SUMMER-TIME CO_2 FLUXES AND CARBONATE SYSTEM BEHAVIOR IN THE MISSISSIPPI RIVER AND ORINOCO RIVER PLUMES

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ABSTRACT

High-resolution underway measurements of surface water pH, CO_2 fugacity (fCO_2), and total dissolved inorganic carbon (DIC), along with discrete bottle sample analyses from depths, were obtained in July 2005 and September 2006 in the Mississippi River Plume (MRP) and the Orinoco River Plume (MRP). The resulting data were analyzed to compare and contrast the CO_2 fluxes and carbonate system behavior of the two river plumes. The surface water within the MRP shows a strong atmospheric CO_2 sink, while oligotrophic waters of the Gulf of Mexico were a CO_2 source. The CO_2 sink of the ORP is much less significant, and the adjacent surface water of the Caribbean Sea was approximately in equilibrium with the atmosphere. The carbonate system inside the MRP is strongly influenced by net biological uptake. This is less significant for the ORP. The strength of the carbon sinks in the two plume systems differs significantly due to both natural and anthropogenic influences.

1. BACKGROUND

Coastal oceans are a critical component of the global carbon cycle, and their capacity to absorb atmospheric CO_2 plays an important role in the global CO_2 budget [1, 2]. Coastal oceans are highly dynamic and heterogeneous due to complex physical, chemical, and biological forcings. Thus the factors that influence air-sea CO_2 flux are often complex and highly variable in coastal waters, making modeling and prediction difficult. A recent synthesis of CO_2 measurements and flux calculations by Chen and Borges [2] indicates open continental shelf waters experience a net influx of atmospheric CO_2 of 0.33 – 0.36 Pg C yr^{-1}. However, these estimates still bear large uncertainty due to limited data coverage in coastal oceans around the globe, and many shelf regions lack any pCO_2 measurements. Arguably the greatest uncertainty in our understanding of the global carbon cycle surrounds biogeochemical processes that occur in coastal oceans. As a community we should move forward and broaden our research scope in coastal CO_2 studies beyond air-sea CO_2 flux to the investigation of biogeochemical mechanisms that control the coastal CO_2 source/sink, since these processes may have important implications for the long-term responses of coastal systems to anthropogenic impacts.

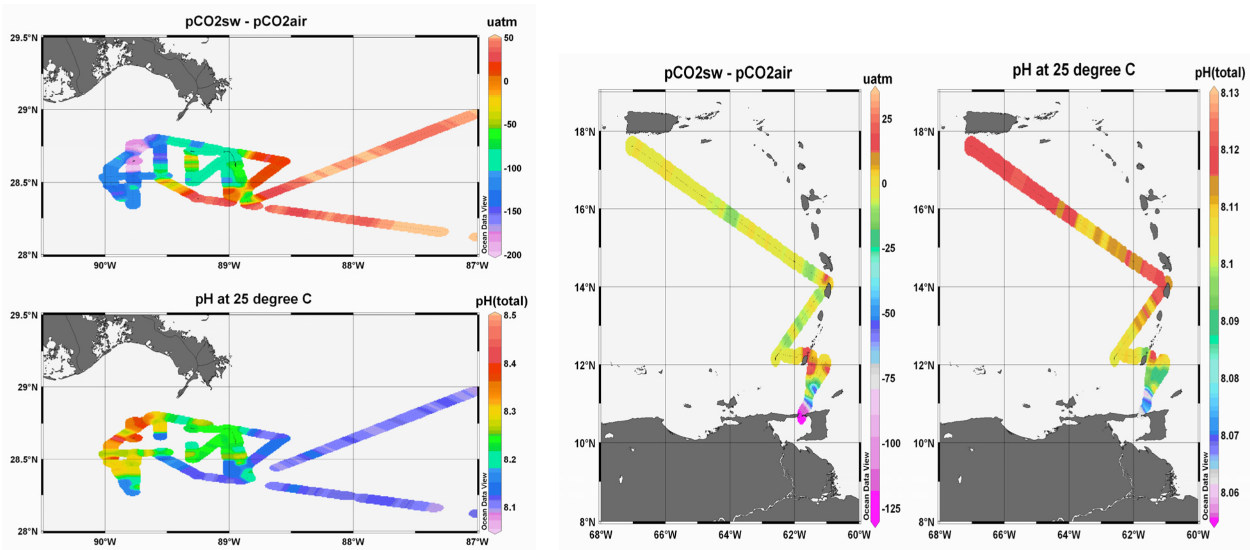
The Mississippi and Orinoco Rivers are the seventh and eighth largest rivers in terms of discharge in the world, respectively. Their impact on the chemistry, geology, physics, and biology of the ocean basins they enter extends thousands of kilometers from their river mouths. At times, the Mississippi River Plume (MRP) can reach the Florida Straits, and be traced as far north as Georgia [3]. The Orinoco River Plume (ORP) influences the entire southern Caribbean [4], and often combines with the Amazon plume to cause surface salinity anomalies over 2000 km away from the river mouths [5]. Nutrients from the Mississippi River fuel net biological uptake of inorganic carbon in its river plume water that generally produces areas under-saturated in CO_2, creating CO_2 sinks on the continental shelf [6,7]. Large river plumes may even make significant contribution to the CO_2 flux on a ocean-basin scale as implied by the CO_2 studies in the Amazon River Plume [8,9].

