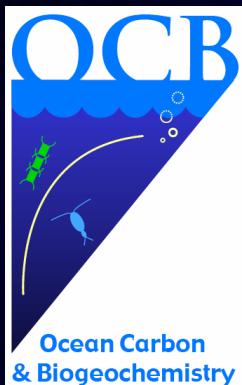


Gulf of Mexico Carbon Cycling

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Introduction

- **Significance of Coastal Ecosystems to Global C Cycling**
 - *As much as 15-30% of ocean primary production occurs in the coastal margin*
 - *80-85% of the organic matter burial, primarily near large river deltas*
 - *90% of the sedimentary mineralization*
 - *50% of the deposition of calcium carbonate*

Introduction

Table 2.1 Carbon Fluxes and Reservoirs Relevant to RiOMar Systems

	C flux (Tg/yr)	Range (Tg C yr ⁻¹)	Reference
<i>Total Riverine Carbon Input to the Ocean</i>		700-1000	
Dissolved Inorganic Carbon (DIC)	450	381-410	1,2,3
Total Organic Carbon (TOC)	450	200-530	2,3,4,5
Particulate Organic Carbon (POC)	200	138-288	4,6,7
Dissolved Organic Carbon (DOC)	250	214-360	2,4,8,9,10
<i>Terrestrial Storage</i>		600-1500	11
<i>Burial in Marine Sediments</i>	130	98-138	5,12,13
Terrestrial		43-104	5,12
Marine		55	5,14

¹Meybeck, 1993

²Meybeck and Vörösmarty, 1999

³Degens et al., 1991

⁴Spitzzy and Ittekkot, 1991

⁵Schlunz and Schneider, 2000

⁶Lyons et al., 2002 (and references within)

⁷Ittekkot and Laane, 1991

⁸Spitzzy and Leenheer, 1991

⁹Aitkenhead and McDowell, 2000

¹⁰Hedges et al, 1997

¹¹Stallard, 1998

¹²Berner, 1982

¹³Hedges and Keil, 1995

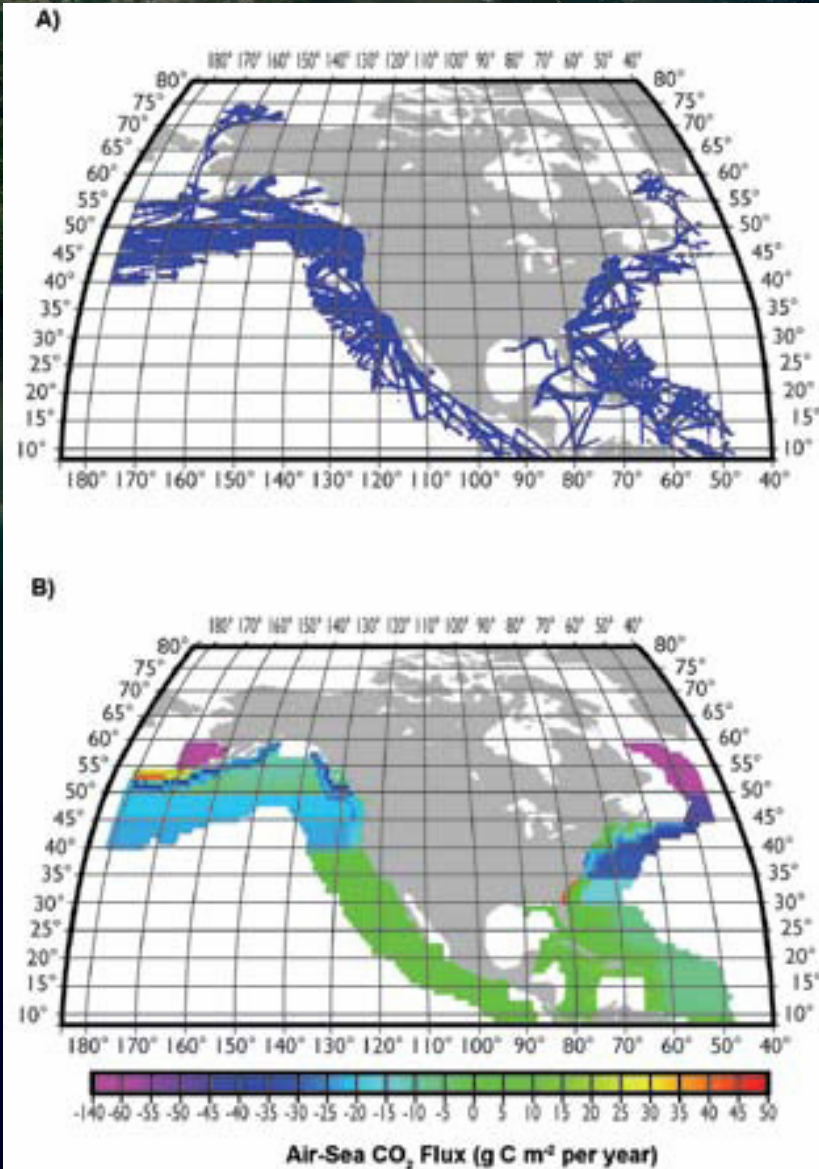
¹⁴Berger et al., 1989



Introduction

- **Chavez and Takahashi - State of the Ocean Carbon Cycle Report – Ch. 15**
 - *“The carbon budgets of ocean margins (coastal regions) are not as well-characterized due to lack of observations coupled with complexity and highly localized geographic variability.”*
 - *“With the exception of one or two time-series sites, almost nothing is known about historical trends in air-sea fluxes and the source-sink behavior of North America’s coastal oceans.”*
 - *“Highly variable air-sea carbon dioxide fluxes in coastal areas may introduce errors in North American carbon dioxide fluxes calculated by atmospheric inversion methods.”*
 - *“Experimental studies involving coastal carbon cycling should be encouraged.”*

Introduction



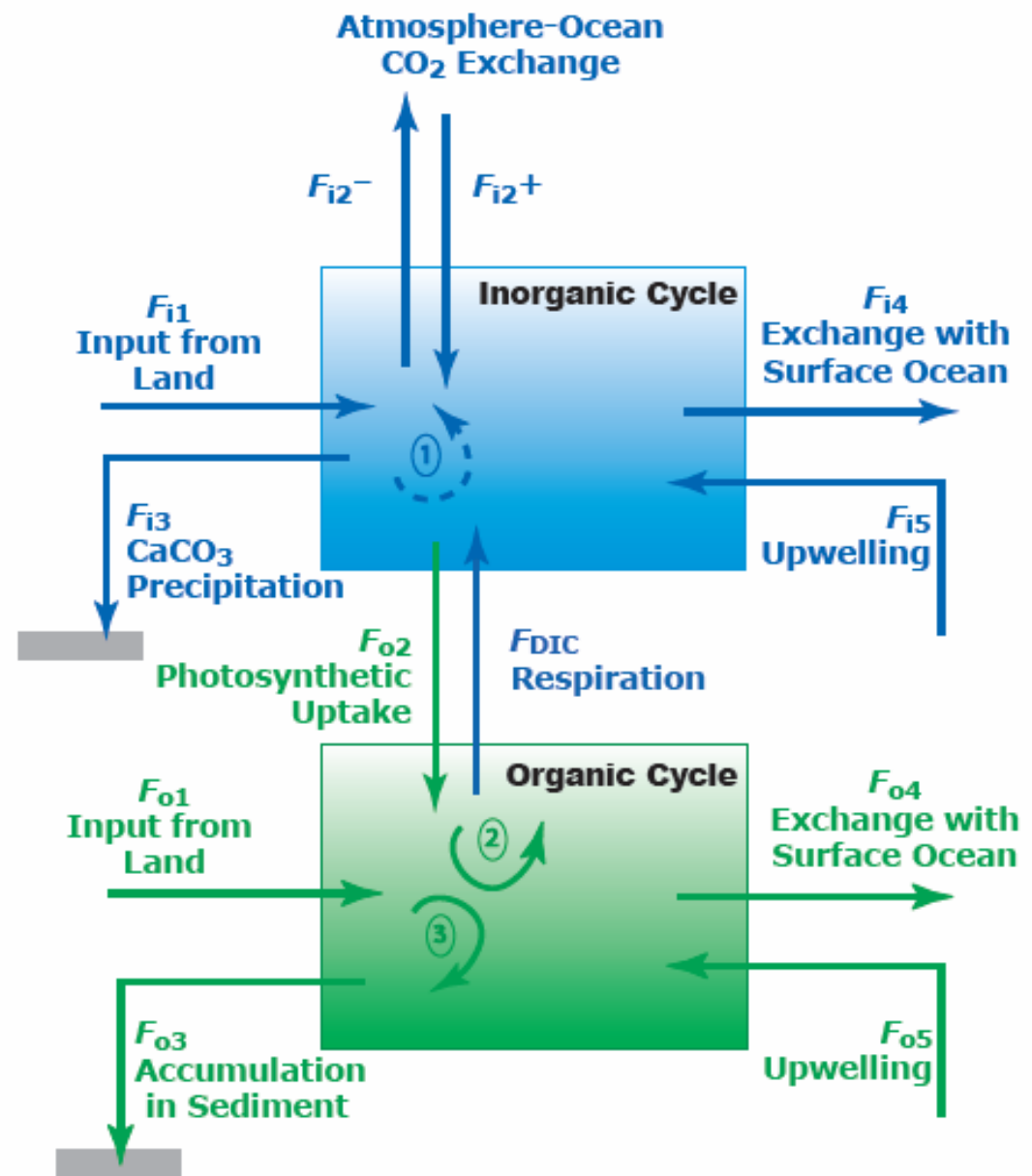
- Distribution of coastal surface water CO_2 partial pressure measurements made between 1979 and 2004, from Chavez and Takahashi showing lack of coverage in the Gulf of Mexico
- The Gulf of Mexico represents a large source of uncertainty in North American carbon budget

An aerial photograph of the Gulf of Mexico coastline, showing the dark blue water of the ocean meeting the lighter green and brown land. The text is overlaid on the upper left portion of the image.

