\text{CO}_2$ 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 CO_2 fluxes for both the open ocean and coastal sites (e.g., Takahashi et al., 2002, 2009, 2014; Tseng et al., 2011; Jiang et al., 2008; Geilfus et al., 2012; Vandemark 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 $p\text{CO}_2$ (e.g., Xue et al., 2014; Arruda et al., 2015), 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 $p\text{CO}_2$ algorithm development (e.g., Ono et al., 2004; Sarma et al., 2006; Jamet et al., 2007; Telszewski et al., 2009; Hales et al., 2012; Nakaoka et al., 2013; Signorini et al., 2013; Bai et al., 2015), there is potential for the use of satellite remote sensing to augment direct field assessments of air/sea CO_2 fluxes. Nevertheless, except for two studies that focused on nearshore waters off the Mississippi River delta (Lohrenz and Cai 2006; Lohrenz 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.

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 *p*CO₂ should play an important role. In particular, with continuous surface *p*CO₂ 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 *p*CO₂ 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 gentle slope, 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 (Jolliff et al., 2003; Weisberg and He, 2003; Hu et al., 2005; Hu et al., 2006; Walsh et al., 2006; Benway 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 (Saul et al., 2013; Chagaris et al., 2015). As one of the broadest continental shelves of United States (He and Weisberg, 2002), the WFS may play a big role in modulating CO₂ flux in the GOM, and knowledge of synoptic surface *p*CO₂ 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 *p*CO₂ data through numerous ship surveys, and one study (Xue et al., 2014) to model *p*CO₂ 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 *p*CO₂ 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 $p\text{CO}_2$ on the WFS. The present work is directed toward bridging knowledge gaps by providing, for the first time, monthly $p\text{CO}_2$ distribution maps at medium resolution (1-km) and their temporal variations on the WFS.

2. Data and methods

2.1. A brief review of $p\text{CO}_2$ remote sensing

While the details of different methods to estimate surface $p\text{CO}_2$ from remote measurements can be found in the literature (as listed in Table 1), for completeness the methods are briefly described here.

Table 1. List of published works on remote sensing of surface ocean $p\text{CO}_2$, arranged in chronological order. Note that studies of surface ocean $p\text{CO}_2$ without the use of remote sensing are not listed here.

Reference	Study area	Model input	Model	Model uncertainty
Stephens et al. (1995)	North Pacific	SST, LON	MPR	RMSE = +/-17 μatm (subtropical), RMS = +/- 40 μatm (subpolar)
Lefevre et al. (2002)	Coast off Chile	SST, SSS, CHL	MLR	STD = 35 μatm , $R^2=0.65$
Sarma (2003)	Arabian Sea	SST, SSS, CHL	MLR for DIC and TA	errors= +/- 5-30 μatm
Olsen et al. (2004)	Caribbean Sea	SST, LAT, LON	MLR	RMSE=9.5 μatm , $R^2=0.8$
Ono et al. (2004)	North Pacific	SST, CHL	MPR	RMSE = +/- 14 μatm (subtropical), RMSE = +/-17 μatm (subpolar)
Rangama et al. (2005)	Southern ocean	SST, CHL	MLR	STD = 2.6~7.9 μatm
Sarma et al. (2006)	North Pacific	SST, SSS, CHL	MLR for DIC and TA	RMSE = 17~23 μatm
Lohrenz and Cai (2006)	Mississippi River delta	SST, SSS, CHL	PCA and MLR	$R^2 = 0.743$, RMSE = 50.2 μatm
Jamet et al. (2007)	North Atlantic	SST, CHL, MLD	MLR	$R = 0.45\sim0.86$, RMSE = 8.98~15.01 μatm
Watanabe et al. (2007)	East China Sea	SST, CHL, SSS	MPR for TA and DIC	Not available
Berryman et al. (2008)	Central Pacific	SST, SSS, CHL	MLR	$R^2 = 0.59$, $p < 0.02$
Evans et al. (2008)	Oregon and Washington Shelf	SST, CHL	Not available	Not available
Zhu et al. (2009)	Northern South China Sea	SST, CHL	MPR	$R^2=0.66$, RMSE = 25.1 μatm , $R^2=0.68$ RMSE = 4.6 μatm
Chierici et al. (2009)	Northern North Atlantic	SST, CHL, MLD	MPR	RMSE = 10.8 μatm , $R^2=0.72$
Telszewski et al. (2009)	North Atlantic	SST, CHL, MLD	SOM	RMSE = 11.6 μatm
Friedrich and Oschlies (2009)	North Atlantic	SST, CHL	KFM	RMSE = 19 μatm
Shadwick et al. (2010)	Scotian Shelf	SST, CHL, wind speed	MLR	STD = 13 μatm , $R^2=0.81$
Borges et al. (2010)	Belgian coastal zone	SST, CHL	MPR	Not available

Lohrenz et al. (2010)	Mississippi River delta	SST, SSS, CHL	PCA and MLR	$R^2 = 0.165\sim0.976$, $p<0.001$
Karagali et al. (2010)	Peru and Namibia	SST, CHL	MPR	$R^2=0.67\sim0.72$
Chen et al. (2011)	Southern Atlantic and Indian Ocean	SST, CHL	MLR	$R^2=0.77, 0.85$, STD=1.21, 21.0 μatm
Wipf et al. (2012)	Santa Barbara Channel	SST, CHL, NO_3^-	MLR	Not available
Jo et al. (2012)	Northern South China Sea	SST, CHL, LAT, LON	FFBP	RMSE = 6.9 μatm , $R^2 = 0.98$
Hales et al. (2012)	North American West Coast	SST, CHL	Quasi-mechanistic model	$R = 0.61\sim0.93$, RMSE = 6.6~65 μatm
Tao et al. (2012)	Huanghai Sea and Bohai Sea	SST, CHL	MPR	RMSE=15.82~31.74 μatm
Nakaoka et al. (2013)	North Pacific	SST, SSS, CHL, MLD	SOM	RMSE = 17.6~20.2 μatm
Signorini et al. (2013)	North American East Coast	SST, SSS, CHL, Jday	MLR	$R^2 = 0.42\sim0.82$, RMSE = 22.4~36.9 μatm
Marrec et al. (2014)	Western English Channel	SST,SSS,CHL,MLD,Jday,LAT,LON	MLR	RMSE = 17.2, 21.5 μatm , $R^2=0.71,0.79$
Parard et al. (2014)	Baltic Sea	SST,CHL,CDOM,NPP,MLD,Jday	MLR and SOM	RMSE = 35 μatm , $R^2 = 0.93$
Qin et al. (2014)	Yellow Sea	SST, CHL	MPR	RMSE=16.68~21.46 μatm
Bai et al. (2015)	East China Sea	TA, DIC, CHL	Mechanistic semi-analytical model	Not available, but large uncertainty can be detected from the model validation.
Marrec et al. (2015)	European shelf	SST, CHL, wind speed, PAR, MLD	MLR	RMSE=16, 17 μatm
Padhy et al. (2015)	Hooghly Estuary	SST, CHL	MPR	RMSE=18 μatm
Moussa et al. (2016)	Tropical Atlantic	SST, SSS, CHL	FNN	RMSE=8.7~9.6 μatm
Note: MLR=Multiple Linear Regression; MPR=Multiple Polynomial Regression; PCA=Principal Component Analysis; SOM=Self Organising Map; FFBP= Feed Forward Back Propagation; KFM=Kohonen Feature Map; FNN=Feedforward Neural Network; STD=Standard Deviation; CDOM=Colored Dissolved Organic Matter; NPP=Net Primary Production; PAR=Photosynthetically Active Radiation; Jday=Julian day; R=Correlation Coefficient.				

