

Satellite Assessment of CO₂ Distribution, Variability and Flux and Understanding of Control Mechanisms in a River Dominated Ocean Margin

**CRUISE PLAN
R/V Cape Hatteras 8 – 20 January 2009**

Overview:

The primary hypothesis of our proposed research is that **large river margin water columns exhibit extreme seasonal and spatial variability in air-sea CO₂ fluxes, characterized by localized uptake driven largely by high rates of autotrophic production and loss of CO₂ driven by high terrestrial inputs and heterotrophic respiration.** Our plan of work will involve a multi-disciplinary but focused research approach comprised of four major activities including: 1) *continuous, shipboard, assessments of carbon system properties and air-sea fluxes of CO₂* and relationships to other variables (pH, DIC, TAlk, DO, nutrients, Chlorophyll, Chlorophyll fluorescence, etc) in the river margin shelf ecosystem of the Mississippi- Atchafalaya River (Fig. 1), 2) *satellite-derived assessments of regional scale pCO₂ and air-sea carbon fluxes* that will be used to quantify and assess spatial and temporal variations; 3) *targeted process measurements* of plankton community net community metabolism and carbon fixation rates, and phytoplankton pigment composition and size structure at representative sites, which will provide information about the net metabolic balance and composition of the plankton community, and 4) *box-model exercises* simulating plume mixing (estuarine mixing model, Officer, 1979, 1980; Cai et al. 2000), acid-base chemistry (using CO₂SYN) and an inverse model to describe biological processes mediating carbon cycling and air-sea flux of CO₂ (Green et al. 2006). A listing of observational efforts and responsibilities is given in Table 1.

Measurements:

Table 1. Sampling Activities and Principle Investigator(s) Responsible

Observation Type	Variable Measured	PI(s) or source
<i>Underway (continuous)</i>	Wind, meteorological data	NDBC
	TS, chlorophyll fluorometry, transmissometry Dissolved oxygen, pCO ₂	Lohrenz, Cai Cai
<i>Underway Water Column (discrete)</i>	HPLC pigments DIC, alkalinity, pH, DO	Chakrabroty Cai, Lohrenz
	Dissolved nutrients, salinity, total suspended matter Chromophoric dissolved organic matter (CDOM) absorption, particulate pigment and detrital absorption	Lohrenz
<i>Satellite Imagery</i>	Water-leaving radiance, chlorophyll, chlorophyll fluorescence line height, suspended solids, CDOM absorption, SST, high resolution true-color imagery, winds, vis/infrared imagery	Lohrenz
<i>Process Studies</i>	Air-sea CO ₂ flux and biological uptake of DIC (i.e., solubility and biological pumps)	Cai
	Community respiration	Cai
	Net surface water metabolic balance	Gundersen
	Dissolved nutrient dynamics	Cai, Lohrenz
<i>Box-model exercise</i>	Photosynthesis-irradiance, primary production	Lohrenz
	Freshwater-seawater mixing, acid-based chemistry, biological processes/net system metabolism	Cai, Lohrenz

Underway $p\text{CO}_2$ monitoring. The flow-through system is attached to a “shower head equilibrator plus infrared detector (Li7000)” system to measure sea surface $p\text{CO}_2$ with field temperature (Wang and Cai 2004). Air $p\text{CO}_2$ will be measured continuously with another Li7000. Our underway $p\text{CO}_2$ data compare well with the NOAA system (R. Wanninkhof) for two recent cruises on the East coast.

Air-sea CO_2 flux calculation will follow standard methods (Wanninkhof, 1992; McGillis et al., 2001; Lohrenz and Cai, 2006). We recognized that bulk parameterization models established in open ocean waters may not be appropriate for coastal ocean applications. However, there is no current consensus on what is the best approach. Thus we plan to use a set of equations to bracket the gas flux range as we did earlier (Lohrenz and Cai 2006) but will discuss with experts in the area for advice. Continuous wind speed records will be available from the ship as well as from several NOAA National Data Buoy Center meteorological stations. Wind fields can also be characterized using QuikSCAT scatterometer imagery.

pH will be measured on board with an Orion Ross glass electrode (Wang and Cai, 2004).

DIC and TAlk. See Wang and Cai (2004). Samples taken from Niskin bottles will be measured for TAlk on board ship and they will be preserved with HgCl_2 and brought back to lab for analysis of DIC. Both analyses have a precision of 0.1% and are calibrated using the Certified Reference Material (CRM) from A. G. Dickson.

DO will be measured underway with an Aanderaa DO sensor. Water samples from the Niskin bottles will also be measured by Winkler titration on board ship with a precision of 0.1-0.2% (a modification of Pai 1993).