Elements of Gulf of Mexico Carbon Cycle:

- Major Carbon Pathways
 - *Terrestrial Inputs*
 - *Shelf/Ocean Exchange*
 - *Air-Sea Flux*
 - *Vertical Flux, Sinking, Burial*
- Carbon Cycling
 - *Primary production*
 - *Remineralization and Biogeochemical Cycling*
 - *Photodegradation/Photoremineralization*

- Mackenzie et al. (2004)
 - *Coupled inorganic and organic carbon cycles*



Air-Sea Flux of CO₂: -2 - >70 Tg a⁻¹



**Terrestrial
Inputs:**
5.5 OC Tg a⁻¹
0.3 PIC Tg a⁻¹
21 DIC Tg a⁻¹

PP=30-550 (~150) g m⁻² a⁻¹
=23 Tg a⁻¹



R=~11-? Tg a⁻¹

**Shelf/Ocean
Exchange: ?**



OC Burial: 0.5-1.0 Tg a⁻¹



Shelf Area (US GOM):
1.56 x 10⁵ km²

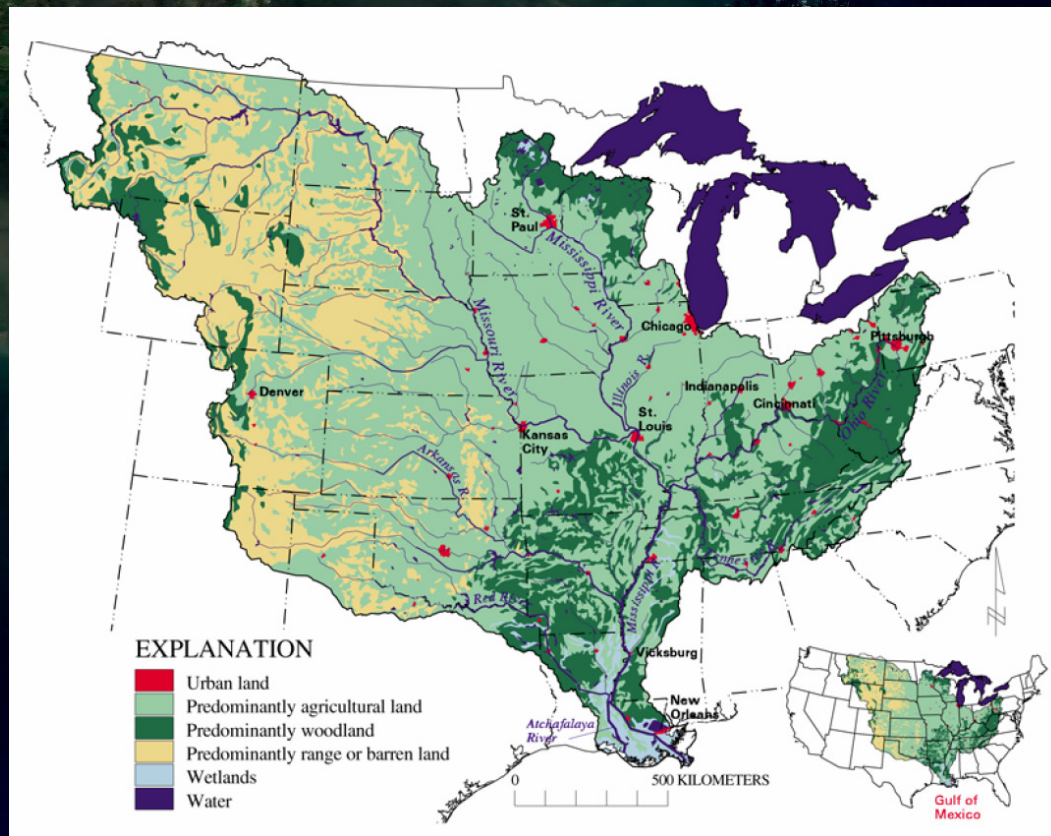


Organization of Talk

- Summary of Riverine and Terrestrial Inputs
- Transformation and Fate of Inputs
 - *Primary Production*
 - *Remineralization/Biogeochemical Cycling*
 - *Shelf/Ocean Exchange*
 - *Vertical Flux/Burial/Sinking*
 - *Air-Sea Flux*

Terrestrial Inputs

- **Mississippi River**



- Drainage basin encompasses 41% of the lower 48 United States
- Largest river basin in North America and third largest in the world

Source: Goolsby et al. 1999. NOAA Coastal Ocean Program Decision Analysis Series No. 17. NOAA Coastal Ocean Program, Silver Spring, MD.

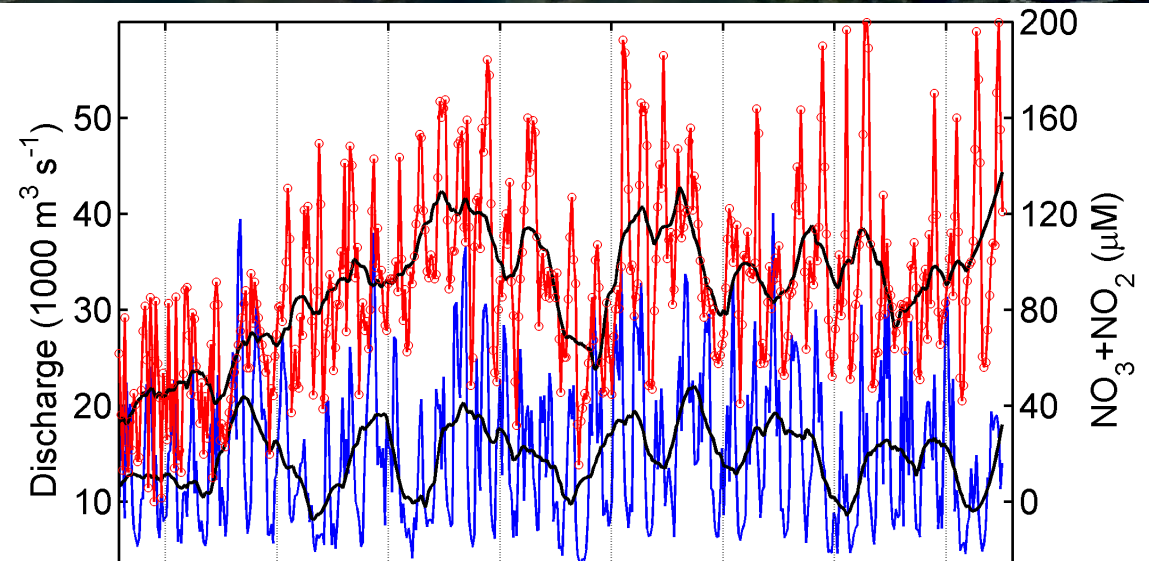
Terrestrial Inputs

- Mississippi River (Cai and Lohrenz, 2007)

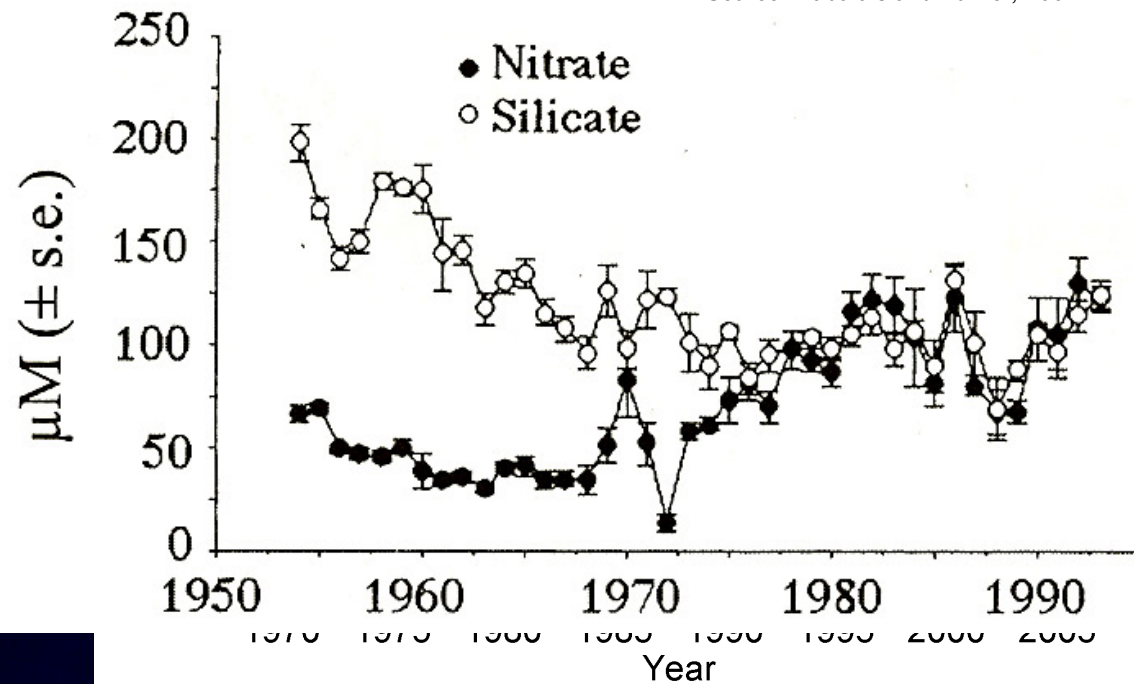
Chemical	Concentration (mM)	Annual Flux Tg y ⁻¹	Reference
TSM	---	210 ^s	Meade and Parker (1985)
POC	1.6% of TSM	3.4	Trefry et al. (1994)
DOC		1.2 ^{&}	Duan and Bianchi 2006
	0.28	1.8	Trefry et al. (1994)
	0.33	2.1	Benner and Opsahl 2001
	0.49	3.1	Bianchi et al. 2004
PIC	0.15% of TSM	0.31	Trefry et al. (1994)
DIC	0.219	21 [*]	Cai (2003)
TAlk	0.216	21 [*]	Cai (2003); Raymond and Cole (2003)
Total Nitrogen (N)		1.57	Goolsby et al. (1999)
NO ₃ + NO ₂		0.95	Goolsby et al. (1999); Howarth et al. (1996)
Ammonium		0.03	Goolsby et al. (1999)
Dissolved Org. N		0.38	Goolsby et al. (1999)
Particulate Org. N		0.20	Goolsby et al. (1999)
Particulate Org. N		0.45 ⁺	Trefry et al. (1994)
Total Phosphorus (P)		0.136	Goolsby et al. (1999)
PO ₄		0.042	Goolsby et al. (1999)
Particulate P		0.095	Goolsby et al. (1999)
Si-dissolved		2.32	Goolsby et al. (1999)