In terms of model inputs, most published works correlated surface $p\text{CO}_2$ 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^{-3}) (e.g., Stephens et al., 1995; Rangama et al., 2005; Wanninkhof et al., 2007; Watanabe et al., 2007; Berryman et al., 2008; Zhu et al., 2009; Friedrich and Oschlies, 2009; Hales et al., 2012; Tao et al., 2012; Signorini et al., 2013; Qin et al., 2014; Bai et al., 2015; Marrec et al., 2015; Padhy et al., 2015; Moussa et al., 2016). These parameters all have the potential to affect surface $p\text{CO}_2$, 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 $p\text{CO}_2$ as CHL increases (e.g., in algal blooms) can cause significant decreases in surface $p\text{CO}_2$ (Sarma 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 $p\text{CO}_2$ (Lefevre and Taylor 2002) were used to model the effect of air-sea CO_2 flux on surface $p\text{CO}_2$. Parard et al. (2014) and Marrec et al. (2014) estimated surface $p\text{CO}_2$ seasonal variations as a function of Julian day, and net primary production (Parard et al., 2014) was used to describe biological effects. Several other studies correlated surface $p\text{CO}_2$ with latitude and longitude (Olsen et al., 2004; Jo et al., 2012; Marrec et al., 2014). The work of Salisbury et al. (2008) related surface $p\text{CO}_2$ to optical measurements (beam attenuation at 660 nm, c_{660} , m^{-1} , provided an indication of the turbidity of the water column), and showed that high $p\text{CO}_2$ was associated with low c_{660} . It is reasonable and generally necessary to correlate surface $p\text{CO}_2$ to the parameters mentioned above (possibly excluding geo-locations) because it is difficult to directly describe $p\text{CO}_2$ 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 $p\text{CO}_2$ to SST, SSS, CHL and MLD in the open ocean (Ono et al., 2004; Sarma et al., 2006; Jamet et al., 2007; Telszewski et al., 2009; Nakaoka et al., 2013; Marrec et al., 2015; Padhy et al., 2015; Moussa et al., 2016). Such parameterizations have provided $p\text{CO}_2$ with Root Mean Square Errors (RMSE) less than 17 μatm . 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 $p\text{CO}_2$. Unlike empirical models, mechanistic methods explicitly explain the physical and biogeochemical processes that control surface $p\text{CO}_2$ 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 $p\text{CO}_2$ (Bai et al. 2015). The $p\text{CO}_2$ RMSE uncertainties of these models for coastal oceans can reach 88.6 μatm (Hales et al., 2012), and the coefficient of determination (R^2) can be as low as 0.165 (Lohrenz et al., 2010). Therefore, while remote estimation of surface $p\text{CO}_2$ 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 tides, coastal upwelling, groundwater discharge and biological factors) (Richey et al., 2002; Bauer et al., 2013; Cyronak et al., 2014), remote estimation of surface $p\text{CO}_2$ is still

challenging.

The monthly mean satellite products or climatology used as inputs in most published works can introduce significant uncertainties in nonlinear $p\text{CO}_2$ models. Likewise, the sensitivity of established models to individual input variables has rarely been studied. As satellite-derived SST and CHL have inherent uncertainties ($0.5 - 1.0^\circ\text{C}$ for SST (Hu et al., 2009) and 12 - 24% for CHL in waters of > 5 m bottom depth (Cannizzaro et al., 2013)), error propagation in model-derived $p\text{CO}_2$ 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 $p\text{CO}_2$ and how errors in input parameters influence the final $p\text{CO}_2$ estimates.

2.2. Field data

The twenty five cruises used to obtain the underway surface water $p\text{CO}_2$ 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 $p\text{CO}_2$, SSS and SST were collected at a depth of 5 meters using a shipboard flow-through seawater system (31,137 observations of each parameter). Full cruise tracks with color-coded surface $p\text{CO}_2$ values are shown in Fig. 1a. Surface $p\text{CO}_2$ data were measured with either a non-dispersive, infrared analyzer Li-CORTM (Feely et al., 1998; Pierrot et al., 2009) or with a Multiparameter Inorganic Carbon Analyzer (MICA; Wang et al., 2007). The Li-CORTM data had an accuracy of $2\ \mu\text{atm}$ (or better) with a measurement interval near 2 minutes, and the MICA data had an accuracy of $2.5\ \mu\text{atm}$ (or better) and a measurement interval around 2 minutes (Wang et al., 2007). The details of data collection, processing, and quality control can be found in Feely et al. (1998), Pierrot 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 $p\text{CO}_2$ system.

Table 2. Underway $p\text{CO}_2$ measurements used in this study. All the cruise tracks listed here are shown in Fig. 1a. The cruises marked in red were selected for model development together with concurrent (± 6 hours) satellite measurements, as shown in Fig. 1b. The cruises marked in black had no concurrent satellite measurements, thus were not used for this study.

Cruise ID	Ship Name^a	Date Range	# of Observations
GU0801	NOAA ship Gordon Gunter	2008/04/04-2008/04/07	2281
GU0802_Leg2	NOAA ship Gordon Gunter	2008/05/13-2008/05/14	344
08FSH01	M/V Here Today	2008/8/11-2008/8/15	1594
GU0805_leg2_2	NOAA ship Gordon Gunter	2008/11/05-2008/11/12	4628
GU0805_Leg3	NOAA ship Gordon Gunter	2008/11/14-2008/11/19	1734
09FSH01	M/V Here Today	2009/2/24-2009/2/28	1067
GU0901_leg2	NOAA ship Gordon Gunter	2009/03/01-2009/03/13	3327
GU0902_Leg3	NOAA ship Gordon Gunter	2009/05/15-2009/05/16	246
09FSH02	M/V Here Today	2009/8/17-2009/8/21	1504
GU0904_Leg1	NOAA ship Gordon Gunter	2009/09/06-2009/09/08	683
GU0904_Leg2	NOAA ship Gordon Gunter	2009/09/17-2009/09/28	3046
GU0905_Leg2	NOAA ship Gordon Gunter	2009/11/07-2009/11/08	383
GU1001L2	NOAA ship Gordon Gunter	2010/04/30-2010/05/01	280
GU1005_Leg1_DWH	NOAA ship Gordon Gunter	2010/10/16-2010/10/25	409
GU1005_Leg2	NOAA ship Gordon Gunter	2010/09/18-2010/09/28	3651
RB0905	NOAA ship Ronald Brown	2009/8/20	111
RB0905T	NOAA ship Ronald Brown	2009/09/15-2009/09/16	150
RB0305	NOAA ship Ronald Brown	2003/09/03-2003/09/04	152
RB0306	NOAA ship Ronald Brown	2003/09/09-2003/09/12	486
RB0606A	NOAA ship Ronald Brown	2006/7/30	97
RB0705	NOAA ship Ronald Brown	2007/07/15-2007/07/16	196
WS1116	R/V Walton Smith	2011/10/21-2011/10/24	1240
WS1202	R/V Walton Smith	2012/02/28-2012/03/02	1130
WS1209	R/V Walton Smith	2012/6/29	344
WS1214	R/V Walton Smith	2012/09/08-2012/09/12	2054
Total from all cruises			31137
Total used in model development and validation			26734

