

**Ocean Carbon and Biogeochemistry Scoping Workshop on  
Terrestrial and Coastal Carbon Fluxes in the Gulf of Mexico  
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POSTER ABSTRACTS**

**Atilla, Nazan, and Nancy Rabalais**

Louisiana Universities Marine Consortium

**Phytoplankton Assemblages and Coastal Hypoxia in the Northern Gulf of Mexico**

Northern Gulf of Mexico experiences seasonal bottom water hypoxia due to high freshwater discharge and nutrient loads from the Mississippi and Atchafalaya Rivers. High nutrients stimulate the phytoplankton blooms where most of the carbon settles to the lower water column and the seabed. Due to decomposition and strong stratification oxygen is nearly depleted in the bottom waters every summer. We studied phytoplankton communities near the Mississippi and Atchafalaya Rivers by their signature pigments 2001 through 2004. Phytoplankton community composition was not different near Mississippi and Atchafalaya Rivers. Phytoplankton biomass was dominated by diatoms in spring and by cyanobacteria in summer. Dinoflagellate blooms were more common near the Mississippi River than the Atchafalaya River. Total biomass was higher in shallower coastal waters than off shore waters, with higher chlorophyll concentrations observed near the Mississippi River.

**Atilla<sup>1</sup>, Nazan, Galen McKinley<sup>1</sup>, Noel Urban<sup>2</sup>, Nobuaki Kimura<sup>1</sup>, Val Bennington<sup>1</sup>, Chin Wu<sup>3</sup>, and Ankur Desai<sup>1</sup>**

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**The Carbon Cycle of Lake Superior: First Results from the Cycles Project**

CO<sub>2</sub> emissions and seasonal cycling from the Great Lakes may be comparable to that of local terrestrial ecosystems. CO<sub>2</sub> fluxes from Lake Superior are of particular interest because they may greatly impact observations at nearby Ameriflux towers. Long residence time of water and limited watershed inputs suggest carbon cycling in Lake Superior is tightly coupled with physical processes. We developed a coupled ecosystem-carbon-hydrodynamic model of Lake Superior to estimate carbon fluxes and their spatio-temporal variations. The ecosystem, including two sizes of phytoplankton, macronutrients and a single grazer is implemented to estimate spatial and temporal patterns of carbon cycling in the lake. Carbon as DOC, DIC and POC, and O<sub>2</sub> (as an indicator of biological productivity) are included as state variables upon which ecosystem processes act. Model predicted chlorophyll concentrations are compared with results of synoptic surveys made in 2006. Spatial and temporal patterns of chlorophyll, pCO<sub>2</sub>, and CO<sub>2</sub> fluxes as predicted by the model is summarized. These patterns will be used to illustrate some of the factors controlling carbon cycling such as temperature and watershed inputs, and some potential consequences of climatic change. Discrepancies between model predictions and measurements will be used to highlight research needs.

**Bauer<sup>1</sup>, James E., David W. Perkey<sup>1</sup>, Thomas S. Bianchi<sup>2</sup> and Edward Keese<sup>1</sup>**

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**Variability of Major Carbon Pools in the Mississippi River: Importance of Tributary Inputs and Regional Land Use on Carbon and Organic Matter Biogeochemistry**

The Mississippi is North America's largest river and drains approximately 2/3 of the continental U.S., yet relatively few studies of carbon and organic matter (OM) biogeochemistry along its mainstem have been

undertaken. Because the spatial distribution of water sources and inputs throughout the Mississippi basin is heterogeneous, it is reasonable to assume that the sources and biogeochemical processes involving C and OM in the river are spatially and temporally variable. Major findings from the first large-scale survey of the distributions and isotopic compositions of dissolved inorganic, dissolved organic, and particulate organic carbon (DIC, DOC and POC, respectively) along the Mississippi mainstem by our group in 2004-2005 include: 1) aged,  $^{14}\text{C}$ -depleted DIC and POC and modern DOC throughout the system in general, and 2) higher concentrations of DIC and DOC, and  $^{13}\text{C}$ -enriched POC, in the Upper Mississippi compared to the Lower Mississippi. These findings further demonstrate how both internal processing, and the different land uses and underlying geologies of areas drained by the major tributaries (most notably the Ohio River), affect the amounts and isotopic character of the major carbon pools discharged by the Mississippi to the Gulf of Mexico ocean margin.

**Butler, Martha, Kenneth Davis, Timothy Hilton, Klaus Keller, Natasha Miles and Scott Richardson**  
The Pennsylvania State University  
**Scott Denning, Nicholas Parazoo, Andrew Schuh, Marek Uliasz and Dusanka Zupanski**  
Colorado State University  
**Daniel Ricciuto**  
Oak Ridge National Laboratory

#### **Data Fusion to Determine North American Sources and Sinks of Carbon Dioxide at High Spatial and Temporal Resolution from 2004 to 2008**

Networked measurements of ecosystem-atmosphere fluxes of carbon dioxide and atmospheric carbon dioxide mixing ratios are being synthesized using models of terrestrial carbon and energy fluxes and atmospheric dynamics to diagnose terrestrial ecosystem sources and sinks of  $\text{CO}_2$  across North America. Our objective is to diagnose fluxes of  $\text{CO}_2$  with higher spatial and temporal resolution, and greater precision and accuracy, than has been achieved to date. An improved network of  $\text{CO}_2$  mixing ratio measurements in the continental atmospheric boundary layer and the integration of  $\text{CO}_2$  flux measurements to create an improved prior estimate of terrestrial fluxes are added to the traditional marine flask  $\text{CO}_2$  mixing ratio measurement network to improve understanding of regional fluxes across North America. Observational density is highest in the mid-continent in support of the Midcontinental Intensive regional study (MCI) of the North American Carbon Program (NACP). Markov Chain Monte Carlo parameter estimation techniques are being used to derive probabilistic prior fluxes from the combination of tower flux measurements and a model describing ecosystem-atmosphere carbon fluxes. The atmospheric inversion scheme uses a coupled, high-resolution ecosystem-atmosphere model, a Lagrangian particle dispersion model, and a maximum likelihood ensemble Kalman filter technique. The observations will be synthesized into regional, monthly flux estimates. Results to date show encouraging space-time coherence of tower flux observations across the U.S. midcontinent and strong variability in atmospheric  $\text{CO}_2$  mixing ratios at small scales across the midcontinental region, indicative of large magnitude, spatially coherent regional variability in terrestrial  $\text{CO}_2$  fluxes. Pseudo-data tests of the atmospheric inversion framework show the ability to derive spatially coherent, climate-driven variability in terrestrial fluxes in the presence of large amplitude, small-scale variability in carbon fluxes. The results to date, while encouraging, do not yet provide definitive answers regarding the limits of our ability to derive monthly, regionally-resolved terrestrial  $\text{CO}_2$  fluxes across North America.