- **Mississippi nutrient fluxes (Cai and Lohrenz, 2007)**

- *Increase in NO_x flux, especially during 1970's*
- *NO_x:PO₄ ratios well above Redfield*

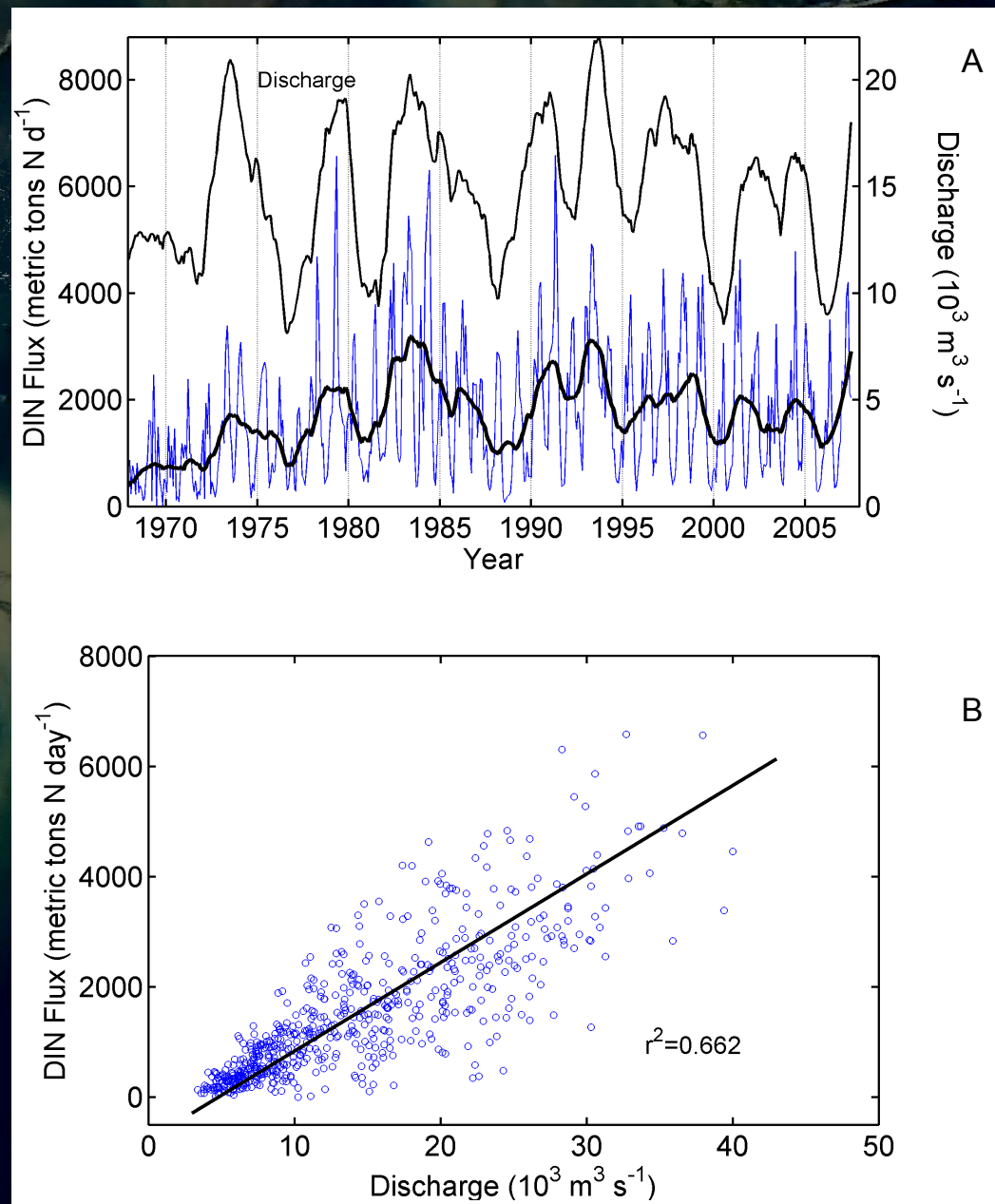


Source: Rabalais and Turner, 2001

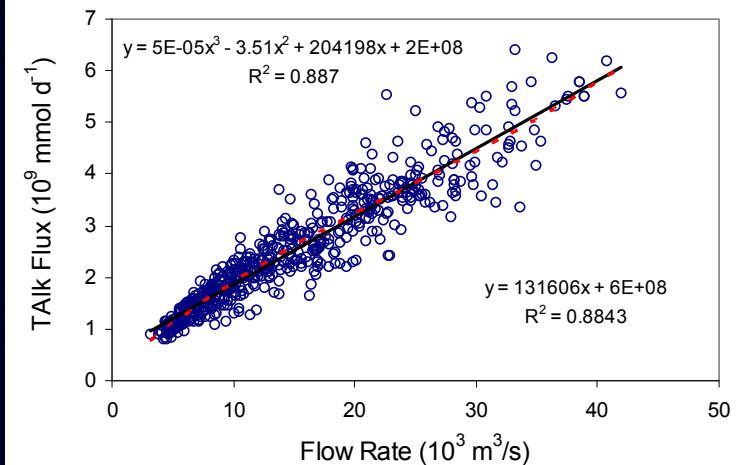
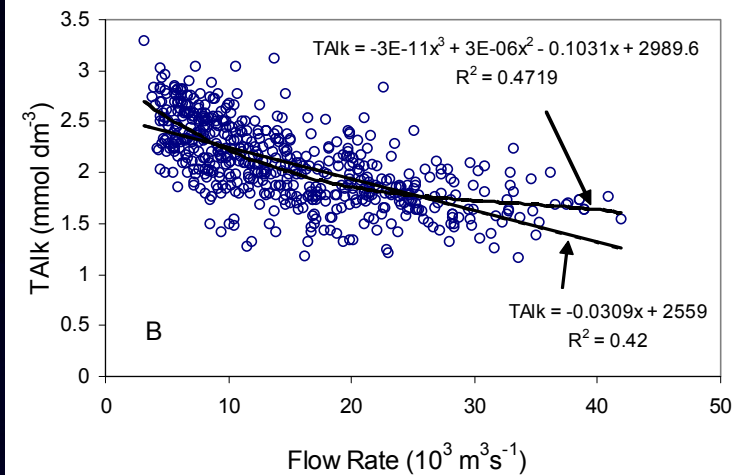
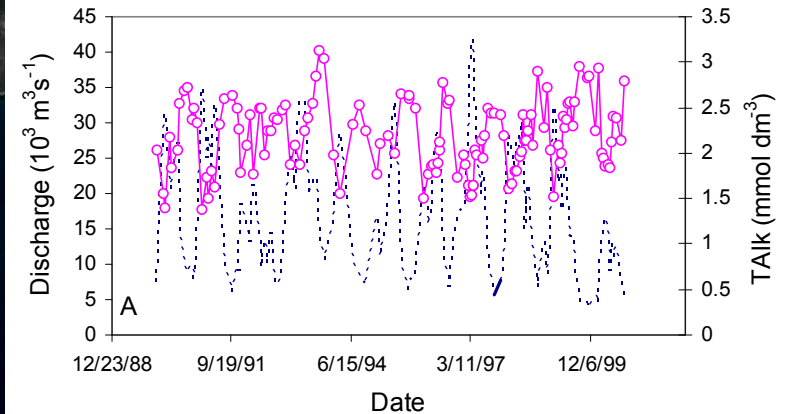


- **Mississippi (Cai and Lohrenz, 2007)**

– *Increase in DIN flux attributable to both increase in concentration and discharge*