This study is one part of the project to study ecology and genomics of CO_2 fixation in the Mississippi and Orinoco River Plumes. The two over-arching goals of this project are: (1) to investigate the CO_2 sink and carbonate system in the two large river plumes; (2) to link gene expression analysis and the carbonate system measurements in order to identify phytoplankton species/groups that are mainly responsible for carbon uptake inside vs. outside the plumes, and to study its possible causes. In this study, we will present the high-resolution data of the CO_2 system (pH, DIC, and pCO_2) measured during the two summer cruises in the Mississippi and Orinoco River Plumes. The main research objectives for this coastal carbon cycle study are:

1) Examine if the two major river plumes consist of significant carbon sink under summer conditions and estimate air-sea CO_2 fluxes in surveyed area;
2) Estimate net biological production of the two river plumes in summer;
3) Compare and contrast the carbonate system behaviors between the MRP and ORP and examine their respective controlling biogeochemical processes.

2. METHODS

High-resolution simultaneous underway measurements of surface water pCO_2, DIC, and pH were obtained during the two summer cruises in the MRP and CTD-Rosette package at the sampling stations with various depths, and analyzed by the MICA.



(A) Mississippi River Plume (B) Orinoco River Plume

Figure 1. Surface water distributions of pCO_2 gradient ($pCO_{2sea} - pCO_{2air}$) and pH along the cruise tracks. (A) Mississippi River Plume, July 2005; (B) Orinoco River Plume, September 2006.

