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Satellite ocean color assessment of air-sea fluxes of CO_2 in a river-dominated coastal margin

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[1] Quantification of the contributions of river-influenced margins to regional CO_2 fluxes is difficult due to the high degree of spatial and temporal variability in these regions. We describe an algorithm for assessment of surface water partial pressure of CO_2 (pCO_2) from MODIS imagery in the northern Gulf of Mexico. Principal component analysis and multiple regression were used to relate surface pCO_2 to environmental variables (T, S, chlorophyll). Subsequent retrieval of corresponding products from MODIS-Aqua L1B data permitted the assessment of regional distributions of pCO_2. An area of low pCO_2 was evident in the vicinity of the Mississippi River delta, consistent with field observations. Regional surface air to sea fluxes of CO_2 were estimated as 2.0–4.2 mmol C m^{-2} d^{-1}. **Citation:** Lohrenz, S. E., and W.-J. Cai (2006), Satellite ocean color assessment of air-sea fluxes of CO_2 in a river-dominated coastal margin, *Geophys. Res. Lett.*, *33*, L01601, doi:10.1029/2005GL023942.

1. Introduction

[2] Recent studies in the East China Sea [*Tsunogai et al.*, 1999; *Wang et al.*, 2000; *Yool and Fasham*, 2001] suggest that continental shelves, particularly those impacted by large rivers, may act as CO_2 pumps that transfer as much as 0.5 to 1 Gt C/yr globally from the atmosphere into the open ocean. Fluxes of this magnitude would account for 25–50% of current ocean uptake of anthropogenic CO_2 and, thus, represent a significant fraction of overall global C budgets [*Sarmiento*, 1993]. This view is supported by findings in other continental shelf regions [*Ternon et al.*, 2000; *Frankignoulle and Borges*, 2001; *DeGrandpre et al.*, 2002; *Cai*, 2003]. However, prevailing arguments have maintained that continental shelves must be net heterotrophic and are likely a source of CO_2 since riverine particulate organic carbon (POC) is largely respired in these areas (*Smith and Hollibaugh* [1993], *Mackenzie et al.* [2000], and others). This latter viewpoint is supported by recent reports in other shelf systems such as the Northern South China Sea [*Zhai et al.*, 2005].

[3] These contrasting and perhaps conflicting reports highlight the need to develop innovative methods to assess regional features based on satellite remote sensing data and to better understand mechanisms regulating air-sea CO_2 fluxes in different types of margins. Because of extreme variability, constructing and characterizing spatially and temporally integrated air-sea fluxes (or in-turn predicting such fluxes) is subject to large uncertainties associated with extrapolation or interpolation from discrete field measurements. A satellite-based regional approach [e.g., *Lefevre et al.*, 2002; *Ono et al.*, 2004; *Olsen et al.*, 2004] can be used to extend the spatial and temporal coverage for broad scale assessments of pCO_2 distributions and air-sea fluxes of CO_2.

2. Methods

[4] Field measurements of total alkalinity (TAlk), dissolved inorganic carbon (DIC), and chlorophyll were acquired during a June 24–31, 2003 cruise on the R/V Pelican in the vicinity of the Mississippi plume and shelf (Figure 1). A Seabird 911 CTD/rosette system equipped with 10-L Niskin bottles was used to collect surface water samples and provide in situ measurements of temperature and salinity. For DIC and TAlk, water samples were stored in 250-mL glass bottles preserved with 20 mL saturated $HgCl_2$. Methods for DIC, TAlk and pH analysis are given by *Wang and Cai* [2004]. pCO_2 was calculated from measured pH and DIC based on constants suggested for estuarine waters by *Cai and Wang* [1998]. Chlorophyll was determined by filtration using GF/F filters and fluorometric assay of 90 % acetone extracts.