^a The original data and metadata for the cruises of NOAA ship Gordon Gunter; NOAA ship Ronald H Brown and R/V Walton Smith can be found at <http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>, These data were acquired with funding from the NOAA Climate Program Office. The original data and metadata for the USGS cruises of M/V Here Today can be found at <http://pubs.usgs.gov/ds/>. These data were acquired with funding from USGS Coastal and Marine Geology Program.

Figure. 1 (a) Spatial distributions of the field-measured $p\text{CO}_2$ along the ship transects (Table 2). (b) The same field data where near-concurrent (± 6 hours) high-quality MODIS data exist.

All cruise data obtained from CDIAC/SOCAT 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ observations were selected for model development and validation (see section 2.4).

2.3. MODIS satellite data

Standard NASA Level-2 data products (version R2014.0) between July 2002 and December 2014 were downloaded from NASA Goddard Space Flight Center (<http://oceancolor.gsfc.nasa.gov/>). These Level-2 data products obtained by the Moderate Resolution Imaging Spectroradiometer (MODIS) on the Aqua satellite included SST and ocean color data such as CHL and spectral remote

sensing reflectance (R_{rs} , sr^{-1}) in 7 spectral bands between 412 and 678 nm. The spectral R_{rs} data were used to calculate the diffuse attenuation coefficient at 490 nm (K_d_Lee , m^{-1}) and the absorption coefficient of colored dissolved organic matter at 440 nm (a_{g440} , m^{-1}) using the semi-analytical algorithm developed by Lee et al. (2005). This algorithm was selected because it is more accurate than empirical K_d algorithms for the large K_d range ($0.03 - 1.29 m^{-1}$) that is typical of turbid coastal waters in the eastern GOM. K_d_Lee has an estimated uncertainty of about 13% (Zhao et al., 2013). Data quality flags - another Level-2 MODIS data product - were used to screen low-quality data. Statistics between 2003 and 2014 showed that after discounting cloud cover, sun glint, and other factors that affect data quality, for any given location in the GOM there was, on average, a valid CHL (or K_d_Lee) observation every 5-10 days and a valid SST observation every 3-5 days (Feng and Hu, 2016).

2.4. Algorithm development and validation

Although the field measurements included several key properties (e.g., SST, SSS, and CHL) that can be used to model surface pCO_2 , MODIS-derived data products for SST, CHL, a_{g440} , 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 will be cancelled to a large extent.

To obtain concurrent field data and MODIS data, a time window of ± 6 hours was used. In order to assure satellite data quality an image pixel was discarded if it was associated with any one of the following quality control flags (Barnes and Hu, 2015): atmospheric correction failure, land, sun glint, high radiance, large sensor viewing angle ($>60^\circ$), stray 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 1,516 conjugate observations of field-measured $p\text{CO}_2$ and MODIS data products were available for algorithm development and validation (Fig. 1b). In this dataset, field-measured $p\text{CO}_2$ ranged between 305.7 and 552.4 μatm , field-measured SSS ranged between 31.75 and 36.56, satellite SST ranged between 15.1 and 31.4 $^{\circ}\text{C}$, satellite CHL ranged between 0.076 and 3.624 mg/m^{-3} , satellite $a_{\text{g}440}$ ranged between 0.009 and 0.185 m^{-1} , and satellite Kd_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 $p\text{CO}_2$) 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, SSS, CHL, Kd_Lee, $a_{\text{g}440}$, Julday) should be used to predict surface $p\text{CO}_2$. Although Julday was not a real bio-chemical variable (more of a “tuning” parameter), it was selected and normalized sinusoidally to emphasize the seasonal cycle of surface $p\text{CO}_2$ (Friedrich and Oschlies, 2009; Lefevre et al., 2005; Signorini et al., 2013). Because CHL, Kd_Lee and $a_{\text{g}440}$ 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 Kd_Lee could be selected with 95% confidence ($p \leq 0.05$) in the final stepwise MLR model, with RMSE of 14.83 μatm and R^2 of 0.75. However, the scatterplot between predicted $p\text{CO}_2$ and field-measured $p\text{CO}_2$ (not shown here, but with statistics listed in Table 3) indicated that the predicted $p\text{CO}_2$ tended to plateau at high $p\text{CO}_2$: for $p\text{CO}_2 > 420 \mu\text{atm}$, the mean bias (MB) and mean ratio (MR) between model-predicted and field-measured $p\text{CO}_2$ from the stepwise MLR were -39.336 μatm and 0.916, respectively, suggesting that $p\text{CO}_2$ was significantly underestimated for $p\text{CO}_2 > 420 \mu\text{atm}$, thus the performance of the MLR approach was not satisfactory and further improvement was required.

Table 3. Statistics of the stepwise multiple linear regression (MLR). With 95% confidence ($p \leq 0.05$), all variables except CHL and Kd_Lee were selected in the final MLR model (p values with CHL or Kd_Lee added in the model are marked in red). Clearly, the stepwise MLR underestimated surface $p\text{CO}_2$ for $p\text{CO}_2 > 420 \mu\text{atm}$. Therefore, this model was not applied in this study.

Model inputs ^a	Variable added	Decision to the new-added variable	p value	RMSE (μatm)	MB(μatm)		MR		R^2
					$p\text{CO}_2 > 420 \mu\text{atm}$	$p\text{CO}_2 \leq 420 \mu\text{atm}$	$p\text{CO}_2 > 420 \mu\text{atm}$	$p\text{CO}_2 \leq 420 \mu\text{atm}$	

Inputs1	SST	In	0.000	16.06	-45.251	1.120	0.903	1.004	0.703
Inputs2	$\log_{10}(a_{g440})$	In	0.000	15.16	-37.025	0.916	0.921	1.004	0.736
Inputs3	SSS	In	0.000	14.86	-39.282	0.972	0.916	1.004	0.746
Inputs4	$\cos(\text{Julday})$	In	0.042	14.83	-39.336	0.973	0.916	1.004	0.748
Inputs5	$\log_{10}(\text{CHL})$	Out	0.644	14.78	-39.443	0.976	0.916	1.004	0.748
Inputs6	$\log_{10}(\text{Kd_Lee})$	Out	0.135	14.75	-38.822	0.961	0.917	1.004	0.749

^a inputs1=[SST]; inputs2=[SST, $\log_{10}(a_{g440})$]; Inputs3=[SST, $\log_{10}(a_{g440})$, SSS]; Inputs4=[SST, $\log_{10}(a_{g440})$, SSS, $\cos(\text{Julday})$]; Inputs5=[SST, $\log_{10}(a_{g440})$, SSS, $\cos(\text{Julday})$, $\log_{10}(\text{CHL})$]; Inputs6=[SST, $\log_{10}(a_{g440})$, SSS, $\cos(\text{Julday})$, $\log_{10}(\text{Kd_Lee})$].