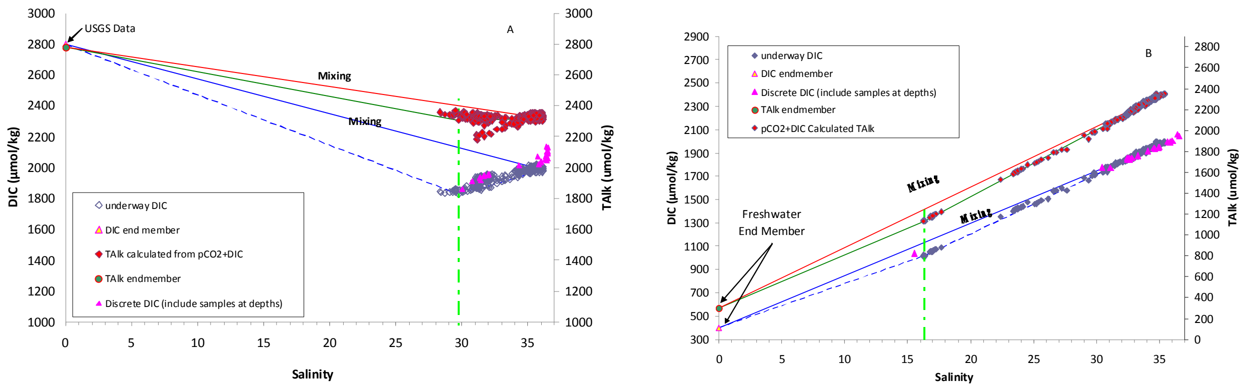


Figure 2. Salinity distributions of DIC and pCO_2-DIC calculated TAlk in (A) the MRP, July 2005 and (B) the ORP, September 2006. The freshwater end-members of DIC and TAlk for the Mississippi River were obtained from the USGS. For the Orinoco River, its end-members of DIC and TAlk were assumed to be the end-members of the Amazon River (Cooley and Yager, 2006).

ORP on board ship of R/V Pelican. The underway system consists of a Multi-parameter Inorganic Carbon Analyzer (MICA) [10], which was recently developed by the College of Marine Science and Center for Ocean Technology at the University of South Florida. All measurements are based on similar spectrophotometric principles, and have achieved high precision and accuracy that are comparable to traditional state-of-art methodologies for measurements of the CO_2 parameters. Discrete DIC samples at depths were also taken by a

3. RESULTS

3.1 Mississippi River Plume

Surface water inside the Mississippi River Plume (MRP) is strongly under-saturated of pCO_2 with respect to the atmosphere. The lowest pCO_2 (~160 uatm) was observed at salinity of ~29, with a pCO_2 air-sea gradient ($pCO_{2sea} - pCO_{2air}$) of ~-200 µatm (Fig. 1). Surface pH (total scale) at 25˚ C is generally greater than 8.20, and reaches as high as ~8.49. The location of observed high pH coincides with that of low pCO_2 (Fig. 1). DIC at surface also shows a significant deficit inside the plume (DIC ~1830 μmol kg^{-1}) relative to the theoretical mixing line between the Mississippi River water (DIC ~2800 μmol kg^{-1}) and the open Gulf of Mexico (GOM) water (DIC ~2000 μmol kg^{-1}) (Fig. 2). These observations indicate an intensive net biological carbon uptake inside the MRP, where photosynthesis surpasses respiration, resulting in a net uptake of proton (H^+). This strong CO_2 sink was estimated to be a flux of -4.9 ~ -7.7 mmol C m^{-2} d^{-1} (negative sign indicates that the direction of the CO_2 flux is from the atmosphere to the surface water) based on the parameterizations of the CO_2 flux calculations by Wanninkhof [11] and Liss and Merlivat [12]. It is also noted that pCO$_2$-DIC calculated TAlk also shows a net removal inside the plume relative to the mixing line (Fig. 2), suggesting net biological calcification/$CaCO_3$ precipitation may also occur along with intensive biological carbon uptake. Calcification/$CaCO_3$ precipitation process will lower DIC and TAlk together with a removal ratio of 1:2 (ΔDIC : ΔTAlk).

Outside the MRP in the open water of the GOM, surface water becomes a source of CO_2 (1.3 ~ 2.9 mmol C m^{-2} d^{-1}) to the atmosphere with pCO$_2$ values above 420 μatm (Fig. 1). Surface pH outside the plume is significant lower than that inside the plume with a mean of ~8.09 (typical GOM pH level). DIC in the open water of the GOM has a concentration of ~2000 μmol kg^{-1} at surface and ~ 2100 μmol kg^{-1} at the bottom (Fig. 2). Surface water pCO$_2$, pH, and DIC vary less spatially outside the plume (Fig. 1).