[5] An empirical relationship between field measurements of surface pCO_2 to environmental variables (T, S, chlorophyll) was derived by applying principal component analysis to the T, S and chlorophyll data and subsequently regressing the derived orthogonal components against in situ pCO_2. The results of the regression analysis were then applied to a MODIS-Aqua image from 26 June 2003. MODIS-Aqua L1B data were acquired from the NASA Goddard Space Flight Center's Distributed Active Archive Center. The L1B data were processed using SeaDAS v4.5, and products were retrieved for sea-surface temperature (SST), chlorophyll (OC4 algorithm) and dissolved/detrital absorption (Garver-Siegel-Maritorena version 1, acdm_gsm01 [*Maritorena et al.*, 2002]). The acdm_gsm01 product was assumed to be representative of a_{CDOM} (absorption of colored dissolved organic matter) after adjusting for differences in wavelength (443 nm versus 412 nm) using an exponential spectral slope of 0.020 nm^{-1}. We assumed that the majority of the acdm_gsm01 product absorption was due to the dissolved fraction; however, the validity of this assumption needs further evaluation. Salinity was estimated using a previously

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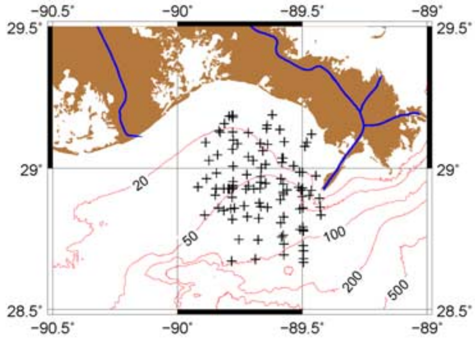

Figure 1. Station locations for surface water samples during the June 2003 R/V *Pelican* cruise.

determined relationship between CDOM absorption (a_{CDOM}) at 412 nm and salinity for the Mississippi delta region [*Wright*, 2005]: Salinity = $-22.4a_{CDOM} + 35.0$, with root mean square error (RMSE) of 3.0 and $r^2 = 0.838$.

3. Results and Discussion

3.1. Surface Measurements of Carbon System Properties

[6] We found evidence of both high CO_2 biological uptake and great variability in this system. The Mississippi River low salinity waters exhibit TAlk and DIC values (range 1500–3000 μM) higher than or similar to adjacent coastal water (Figure 2 and *Cai* [2003]), and are a source of CO_2 to the atmosphere. The relatively high alkalinity of Mississippi River imparts a strong buffering capacity to its outflow waters. Physical mixing of river and ocean waters decreases plume pCO_2. However, this process alone cannot account for observations of pCO_2 below atmospheric levels (i.e., the plume is a CO_2 sink) (Figure 2). The very low pCO_2 observed in the plume (~100 μatm) must be the result of strong biological removal (net autotrophy). In contrast, very high pCO_2 (>600 μatm) immediately adjacent to the plume indicates that the system varies from a CO_2 source in the river and initial outflow, to a strong sink in the optimal growth zone, and to a weak CO_2 source in offshore waters (Figure 2). In addition, areas between the plume and the coast marshes are likely a source of CO_2 [*Cai et al.*, 2003].

3.2. Principal Component and Multiple Linear Regression Analyses of Relationships of Environmental Variables to pCO_2

[7] We sought to identify empirical relationships of pCO_2 with physical (salinity, temperature) and biological (chlorophyll as a proxy for primary production) variables. Prior to principal component analysis, data were partitioned according to salinities of less than 10 or greater than or equal to 10 to account for the change in slope in the relation to pCO_2 (Figure 2). Principal component analyses of salinity, temperature and chlorophyll data revealed that more than 98% of the variation could be accounted for by the first two components for both the low salinity and high salinity data. Component scores for first two orthogonal components were regressed against surface pCO_2 using multiple linear regression (Figure 3). The RMSE for the test data relationship in Figure 3 was 50.2 μatm.