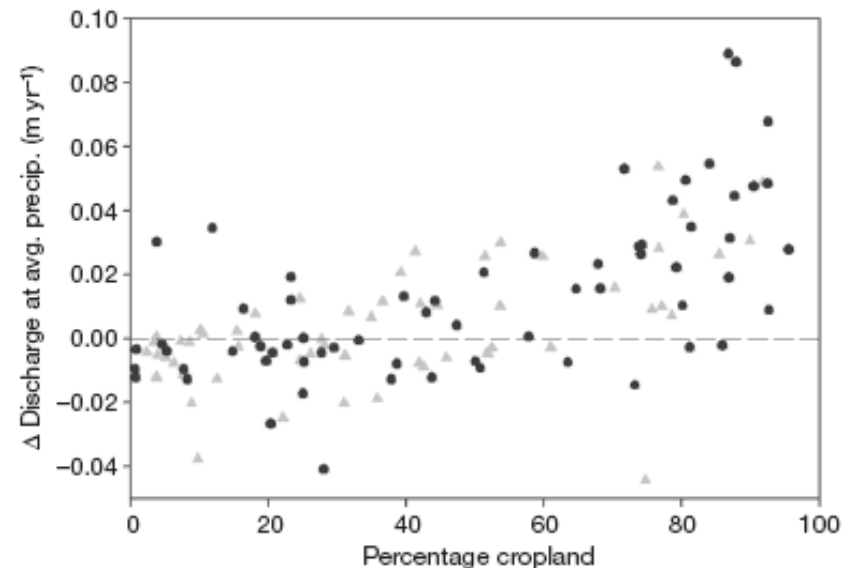
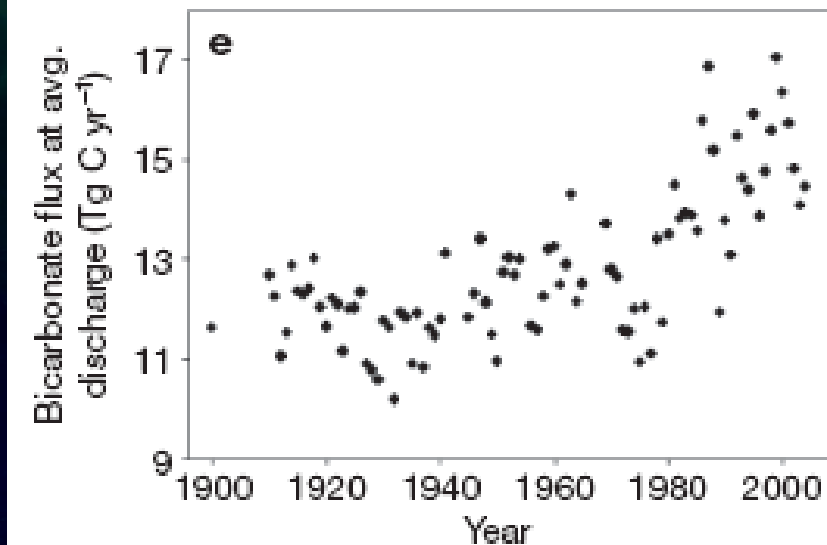


- Mississippi (Cai and Lohrenz, 2007; Cai et al., 2008)
 - *Negative correlation of TAlk to discharge*
 - *Weathering rates related to precipitation*



Terrestrial Inputs

- **Mississippi (Raymond et al., 2008)**
 - increase in bicarbonate and water fluxes is caused mainly by an increase in discharge from agricultural watersheds that has not been balanced by a rise in precipitation





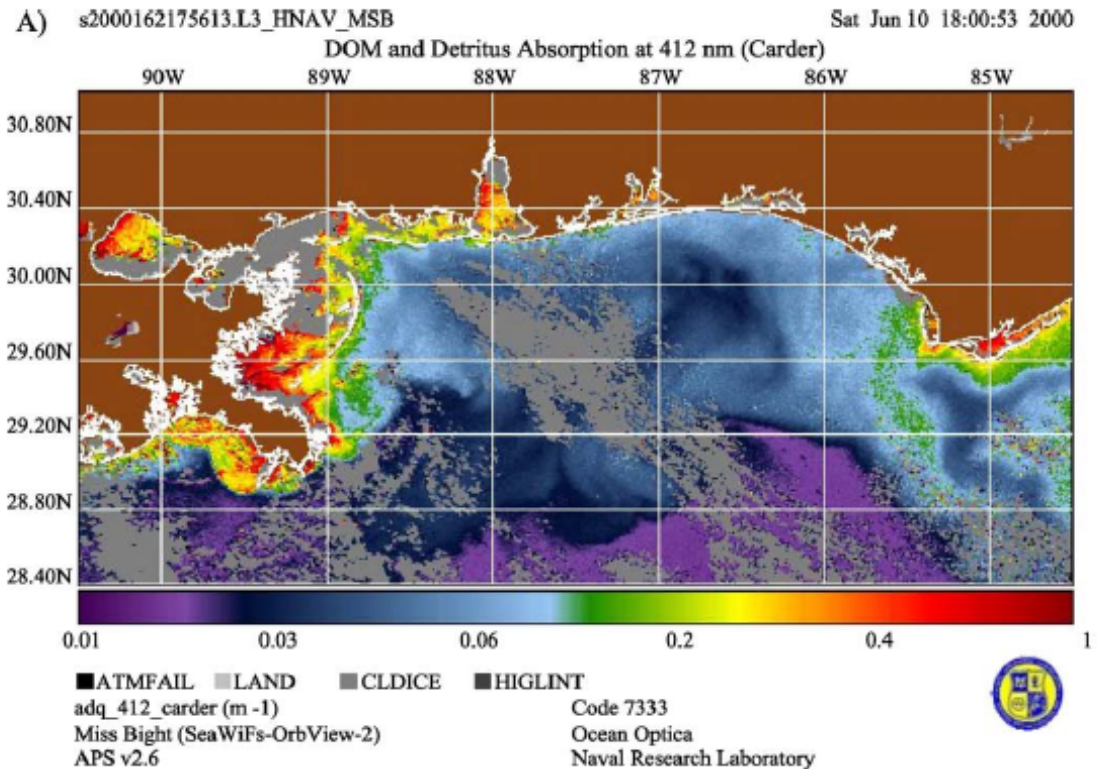
Terrestrial Inputs

- Combined export of POC and DOC by Mississippi River represents more than 10% of total POC+DOC for North America based estimated POC+DOC by Seitzinger et al. (2005)
- POC flux higher during high discharge period
 - *Strong relationship to TSM (Trefrey et al., 1994; Cai and Lohrenz, 2007)*
 - *Ratio of DOC to POC varies in relationship to discharge (Cai and Lohrenz, 2007)*
- DOM and DOC
 - *Mississippi end member less variable than Atchafalaya (Chen et al., 2004)*
 - *Significant biological production of DOM (Benner and Opsahl, 2001; Chen et al., 2004)*
 - *Losses of terrestrially-derived material through degradation and flocculation (Benner and Opsahl, 2001)*

Terrestrial Inputs

- **DOM and DOC**
 - *Riverine CDOM extensively dispersed (Chen et al., 2004)*
 - *Subsurface CDOM more biologically labile and photochemically refractory than the surface CDOM*
 - *Much of riverine DOC photochemically converted to DIC over period of weeks (Miller and Zepp, 1995; Hernes and Benner, 2003)*

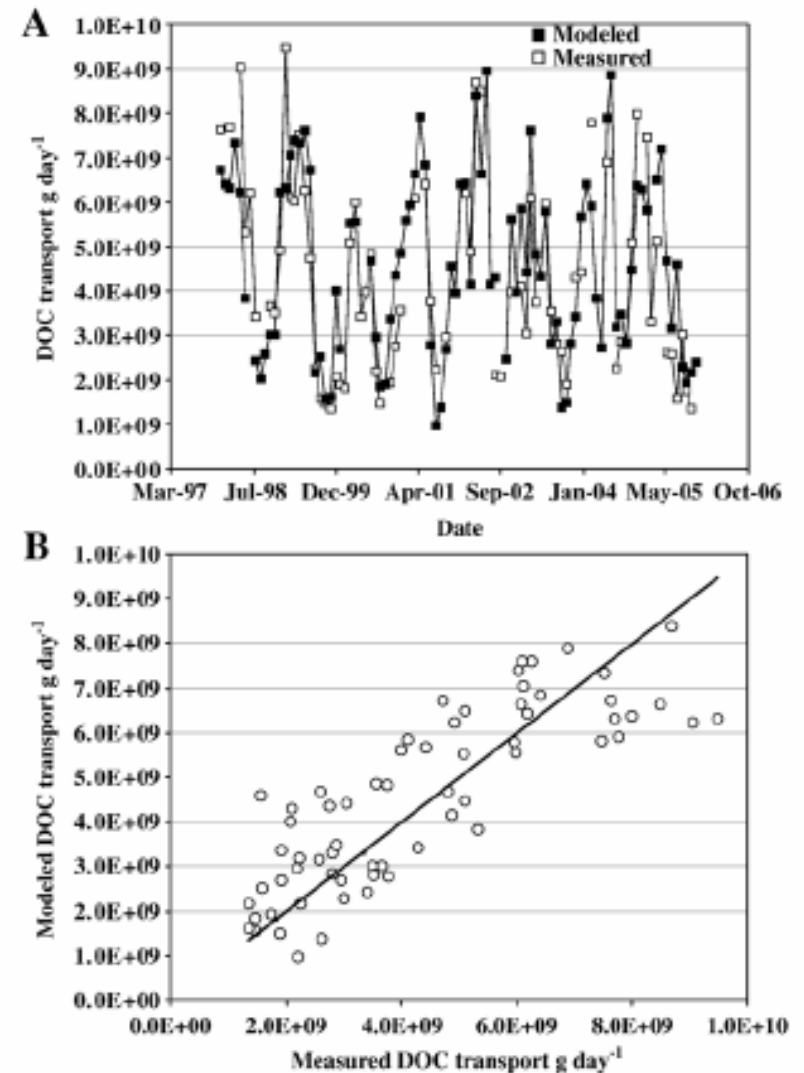
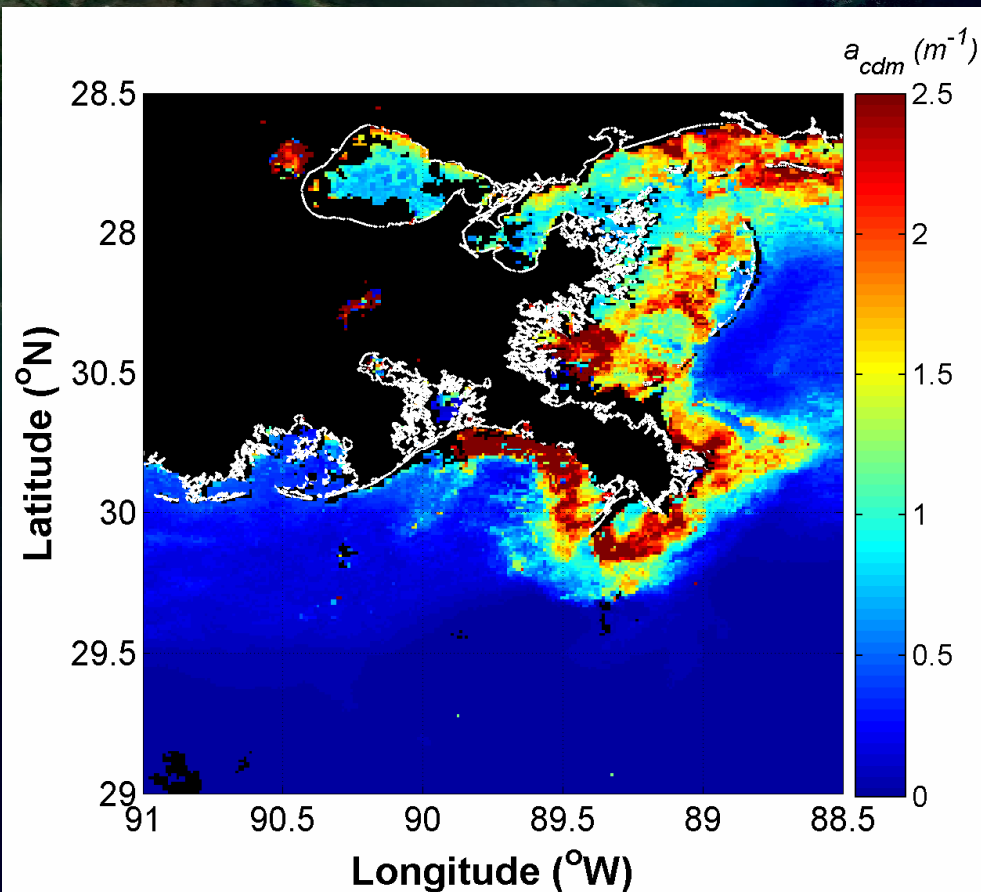
R.F. Chen et al. / Marine Chemistry 89 (2004) 257–272