3.2 Orinoco River Plume

The CO_2 sink inside the ORP is much weaker than the MRP. Lowest surface pCO$_2$ (~250 uatm) was observed near salinity of 16 at the Dragon Mouth in the Gulf of Paria (Fig. 1). Surface CO_2 influx was estimated to be -0.7 ~ -1.1 mmol C m^{-2} d^{-1}, about one fourth of that in the MRP. In contrast to the MRP, surface pH at 25° C is less than 8.10. The location of observed low pH coincides with that of low pCO$_2$. DIC at the low salinity encountered is only ~1000 μmol kg^{-1}, much lower than the MRP. However, the net biological uptake of inorganic carbon seems to be much less substantial than the MRP as evidenced by the salinity-DIC diagram (Fig. 2). The net removal of TAlk is also less apparent in the ORP.

Surface water for most of the surveyed area in the southwestern Caribbean Sea is near CO_2 equilibrium with or slightly lower than (pCO$_2$ 360 – 375 μatm) the atmosphere (Fig. 1). Surface pH outside the plume is higher than that inside the plume with a range of 8.10 – 8.12, which is close to oligotrophic waters of the GOM. There is little spatial variability for all carbonate parameters (pH, pCO$_2$, DIC, and TAlk) outside the plume.

4. DISCUSSION

4.1 River influence and net biological uptake rates

The Mississippi River water contains high concentration of HCO_3^- (weathering products), which results in high DIC concentration and TAlk content (~2800 μmol kg^{-1}) (Fig. 2), thus high buffering capacity. During the low flow season (summer and fall), the river-ocean mixing of both DIC and TAlk shows a positive gradient (high to low concentration) from river to ocean (Fig 4). Salinity-normalized DIC and TAlk also show a strong positive gradient (high to low concentration) relative to the ocean end-member (data not shown), indicating that the MR is a significant source of inorganic carbon to the GOM. In contrast, the Orinoco River discharges freshwater containing little TAlk and DIC, but high concentration of humic material from its drainage basin [4]. A negative gradient of DIC and TAlk (low to high concentration) from river to ocean was observed in summer (Fig. 2). Much less inorganic carbon outflows from the OR compared to the MR as suggested by potential low concentration of DIC at the river end-member of the OR (Fig. 2).

DIC and TAlk data can be used to estimate net biological production for the two river plumes based on a standard mixing model assuming a mixing scenario with two end-members (a freshwater end-member and an open ocean end-member) [13] (Fig. 2). This model uses the concept of Effective Concentration (C*), which is defined as the expected concentration of a dissolved material at the zero salinity after correcting a measured concentration at a certain salinity for physical mixing. Then a product of the river discharge rate (Q) and this effective concentration (C*) represents the flux of a dissolved material across that iso-salinity surface (Flux = QC*). The difference between this flux and the flux (Flux = QC) across the zero salinity (at the freshwater end-member) then indicates the net removal (or addition) flux of this dissolved material during the mixing at the salinity where the dissolved material is measured. Based on the salinity-DIC and TAlk diagrams (Fig. 2), the net removal fluxes of DIC and TAlk in the MRP and ORP were estimated using the above described mixing model. The net removal of DIC calculated here includes net biological DIC uptake and changes of DIC during calcification/$CaCO_3$ precipitation (ΔTAlk : ΔDIC = 2 : 1). Therefore, the net biological carbon uptake rate can be assessed by correcting net DIC removal by net calcification/$CaCO_3$ precipitation given the plume area:

$$\text{Net Biological Uptake} = \frac{\Delta(\text{DIC Flux}) - 1/2\Delta(\text{TAlk Flux})}{\text{Plume Area}} \quad (1)$$