**Cai<sup>1</sup>, Wei-Jun, Xianghui Gao<sup>1</sup>, Feizhou Chen<sup>1</sup>, Wei-Jen Huang<sup>1</sup>, Yongchen Wang<sup>1</sup>, and Steven E. Lohrenz<sup>2</sup>**

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**The Dynamics of  $\text{CO}_2$  in the Mississippi River Plume and Northern Gulf of Mexico**

We report the distributions of  $p\text{CO}_2$  in the northern Gulf of Mexico (GOM) during several cruises.  $p\text{CO}_2$  at the river mouth was well above the atmosphere. Very low  $p\text{CO}_2$  was observed in the Mississippi River plume in all seasons except October 2005 when the system was disturbed by Katrina. The offshore  $p\text{CO}_2$  was relatively high and appeared to be controlled by temperature and the regeneration of organic carbon. In all seasons, surface  $p\text{CO}_2$  values correlated with salinity. Correlations were also found among  $p\text{CO}_2$ , fluorescence, and SST. Nearshore effects in areas away from the river plume were also significant.

Total Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TAlk) values were generally higher in the river end-member than that of the seawater. Strong biological uptake was clearly seen from the very low DIC to TAlk ratio and the high pH (8.2-8.6) in the mid salinity plume area. DIC and TAlk are used to estimate net biological production rates and to discuss possible controlling processes. The relationship between nutrient removal and DIC removal in the plume will be examined.

A background synthesis of carbon and nutrient flux from the Mississippi River to the GOM is also provided. It is concluded while the river plume area is net autotrophic, the role of terrestrial carbon on the metabolic state of the coastal water is equivocal, requiring further study to determine whether the system is autotrophic or heterotrophic and whether the system is a net source or sink of  $\text{CO}_2$  to the atmosphere.

**Chipman<sup>1</sup>, Lindsay, William T. Cooper<sup>2</sup>, Thorsten Dittmar<sup>1</sup>, Joel E. Kostka<sup>1</sup> and Markus Huettel<sup>1</sup>**

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#### **Degradation of Dissolved Organic Matter in Percolated Permeable Shelf Sands**

Bottom currents caused by wind, waves and tides pump coastal sea water loaded with dissolved organic matter (DOM) through the ripples and uppermost surface layer of highly permeable nearshore sand beds. We tested the hypothesis that this filtering over distances of a few centimeters through the sediment enhances the degradation of diatom-derived DOM that is flushed through the sand. Within the sediment, DOM is exposed to enzymes of the microbial community that colonizes the sand grains, and abundance and diversity of these bacteria is higher than in the overlying water column. Through a combination of in-situ measurements in the Gulf of Mexico and laboratory experiments we show that filtration through 5 cm permeable shelf sediments promotes the degradation of diatom-derived and riverine DOM. Analysis using FT-ICR MS showed distinct differences in the DOM after transition through the sand. Our results indicate that the nearshore filtering sands may have a significant influence on the decomposition of labile DOM in the coastal zone.

**Conmy, R.N., and P.G. Coble**

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#### **Temporal and Spatial Patterns in Optical Properties of CDOM on Florida's Gulf Coast: Shelf to Stream to Aquifer**

On river-dominated margins, such as the West Florida Shelf on Florida's Gulf Coast, CDOM distributions are, to the first-order, controlled by mixing of fresh and marine waters. In this region, the underwater light field is also affected by hurricanes and resuspension events, which is linked closely with a number of factors prior to a storm's passing such as the presence of persistent blooms, rainfall and discharge. Additionally, storm track and wind direction play a significant role in resultant CDOM signatures.

Gulf Coast riversheds (Mississippi River to Everglades System) that supply the shelf exhibit strong seasonality and affect CDOM signatures. A regional dependency also exists, where highest aromaticity and concentration of organic material is found for the southernmost watersheds. Basin characteristics, land use and climatic patterns are implicated in the cause for regional differences. In addition to surface flow, groundwater discharge can introduce organic material to surface waters. For the Tampa Bay region,

strong hydrologic links exist between shallow aquifers and the overlying surface waters, resulting in similar CDOM quantity and quality in both reservoirs. Deep aquifers, however are less concentrated and have CDOM signatures more similar to marine waters, suggesting like biogeochemical pathways of the material, including the influence of the aquatic microbial community.

Investigating CDOM distribution and signatures is vital to carbon budget and cycling questions. The amount and quality of organic material has significant implications for ecosystems, thereby affecting organisms that use CDOM as a food source, light availability for photosynthesis, UV shading provided to biota, satellite estimates of chlorophyll, metal binding, materials transport and overall water quality.

**Cooper<sup>1</sup>, Bill, Juliana D'Andrilli<sup>1</sup>, David Padgorski<sup>1</sup>, Thorsten Dittmar<sup>2</sup>, Markus Huettel<sup>2</sup>, and Joel Kostka<sup>2</sup>, Lindsay Chipman<sup>2</sup>**

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### **Ultrahigh Resolution Mass Spectrometry of Dissolved Organic Matter in Estuaries**

Electrospray ionization combined with high-field Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) can now identify individual compounds in complex dissolved organic matter (DOM) mixtures. This ultrahigh resolution (UHR) technique generates large databases of chemical formulae for individual samples which can be searched for specific compounds and compound classes or integrated across the entire dataset to summarize the molecular characteristics of DOM (e.g., aromaticity, elemental ratios, degree of unsaturation). In this presentation we will demonstrate how UHR MS data can define the molecular changes that accompany terrestrial DOM as it moves from its fresh water sources through estuaries and into the coastal zone. Specific examples to be discussed include microbial alteration of riverine DOM as it percolates through coastal sands, and photochemical processes that change fluorescence signatures. A combination of in-situ measurements in the Gulf of Mexico and laboratory experiments were carried out that showed that filtration through 5 cm permeable shelf sediments promotes the degradation of diatom-derived and riverine DOM. Photochemical effects were identified by irradiating riverine DOM in a solar simulator for 21 hours. Photodegradation induced by the irradiation was 4-fold higher for fluorescent compounds compared to only absorbing compounds. Results from UHR MS analyses indicated that the number of highly unsaturated molecular masses decreased and the number of saturated masses increased, as evidenced by an increase in the H/C ratios and decrease in the oxygen-subtracted double bond equivalent (DBE-O) values.

**Corbett<sup>1</sup>, D. Reide, J.P. Walsh<sup>1</sup>, and Miguel Goñi<sup>2</sup>**

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### **The Impact of Storms on Continental Margins: Sediment and Biogeochemical Dynamics**

The complex sediment processes that occur along continental margins (deposition, benthic diagenetic transformation, resuspension/redistribution and burial) play an important role in the overall function of the ecosystem. The deposition and decomposition of organic matter influences nutrient and oxygen concentrations in porewaters and the overlying water column. Physical processes, such as winds, tides, and groundwater infiltration, can play an important part in the overall disposition of these sediments and biogeochemical coupling with surface waters. Waves and strong currents, associated with storm events, can resuspend sediment previously deposited and redeposit farther seaward, affecting regions of the seabed that rarely experience such energetic conditions. As a result, large-magnitude storms can play a key role in the cross-shelf transport of sediment and advective transport of nutrient-rich porewaters. These disturbances will have a direct influence on the characteristics of the seabed, affecting the composition of benthic communities and the cycling of carbon, nutrients and oxygen. The biogeochemical ramifications

associated with the dynamic nature of the seabed have yet to be completely understood. Here, we present evidence for a massive sediment remobilization and deposition event on the Mississippi-Atchafalaya margin associated with the passage of Hurricanes Katrina and Rita. The erosion and subsequent deposition of vast amounts of sediments and associated organic matter had a major impact on the composition and characteristics of the seabed over a broad area of the northern Gulf of Mexico shelf and slope, affecting benthic communities throughout the region and delivering a significant load of nutrients into the overlying water column.