Isotope Tracers. Additionally, on selected water samples, $\delta^{13}\text{C}(\text{DIC})$ (indicates biological processes, Spiker 1980; Coffin et al. 1994) and $\delta^{18}\text{O}$ and D/H ratio (water mass tracers; Fairbanks, 1982) will be measured at the UGA Center for Applied Isotope Study. Preliminary $\delta^{18}\text{O}$ and D/H ratio data from the June 2006 cruise indicate that waters in the area are largely a mixture of the Mississippi River water and seawater with some additional inputs.

Community respiration. Water samples (in 300-mL acid clean bottles) will be incubated in darkness at ambient temperature for 24 hours. Both DIC increase and O_2 decrease (Winkler method) will be measured. Rates will be determined from the difference between the intact group and the HgCl_2 -killed reference group (each 3-5 bottles).

Net metabolic balance (P/R) of surface waters. The upper water column-integrated balance between plankton community gross production (Pg) and respiration (R) defines the net metabolic status of the surface waters. Rates of Pg and R will be based on depth-integrated light/dark bottle O_2 incubations (described in detail in Smith and Kemp, 2003). Briefly, integrated rates of Pg (defined as O_2 changes in light bottles plus dark bottles minus initial bottles) will be determined in 8-12 h simulated in situ incubations for average light levels over the depth of the euphotic zone. Integrated rates of R will be determined by extrapolating volumetric rates (described above) to 24 h and summing over the depth of the

euphotic zone. This measurement can be compared to the net metabolic rate constrained from surface water CO₂/DIC mass balance.

Characterization of Phytoplankton Pigment Composition and Size Structure. Phytoplankton pigments will be determined for total and <5- μ m size fractions by filtering through GF/F filters and storage in liquid nitrogen. HPLC analysis will follow the protocol of Wright et al. (1991) on a Waters HPLC system. Phytoplankton counts will be determined from water preserved in 0.5% glutaraldehyde, refrigerated for 1 h, and filtered onto 0.2-, and 5- μ m polycarbonate filters, the larger size fraction stained with proflavin and counted using epifluorescence microscopy (Dortch et al. 1992, 1997).

Nutrient Analyses and Total Suspended Matter (TSM) Analyses. Inorganic nutrients (NH₃, NO₂/NO₃, PO₄, and Si) will be quantified in samples collected from the underway flow-through mapping effort, and in discrete samples collected from the CTD/Niskin casts. In order to understand the variability in the river (source), we will rely on monitoring data provided by the U.S. Geological Survey at various river sites (http://toxics.usgs.gov/hypoxia/real_time.html). Discrete samples collected on the cruises for inorganic nutrients will be analyzed using an Astoria-Pacific 2+2. Nutrient Analyzer. For TSM, samples will be filtered onto pre-tared 0.45 μ m polycarbonate filters (Poretics), rinsed with isotonic ammonium formate to remove sea salt, and dried until weight is stable.

Inherent and Apparent Optical Properties. Optical measurements and modeling will provide a basis for the interpretation of satellite ocean color and its relationship to biogeochemical constituents and will provide ancillary information in support of satellite-based estimations of primary production. Optical profiles of inherent optical properties (IOPs), including total absorption, scattering, backscattering and attenuation, will be made using a package equipped with various sensors. A WETLabs ac-s will provide estimates of in situ spectral absorption and beam attenuation at 99 wavelengths. An ac-9 can be equipped with a filter cartridge to provide simultaneous measurements of absorption by CDOM (Twardowski et al., 1999). The optical package also contains a backscattering sensor (WETLabs, Inc. ECO BB9). Measurements of IOPs can be used to model irradiance fields using semi-analytical (e.g., Morel, 1991, Lohrenz et al., 2002) or radiative transfer (Hydrolight 4.1, Sequoia Scientific) models. Validation of this approach will be achieved by comparing modeled apparent optical properties with measurements made using a 14 channel Satlantic MicroPro profiling spectroradiometer. The measurements of particulate and dissolved absorption will be made on discrete samples. Particulate spectral absorption will be determined by the quantitative filter pad absorption technique (Lohrenz, 2000; Mitchell et al., 2000, Lohrenz et al., 2003). Pigments are extracted from the filter pad in hot methanol and measurements repeated to obtain the absorption spectrum of the particulate detrital material. Correction for pathlength amplification is performed following the method given by Lohrenz (2000). Spectral absorption of chromophoric dissolved organic matter (CDOM) is determined by filtering samples through a rinsed 0.2 μ m polycarbonate membrane (Poretics) filter and scanning in a dual beam instrument using 10 cm quartz cuvettes.