Terrestrial Inputs

DelCastillo and Miller, 2007

- CDOM/DOC

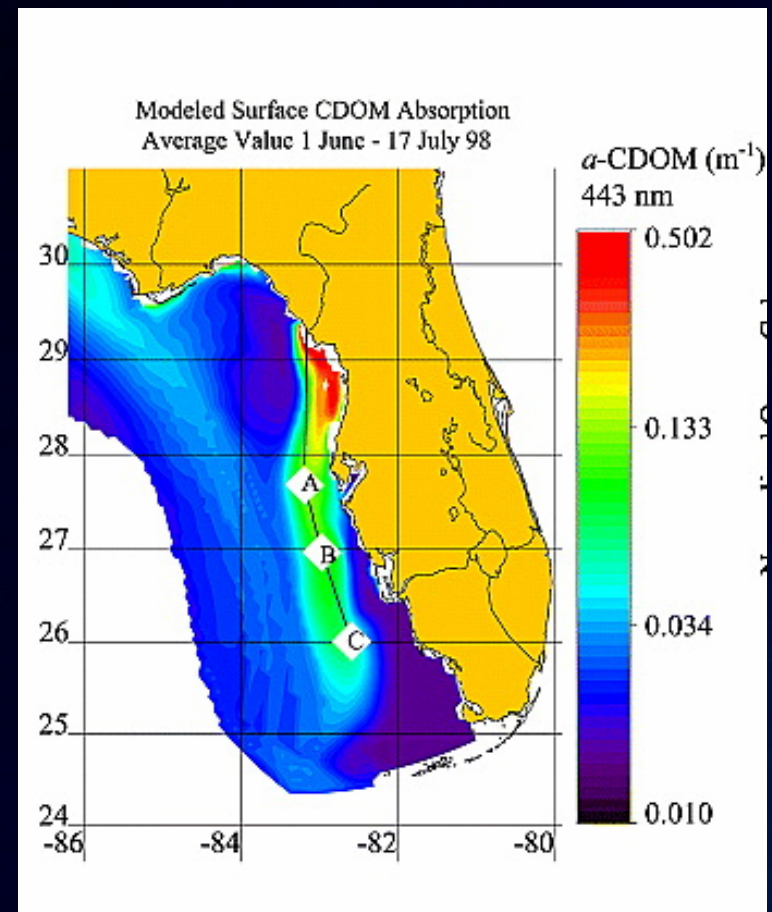


Terrestrial Inputs

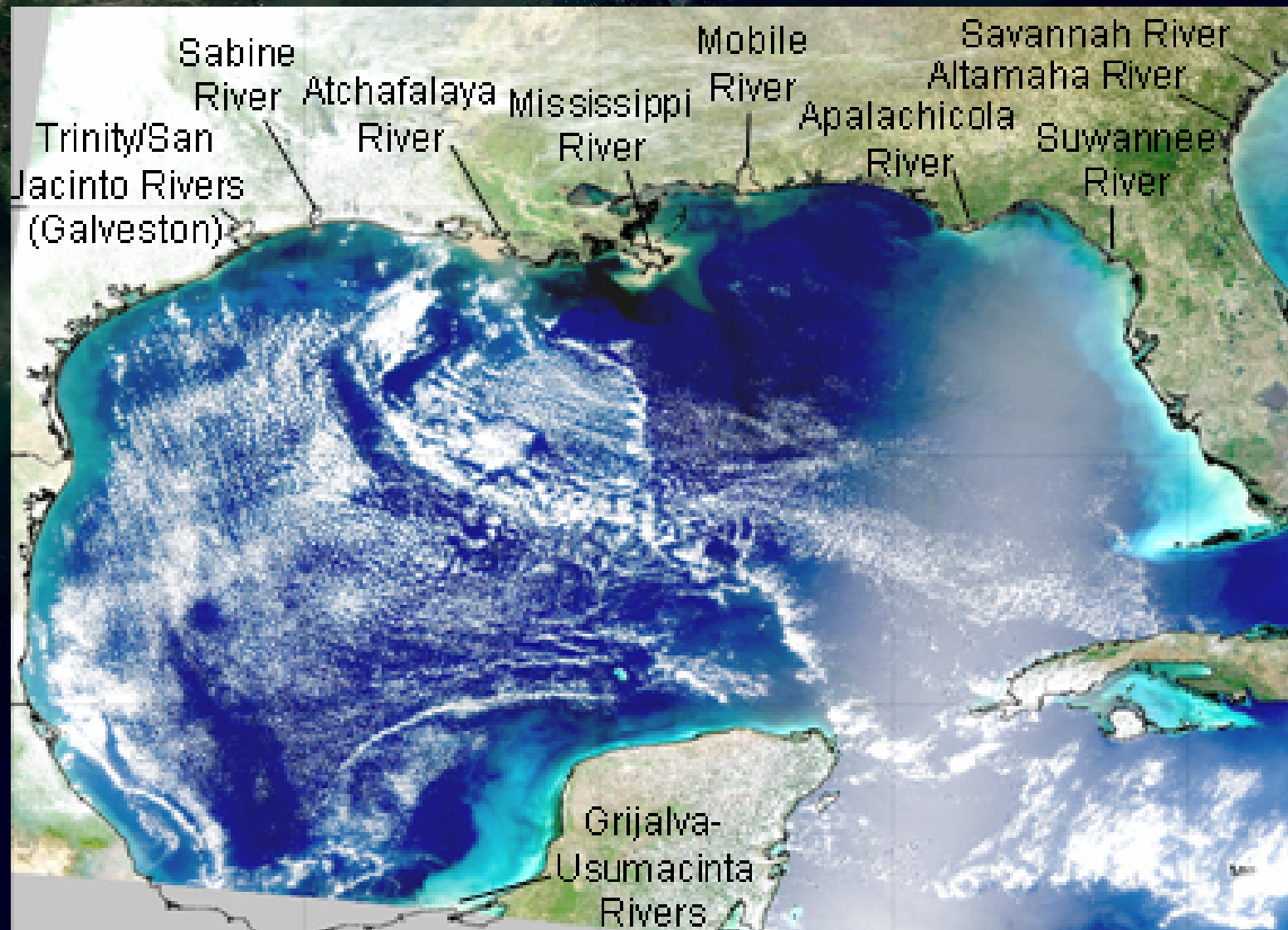
- **West Florida Shelf CDOM**

- *Photochemical production of N probably a minor fraction of total N requirements for phytoplankton*