**DeGrandpre<sup>1</sup>, Mike, and Sarah Cullison<sup>1</sup>, and Jim Beck<sup>2</sup>**

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### **Quantification of Inorganic Carbon Using Autonomous Sensors**

We present the latest technologies developed in our lab for autonomous quantification of inorganic carbon parameters. The poster will describe an improved version of the Submersible Autonomous Moored Instrument for CO<sub>2</sub> (SAMI-CO<sub>2</sub>) that is in the advanced stages of development. A design of a new sensor, SAMI-pH, developed directly from the SAMI-CO<sub>2</sub> technology, is also described. Results from recent field studies using SAMI-pH are presented. The sensor has been deployed on Scripps pier, in Monterey Bay (MBARI M0 mooring), in the northeast Pacific, and on a coral reef in Puerto Rico. These studies are characterizing the natural range of pH variability over diurnal to seasonal time scales. Calculation of total dissolved inorganic carbon (DIC) from combined autonomous measurements of the partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>) and pH is examined. These preliminary results show that, as expected, the pH-*p*CO<sub>2</sub> combination is sensitive to errors; however, very good DIC prediction is obtained from both pH and *p*CO<sub>2</sub> when combined with salinity-derived alkalinity. Our future plans are to combine pH and *p*CO<sub>2</sub> sensors with an autonomous total alkalinity system currently under development. These combined measurements will make it possible to quantify DIC while simultaneously checking internal consistency of the inorganic carbon parameters.

**Del Castillo<sup>1</sup>, Carlos E., and Richard L. Miller<sup>2</sup>**

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<sup>2</sup>National Aeronautics and Space Administration, Stennis Space Center, Mississippi

### **On the Use of Ocean Color Remote Sensing to Measure the Transport of Dissolved Organic Carbon by the Mississippi River Plume**

We investigated the use of ocean color remote sensing to measure the transport of dissolved organic carbon (DOC) by the Mississippi River to the Gulf of Mexico. From 2000 to 2005 we recorded surface measurements of DOC, colored dissolved organic matter (CDOM), salinity, and water-leaving radiances during five cruises to the Mississippi River Plume. These measurements were used to develop empirical relationships to derive DOC, CDOM, and salinity from monthly composites of SeaWiFS imagery collected from 1998 through 2005. We compared our remote sensing estimates of river flow and DOC transport with data collected by the United States Geological Survey (USGS) from 1998 through 2005.

Our remote sensing estimates of river flow and DOC transport correlated well ( $r^2 \sim 0.70$ ) with the USGS data. Our remote sensing estimates and USGS field data showed low variability in DOC concentrations in the river end-member (7-11%), and high seasonal variability in river flow (~50%). Therefore, changes in river flow control the variability in DOC transport, indicating that the remote sensing estimate of river flow is the most critical element of our DOC transport measurement. We concluded that it is possible to use this method to estimate DOC transport by other large rivers if there are data on the relationship between CDOM, DOC, and salinity in the river plume.

**Dixon<sup>1,2</sup>, L.K., P.G. Coble<sup>2</sup>, and R.N. Conmy<sup>2</sup>**

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### **Development of a PARAFAC Model of Gulf of Mexico CDOM Fluorescence: A Tool for Quantitative Evaluation of Dissolved Organic Carbon Properties and Processes**

The eastern Gulf of Mexico represents a large region with numerous river inputs, ranging from the large temperate Mississippi River with low DOC and CDOM concentrations to smaller subtropical rivers with high dissolved carbon of terrestrial origin and relatively low sediment burdens (blackwater rivers). Mixing of freshwater from these various rivers along with autochthonous production by plankton and transformation and removal by photobleaching all affect the fluorescence signature (excitation-emission matrices or EEM spectra) of the CDOM in the Gulf. Seasonal and annual variability also plays a role in CDOM concentrations across the region. In order to quantitatively describe CDOM composition and identify processes controlling its distribution, a PARAFAC (Parallel Factor Analysis) model was developed using EEMs collected from the panhandle of Florida to the Florida Keys over multiple years. Model development was optimized to account for both very low and very high fluorescent samples. Unlike the development of PARAFAC models when known compounds with discrete fluorescent signatures are examined, successful models for widely varying ambient samples requires reliance on robust results (successful split-half analysis) rather conventional statistical measures of sufficiency. A total of seven factors can be identified with this model, including all components previously identified by spectral analysis from terrestrial and marine humic substances, proteins and amino acids, and photobleaching. Mapping of factors is presented for selected semi-synoptic sampling events and can now be used for quantitative descriptions of Gulf of Mexico carbon processes.

**D'Sa<sup>1</sup>, Eurico, Dong S. Ko<sup>2</sup>, and S. DiMarco<sup>3</sup>**

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### **Short-term Physical Influences on Chromophoric Dissolved Organic Matter (CDOM) in the Northern Gulf of Mexico**

Short-term temporal and spatial patterns of chromophoric dissolved organic matter (CDOM) absorption properties were studied in waters influenced by the Mississippi-Atchafalaya river system in the spring of 2005 during a frontal passage using field, model and satellite data. A well-correlated inverse relationship between CDOM absorption at 412 nm and salinity indicated conservative mixing throughout the water column between the riverine freshwater sources and the oceanic end member with mean CDOM absorption of lower salinity surface waters being higher than the higher salinity sub-surface waters. A high-(~ 1.9 km horizontal) resolution 3-dimensional Navy Coastal Ocean Model (NCOM) model being developed as part of a monitoring system for the coastal states of Mississippi, Louisiana and Texas (27 – 30.5 N; 88.2 – 95.5 W) suggested a strong response of the currents and sea level to wind forcing. CDOM estimates derived from SeaWiFS using an empirical two-band ratio algorithm indicated correlations to the modeled current field and a general change in the pattern of CDOM distribution associated with the physical forcing.

**Easley, Regina A.<sup>1</sup>, Lori R. Adornato<sup>2</sup>, Robert H. Byrne<sup>1</sup>, Eric A. Kaltenbacher<sup>2</sup>, and Danielle Greenhow<sup>1</sup>**

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### **The In-Situ Analysis of Nitrate, Phosphate, and Nitrite Using the Spectrophotometric Elemental Analysis System II (SEAS II): Observations of Diurnal and Seasonal Nutrient Variations in the Gulf of Mexico and Tampa Bay, Florida**

Quantification of carbon fluxes along coastal margins is necessary to improve constraints on global carbon budget estimates. Since approximately 15 to 30% of oceanic primary production occurs along ocean margins, understanding annual variations in productivity along the coasts is essential. The availability and distribution of nutrients play significant roles in regulating primary productivity by controlling phytoplankton community structure and net growth. The West Florida Shelf (WFS), an oligotrophic continental shelf, receives its primary nutrient inputs from riverine sources, the Gulf Stream's Loop Current, and atmospheric deposition. Low-frequency events such as red tides also play significant but poorly understood roles in recycling nutrients across the WFS. Knowledge of temporal and spatial nutrient distributions is therefore important in attempts to understand and predict the flow of carbon throughout the region. The in situ Spectrophotometric Elemental Analysis System (SEAS), an instrument with sub-nanomolar detection capabilities, provides the high-resolution nutrient measurements necessary for observations of fine-scale features in oligotrophic environments. With a 1 Hz sampling frequency, SEAS can provide vertical resolutions on the order of one meter. Data from the Gulf of Mexico and Tampa Bay provide unique observations of diurnal variations of phosphate and nitrate concentrations and in the primary nitrite maximum.