Primary Production. At selected stations, photosynthesis-irradiance (P-E) parameters will be determined by incubation with ¹⁴C-HCO₃⁻ similar to that described in Lohrenz et al. (1994). The derived photosynthetic parameters will be used in conjunction with biomass and irradiance distributions to model water column-integrated primary production in the

system. Lohrenz has successfully used a wavelength-integrated (WIM) model (after Behrenfeld and Falkowski, 1997) for estimation of primary production on the Texas shelf (Chen et al., 2000), and a wavelength-resolved model (WRM) in shelf waters off North Carolina (Lohrenz et al., 2002; Carr et al., 2006). These models will be implemented at various spatial scales using observations from vertical profiles, underway-mapped surface distributions, and satellite imagery. A large database of photosynthetic parameters for the Mississippi delta region (Lohrenz et al. 1994) is available and will be supplemented by additional measurements in this study.

Cruise Personnel and Affiliations:

Name		Gender	Institution
Steven	Lohrenz	Male	University of Southern Mississippi (USM)
Wei-Jun	Cai	Male	University of Georgia (UGA)
Kjell	Gundersen	Male	USM
Kevin	Martin	Male	USM
Sarah	Epps	Female	USM
Sumit	Chakrabroty	Male	USM
Alyson	Azzara	Female	USM
Matt	Dornback	Male	USM
Yongchen	Wang	Male	UGA
Wei-Jen	Huang	Male	UGA
Xinping	Hu	Male	UGA
Leanne	Powers	Female	UGA
Cedric	Fichot	Male	University of South Carolina

Leg No., Name	Ending Waypoint Lat/Lon	Time Sum	Completion
1,	30 21.194 N 089 05.130 W	0:00:00	1/9/2009 4:00
2,	30 15.515 N 089 00.296 W	1:24:36	1/9/2009 5:24
3,	30 11.374 N 088 59.324 W	2:15:21	1/9/2009 6:15
4,	30 07.082 N 088 55.781 W	2:46:58	1/9/2009 6:46
5,	30 08.505 N 088 28.989 W	5:06:18	1/9/2009 9:06
6,	30 07.676 N 088 04.004 W	7:16:01	1/9/2009 11:16
7,	30 13.574 N 088 02.111 W	7:52:44	1/9/2009 11:52
8, A1	30 14.190 N 088 01.616 W	7:57:14	1/9/2009 11:57
9,	30 13.474 N 088 02.121 W	10:02:16	1/9/2009 14:02
10, A2	30 07.321 N 088 02.418 W	10:39:14	1/9/2009 14:39
11, A3	29 48.785 N 088 03.022 W	13:30:28	1/9/2009 17:30
12, A4	29 29.689 N 088 03.225 W	16:25:04	1/9/2009 20:25
13, A5	29 08.088 N 088 02.707 W	19:34:44	1/9/2009 23:34
14, A6	28 41.378 N 088 03.043 W	24:15:00	1/10/2009 4:14
15, A7	28 00.232 N 088 03.463 W	30:21:54	1/10/2009 10:21
16,	28 50.165 N 089 25.728 W	50:56:49	1/11/2009 6:56
17,	28 53.028 N 089 25.856 W	51:31:15	1/11/2009 7:31
18,	28 54.233 N 089 25.913 W	54:45:46	1/11/2009 10:45
19,	28 54.674 N 089 25.514 W	54:52:30	1/11/2009 10:52
20,	28 55.886 N 089 24.631 W	55:09:46	1/11/2009 11:09
21,	28 57.153 N 089 23.738 W	55:27:39	1/11/2009 11:27
22,	28 59.376 N 089 21.856 W	56:00:53	1/11/2009 12:00
23, MR1	29 01.798 N 089 19.918 W	56:36:25	1/11/2009 12:36
24,	28 59.342 N 089 21.920 W	57:54:32	1/11/2009 13:54
25,	28 57.214 N 089 23.728 W	58:10:26	1/11/2009 14:10
26,	28 55.945 N 089 24.624 W	58:19:22	1/11/2009 14:19
27,	28 54.717 N 089 25.506 W	58:36:46	1/11/2009 14:36
28, MR2	28 54.279 N 089 25.945 W	58:43:44	1/11/2009 14:43
29,	28 50.103 N 089 26.109 W	59:08:49	1/11/2009 15:08
30, MR3	28 42.119 N 089 29.868 W	60:00:39	1/11/2009 16:00
31, B1	28 00.069 N 089 45.879 W	65:26:45	1/11/2009 21:26
32, B2	28 27.237 N 089 45.992 W	68:09:46	1/12/2009 0:09
33, B3	28 44.314 N 089 45.597 W	69:52:15	1/12/2009 1:52
34, B4	28 57.425 N 089 45.372 W	72:10:55	1/12/2009 4:10
35, B5	29 15.900 N 089 45.323 W	75:01:47	1/12/2009 7:01
36,	29 06.014 N 090 05.446 W	78:02:45	1/12/2009 10:02
37, C1	28 58.516 N 090 21.753 W	79:39:25	1/12/2009 11:39
38, C2	28 38.594 N 090 21.866 W	82:38:56	1/12/2009 14:38
39, C3	28 18.057 N 090 21.641 W	85:42:10	1/12/2009 17:41
40, C4	27 55.651 N 090 21.641 W	88:56:38	1/12/2009 20:56
41, C5	27 32.161 N 090 21.641 W	93:17:34	1/13/2009 1:17
42, D1	27 32.362 N 091 01.802 W	98:51:17	1/13/2009 6:51
43, D2	27 56.453 N 091 01.802 W	103:15:50	1/13/2009 11:15