The net biological carbon uptake evaluated in this method represents the net community production (primary production – community respiration). The plume area for the MRP and ORP can be estimated from the satellite images (C. Hu, University of South Florida, personal communication). The net biological carbon uptake rate in the MRP was calculated to be 1.8 g C m^{-2} d^{-1}, which is one order of magnitude higher than the ORP (0.1 g C m^{-2} d^{-1}). The estimated net biological carbon uptake for the MRP agrees well with previously estimated values [6], and is among the highest in the coastal systems studied so far. This estimate also indicates that the surface area of the MRP is net autotrophic, where primary production greatly exceeds community respiration, resulting in a net production of organic carbon. Since the freshwater end-member in the OR is not exactly known (Fig. 2), and was assumed to be the same as the Amazon River, the estimate of the net biological DIC uptake in the ORP likely bears large uncertainty. However, it is reasonably to argue that the DIC and TAlk values in the OR would be fairly close to the Amazon River given that they drains similar geological area. In this regard, the net community production in the surface area of the ORP should be much less than the MRP.

Table 1. Riverine fluxes and the CO_2 systems for the Mississippi and Orinoco Rivers, and their river plumes.

	Mississippi	**Orinoco**
Annual Water Discharge (10^{11} m^3 yr^{-1})	5.3	9.8
Total Riverine N Flux (10^{12} gC yr^{-1})	1.57	0.57
Total Riverine OC Flux (10^{12} gC yr^{-1})	5.6	6.8
Riverine DIN Flux (10^{12} gC yr^{-1})	0.98	0.13
Mean Riverine DIN Concentration (µM)	100	6.6
Mean Riverine DIP Concentration (µM)	3.1	0.2
Mean Riverine SiO_3 (µM)	108	86
(The above data are from Dagg et al. [14] and Cai [6])		
Riverine DIC/TAlk Flux (10^{12} gC yr^{-1})	21	2.2 – 7/ 1.1 - 7
Riverine DIC/ TAlk (µmol kg^{-1})	2799/2780	187-600/ 95-600 ?
CO_2 flux inside the river plume (mmol m^{-2} d^{-1})	-7.7	-1.3
CO_2 flux outside the river plume (mmol m^{-2} d^{-1})	2.9	-0.4
Plume area-integrated net biological uptake (gC m^{-2} d^{-1})	1.8	0.1
Primary production (gC m^{-2} d^{-1})	1.0 - 8.0	0.1 - 1.0

(The above data are for the summer conditions estimated from this study.)

4.2 Comparison between the MRP and ORP

The MR and OR bear many differences in terms of river chemistry, which significantly affect the carbonate chemistry in their respective river plumes. Table 1 summarizes the major differences in river chemistry and the corresponding carbon system behaviors in the MRP and ORP. It is clear from this comparison that the MRP consists of a significant biological sink of atmospheric CO_2, which is mainly fueled by large loading of inorganic nutrients discharged by the Mississippi River. Large portion of this nutrient flux (N, P, and Si) has an anthropogenic origin as agriculture (e.g. use of fertilizer) and land change in the MR drainage area are mainly responsible for such a high nutrient flux in the MR. In this sense, human-activity may essentially enhance the CO_2 sink in the MRP that otherwise would be much smaller. In contrast, the OR delivers only a fraction (~1/10) of the MR nitrogen and phosphorous fluxes to the ocean, and the net biological carbon uptake rate in the ORP is only about 1/10 of that in the MRP (Table 1). As a result, the MRP is a net autotrophic system that produces a significant net amount of organic carbon, while the level of the net autotrophy for the ORP is likely one order of magnitude lower than the MRP. The exact fate of organic carbon produced in the MRP is not clearly known and it worth further investigation. However, intensive hypoxia occurred at the bottom in the plume area and over-saturation of surface CO_2 outside the plume in summer may suggest that much of this produced organic carbon is respired adjacent to the plume before making exchange with the open ocean. It is also worth to point out that this study may have implication for long-term change of coastal ecosystem functioning resulting from increasing anthropogenic impacts (such as increase of nutrient and bicarbonate fluxes due to increasing use of fertilizer and increase in weathering rate in the drainage basin). How the carbonate system responds to these anthropogenic influences is a critical issue that warrants future efforts of studying.