**Gundersen<sup>1</sup>, Kjell, Karen Orcutt<sup>1</sup> and Rodney Powell<sup>2</sup>**

<sup>1</sup>University of Southern Mississippi, Department of Marine Science and <sup>2</sup>Louisiana Universities Marine Consortium

### **A Carbon Based Assessment of New Production on the Louisiana Shelf and Its Impact on the Seasonal Hypoxia in the Region**

This project assesses the biogeochemical significance of diazotrophs and their impact on regional hypoxia in coastal waters influenced by the Mississippi River plume. Currently, the biological component to hypoxia on the Louisiana shelf is poorly constrained. In order to determine daily dissolved oxygen budgets for the water column and benthic sediment during hypoxia, we propose to measure daily rates of net primary productivity and respiration by including filamentous diazotrophic cyanobacteria (*Trichodesmium* sp.) in these estimates.

We propose that many large river systems such as the Mississippi River plume, characterized by high levels of trace metals, bioavailable Fe-ligands and excess phosphate, can provide ideal habitats for diazotrophic organisms. We will test this hypothesis by quantifying the *nifH* abundances of *Trichodesmium* and other diazotrophs. Physical (photosynthetic light, salinity and temperature) as well as chemical parameters (particulate and dissolved macro and trace nutrients) will identify the environmental constraints put on these diazotrophic organisms on the Louisiana shelf. Molecular detection of the diazotrophs will be combined with C-incorporation and N-fixation rates and the resulting C:N incorporation ratio ( $C:N_{RATE}$ ) will determine their significance to new production of the plankton communities in the mid and far-field regions of the Mississippi River plume. Our direct observations will provide a better understanding of the seasonal biogeochemical dynamics that may cause hypoxia in this unique estuarine environment.

**Hitchcock<sup>1</sup>, Gary, and Will Drennan<sup>2</sup>**

<sup>1</sup>Marine Biology and Fisheries, and <sup>2</sup>Applied Marine Physics, RSMAS, University of Miami

### **The Trophic Status of Gulf of Mexico Coastal Waters**

On a global scale the coastal ocean is net heterotrophic with community respiration ( $R$ ) exceeding community production ( $P$ ) such that the trophic status, or net ecosystem production ( $NEP = P - R$ ), is negative. While an isolated ecosystem cannot function indefinitely in this state, coastal ecosystems receive large inputs of allochthonous carbon from terrestrial sources that support high community respiration rates, effectively producing respiratory  $CO_2$  in excess of that fixed through  $P$  over diel cycles. Although there have been many productivity studies in coastal waters, few have simultaneously measured

respiration, a key component in assessing the *NEP* of coastal ecosystems. The trophic status of coastal waters varies markedly in space and time. A limited number of studies in Gulf of Mexico estuaries show strong heterotrophic signals over annual cycles with only a limited number of observations from coastal waters. We are developing an automated *in situ* system to quantify *P*, *R* and *NEP* in coastal communities with a production/respiration chamber and *in situ* O<sub>2</sub> sensors. A major goal is to correct *P*, *R*, and therefore *NEP* estimates, for the effect of air-sea exchange which varies as a function of wind speed. Many previous estimates of whole ecosystem *P* and *R* have oversimplified the effects of air-sea exchange. This correction, combined with diel *P/R* signals, should yield an improved assessment of the seasonal variability in the trophic status of coastal ecosystems and their potential contribution to coastal carbon dynamics.

**Holmes, Charles W.**, U.S. Geological Survey, Center for Coastal and Watershed Studies, 600 Fourth Street South St. Petersburg, FL 33701

### **The Carbon Flux as Recorded in Black Corals from the Atlantic and Gulf of Mexico**

Black corals (antipatharians) are found in all oceans, grow very slowly, subsist on plankton, and live in water depths from 100 to >1000 meters. Their skeletons are composed of chitinous concentric bands. Because these bands can be easily separated, sampling of individual bands provide highly temporally resolvable samples for analyses.

228 stable and radiometric carbon isotope measurements were made on three specimens; one from the Jacksonville lithoherm in the Western Atlantic and two from the northeastern Gulf of Mexico. In the Jacksonville specimen, the  $\delta^{13}\text{C}$  record is  $-16 \pm 0.2\text{‰}$  till about the middle of the nineteenth century when it begins to trend lighter, reaching  $-19 \pm 0.2\text{‰}$  in the outer layers. In the Gulf specimens, the  $\delta^{13}\text{C}$  is highly variable, averaging  $-16\text{‰}$  with a range of  $2.0\text{‰}$ . They do not exhibit the progressive twentieth century lightening.

The differences between these two sites suggest different sources of carbon. The decreasing  $\delta^{13}\text{C}$  in the Atlantic coral indicates an atmospheric anthropogenic source; whereas in the Gulf of Mexico coral, the  $\delta^{13}\text{C}$  atmospheric lightening is counter balanced by a flux of heavy carbon. Recently published carbon data on the composition of Mississippi River water demonstrated that the water has become increasingly alkaline over the last half century. As the isotopic composition of alkaline carbon is usually heavy ( $\delta^{13}\text{C} \approx 0\text{‰}$ ), such an increase in heavy alkaline carbon could be a counter balance, resulting in the constant carbon isotopic record.

**John<sup>1</sup>, David E., Zhaohui A. Wang<sup>1</sup>, Xuewu Liu<sup>1</sup>, Robert H. Byrne<sup>1</sup>, Jorge E. Corredor<sup>2</sup>, Deborah A. Bronk<sup>3</sup>, and John H. Paul<sup>1</sup>**

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### **Phytoplankton Carbon Fixation Gene (RuBisCO) Transcripts and Air-Sea CO<sub>2</sub> Flux in the Mississippi River Plume**

River plumes deliver large quantities of nutrients to oligotrophic oceans, often resulting in significant CO<sub>2</sub> drawdown. To determine the relationship between expression of the major gene in carbon fixation (large subunit of ribulose-1,5-bisphosphate carboxylase/oxygenase) and CO<sub>2</sub> dynamics, we evaluated *rbcL* mRNA abundance using novel quantitative PCR assays, phytoplankton cell analyses, photophysiological parameters, and *pCO*<sub>2</sub> in and around the Mississippi River plume (MRP) in the Gulf of Mexico. Lower salinity (30-32) stations were dominated by *rbcL* mRNA from heterokonts, such as diatoms and pelagophytes, at least an order of magnitude greater than haptophytes, *α-Synechococcus* or high-light *Prochlorococcus*. However, *rbcL* transcript abundances were similar among these groups at oligotrophic

stations (salinity 34 – 36). Diatom cells and heterokont *rbcL* RNA showed a strong negative correlation to seawater  $p\text{CO}_2$ . While *Prochlorococcus* cells did not exhibit a large difference between low and high  $p\text{CO}_2$  water, *Prochlorococcus rbcL* RNA concentrations had a strong positive correlation to  $p\text{CO}_2$ , suggesting a very low level of RuBisCO RNA transcription among *Prochlorococcus* in the plume waters. These results provide molecular evidence that diatom/pelagophyte productivity is largely responsible for the large  $\text{CO}_2$  drawdown occurring in the MRP. This may partly be due to efficient carbon concentrating mechanisms that enable heterokont eukaryotes such as diatoms to continue fixing  $\text{CO}_2$  in the face of strong  $\text{CO}_2$  drawdown. Our work represents the first attempt to relate in-situ microbial gene expression to contemporaneous  $\text{CO}_2$  flux measurements in the ocean.