Exclusion of CHL and Kd_Lee in the MLR model was consistent with the parsimony step-wise test, even though they were used in other studies to model surface $p\text{CO}_2$ (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, Kd_Lee, a_{g440} , Julday) and dependent variable (surface $p\text{CO}_2$) were examined and listed in Table 4. With 95% confidence ($p \leq 0.05$), 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_{g440} and CHL (or Kd_Lee), and higher correlation between surface $p\text{CO}_2$ and a_{g440} than between surface $p\text{CO}_2$ and CHL (or Kd_Lee). Therefore, once a_{g440} was explicitly included in the MLR model, CHL and Kd_Lee were implicitly included.

Table 4. Correlation coefficients among independent variables and dependent variables used in the selected model in this work, with 95% confidence. Coefficients with <95% confidence are marked in red, and the corresponding p values are listed in the parentheses.

Variables	SST	$\log_{10}(\text{CHL})$	$\log_{10}(\text{Kd_Lee})$	$\log_{10}(a_{g440})$	SSS	$\cos(\text{Julday})$	$p\text{CO}_2$
SST	1	-0.532	-0.471	-0.681	0.212	-0.081	0.839
$\log_{10}(\text{CHL})$	-0.532	1	0.950	0.927	-0.342	-0.073 (0.052)	-0.324
$\log_{10}(\text{Kd_Lee})$	-0.471	0.950	1	0.858	-0.314	-0.009 (0.812)	-0.266
$\log_{10}(a_{g440})$	-0.681	0.927	0.858	1	-0.475	-0.077	-0.438
SSS	0.212	-0.342	-0.314	-0.475	1	0.198	0.007 (0.852)
$\cos(\text{Julday})$	-0.081	-0.073 (0.052)	-0.009 (0.812)	-0.077	0.198	1	-0.154
$p\text{CO}_2$	0.839	-0.324	-0.266	-0.438	0.007 (0.852)	-0.154	1

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 $p\text{CO}_2$ using the six PCs. The RMSE and R^2 of the PCR were 14.69 μatm and 0.75, respectively. Similar to the MLR results, the predicted $p\text{CO}_2$ tended to plateau at high $p\text{CO}_2$ values: for $p\text{CO}_2 > 420 \mu\text{atm}$, MB

and MR of the PCR were -38.695 μatm and 0.917, respectively, indicating model deficiency of the PCR and a necessity for further effort to improve the model.

Table 5. Coefficients between each principal component (PC) and the independent variables, as well as the percentage of variance explained by each PC.

Variables	PC1	PC2	PC3	PC4	PC5	PC6
SST	0.996	-0.066	0.024	0.053	0.014	-0.004
$\log_{10}(\text{CHL})$	-0.037	-0.063	-0.022	0.702	-0.089	0.702
$\log_{10}(\text{Kd_Lee})$	-0.023	-0.040	0.005	0.497	-0.642	-0.583
$\log_{10}(\text{a}_{\text{g}440})$	-0.044	-0.081	-0.012	0.495	0.761	-0.409
SSS	0.063	0.972	-0.198	0.104	0.029	-0.015
$\cos(\text{Julday})$	-0.013	0.196	0.980	0.038	0.016	0.011
Variance explained (%)	90.59	6.69	2.15	0.53	0.02	0.01

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, the following model development and tuning were based on multi-variate nonlinear regression (MNR) between field-measured $p\text{CO}_2$ and the independent variables. After extensive trial and error, it was found that the use of MODIS-derived SST, CHL, and Kd_Lee provided optimal results (Table 6). Other parameters, such as MODIS-derived $\text{a}_{\text{g}440}$ (often inversely related to SSS 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 $p\text{CO}_2$ (Table 6). The functional relationship between field-measured $p\text{CO}_2$ 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:

$$p\text{CO}_2 = k_0x_1 + k_1x_2 + k_2x_3 + k_3x_4 + k_4x_1x_2 + k_5x_1x_3 + k_6x_1x_4 + k_7x_2x_3 + k_8x_2x_4 + k_9x_3x_4 + k_{10}x_1^2 + k_{11}x_2^2 + k_{12}x_3^2 + k_{13}x_4^2 \quad (1)$$

where $x_1 = \text{SST}$, $x_2 = \log_{10}(\text{Kd_Lee})$, $x_3 = \log_{10}(\text{CHL})$, $x_4 = \cos(2\pi(\text{Julday} - \gamma)/365)$.

In the equation above, γ 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 $\text{a}_{\text{g}440}$ instead of satellite Kd_Lee, and use of original CHL or Kd_Lee instead of logarithmic CHL or Kd_Lee. 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_{g440} and CHL, and a_{g440} and SSS (last three rows in Table 6). However, models with combinations of a_{g440} and CHL, and a_{g440} and SSS tended to plateau for high pCO_2 values ($> 420 \mu atm$), with MB of $-18.303 \mu atm$ and $-16.305 \mu atm$, and MR of 0.962 and 0.966, respectively, indicating underestimation at high pCO_2 values. Although the model with combination of SSS and CHL showed a slightly lower MB for $pCO_2 > 420 \mu atm$ as compared to the model in Eq. 1, this model had a slightly higher RMSE and lower R^2 , and its pCO_2 prediction was significantly biased for $pCO_2 > 480 \mu atm$ (MB= $-23.804 \mu atm$, MR= 0.957). Furthermore, it is currently difficult to estimate SSS from satellite measurements over coastal waters. Therefore, Eq. 1 was preferred as the potential pCO_2 model for this study. For reference and to follow the principle of model parsimony, again a stepwise MNR 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 MNR had a RMSE of $19.98 \mu atm$ (5.0%) and a R^2 of 0.62, and its ability in estimating pCO_2 for $pCO_2 > 420 \mu atm$ was also limited (MB = $-37.922 \mu atm$, MR = 0.916). Therefore, this stepwise MNR did not show improvement over the stepwise MLR or PCR or MNR above, and was not selected in this study to model surface pCO_2 .

$$pCO_2 = 2.0105x_1 + 339.2493x_2 + 0.5330x_1x_3 - 0.1784x_1x_3 - 0.0035x_1^2 + 234.2682x_2^2 - 86.8151x_3^2 \quad (2)$$

where $x_1 = SST$, $x_2 = \log_{10}(Kd_Lee)$, $x_3 = \log_{10}(CHL)$.