References

1. Cai, W.J., Dai, M. & Wang, Y. (2006). Air-sea Exchange of Carbon Dioxide in Ocean Margins: A Province-based Synthesis. *Geophysical Research Letters* **33**, L12603.

2. Chen, C.A. & Borges, A.V. (2009). Reconciling Opposing Views on Carbon Cycling in the Coastal Ocean: Continental Shelves as Sinks and Near-shore Ecosystems as Sources of Atmospheric CO_2. *Deep-Sea Research II* **56**, 578–590.

3. Hu, C.M., Nelson, J.R., Johns, E., Chen, Z.Q., Weisberg, R.H. & Muller-Karger, F.E. (2005). Mississippi River Water in the Florida Straits and in the Gulf Stream off Georgia in Summer. (2004). *Geophysical Research Letters* **32**, L14606.

4. Morell, J.M. & Corredor, J.E. (2001). Photomineralization of Fluorescent Dissolved Organic Matter in the Orinoco River Plume: Estimation of Ammonium Release. *J. Geophys. Res.* **106**, 16807–16813.

5. Hu, C.M., Montgomery, E.T., Schmitt, R.W. & Muller-Karger, F.E. (2004). The Dispersal of the Amazon and Orinoco River water in the Tropical Atlantic and Caribbean Sea: Observation from Space and S-PALACE floats. *Deep-Sea Research Part II-Topical Studies in Oceanography* **51**, 1151-1171.

6. Cai, W.J. (2003). Riverine Inorganic Carbon Flux and Rate of Biological Uptake in the Mississippi River Plume. *Geophysical Research Letters* **30**, 1032.

7. Lohrenz, S.E. & Cai, W.J. (2006). Satellite Ocean Color Assessment of Air-sea Fluxes of CO_2 in a River-dominated Coastal Margin. *Geophys. Res. Lett.* **33**, L01601.

8. Cooley, S.R. & Yager, P. L. (2006). Physical and Biological Contributions to the Western Tropical North Atlantic Ocean Carbon Sink Formed by the Amazon River Plume. *Journal of Geophysical Research-Oceans* **111**, C08018.

9. Cooley, S.R., Coles V.J., Subramaniam, A. & Yager, P.L. (2007). Seasonal Variations in the Amazon Plume-related Atmospheric Carbon Sink. *Global Biogeochemical Cycles* **21**, GB3014.

10. Wang, Z.A., Liu, X., Byrne, R.H., Wanninkhof, R.H., Bernstein, R.E., Kaltenbacher, E.A. & Patten, J. (2007). Simultaneous Spectrophotometric Flow-through Measurements of pH, Carbon Dioxide Fugacity, and Total Inorganic Carbon in Seawater. *Analytica Chimica Acta* **596**, 23-36.

11. Wanninkhof, R. (1992). Relationship Between Wind Speed and Gas Exchange Over the Ocean. *J. Geophys. Res.* **97**, 7373-7382.

12. Liss, P.S. & Merlivat, L. (1986). Air-sea Gas Exchange Rates: Introduction and Synthesis. In Buat-Menard, P. (Ed.), *The Role of Air-sea Exchange in Geochemical Cycling*. NATO Advanced Studies, Reidel Publishing, pp. 113-127.

13. Officer, C.B. (1979). Discussion of the Behavior of the Non-conservative Dissolved Constituents in Estuaries. *Estuar. Coast. Mar. Sci.* **9**, 911-914.

14. Dagg, M., Benner, R., Lohrenz, S., O'Donnell, J. & Lawrence, D. (2004). Transport and Transformation of Dissolved and Particulate Materials on Continental Shelves Influenced by Large Rivers: Plume Processes. *Continental Shelf Research* **24**, 833-858.