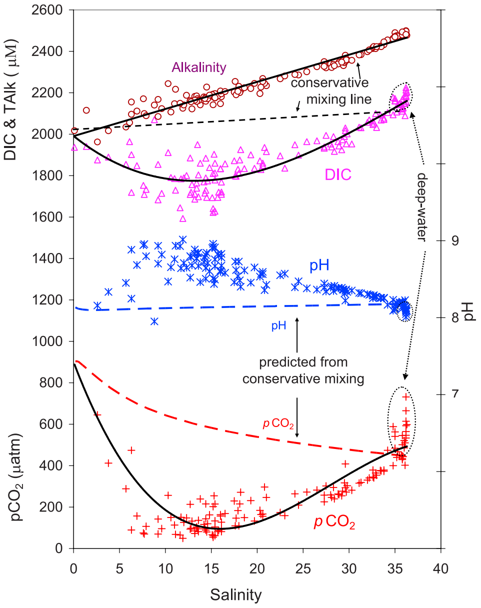

Figure 2. Dissolved inorganic carbon (DIC), total alkalinity (Talk) and pH values measured in the Mississippi River plume in June 2003 (Cai, unpublished data). Solid lines are regression lines and dashed lines are either conservative mixing line (DIC) or lines (pH and pCO_2) predicted from conservation mixing. In the mixing calculation river end-member DIC and TAlk (not shown) were used. Data from deep-water samples were included in the regression. This created an offset in the pCO_2 case. Also the river end-member value (900 μatm) was used to set the intercept in the pCO_2 regression.

[8] The results of the regression analysis were then applied to a MODIS-Aqua image from 26 June 2003 to estimate pCO_2 using retrieved products for T (SST), S (estimated from a_{CDOM}), and chlorophyll (Figure 4).

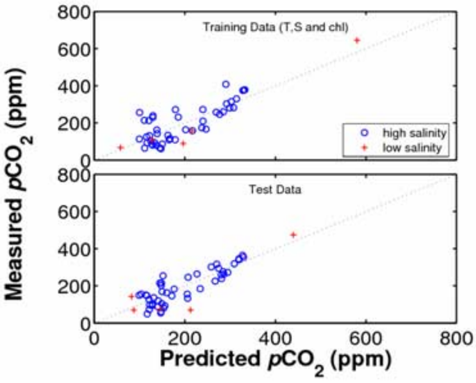

Figure 3. Observed versus predicted pCO_2 based on regression of principal components derived from in situ T, S and chlorophyll data during June 2003. Dotted lines are 1:1 relationship. The top panel shows the data set used to derive the component loads and regression coefficients. The bottom panel shows the comparison when the results were applied to the second half of the data. The r^2 for the combined test data was 0.743.

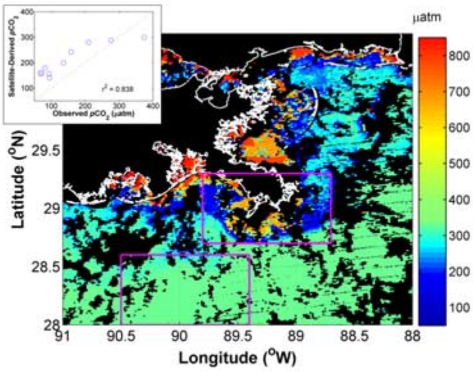

Figure 4. Satellite-derived pCO_2 distribution in the shelf region near the Mississippi River delta derived from MODIS-Aqua imagery 26 June 2003. The image shows a large area of low pCO_2 waters subject to the outflow of the Mississippi River that was consistent with in situ measurements (Figure 2). The magenta boxes delineate plume and shelf subregions for which air-sea flux calculations were made (Table 1). Inset shows matchups between satellite-derived and ship-based measurements of pCO_2 in relationship to 1:1 line.

Estimated pCO_2 values less than zero were discarded. An area of low pCO_2 can be seen in the vicinity of the Mississippi River delta, consistent with field observations (Figure 2). Match-up between neighboring pixels and contemporaneous (within 12 h) field observations revealed a strong correlation (r^2 = 0.838; Figure 4 inset), but with a positive bias in satellite estimates at low pCO_2 levels (RMSE = 72.8 µatm). The positive bias could be explained, at least partially, by a small negative bias in satellite estimates of salinity (from a_{CDOM}) at low salinities (not shown). Briefly, additional sources of error included uncertainty in the regression relationship in Figure 3, as well as in satellite estimates of chlorophyll and temperature. Temporal offsets between satellite and in situ observations, and within-pixel variability would contribute additional error. With regard to shipboard measurements, uncertainties of pH measurements in estuarine waters are well known [*Cai and Wang*, 1998] and were estimated as ±0.05 pH unit at low salinity, which would lead to uncertainties of 25 (for low pCO_2) to 80 (for high pCO_2) µatm. Despite such errors and biases, the agreement between observed and satellite-derived estimates is encouraging, and trends in satellite-derived pCO_2 were representative of ship-based measurements.