44, D3	28 16.659 N 091 01.802 W	107:17:05	1/13/2009 15:16
45, D4	28 35.656 N 091 01.175 W	110:11:09	1/13/2009 18:10
46, D5	28 47.197 N 091 00.730 W	112:20:27	1/13/2009 20:20
47,	28 56.780 N 091 24.534 W	115:38:05	1/13/2009 23:37
48,	29 01.789 N 091 39.989 W	118:04:37	1/14/2009 2:04
49, E1	29 10.156 N 091 33.820 W	120:04:19	1/14/2009 4:04
50, E2	29 02.037 N 091 40.384 W	122:03:57	1/14/2009 6:03
51, E3	28 47.095 N 091 41.382 W	123:33:46	1/14/2009 7:33
52, E3	28 28.095 N 091 41.123 W	126:27:46	1/14/2009 10:27
53, E4	28 01.060 N 091 40.609 W	130:10:01	1/14/2009 14:09
54, E5	27 33.367 N 091 40.384 W	134:56:09	1/14/2009 18:55
55, F1	28 00.753 N 092 21.331 W	141:28:37	1/15/2009 1:28
56, F2	28 30.387 N 092 21.071 W	146:26:27	1/15/2009 6:26
57, F3	28 54.405 N 092 20.812 W	149:50:34	1/15/2009 9:50
58, F4	29 12.538 N 092 25.396 W	152:41:59	1/15/2009 12:41
59, F5	29 25.318 N 092 26.073 W	154:58:44	1/15/2009 14:58
60, G1	29 26.478 N 092 59.917 W	158:55:44	1/15/2009 18:55
61, G2	29 08.088 N 093 00.241 W	161:46:04	1/15/2009 21:45
62, G3	28 48.924 N 093 00.500 W	164:41:05	1/16/2009 0:40
63, G4	28 31.762 N 093 00.760 W	167:24:03	1/16/2009 3:23
64, G5	28 13.635 N 093 00.760 W	170:12:50	1/16/2009 6:12
65, H1	28 13.175 N 093 39.670 W	174:38:34	1/16/2009 10:38
66, H2	28 35.427 N 093 39.929 W	177:52:04	1/16/2009 13:51
67, H3	28 56.185 N 093 40.078 W	180:56:38	1/16/2009 16:56
68, H4	29 18.820 N 093 39.965 W	184:12:28	1/16/2009 20:12
69,	29 28.552 N 093 39.908 W	186:10:51	1/16/2009 22:10
70, H5	29 36.838 N 093 48.764 W	188:18:43	1/17/2009 0:18
71,	29 34.718 N 092 57.999 W	192:43:51	1/17/2009 4:43
72,	29 16.298 N 092 45.364 W	194:52:37	1/17/2009 6:52
73,	28 43.369 N 090 56.951 W	204:54:54	1/17/2009 16:54
74,	28 42.872 N 089 59.981 W	209:54:43	1/17/2009 21:54
75,	28 45.679 N 089 22.606 W	213:12:03	1/18/2009 1:11
76,	29 06.367 N 088 54.211 W	219:40:08	1/18/2009 7:39
77,	29 51.035 N 088 45.909 W	224:11:38	1/18/2009 12:11
78,	30 06.621 N 088 47.575 W	225:45:32	1/18/2009 13:45
79,	30 06.558 N 088 55.337 W	226:25:51	1/18/2009 14:25
80,	30 11.261 N 088 59.394 W	227:01:04	1/18/2009 15:00
81,	30 15.528 N 089 00.271 W	227:27:03	1/18/2009 15:26
82,	30 21.159 N 089 05.195 W	228:09:25	1/18/2009 16:08