Table 6. Model performance for different combinations of input parameters using regression formula in Eq. 1. Note that although the last two rows show the same R^2 values as the first row with even lower RMSE, both tend to plateau for $pCO_2 > 420 \mu atm$ (i.e., negatively biased MB and MR values). The third row from bottom shows slightly lower MB for $pCO_2 > 420 \mu atm$ than the first row, but this row also shows higher RMSE, lower R^2 , and plateaued performance for $pCO_2 > 480 \mu atm$ (MB= $-23.804 \mu atm$, MR= 0.957). Because currently SSS is difficult to derive from satellites for coastal waters, **the first row was selected as the final pCO_2 model in this study.**

Model inputs ^a	R^2	RMSE ($\mu atm/\%$)	MB (μatm)		MR		Relationship between modeled pCO_2 and in situ pCO_2	Range of modeled pCO_2 (μatm)
			$pCO_2 > 420 \mu atm$	$pCO_2 \leq 420 \mu atm$	$pCO_2 > 420 \mu atm$	$pCO_2 \leq 420 \mu atm$		
Inputs1	0.89	10.98/2.9	-8.536	0.561	0.981	1.002	$Y = 0.899X + 38.1$	312.5–558.0
Inputs1 [*]	0.62	19.98/5.0	-37.922	1.917	0.916	1.007	$Y = 0.605X + 147.57$	312.3–516.2
Inputs2	0.87	11.60/3.1	-12.269	0.628	0.973	1.002	$Y = 0.871X + 48.1$	312.9–566.1
Inputs3	0.84	13.10/3.4	-11.590	0.703	0.974	1.003	$Y = 0.856X + 54.1$	316.5–529.0
Inputs4	0.84	13.12/3.4	-9.187	0.933	0.979	1.003	$Y = 0.887X + 42.6$	310.3–562.1
Inputs5	0.86	11.94/3.1	-6.251	0.765	0.987	1.002	$Y = 0.911X + 33.7$	315.6–498.2
Inputs6	0.89	9.97/2.6	-18.303	0.369	0.962	1.001	$Y = 0.880X + 44.7$	311.9–477.8
Inputs7	0.89	9.86/2.6	-16.305	0.303	0.966	1.001	$Y = 0.889X + 40.4$	311.2–488.2

^a Inputs1=[SST, $\log_{10}(Kd_Lee)$, $\log_{10}(CHL)$, $\cos(Julday)$]; Inputs2=[SST, Kd_Lee , $\log_{10}(CHL)$, $\cos(Julday)$]; Inputs3=[SST, $\log_{10}(Kd_Lee)$, CHL, $\cos(Julday)$]; Inputs4=[SST, Kd_Lee , CHL, $\cos(Julday)$]; Inputs5=[SST, SSS, $\log_{10}(CHL)$, $\cos(Julday)$]; Inputs6=[SST, $\log_{10}(a_{g440})$, $\log_{10}(CHL)$, $\cos(Julday)$]; Inputs7=[SST, $\log_{10}(a_{g440})$, SSS, $\cos(Julday)$].

* This model was a stepwise MNR, as shown in Eq. 2.

Table 7 is a summary of the model performance with the stepwise MLR, PCR, stepwise MNR, and MNR. Clearly, the MNR model with Eq. 1 showed the best performance in terms of RMSE, R^2 , MB, MR, the relationship between modeled and measure pCO_2 , and the range of modeled versus measured pCO_2 . Thus, the final empirical pCO_2 model was determined as:

$$pCO_2 = -124.076x_1 + 790.201x_2 - 753.952x_3 + 704.22x_4 + 35.217x_1x_2 - 7.044x_1x_3 - 34.737x_1x_4 - 1075.65x_2x_3 - 108.248x_2x_4 - 10.091x_3x_4 + 3.525x_1^2 + 947.627x_2^2 + 285.986x_3^2 + 105.661x_4^2 \quad (3)$$

where $x_1 = SST$, $x_2 = \log_{10}(Kd_Lee)$, $x_3 = \log_{10}(CHL)$, $x_4 = \cos(2\pi(Julday - 255)/365)$.

Table 7. Comparison of model performance. The stepwise MNR and MNR are both based on Eq. 1, with model coefficients shown in Eq. 2 and Eq. 3, respectively. Clearly, the stepwise MLR, PCR, and stepwise MNR all show large underestimations for $pCO_2 > 420 \mu atm$. Therefore, the MNR model was selected as the final pCO_2 model in this study (Eq. 3).

Model type	R^2	RMSE (μatm)	MB(μatm)		MR		Relationship between modeled pCO_2 and <i>in situ</i> pCO_2	Range of modeled pCO_2 (μatm)
			$pCO_2 > 420 \mu atm$	$pCO_2 \leq 420 \mu atm$	$pCO_2 > 420 \mu atm$	$pCO_2 \leq 420 \mu atm$		
Stepwise MLR	0.75	14.83	-39.336	0.973	0.916	1.004	$Y = 0.748X + 93.7$	323.2–416.5
PCR	0.75	14.69	-38.695	0.958	0.917	1.004	$Y = 0.751X + 92.6$	323.4–414.6
Stepwise MNR	0.62	19.98	-37.922	1.917	0.916	1.007	$Y = 0.605X + 147.57$	312.3–516.2
MNR	0.89	10.98	-8.536	0.561	0.981	1.002	$Y = 0.899X + 38.1$	312.5–558.0

The MNR model in Eq. 3 was subsequently applied to the half of the dataset that was not used in the model development. The model-predicted pCO_2 was compared with the field-measured pCO_2 , where R^2 , RMSE, MR and MB were used to gauge model performance. A histogram of the difference between field-measured pCO_2 and model-predicted pCO_2 was generated to examine the error distributions.

To examine which independent variable is mostly responsible for the predictive capacity of the pCO_2 model, the variance that is explained by each variable was investigated by comparing the full model (Eq. 3, with all the 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 SST, CHL, Kd_Lee , and Julday, respectively. In each case, variance in the surface pCO_2 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 $p\text{CO}_2$ distributions derived from MODIS

The model in Eq. 3 was applied to the daily Level-2 MODIS data for the period of July 2002 – December 2014 to generate daily surface $p\text{CO}_2$ maps. The daily maps were used to compose monthly mean $p\text{CO}_2$ maps for each year, and these monthly mean maps were then used to compose monthly $p\text{CO}_2$ climatology. All parameters, including monthly $p\text{CO}_2$, CHL, K_d _Lee, and SST, 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 $p\text{CO}_2$ prediction. The RMSE during model training was 10.51 μatm , with a coefficient of variation (CV) of 2.8% and R^2 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 R^2 of 0.88. The validation showed that model-predicted $p\text{CO}_2$ was almost non-biased, as MR (which was 1.0006) was close to 1 and MB (which was 0.033 μatm) was close to 0 μatm . A histogram of residuals (measured $p\text{CO}_2$ minus predicted $p\text{CO}_2$) 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 32.45 μatm $p\text{CO}_2$ standard deviation ($\pm$ -sigma).

Figure 2. (a) $p\text{CO}_2$ model development, where the modeled $p\text{CO}_2$ (y-axis) was estimated through coefficient tuning using the multi-variate regression Eq. (1). (b) $p\text{CO}_2$ model validation using a separate dataset that was not used for model development. (c) Histogram of error distributions for both model development and validation.