3.3. Air-Sea Fluxes of CO_2

[9] Satellite-derived regional assessments of pCO_2 were used in conjunction with estimates of wind fields to produce regional-scale estimates of air-sea fluxes. Various sets of the gas transfer velocity, *k*, vs. wind speed relationships (Table 1) were used to provide a range of values bracket the gas flux. The daily average wind speed for June 2003 (5.28 m s^{-1}) was estimated for data obtained from the NOAA National Data Buoy Center C-Man station located at 28.90°N 89.43°W near Southwest Pass. Estimates were made using the various flux parameterizations for a subregion (see Figure 4) near the plume, the outer shelf, and for the entire image (Table 1). As noted by *Thomas et al.* [2004], estimates for more recent flux parameterizations show a convergence of values (Table 1). In all cases, estimated air-sea fluxes were negative (net sink for CO_2). Overall, for the region encompassed by the entire image, there was a net surface in-water flux estimated at 2.0–4.2 mmol C m^{-2} d^{-1}. The plume subregion had slightly more negative fluxes than the shelf subregion, and both the shelf and plume regions displayed higher uptake than for the entire image. Uncertainty analyses indicated that the positive bias in satellite pCO_2 estimates would have resulted in as much as a 60% underestimation of in-water fluxes in the plume region, with smaller impacts for the shelf and regional estimates (20–30%).

4. Synthesis

[10] Our findings support the views expressed in prior studies that conditions in the Mississippi River can result in high net uptake of carbon dioxide [*Cai*, 2003] and enhanced biological production [*Lohrenz et al.*, 1990, 1997, 1999]. *Cai and Lohrenz* [2006] similarly noted the regional importance of the Mississippi River in influencing carbon dynamics of the northern Gulf of Mexico coastal ecosystem. High productivity in surface waters and accompanying export of organic matter to bottom waters has been cited as a cause of recurrent hypoxia in the northern Gulf of Mexico [*Rabalais et al.*, 2002].

[11] Globally, it was reported the estuaries of small and medium rivers were major sources of CO_2 to the atmosphere [*Frankignoulle et al.*, 1998; *Cai et al.*, 1999; *Raymond et al.*, 2000]. This work and others [*Tsunogai et al.*, 1999; *Ternon et al.*, 2000; *Cai*, 2003] demonstrate that enhanced biological production in large river plumes may lower surface pCO_2 levels such that these regions may exhibit a net surface influx of atmospheric CO_2. Systems are likely to differ depending on the both biological and chemical properties. For example, *Cai* [2003] noted that net biological uptake of carbon was higher in the Mississippi River plume than the Amazon system [*Ternon et al.*, 2000].

[12] Our findings illustrate the highly heterogeneous nature of pCO_2 distributions in river-impacted coastal margins (Figure 4) and show considerable promise for synoptic, regional scale estimates of air-sea flux of CO_2 using satellite imagery. Future studies will likely require a combination of both in situ and satellite observations to constrain variations in empirical algorithms. For example, horizontal temperature variations were relatively small and so were presumably a minor factor in the observed variations in pCO_2 in Figures 3 and 4. However, temperature may play a larger role at other times of the year. Similarly, seasonal variations in river discharge, meteorological forc-

Table 1. CO_2 Air-Sea Flux Estimates Determined Using Different Flux Parameterizations[a]

Plume	Shelf	Region	Reference
−4.6	−3.3	−2.5	*Liss and Merlivat* [1986]
−7.7	−5.5	−4.2	*Wanninkhof* [1992]
−3.7	−2.7	−2.0	*Wanninkhof and McGillis* [1999]
−6.8	−4.9	−3.7	*Nightingale et al.* [2000a]
−6.8	−4.9	−3.7	*Nightingale et al.* [2000b]
−6.8	−4.9	−3.7	*McGillis et al.* [2001]

[a] Estimates are in mmol C m^{-2} d^{-1}. Negative flux indicates a direction from air to sea.

ing, and physicochemical and biological factors will influence carbon system properties and predictive relationships.

[13] **Acknowledgments.** We are grateful to V. Wright, C. DelCastillo, M. Dagg, Y. Wang, L. Jiang and G. Han for data and technical support. J. Salisbury and an anonymous reviewer provided valuable comments on earlier versions of the paper. Funding for this research was provided by NASA (NNG05GD22G and NNS04AB84H).

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