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### **Sources of Sedimentary Organic Matter in the Mississippi River and Adjacent Gulf of Mexico as Revealed by Lipid Biomarker and $\delta^{13}\text{C}_{\text{TOC}}$ Analyses**

Changes in the organic matter (OM) composition (C/N,  $\delta^{13}\text{C}_{\text{TOC}}$ , and lipid biomarker compounds) of surface sediments (0–1 cm) were examined along the dispersal pathway from Mississippi River and marsh/estuarine end-members to the adjacent shelf and canyon regions of the Gulf of Mexico. Biomarkers representing allochthonous (higher plant) and autochthonous (algal/plankton/bacteria) sources demonstrated regional differences in the sources of sediment organic matter (SOM). A two end-member mixing model using  $\delta^{13}\text{C}_{\text{TOC}}$  indicated that C3 vascular plant sources comprised 80% and 50% of the TOC at the river and marsh sites, respectively. However, contributions from soil organic matter/terrestrial plant sources dominated in the river ( $\delta^{13}\text{C}_{\text{TOC}} = 25\text{‰}$ ) while marsh plants likely contributed to the enriched signatures found in the marsh sediments ( $\delta^{13}\text{C}_{\text{TOC}} = 18\text{‰}$ ). Allochthonous OM contributions calculated from fatty acid and sterol biomarkers in the river and marsh regions (39–48% and 50–72%, respectively) differed from those determined using  $\delta^{13}\text{C}_{\text{TOC}}$ . This was likely due to overlapping  $\delta^{13}\text{C}_{\text{TOC}}$  values for vascular plants and freshwater microalgae and the higher lipid content of the autochthonous sources. Although biomarkers representing terrigenous sources decreased with distance offshore, they comprised approximately 17–34% of the fatty acid and sterols at even the most distal slope and canyon sites, suggesting that these deeper regions could be an important sink for terrigenous carbon. In contrast, the shelf sites were enriched in algal material (60–78% autochthonous OC), with biomarkers for diatoms dominating, suggesting that terrigenous carbon is either diluted in, or bypasses, this region.

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### **Impacts of Climate and Land-Use Changes on Water Yield in Southeastern United States during the 20<sup>th</sup> Century**

Climate and land use have been suggested as two major factors that control water yield dynamics in the southeastern United States. Landscapes in the southeast have been intensively disturbed or managed by human activities and are now involved in rapid economic development and urbanization. A number of previous studies through long-term hydrological observations have investigated the effects of land-use change, forestry management, and natural disturbances on the dynamics of water yield, sediment load, peak stream flow, water table, and nutrients cycling on watershed levels. However, few integrated regional studies had been put forward to estimate how climate variations, land-use change and management have affected regional hydrological cycles and water budget. In this study, we have used the Dynamic Land Ecosystem Model (DLEM), which coupled vegetation dynamics, biogeochemical and hydrological cycles, to examine how climate variability/change and land-use change had influenced the dynamics of water yield in the 20<sup>th</sup> Century. The gridded time-series data sets of land-use change from

1865 to 2000 have been developed by using multiple sources of data including Landsat TM/ETM and census records. Our preliminary results indicate that water yield shows substantial interannual and decade variations, and largely varied from location to location. The simulated water yield has been evaluated against USGS long-term discharge data. Finally, we discuss how to tie water fluxes with carbon and nitrogen fluxes from terrestrial ecosystem to Gulf of Mexico by soil erosion, nutrient leaching, and transportation through river systems.

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#### **MICA – A Multiparameter Inorganic Carbon Analyzer**

An autonomous multi-parameter flow-through CO<sub>2</sub> system – MICA has been developed for simultaneous measurements of surface seawater pH, carbon dioxide partial pressure ( $f\text{CO}_2$ ), total dissolved inorganic carbon (DIC) and total alkalinity (TA). All of the measurements are based on spectrophotometric determinations of solution pH at multiple wavelengths using sulfonephthalein indicators. The pH and TA optical cells are machined from a PEEK polymer rod, and have a 15 cm optical pathlength. The  $f\text{CO}_2$  and DIC optical cells consist of Teflon AF 2400 (DuPont) capillary tubing sealed within a bore hole also machined from PEEK. The Teflon AF tubing, filled with a standard indicator solution that has a fixed total alkalinity, forms a liquid core waveguide (LCW). The LCW functions as both a long pathlength (15 cm) optical cell and a membrane that equilibrates the internal standard solution with either external air (providing air  $p\text{CO}_2$ ), seawater (providing seawater  $f\text{CO}_2$ ) or acidified seawater (providing DIC measurements). Both  $p\text{CO}_2$  and DIC are then determined by measuring the pH of the internal solution. TA is measured by mixing seawater samples with an indicator/acid mixture. The system runs repetitive cycles with a measurement frequency of approximately seven samples per hour. Field precisions were evaluated as 0.0008 units for pH, 0.9  $\mu\text{atm}$  for  $p\text{CO}_2$ , and 2.4  $\mu\text{mol kg}^{-1}$  for DIC. These precisions are close to those obtained with conventional methods in the laboratory. This system integrates spectrophotometric measurements of multiple CO<sub>2</sub> parameters into a single package suitable for observations of both seawater and freshwater.

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#### **In-Situ Spectrophotometric pH Measurements in Riverwater and Seawater**

Automated in-situ instrumentation has been developed for precise and accurate measurements of a variety of analytes in natural waters. In this work we describe the use of SEAS (spectrophotometric elemental analysis system) instrumentation for measurements of solution pH. SEAS - pH incorporates a CCD-based spectrophotometer, an incandescent light source, and dual pumps for mixing natural water samples with a sulfonephthalein indicator. The SEAS - pH optical cell consists of a custom-made PEEK cell. Deployments in the Equatorial Pacific and the Gulf of Mexico demonstrate that SEAS - pH instruments are capable of obtaining vertical pH profiles with high spatial resolution. SEAS-pH deployments at a fixed river-site (Hillsborough River, FL) demonstrate the capability of SEAS for observations of diel pH cycles with high temporal resolution. The in-situ precision of SEAS - pH is assessed as 0.0014 pH units, and the system's measurement frequency is approximately 0.5 Hz. This work indicates that in-situ instrumentation can be used to provide accurate, precise, and highly resolved observations of carbon-system transformations in the natural environment.