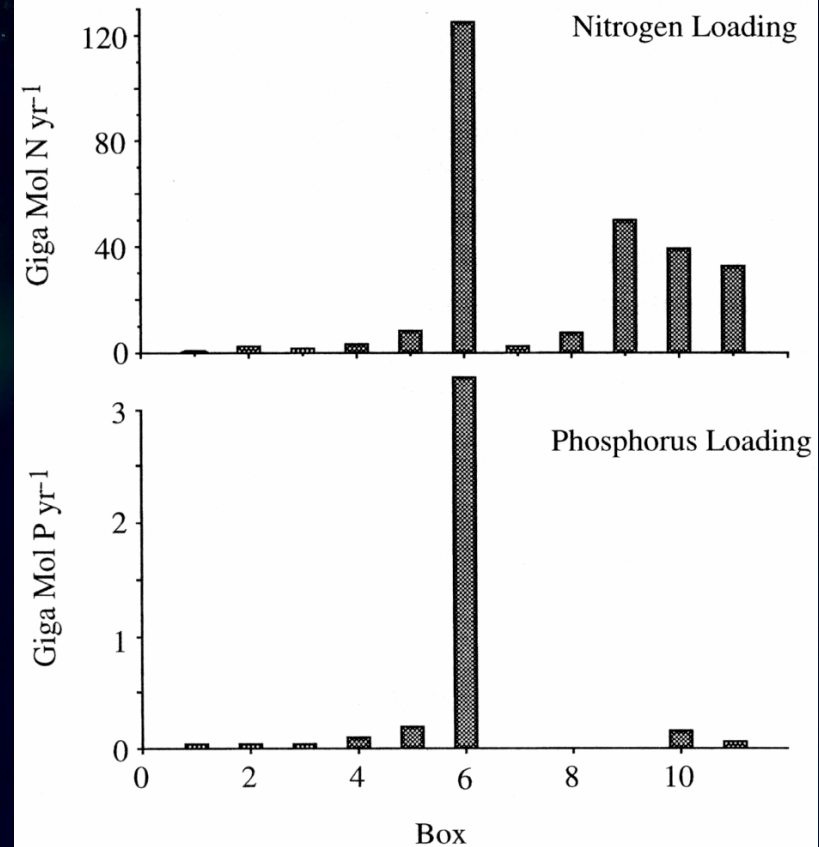
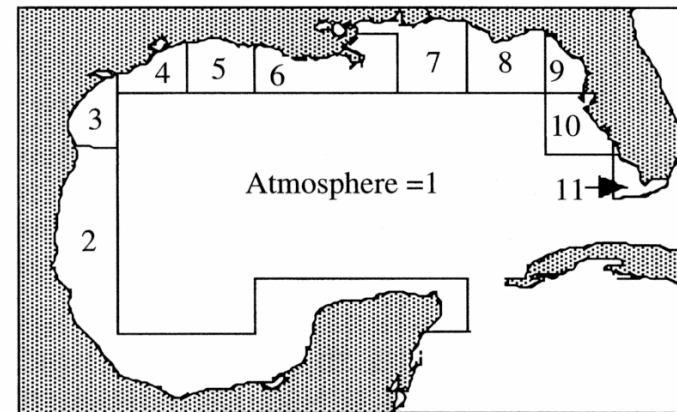
Jolliff et al., 2003



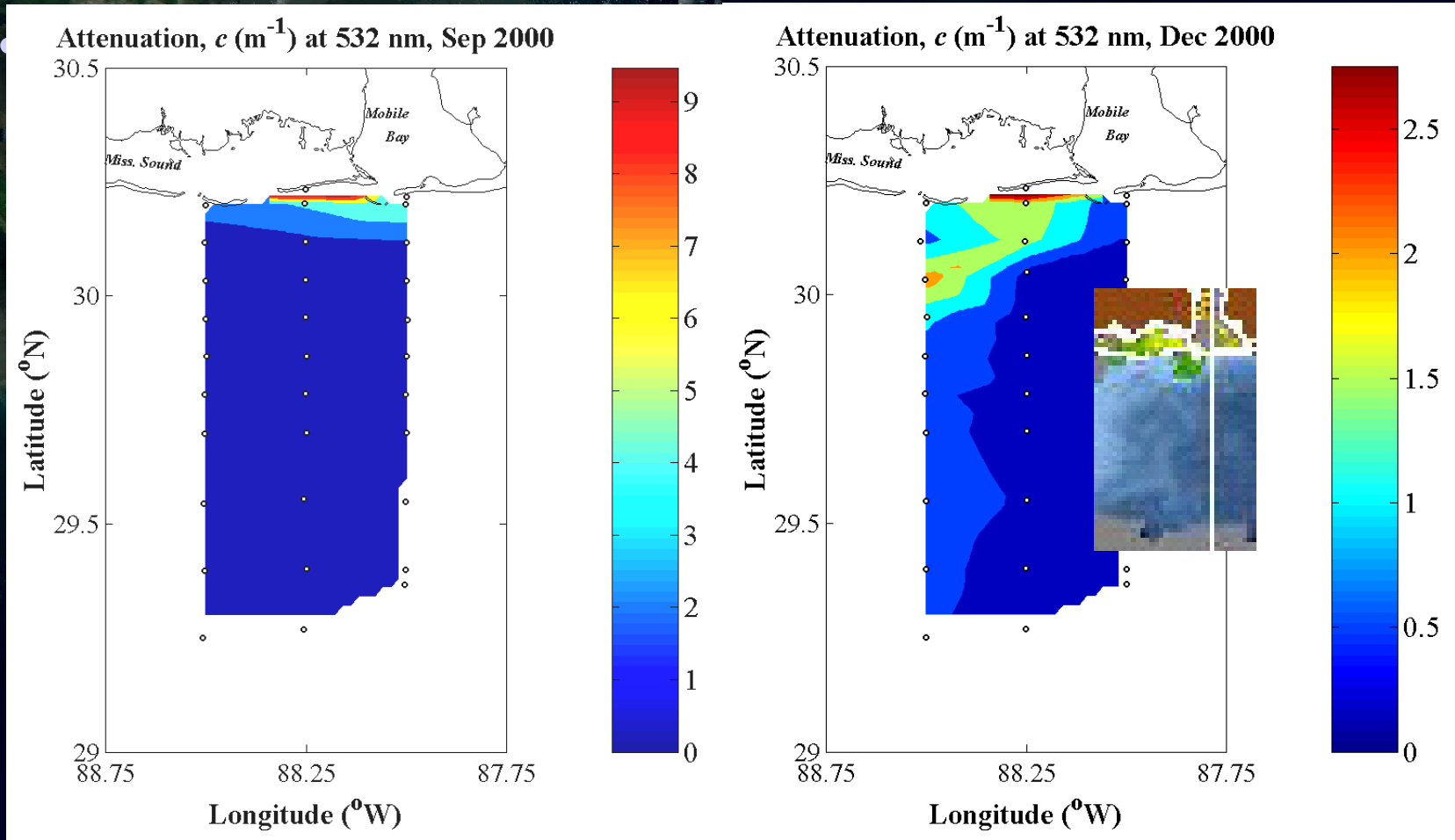
Other Terrestrial Sources



- *Mississippi River dominates terrestrial inputs of N and P (Turner and Rabalais, 2004)*
- *Watershed sources linked to land use practices (Turner and Rabalais, 2004; Donner et al., 2004)*
- *Other inputs important regionally*



Terrestrial Inputs





Terrestrial Inputs

- **Groundwater sources**
 - ***Northern Gulf of Mexico***
 - › Cable et al., 1996
 - › Krest et al., 1999
 - ***West Florida***
 - › Corbett et al., 2000
 - › Hu et al., 2006
 - ***Northeastern Gulf***
 - › Rutkowski et al., 1999

Terrestrial Inputs

- **Coastal Wetlands**
 - *Contribution to carbon delivery to coastal zone poorly quantified*
 - *Outwelling significant in other systems (e.g., Moran et al. 1991)*
 - *Large land losses in Louisiana and northern Gulf may be associated with higher export rates (Dagg et al., 2007)*