The results shown in Table 8 indicated that variables used in our model (the full model) could explain 88.92% of the $p\text{CO}_2$ variance. When SST was excluded in the model, the remaining variables could only explain 68.62% of the $p\text{CO}_2$ variance. When Julday was excluded in the model, 74.45% $p\text{CO}_2$ 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 Julday. This is consistent with those reported in previous studies (Friedrich and Oschlies, 2009; Lefevre et al., 2005; Signorini et al., 2013). CHL and Kd_Lee were the least important variables in explaining the $p\text{CO}_2$ variance, consistent with later sensitivity analysis (see section 4.1). Note that although Julday is not a real biochemical variable, its use improved the model performance more than the use of CHL or Kd_Lee.

Table 8. Statistics of the full model and reduced models for explaining variance in the estimated surface $p\text{CO}_2$. 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.

Model inputs	Excluded variable	Variance explained (%)	Variance explained by the excluded variable (%)
SST, log(Kd_Lee), log(CHL), Julday	NaN	88.92	NaN
log(Kd_Lee), log(CHL), Julday	SST	68.62	20.3
SST, log(CHL), Julday	Kd_Lee	79.63	9.29
SST, log(Kd_Lee), Julday	CHL	82.06	6.86
SST, log(Kd_Lee), log(CHL)	Julday	74.45	14.47

3.2. Temporal and spatial variation of surface $p\text{CO}_2$

Fig. 3 shows mean monthly $p\text{CO}_2$, CHL, Kd_Lee and SST over the entire WFS where $p\text{CO}_2$ is within the model range. Monthly climatologic maps of surface $p\text{CO}_2$ are presented in Fig. 4, with the model range outlined by red dashes. Distinct seasonal $p\text{CO}_2$ patterns can be seen in both Fig. 3 and Fig. 4, corresponding to the seasonal variation of CHL, Kd_Lee and SST.

Figure 3. Monthly time series showing seasonality and inter-annual variations of $p\text{CO}_2$, CHL, K_d_{Lee} , and SST on the West Florida Shelf (calculated from the entire WFS, outlined in Fig. 4). The data were generated from monthly mean satellite data products from July 2002 to December 2014.

Figure 4. $p\text{CO}_2$ monthly climatology derived from satellite data using the multi-variate regression model for the period of July 2002 to December 2014. The maps showed the eastern Gulf of Mexico between 24°N to 31°N and 90°W to 80°W. The West Florida Shelf is outlined by the red dashed line. The red solid circles outline some high-spatial gradient features that were possibly caused by upwelling.

On a temporal scale the seasonal variation of $p\text{CO}_2$ was positively correlated with SST (in phase), and negatively correlated with CHL and K_d_{Lee} . In summer, surface $p\text{CO}_2$ 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 CO_2 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 $p\text{CO}_2$ attains a minimum of around $350 \mu\text{atm}$. During this time, with the breakdown of the thermocline and increase of MLD ($> \sim 50\text{m}$; 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 $p\text{CO}_2$ (see section 4), surface $p\text{CO}_2$ 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 submarine groundwater discharge (Hu et al., 2006; Cyronak et al., 2014). Thus the combined effect of enhanced vertical mixing and decreased SST is that $p\text{CO}_2$ reaches a minimum during winter but is not severely diminished. Although the interannual patterns of $p\text{CO}_2$, 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/m^3 (Fig. 3c). Concomitantly, surface $p\text{CO}_2$ estimates decreased by $38 \mu\text{atm}$ relative to $p\text{CO}_2$ estimates in the previous month, but did not reach a minimum. The highest value of surface $p\text{CO}_2$ was attained in 2010 June (Fig. 3a) and was about $58 \mu\text{atm}$ 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 $15.7 \mu\text{atm}$ in surface $p\text{CO}_2$, the appearance of the $p\text{CO}_2$ maximum in June was reasonable. Comparing this interannual variability of spatially averaged $p\text{CO}_2$ on the WFS to modeled $p\text{CO}_2$ results for the whole 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 4.1) indicates that the results obtained in the present work exhibits improved accuracy and less uncertainty.

In terms of observations on spatial scales (Fig. 4), although there were distinct gradients in CHL and Kd_Lee climatologic maps (not explicitly shown here), $p\text{CO}_2$ 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 $p\text{CO}_2$ relative to

their surroundings (red solid circles in Fig. 4). Among other possible influences, because there are large springs in this region (Rosenau et al., 1977) with low temperature and high $p\text{CO}_2$, this could be due to upwelling of submarine groundwater discharge, as $p\text{CO}_2$ is usually higher in fresh groundwater than surroundings (Macpherson, 2009; Cyronak et al., 2014). From early spring to late fall (April to October), obvious $p\text{CO}_2$ gradients were observed, changing from high to low in the offshore direction. High $p\text{CO}_2$ 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 $p\text{CO}_2$ values are commonly observed. However, the extremely high $p\text{CO}_2$ values ($>550 \mu\text{atm}$) in the nearshore regions of South Florida may not be reliable, as there was little $p\text{CO}_2$ data in this region and the $p\text{CO}_2$ model developed here was only valid for $p\text{CO}_2$ ranging from 300 to 550 μatm . On the other hand, such extremely high $p\text{CO}_2$ values could be realistic as $p\text{CO}_2$ 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 $p\text{CO}_2$ was lower than for inshore waters. Nevertheless, in temporal terms, offshore surface $p\text{CO}_2$ values during the summer are higher than offshore $p\text{CO}_2$ values in the winter and early spring. In the area around the Florida Keys, $p\text{CO}_2$ 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 climatology map) and potentially submarine groundwater discharge in this very shallow region. Compared with the modeled multi-year $p\text{CO}_2$ 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 $p\text{CO}_2$ is mainly controlled by ocean thermodynamics, physical processes, biological processes, and air-sea exchange (Takahashi et al., 2002; Inoue et al., 2003; Rangama et al., 2005; Bai et al., 2015). Ocean thermodynamic effects are dependent on SST, and the relationship between surface $p\text{CO}_2$ and SST can be estimated using a simple exponential relationship: ($p\text{CO}_{2@T2} = p\text{CO}_{2@T1} * \exp[0.0423 * (T_2 - T_1)]$) (Takahashi et al., 2002, 2009). Physical processes such as advection, upwelling and water mixing affect $p\text{CO}_2$ 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 photosynthesis, production of CO₂ by respiration, and utilization of carbonate during calcification also have important direct effects on the $p\text{CO}_2$ of seawater (Reynaud et al., 2003). Air/sea CO₂ exchange can exert especially strong controls on surface $p\text{CO}_2$ 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 sea surface $p\text{CO}_2$ (Bai et al., 2015).

In order to better understand how surface $p\text{CO}_2$ responds to input variables, a sensitivity analysis was conducted. For each analysis, one input variable was varied while the others remained constant. Surface $p\text{CO}_2$ 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.