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## Variability in Satellite Algorithms for Regional Assessments of pCO<sub>2</sub>

Recent studies in the northern Gulf of Mexico and elsewhere demonstrate that enhanced biological production in large river plumes may influence surface pCO<sub>2</sub> levels resulting in a net surface influx of atmospheric CO<sub>2</sub>. However, such systems deliver large amounts of terrestrial carbon into continental margin waters, and hence, the potential for large and variable signals in carbon flux exist in these regions. Our findings suggest the late spring and early summer is a period of lower surface pCO<sub>2</sub> corresponding to a strong biological pump and autotrophic fixation of inorganic carbon. Other key environmental drivers appear to be seasonal variations in temperature and freshwater discharge. Algorithms relating surface pCO<sub>2</sub> to environmental variables, for example, as can be retrieved from satellite imagery, will necessarily have to account for such changes in system properties. Here, we use a combination of satellite and ship-based observations to examine variability in surface pCO<sub>2</sub> and air-sea flux of carbon dioxide in relation to variations in river discharge and seasonal conditions. A key question will be the degree to which satellite imagery can be used to provide regional assessments of carbon system properties over seasonal time scales. This will depend on the extent to which algorithms can be generalized beyond a single set of in situ observations. We examined this question by comparing principal component loadings and regression coefficients for four different periods. Results of the multiple regression analysis of component variables versus pCO<sub>2</sub> revealed both similarities and differences among the different cruise periods. In all cases for the low salinity data sets, negative relationships to salinity were consistent with the observed decrease in surface pCO<sub>2</sub> in relationship to increasing salinity as seen in the underway survey data. Negative coefficients related to chlorophyll could be explained by decreasing pCO<sub>2</sub> in relationship to increasing chlorophyll as light availability increased along the river-ocean mixing gradient. Efforts to improve performance of algorithms and extend their applicability will require a better understanding of underlying processes driving variations in carbon system properties coupled with more sustained and extensive in situ data. This is particularly critical for highly dynamic near shore environments.

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## Matrix Protected Organic Matter in a River Dominated Margin: A Possible Mechanism to Sequester Terrestrial Organic Matter?

The provenance of organic matter in surface sediments from the northern Gulf of Mexico was investigated by analyzing the compositions of lipid biomarkers (*n*-alkanes, fatty acids, sterols) liberated after a series of chemical treatments designed to remove different organo-mineral matrix associations (i.e., freely-extractable, base-hydrolyzable, unhydrolyzable). Bulk analyses of the organic matter (carbon content, carbon:nitrogen ratios, stable and radiocarbon isotopic analyses) were also performed on the intact sediments and their non-hydrolyzable, demineralized residue. We found recognizable lipids from distinct sources, including terrestrial vascular plants, bacteria and marine algae and zooplankton, within each of the isolated fractions. Based on the lipid signatures and bulk compositions, the organic matter within the unhydrolyzable fractions appeared to be the most diagenetically altered, was the oldest in age, and had the highest abundance of terrigenous lipids. In contrast, the base-hydrolyzable fraction was the most diagenetically unaltered, had the youngest ages and was most enriched in N and marine lipids. Our results indicate that fresh, autochthonous organic matter is the most important contributor to base-hydrolyzable lipids, whereas highly altered allochthonous sources appear to be predominant source of unhydrolyzable lipids in the surface sediments from the Atchafalaya River shelf. Overall, the lipid biomarker signatures of intact sediments were biased towards the autochthonous source because many of the organic compounds indicative of degraded, terrigenous sources were protected from extraction and saponification by organo-mineral matrices. It is only after these protective matrices were removed by treatment with HCl and HF that these compounds became evident.

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### **The Importance of Refractory Black Carbon in Coastal Systems**

Continental margin sediments are responsible for about 90% of the ocean's 'sequestered' organic matter (OM), yet most of this carbon is difficult to characterize due to its chemical complexity. A large portion of this OM may be refractory and is likely to be preserved in the coastal zone. But, we have a poor understanding of its source and temporal and spatial variability. Understanding the composition of refractory carbon in coastal systems is important as some of it may represent recent transfers of carbon from the atmosphere to the geosphere (i.e., atmospheric CO<sub>2</sub> drawdown) or some may stem from C fixed from land to the ocean much earlier.

Much refractory carbon in coastal systems may actually be comprised of black carbon (BC). For this reason, any examination of the production, dispersion or storage of OM in a coastal system should consider the influence of BC. We analyzed OM composition in three archetypical coastal systems and found that a substantial portion of the total organic carbon (TOC) in sediments from these systems was comprised of dichromate-oxidized BC. The Eel River, a small mountainous river, the Chesapeake Bay estuary, and the Mississippi/Atchafalaya River deltaic system, contained BC/TOC of 2-30%, 0.5-12% and, 2-16%, respectively. Stable and radio-isotopic carbon signatures indicate that generally, BC was significantly older and more terrestrial plant-derived than TOC in sediments from these systems. These trends suggest that there is a need to examine in greater detail the abundance and composition of BC in North American coastal systems.

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### **The Balance of <sup>228</sup>Ra in the Upper Atlantic Ocean: Implications for Continental Input of DIC and DOC**

I have used data from the Transient Tracers in the Ocean project (TTO) to establish the inventory of <sup>228</sup>Ra (half life = 5.7 years) in the upper Atlantic Ocean. There are approximately 4.8 moles of <sup>228</sup>Ra in the upper (0-1000m) Atlantic. Each year 12% of this inventory decays. If <sup>228</sup>Ra is in steady state, the loss must be balanced by a <sup>228</sup>Ra flux from the continental margins. No other isotope, element, or compound shares these attributes of widespread distribution through the upper ocean, removal that is highly constrained by radioactive decay, and a source due almost entirely to input from continental margins. Thus, the <sup>228</sup>Ra inventory is a proxy for interactions between the upper ocean and the continental margins.

Fluxes of <sup>228</sup>Ra from rivers, the atmosphere, and near-surface sediments support less than half the <sup>228</sup>Ra loss. The remainder must derive from submarine groundwater discharge (SGD). By evaluating <sup>228</sup>Ra concentrations in samples of coastal groundwater collected throughout the Atlantic margin, a total SGD flux of (2 to 4) x 10<sup>16</sup> L/yr was obtained. This is equivalent to 80 to 160 % of the river water flux to the Atlantic.

Other studies have demonstrated a correlation of DIC and DOC with radium in coastal groundwaters. Thus, fluxes of SGD are expected to contribute significant DIC and DOC to estuarine and coastal waters. Because SGD often contains higher concentration of carbon compared to rivers, the SGD fluxes of DIC and DOC almost certainly exceed their riverine fluxes to the Atlantic.