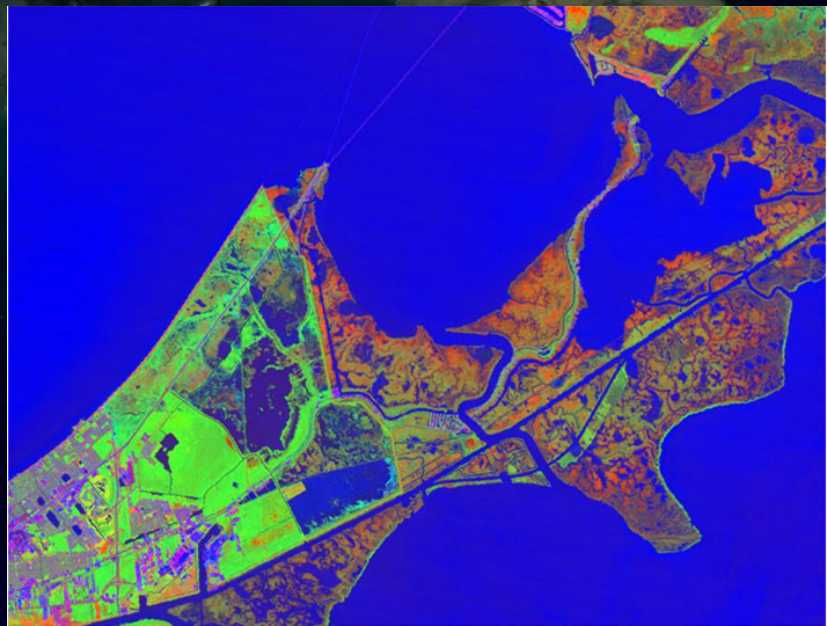


Chandealeur
Islands

31 18 35

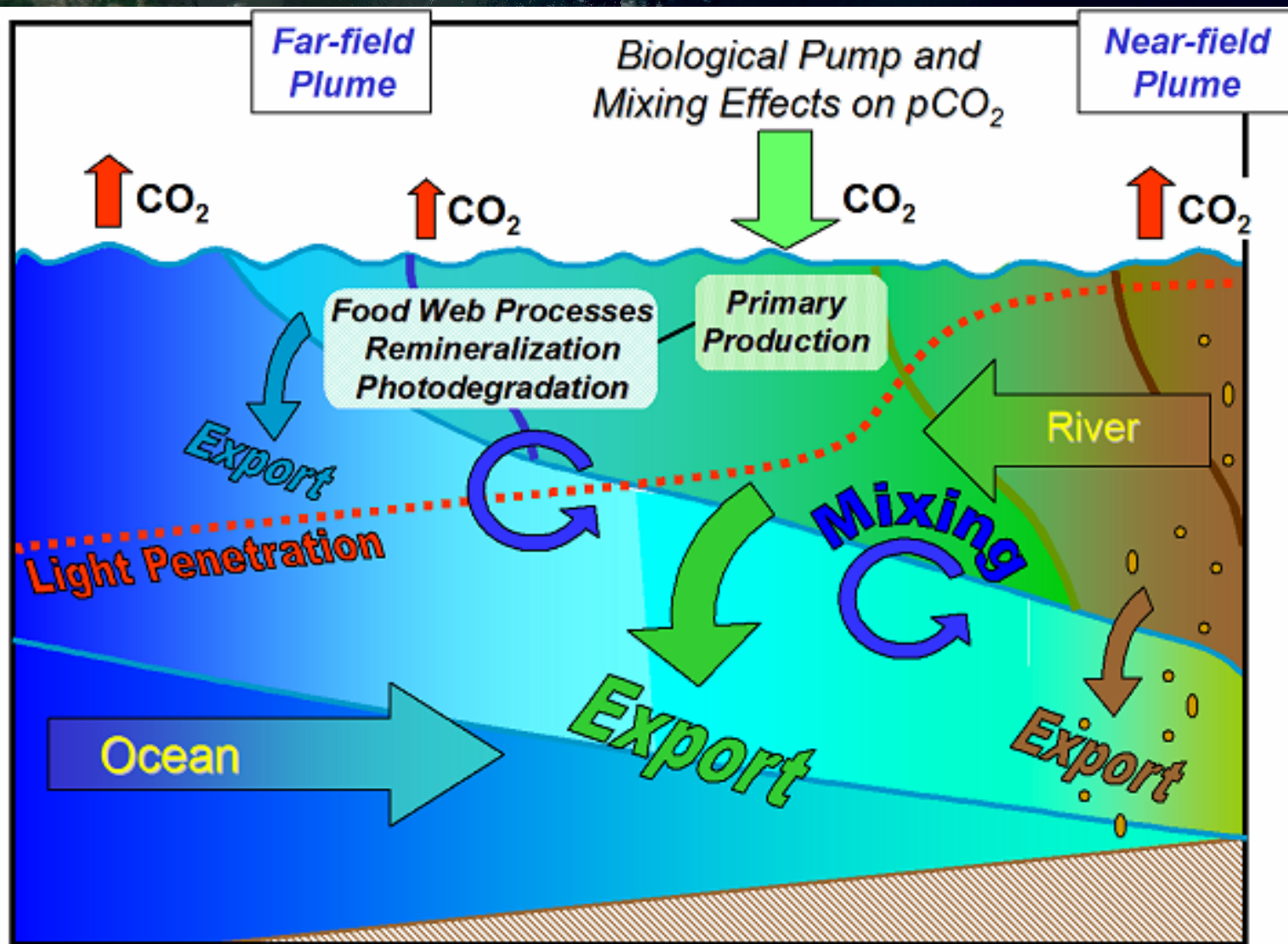
Terrestrial Inputs

- Coastal Wetlands
 - *This may extend to forested regions impacted by storms and extreme events*



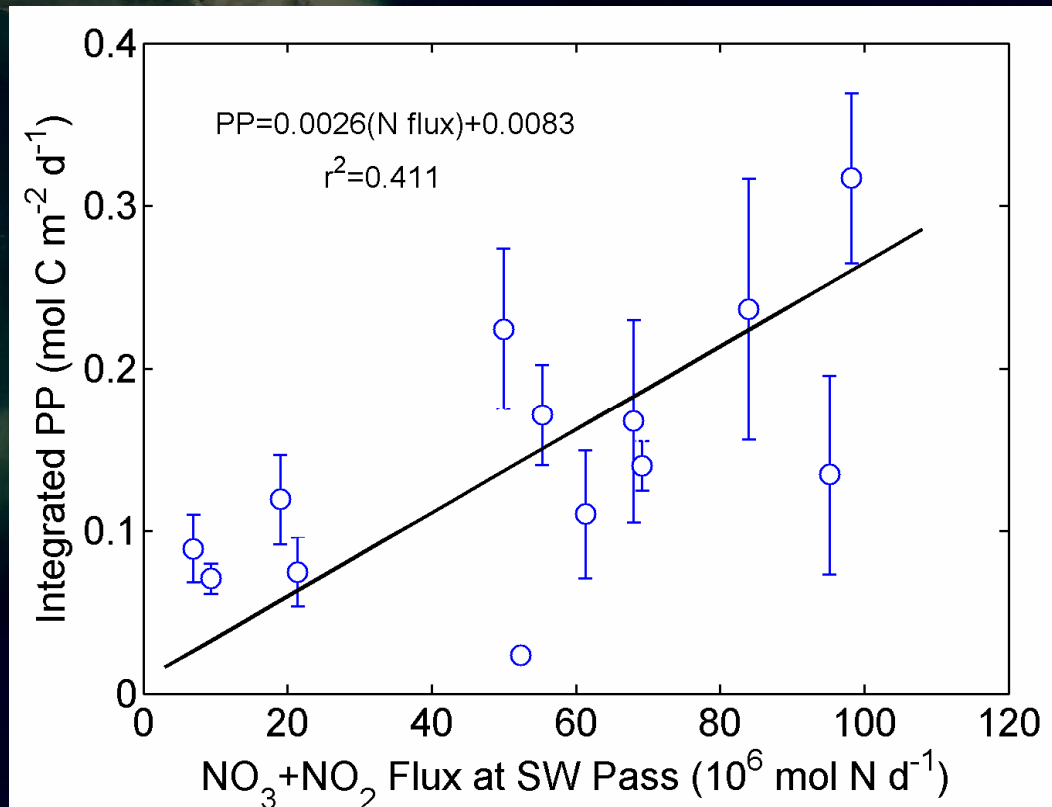
Pre- and post-Katrina LandSat imagery in eastern New Orleans showing forest damage, courtesy of NASA Carbon Cycle and Ecosystems program

Transformation and Fate



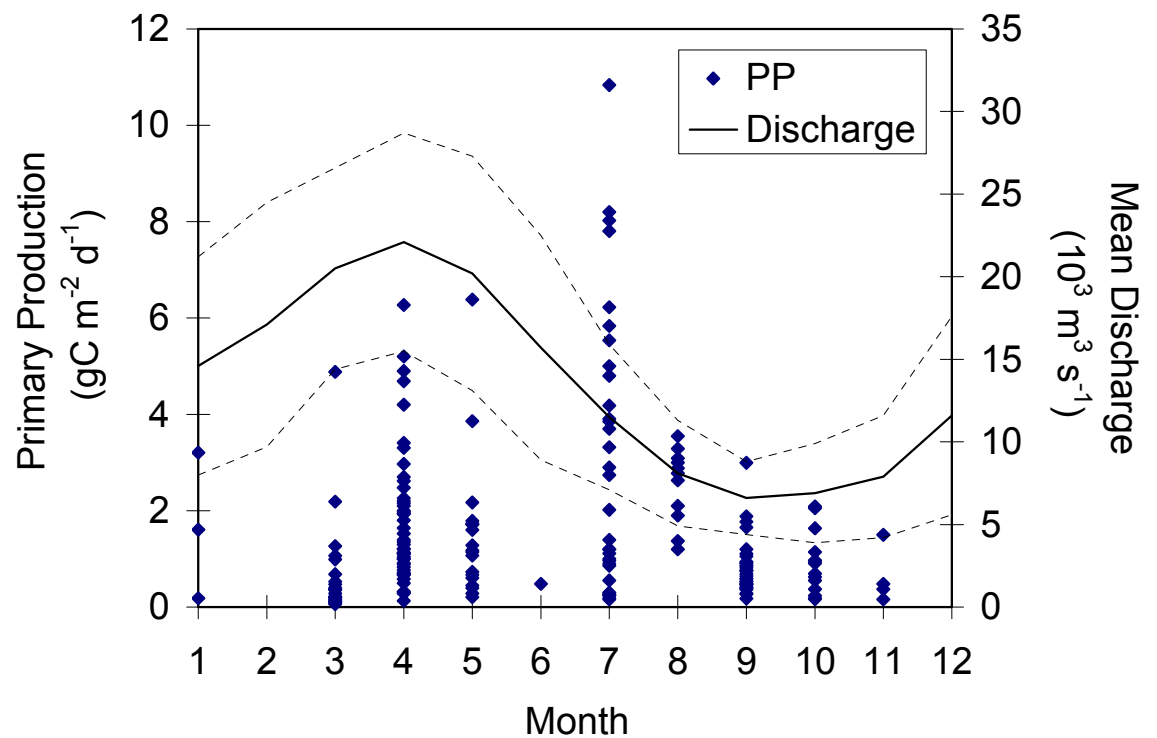
Transformation and Fate

- Linkage between terrestrial DIN flux and primary production (Lohrenz et al., 1997; Cai and Lohrenz, 2007)