Figure 5. $p\text{CO}_2$ model sensitivity to changes in CHL, $K_d\text{_{Lee}}$, or SST. Data used here are from both model development and model validation. In all panels, blue points represent the original prediction while red points represent the prediction corresponding to the artificial changes in either CHL (+/- 20%) (a and b), $K_d\text{_{Lee}}$ (+/- 20%) (c and d), or SST (+/- 1 °C) (e and f) while all other algorithm input variables are kept the same. Statistical results are listed in Table 9.

Figure 6. Comparison between original $p\text{CO}_2$ and predicted $p\text{CO}_2$ with incremental changes in CHL, $K_d\text{_{Lee}}$, or SST, corresponding to Fig. 5. The red solid line is the 1:1 line, red points in panel a and b represent data with CHL above 1.5 mg/m^3 , and red points in panel c and d represent data with $K_d\text{_{Lee}}$ above 0.2 m^{-1} .

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, MR (mean ratio between model-predicted $p\text{CO}_2$ and field-measured $p\text{CO}_2$) and MB (mean bias between model-predicted $p\text{CO}_2$ and field-measured $p\text{CO}_2$) were calculated by comparing the new-predicted $p\text{CO}_2$ with the original-predicted $p\text{CO}_2$. The model was more sensitive to changes in the input variables when CHL was $> 1.5 \text{ mg/m}^3$, Kd_Lee was $> 0.2 \text{ m}^{-1}$, or SST was $> 16 \text{ }^\circ\text{C}$.

Cases	RMSE (μatm)	MR	MB (μatm)
20% increase in CHL	10.34	1.022	8.06
20% decrease in CHL	9.36	0.986	-4.98
20% increase in Kd_Lee	10.02	0.997	-0.68
20% decrease in Kd_Lee	20.95	1.047	17.01
1 °C increase in SST	16.03	1.030	11.57
1 °C decrease in SST	11.98	0.989	-4.52

A visual interpretation of Figs. 5 and 6 indicates that the model is more sensitive to input changes in CHL when CHL is $> 1.5 \text{ mg m}^{-3}$. For CHL greater than 1.5 mg m^{-3} , a 20% increase in CHL (Figs. 5a and 6a) produced $p\text{CO}_2$ predictions that were lower than the original $p\text{CO}_2$, while for CHL less than 1.5 mg m^{-3} the same 20% increase in CHL caused a substantially smaller change in the predicted $p\text{CO}_2$. For the entire data range tested in this analysis (Table 9), the RMSE, MR and MB were $10.34 \mu\text{atm}$, 1.022, and $8.06 \mu\text{atm}$, indicating that a 20% increase in CHL resulted in an $8.06 \mu\text{atm}$ $p\text{CO}_2$ overestimate. For data with CHL $> 1.5 \text{ mg m}^{-3}$, the RMSE, MR and MB were $16.44 \mu\text{atm}$, 0.968, and $-12.44 \mu\text{atm}$. In contrast, for data with CHL $\leq 1.5 \text{ mg m}^{-3}$, the RMSE, MR and MB were $10.07 \mu\text{atm}$, 1.024, and $8.79 \mu\text{atm}$, respectively. A similar disparity in model sensitivity was observed for a 20% decrease in CHL when CHL $> 1.5 \text{ mg m}^{-3}$ and CHL $\leq 1.5 \text{ mg m}^{-3}$ (Figs. 5b and 6b). For the entire data range, RMSE, MR, and MB were $9.36 \mu\text{atm}$, 0.986, and $-4.98 \mu\text{atm}$. For data with CHL $> 1.5 \text{ mg m}^{-3}$, $p\text{CO}_2$ was overestimated, with RMSE, MR, and MB being $24.09 \mu\text{atm}$, 1.053 and $20.11 \mu\text{atm}$. Consistent with the observations described above, for data with CHL $\leq 1.5 \text{ mg m}^{-3}$ the model showed much reduced sensitivity to a 20% decrease in CHL, with an RMSE of $8.40 \mu\text{atm}$, an MR of 0.984, and an MB of $-5.87 \mu\text{atm}$. Based on the characteristics shown in Figs. 5a, 6a, 5b and 6b, the $p\text{CO}_2$ algorithm is especially sensitive to CHL at high concentrations. To some extent, this reflects the complex role of CHL in controlling surface $p\text{CO}_2$.

As Kd_Lee is not entirely independent from CHL, it is also clearly seen that the $p\text{CO}_2$ algorithm is more sensitive to Kd_Lee as this variable becomes larger ($> 0.2 \text{ m}^{-1}$). For Kd_Lee values greater than 0.2 m^{-1} , a 20% increase in Kd_Lee (Figs. 5c and 6c) resulted in substantial increases in

predicted $p\text{CO}_2$, while for $K_d\text{_{Lee}}$ values less than 0.2 m^{-1} , a 20% increase in $K_d\text{_{Lee}}$ produced $p\text{CO}_2$ values close to the original $p\text{CO}_2$ prediction. When all data were used in the analysis the RMSE, MR and MB values for this experiment were $10.02 \text{ } \mu\text{atm}$, 0.997 , and $-0.68 \text{ } \mu\text{atm}$. For data with $K_d\text{_{Lee}} > 0.2 \text{ m}^{-1}$, they were $29.43 \text{ } \mu\text{atm}$, 1.066 , and $24.51 \text{ } \mu\text{atm}$, while for data with $K_d\text{_{Lee}} \leq 0.2 \text{ m}^{-1}$ the RMSE, MR and MB were $8.13 \text{ } \mu\text{atm}$, 0.994 , and $-1.83 \text{ } \mu\text{atm}$. Likewise, with a 20% decrease in $K_d\text{_{Lee}}$ (Figs. 5d and 6d), $p\text{CO}_2$ was predicted to be lower than the original $p\text{CO}_2$ if $K_d\text{_{Lee}}$ values were greater than 0.2 m^{-1} (RMSE = $24.04 \text{ } \mu\text{atm}$, MR = 0.966 , MB = $-13.83 \text{ } \mu\text{atm}$) but higher if $K_d\text{_{Lee}}$ values were less than 0.2 m^{-1} (RMSE = $20.81 \text{ } \mu\text{atm}$, MR = 1.050 , MB = $18.41 \text{ } \mu\text{atm}$). When all data were used in the calculation, RMSE, MR and MB were $20.95 \text{ } \mu\text{atm}$, 1.047 , and $17.01 \text{ } \mu\text{atm}$. The differences in model sensitivity for $K_d\text{_{Lee}} > 0.2 \text{ m}^{-1}$ and $K_d\text{_{Lee}} \leq 0.2 \text{ m}^{-1}$ are consistent with those for CHL changes, as coastal waters typically have higher CHL and $K_d\text{_{Lee}}$ than offshore waters.