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### **Linkage between Production and Respiration on the Louisiana Continental Shelf**

We examined water column metabolic characteristics in the northern Gulf of Mexico offshore of Louisiana, a region characterized by widespread hypoxia during summers. The prevailing paradigm is that historical increases in anthropogenic nutrient pollution have shifted metabolism on the shelf towards heterotrophy, thereby increasing the incidence of hypoxia. However, few studies have examined metabolism outside of the immediate plume region. We conducted five cruises from April 2006 to August 2007. On each cruise, we occupied 3 sites and conducted intensive (3-6 hour interval) sampling over a 30-36 hour period. The sites were widely distributed along the Louisiana coastline, but all were within the region that frequently experiences hypoxia during summer (depth range ~7-20 m). In addition to CTD casts, discrete water samples were analyzed for chlorophyll-a, bacterioplankton abundance, bacterioplankton production, and community respiration. The sites varied markedly, but coherently, in freshwater content, phytoplankton biomass, bacterioplankton biomass, bacterioplankton production and community respiration. As expected, the site nearest the Mississippi River tended to have the highest autotrophic (chlorophyll) and heterotrophic (bacterioplankton) biomass and metabolic activity. A surprising result was that bottom waters underneath highly productive surface waters exhibited no evidence of enhanced metabolic activity. This finding is in contrast with the classic paradigm that hypoxia is caused by increased metabolism underlying regions of intense surface layer production. Furthermore, this apparent decoupling in organic matter supply between surface and bottom waters indicates that physical processes are relatively more important than metabolic processes in predicting the location and extent of hypoxia.

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#### **Autonomous Cross-Shelf Transects of Air-Sea CO<sub>2</sub> Flux with OASIS ASVs**

It would take at least 1000 days of ship time for one year of observations to quantify the carbon budget of the U.S. continental shelf, conservatively assuming a 5 knot mean vehicle speed and scales of variability of 50 km and 1 month. Regardless of the likelihood of obtaining this level of support (or even extending it to include tropical regions), it is clear that autonomous vehicles capable of observing the ocean, atmosphere and their interaction could be useful. An Autonomous Surface Vehicle (ASV) called OASIS (Ocean-Atmosphere Sensor Integration System) has been developed at the NASA Wallops Flight Facility. This spring, one of three presently fabricated OASIS vehicles is performing autonomous cross-shelf transects within the Mid-Atlantic Bight. Additional field tests are being conducted to develop techniques to map harmful algal blooms. The OASIS platform measurement suite currently includes: subsurface pCO<sub>2</sub>, atmospheric CO<sub>2</sub> concentration at two heights in the lower atmosphere, turbulent vertical transport of CO<sub>2</sub> in the lower atmosphere, wind velocity, relative humidity, atmospheric pressure, upper ocean velocity profiles, surface ocean salinity, temperature, CDOM, phycoerythrin and chlorophyll. Air-sea flux of CO<sub>2</sub> is computed using both the direct eddy covariance and gradient flux methods. Future capabilities will include a vertical profiling system for the upper 200 m of the ocean. Preliminary results from a recent transect will be presented. A fleet of remote-controlled OASIS vehicles can sample large coastal regions at relatively low expense, helping provide the observations needed to quantify the role of continental shelves in the global carbon cycle.

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#### **Optical and Geochemical Tracers of Terrestrial DOM in the Coastal Ocean**

Terrestrial inputs of DOM to the coastal ocean are important features of the marine carbon cycle. The optical and chemical properties of terrestrial DOM are related, but bulk properties are difficult to resolve. However, molecular chemical information, such as the stable isotope values of DOM and the quantity of

biomarkers such as dissolved lignin, are more specific to DOM sources and that information might better correspond to optical measurements such as ultraviolet-visible absorption and fluorescence. Recent advances in stable isotope analyses and statistical data processing offer the possibility for high-resolution studies that might better resolve these measurements. Here, results from the Gulf of Mexico and from the Baltic Sea show the relationships between DOM stable isotope values, dissolved lignin, and absorption and fluorescence. The goal is to develop models based on high resolution empirical observations to fine-tune optical measurements of terrestrial DOM in coastal waters.

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### **Results of GOMECC Cruise in July 2007**

The first GOMECC Cruise on board the R/V *Ronald H. Brown* from Galveston in the northern Gulf of Mexico (GOM) to Boston on the East coast was designed to obtain a snapshot of concentrations and fluxes of key carbon, physical, and biogeochemical parameters in the coastal realm. The cruise included a series of three transects approximately orthogonal to the coastline in the GOM and a comprehensive set of underway measurements along the entire transect. Full water column CTD/rosette stations were occupied at 28 specified locations in the GOM. A total of 29 scientists from AOML and other government agencies and universities participated on the 26-day cruise. Water samples were collected from the 24-bottle rosette at each station and analyzed for salinity, oxygen, nutrients, dissolved inorganic carbon, total alkalinity, pCO<sub>2</sub>, dissolved organic matter, colored dissolved organic matter, particulate organic carbon, halocarbons, alkyl nitrates, CO and phytoplankton pigments. Underway systems were in operation for measuring atmospheric CO<sub>2</sub> and near-surface water pCO<sub>2</sub>, DIC, halocarbons, pH, NH<sub>3</sub>, CO and bio-optical properties. An *in situ* spectrophotometric pH profiler was used with the CTD to measure pH profiles to a depth of 1000m. Air-sea fluxes of CO<sub>2</sub> and ozone were also measured using eddy correlation methods. A web site is set up to make these data available to the coastal science community.

The pCO<sub>2</sub> underway systems made the atmospheric and near surface water pCO<sub>2</sub> measurements. The distribution of surface water pCO<sub>2</sub> shows that surface water pCO<sub>2</sub> values are elevated almost everywhere along the cruise tract, except some local areas near the coast. With atmospheric CO<sub>2</sub> measurements made at the same time, the distribution of delta pCO<sub>2</sub> can be evaluated for determining the air-sea CO<sub>2</sub> fluxes. In the coastal regions, delta pCO<sub>2</sub> value is affected not only by the surface water pCO<sub>2</sub> but also by highly variable atmospheric pCO<sub>2</sub>. We see low surface pCO<sub>2</sub> in the northern Gulf of Mexico near the river delta regions. The results of oxygen measurement show that oxygen was supersaturated at the stations located closest to the coast due to high rates of primary production as indicated by elevated chlorophyll levels fueled by river borne nutrients. The surface water pCO<sub>2</sub> values show inverse correlation with oxygen saturation and chlorophyll values, suggesting that the drawdown of CO<sub>2</sub> is caused by biological processes.

Air-sea CO<sub>2</sub> fluxes were estimated from the bulk method utilizing the underway pCO<sub>2</sub> data. On the whole, the coastal region is a strong source of CO<sub>2</sub> during the GOMECC cruise punctuated by sink regions directly associated with continental run-off. The observations show a strong positive correlation between ΔpCO<sub>2</sub> and salinity in the Gulf of Mexico with the low salinity waters of the riverine outflows being a strong CO<sub>2</sub> sink. This contrasts with the Southeast region where there is a negative correlation between ΔpCO<sub>2</sub> and salinity. This is likely due to different TA and DIC end members for the continental run-off in these regions. Initial air-sea CO<sub>2</sub> flux within the coastal region estimates for 10-days spanning the cruises are:

Northern Gulf of Mexico:	$0.74 \pm 0.74 \text{ mol/m}^2/\text{yr}$
East Atlantic Coast:	$1.19 \pm 0.81 \text{ mol/m}^2/\text{yr}$
North East Coast:	$1.19 \pm 0.81 \text{ mol/m}^2/\text{yr}$