The sensitivity of the $p\text{CO}_2$ model to SST varied over the modeled range of SST. For SST greater than $16 \text{ } ^\circ\text{C}$ (Figs. 5e and 6e), a $1 \text{ } ^\circ\text{C}$ increase in SST produced $p\text{CO}_2$ predictions higher than the original $p\text{CO}_2$, while for SST less than $16 \text{ } ^\circ\text{C}$, the predicted $p\text{CO}_2$ was much closer to the original prediction. As would be expected from the above analyses, a $1 \text{ } ^\circ\text{C}$ decrease in SST (Figs. 5f and 6f) for SST greater than $16 \text{ } ^\circ\text{C}$ resulted in predicted $p\text{CO}_2$ values that were lower than the original $p\text{CO}_2$ while for SST less than $16 \text{ } ^\circ\text{C}$ $p\text{CO}_2$ predictions were closer to the original $p\text{CO}_2$. The RMSE values for these two experiments ($1 \text{ } ^\circ\text{C}$ increase and $1 \text{ } ^\circ\text{C}$ decrease in SST) were 16.03 and $11.98 \text{ } \mu\text{atm}$, with MR values of 1.030 and 0.989 and MB values of 11.57 and $-4.52 \text{ } \mu\text{atm}$.

In summary, $p\text{CO}_2$ variations created by a $1 \text{ } ^\circ\text{C}$ change in SST, 20% variations in CHL and 20% variations in $K_d\text{_{Lee}}$ 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 $K_d\text{_{Lee}}$ did 20% variations produce $p\text{CO}_2$ variations somewhat higher than the RMSE of the model. However, considering the range of SST in this region (minimum around $15 \text{ } ^\circ\text{C}$, maximum around $35 \text{ } ^\circ\text{C}$), a $1 \text{ } ^\circ\text{C}$ 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 $K_d\text{_{Lee}}$. Indeed, although coastal waters may occasionally have $\text{SST} < 16 \text{ } ^\circ\text{C}$, $\text{CHL} > 1.5 \text{ mg m}^{-3}$, and $K_d\text{_{Lee}} > 0.2 \text{ m}^{-1}$, 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 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 $p\text{CO}_2$ 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 R^2 , 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 $p\text{CO}_2$ distributions (e.g., 2005 algal blooms and storms), although no such events were considered in the model tuning or validation. In addition, air-sea CO_2 flux ($F_{\text{CO}_2} = kK_0(p\text{CO}_{2\text{sw}} - p\text{CO}_{2\text{air}}$, where k is the gas transfer velocity of CO_2 , and K_0 is the solubility coefficient of CO_2) can be calculated with auxiliary wind speed and atmospheric $p\text{CO}_2$ data, allowing broad-scale assessments of the extent to which the WFS serves as a CO_2 source or sink. Similarly pH ($\text{pH} = -\log_{10}([\text{H}^+]_{\text{T}})$, where $[\text{H}^+]_{\text{T}}$ is the total concentration of hydrogen ions) or carbonate ion concentrations ($[\text{CO}_3^{2-}]_{\text{T}}$) and carbonate saturation states ($[\text{Ca}^{2+}]_{\text{T}} [\text{CO}_3^{2-}]_{\text{T}} / K_{\text{sp}}$) can be derived from modeled $p\text{CO}_2$ 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 for the data range within which it was tuned. Specifically, all data used in the tuning had $p\text{CO}_2$ values between 300 and 550 μatm as the lower and upper bounds of the model's applicability. Field data showed that $p\text{CO}_2$ could occasionally be $> 600 \mu\text{atm}$ or even $> 1000 \mu\text{atm}$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ measurements in other regions of GOM between April 2002 and May 2014 (obtained from <http://cdiac.ornl.gov/oceans/Coastal/> and <http://www.aoml.noaa.gov/ocd/gcc/>), we also tested how the algorithm (Eq. 3) performed in other GOM waters. Based on the distributions of cruise data after matching up with satellite products, the validation was examined mainly in three regions (see Fig. 7): around the Mississippi delta, the northwestern GOM, and LC affected regions (open GOM, northern Caribbean and the Florida Strait). For region around the Mississippi River delta (Figs. 7a, 7b, 8a), predictions for the offshore region were better than the inshore. For the inshore region, predicted $p\text{CO}_2$ deviated substantially from the *in situ* $p\text{CO}_2$. 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 $p\text{CO}_2$. Compared with the satellite-derived $p\text{CO}_2$ map for Mississippi delta generated by Lohrenz and Cai (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, 7b and 8b), the modeled $p\text{CO}_2$ generally followed the *in situ* $p\text{CO}_2$ variations, but with an RMSE of 44.1 μatm . For prediction in the LC affected region, $p\text{CO}_2$ was well estimated (RMSE of 13.7 μatm) between July and December (Figs. 7c, 7d and 8d), while between January and June (Figs. 7e, 7f and 8c), 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 $p\text{CO}_2$ influencing mechanisms may be different from the mechanisms that are dominant between July and December. Accordingly, $p\text{CO}_2$ 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://www7320.nrlssc.navy.mil/GLBhycom1-12_mnsd/navo/arc_list_glfmexspdcurnMN.html). The extension of the LC shows different distribution patterns during these two periods. Because the controlling mechanisms for surface $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$. For both the western and southern GOM, additional *in situ* data are needed for algorithm development.

Figure 7. Spatial distribution of *in situ* and satellite-predicted $p\text{CO}_2$ in other GOM regions except WFS, with *in situ* measurements after matchup with concurrent satellite products shown in top panels and the corresponding satellite prediction below. This validation is divided into three parts according to the location: northwestern GOM (white circles in panel a and b), the region near the Mississippi delta (all points outside the white circles in panels a and b), and LC affected region (panel c-f), based on different backgrounds. Validation for LC affected region is divided into two time regimes with Jul-Dec showed in panel c and d, and Jan-Jun shown in panel e and f. The time span of all the *in situ* measurements shown here is from April 2002 to May 2014.

Figure 8. Algorithm performances in the region near the Mississippi delta, northwestern GOM, and the LC affected

region as specified in Fig. 7. X axis is the pixel number, and Y axis is $p\text{CO}_2$ in unit of μatm .

5. Conclusion

With extensive field and satellite observations and after testing several algorithm approaches, an empirical algorithm for predicting the surface $p\text{CO}_2$ on the West Florida Shelf was developed and validated. The algorithm took Julian day and MODIS-derived CHL, K_d _Lee, and SST as inputs, and determined algorithm coefficients through multi-variate nonlinear regression against concurrent *in situ* $p\text{CO}_2$ measurements. The algorithm showed reasonably good performance and was used to derive spatial distribution maps of surface $p\text{CO}_2$ 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 $p\text{CO}_2$ controlling mechanisms exist in different regions.

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Notations

CDIAC	Carbon Dioxide Information Analysis Center
CHL	Chlorophyll-a Concentration
GOM	Gulf of Mexico
Kd_Lee	Diffuse light attenuation coefficient at 490 nm
LC	Loop Current
MB	Mean Bias
MLR	Multi-variate Linear Regression
MNR	Multi-variate Nonlinear Regression
MODIS	Moderate Resolution Imaging Spectroradiometer
MR	Mean Ratio
PCA	Principle Component Analysis
PCR	Principle Component Regression
RMSE	Root Mean Square Error
SSS	Sea Surface Salinity
SST	Sea Surface Temperature
USGS	U. S. Geological Survey
WFS	West Florida Shelf

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