**Robbins<sup>1</sup>, L.L., I.B. Kuffner<sup>1</sup>, E. Raabe<sup>1</sup>, P. Knorr<sup>1,2</sup>, D. Gledhill<sup>3</sup>, M. Eakin<sup>3</sup>, and R. Byrne<sup>4</sup>**  
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### **Monitoring and Modeling of Florida Shelf Carbonate Saturation State**

A new USGS project will provide key baseline data on carbonate saturation state and the fundamental process of marine biogenic calcification in nearshore waters of the west Florida Shelf and Keys. The rate of change in seawater chemistry resulting from the absorption of anthropogenic carbon dioxide by the oceans is accelerating. The measured change in acidity of -0.03 pH units (“ocean acidification”) over the past two decades in Bermuda is approximately one third of the change since the beginning of the industrial revolution. A change concomitant to decreases in surface ocean pH levels is the decrease in bicarbonate ions available for biogenic calcification, resulting in a decrease in saturation state with respect to carbonate minerals such as aragonite. Fieldwork aimed at measuring and modeling the changes in seawater chemistry in Florida nearshore waters, particularly in the Gulf of Mexico, is lacking. Work investigating the impacts of changing seawater chemistry on regional habitats in Florida waters has not been conducted to date. To address these critical information gaps, USGS is working with USF and NOAA to acquire baseline pCO<sub>2</sub>, pH, and alkalinity data to create an offshore regional carbonate saturation state model for the west Florida shelf. These data will be used in conjunction with habitat data to monitor habitat change over time.

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### **Multispectral Remote Sensing Algorithms for Particulate Organic Carbon (POC): The Gulf of Mexico**

POC plays a key role in the transport of carbon in the ocean through the biological pump. While CO<sub>2</sub> and DOC move with the water, POC can settle through the water column, across isopycnals, scavenging or aggregating other particles and transporting carbon and associated elements to deeper waters. Thus, POC is a key component in the ocean’s role in sequestering and isolating carbon from the atmosphere. Because POC is produced/cycled on day-to-weeks time scales, a synoptic picture can only be obtained employing remote sensing techniques. We have developed remote sensing algorithms for particulate organic carbon (POC) by matching in-situ POC measurements in the Gulf of Mexico with matching SeaWiFS remote sensing reflectance. Data on total particulate matter (PM) as well as POC collected during nine cruises in spring, summer and early winter from 1997-2000 as part of the Northeastern Gulf of Mexico (NEGOM) study were used to test algorithms across a range of environments that may be related to Case I versus Case II waters. Finding that the remote-sensing reflectance clearly exhibited a peak shift from blue to green wavelengths with increasing POC concentration, we developed a maximum normalized difference carbon index (MNDCI) algorithm which uses the maximum band ratio of all available blue-to-green wavelengths, and provides a very robust estimate over a wide range of POC and PM concentrations ( $R^2=0.99$ ,  $N=58$ ). The algorithm can be extended to areas within the vicinity of shipboard sampling for more detailed spatial and temporal studies.

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### **Changes in Terrestrial Carbon Storage in Southeastern US Induced by Multiple Environmental Stresses: Implications to Coastal Carbon Fluxes in the Gulf of Mexico**

Terrestrial ecosystems in the southeastern United States have experienced a complex set of multiple changes in climate, atmospheric composition, land use and natural disturbances. In this study, we have examined how terrestrial carbon fluxes and storage in southeastern United States (13 states in the gulf of Mexico) on inter-annual to century time scales have changed as a result of multiple stresses/changes and interactions among those stresses including land-cover/land use change, climate variability, atmospheric composition (carbon dioxide and tropospheric ozone), precipitation chemistry (nitrogen composition), and natural disturbances using estimates of carbon fluxes and storage from factorial simulation experiments with the Dynamic Land Ecosystem Model (DLEM) in conjunction with remotely sensed and field data. Our analysis suggests that the net carbon exchange of terrestrial ecosystems with the atmosphere in this region show substantially interannual, decadal and spatial variations. Forest recovery after cropland abandonment and natural disturbances have resulted in a carbon uptake, but rapid urbanization and rising tropospheric ozone pollution have led to a significant reduction in carbon storage in the region. Land-use/land cover change appears to be an important control over regional carbon dynamics in this area. Finally, we discuss how to tie the land carbon cycle to the coastal/ocean carbon cycle in the Gulf of Mexico.

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### **Summer-Time CO<sub>2</sub> Fluxes and Carbon System Behavior in the Mississippi River and Orinoco River Plumes**

High-resolution simultaneous spectrophotometric underway measurements of  $p\text{CO}_2$ , DIC, and pH 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<sub>2</sub> fluxes and carbon system behavior of the two river plumes under summer conditions. The surface water within the MRP shows a strong atmospheric CO<sub>2</sub> sink ( $-4.9 \sim -7.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ), while oligotrophic waters of the Gulf of Mexico were a CO<sub>2</sub> source ( $1.3 \sim 2.9 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ). The CO<sub>2</sub> sink of the ORP is much less significant ( $-0.7 \sim -1.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ), and the adjacent surface water of the Caribbean Sea was approximately in equilibrium with the atmosphere. The carbon system inside the MRP exhibits patchiness (strong temporal and spatial variation). Such behavior is much less significant for the ORP, where both DIC and TALK show strong conservative mixing. This study confirms that the two large river plumes constitute carbon sinks under summer conditions. However, the strength of the sinks in these two coastal systems differs significantly due to both natural and anthropogenic influences.

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### **Seasonal Variability of Biogeochemical Processes within a Coupled Model of Chesapeake Bay**

Seasonal variability of biological and chemical properties of Chesapeake Bay is studied through application of a numerical ocean general circulation model with a fully coupled ecosystem. The physical model applied here is the Regional Ocean Modeling System (ROMS). The ecosystem model has been modified from the standard Fasham-type formulation packaged as part of the ROMS distribution to include components that explicitly simulate the impact of river borne sediments, inorganic nutrients and dissolved organic matter. Wet and dry deposition of atmospheric nitrogen, spatio-temporal variation in phosphorus limitation and sediment resuspension have also been incorporated. Finally, dissolved oxygen is explicitly tracked, which allows for resolving the seasonal transition to denitrification within the water

column and underlying benthos. In this initial application of the biogeochemical version of Chesapeake Bay ROMS (ChesROMS), results for 1999 are presented and characterized with respect to available in situ observations obtained by the Chesapeake Bay Program.

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### **Aircraft Assessment of Spatial Variations in Surface Exchange**

While point measurements of surface fluxes have improved and become very common over the past thirty years, many questions remain about spatial variation in surface fluxes. Variability in flux becomes important when assessing the impact of climate change on surface exchange and ecosystem functioning and when scaling and modeling surface exchange processes. The impact of variability on surface exchange will only become more pronounced as landscapes become increasingly fractionated and heterogeneous. Spatial trends in fluxes are not well understood in coastal and near coastal environments. Aircraft have been used for decades in terrestrial environmental to study fluxes, boundary layer dynamics, and CO<sub>2</sub> patterns. However, comparatively little work has been performed in coastal areas and transitioning to open oceans. A new technique in aircraft flux analysis is presented that may help understand spatial behavior of fluxes in coastal environments and in connected watersheds and how such ecosystems respond to impacts such as: major weather storms, droughts, and land and water management practices. This technique was recently developed using the University of Alabama's flux aircraft.