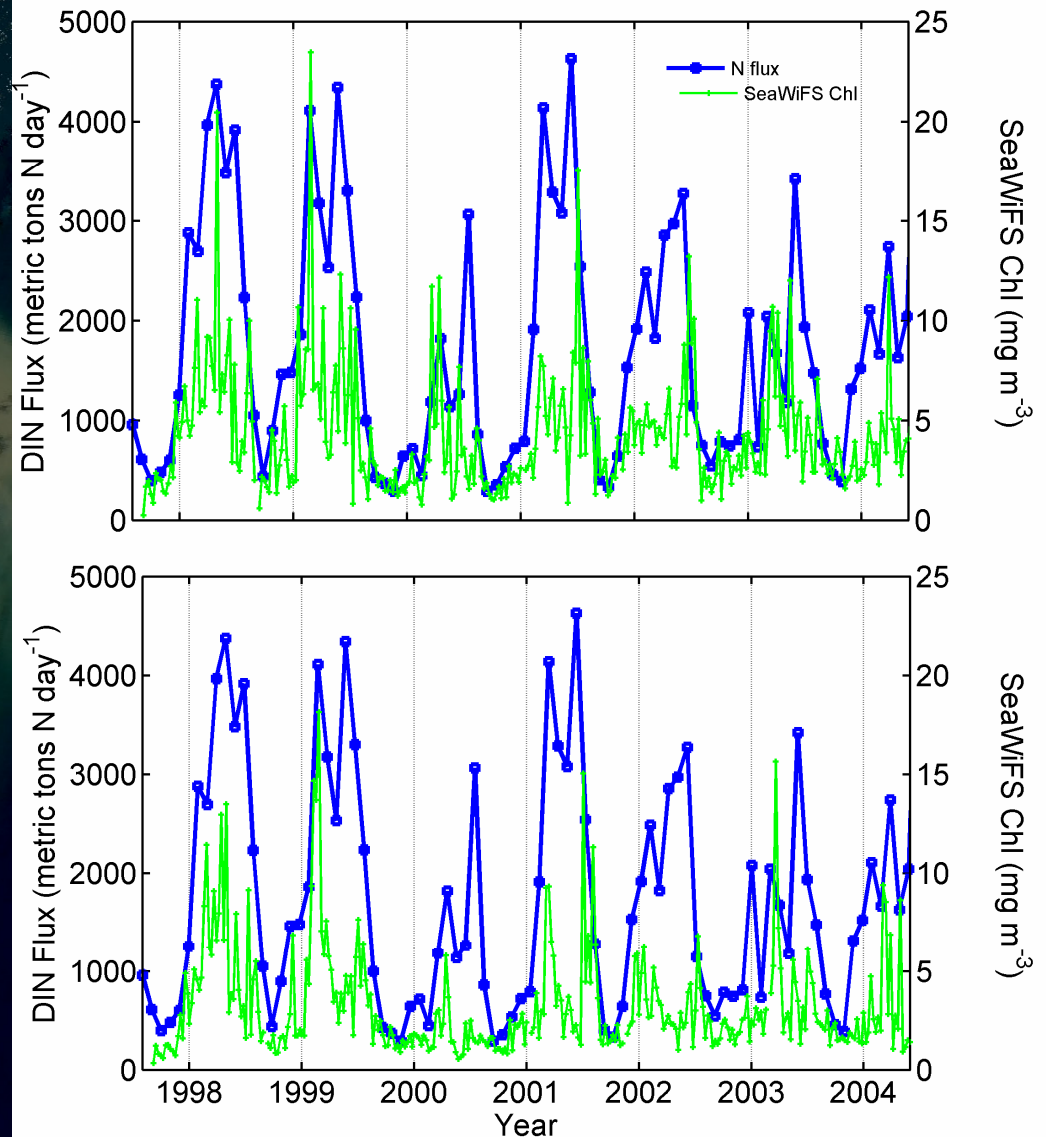
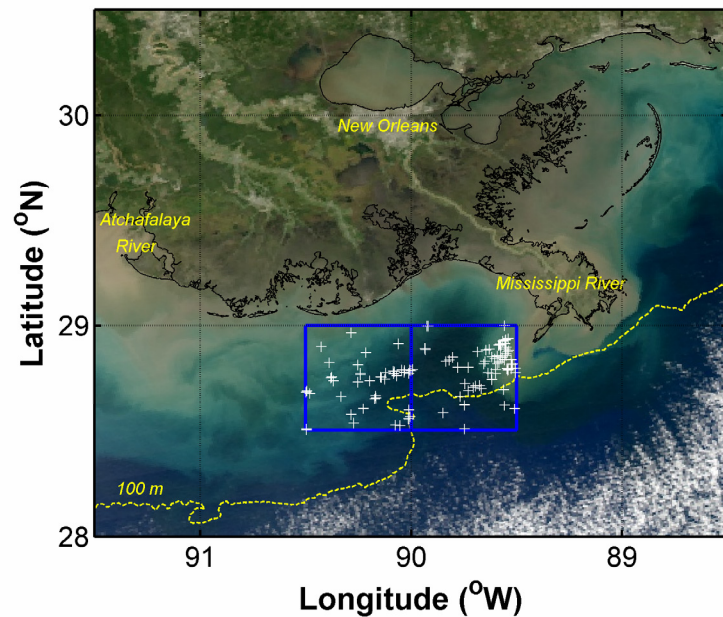
Primary Production

- Productivity generally higher in river-estuarine-influenced regions (Lohrenz et al., 1999)
- Seasonal pattern in productivity, but limited data



Primary Production

- Correspondence between satellite-derived chlorophyll and riverine N flux (Lohrenz et al., 2008)
- See also Walker et al., 2006





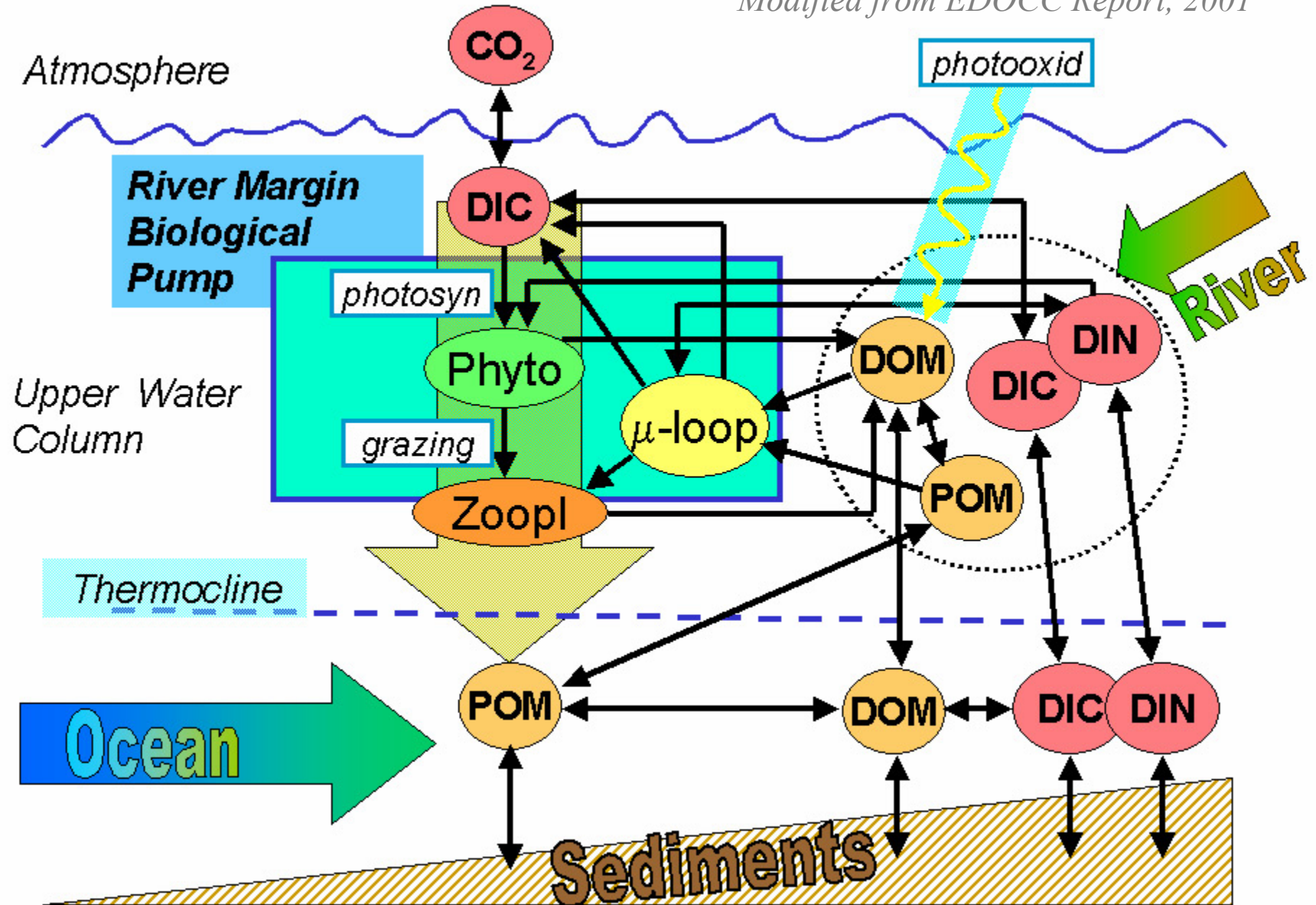
Primary Production

- Off Louisiana, annual average primary production estimated as annual average productivity was approximately $550 \text{ gC m}^{-2} \text{ y}^{-1}$ (Lohrenz and Verity, 2004)
- In the northwestern Gulf of Mexico, primary production was lower, averaging $160 \text{ gC m}^{-2} \text{ y}^{-1}$ (Chen et al., 2000)
- Primary production rates on the western shelf of Florida during non-bloom conditions have been reported to range from 30 to $180 \text{ gC m}^{-2} \text{ y}^{-1}$ (Vargo et al., 1987)

Remineralization/Biogeochemical Cycling

- Largest fluxes of carbon in plume and marine food webs are through the phytoplankton and bacterioplankton
- Major fate of phytoplankton is grazing
 - *Microzooplankton grazing generally dominates grazing*
 - *Grazing by larger zooplankton (e.g., copepods) may have greater impact on vertical flux of carbon (e.g., Dagg et al., 2007)*

Modified from EDOCC Report, 2001





Remineralization/Biogeochemical Cycling

- High rates of N recycling (Dagg et al., 2004)
 - *Close coupling of autotrophic and heterotrophic production*
 - *High rates of respiration and remineralization at intermediate salinities (Gardner et al., 1994; Bode and Dortch, 1996; Gardner et al., 1997)*
 - *High rates of ammonium regeneration in offshore waters (Warwik et al., 2004)*



Remineralization/Biogeochemical Cycling

- Information about nitrogen transformations (denitrification, nitrification, fixation, DNRA) will be a key to understanding its role in carbon cycling (Dagg et al., 2007)
 - *Gulf of Mexico denitrification rates ($195 \times 10^9 \text{ mol y}^{-1}$, Seitzinger and Giblin, 1996) are comparable to estimated land-derived inputs of total N ($136\text{--}159 \times 10^9 \text{ mol y}^{-1}$, Nixon et al., 1996)*
 - *Denitrification in terrestrial ecosystems also represents a substantial path for removal of nitrogen, but estimates vary (Royer et al., 2004)*
 - *High apparent rates of nitrification in plume waters (Pakulski et al., 2000)*



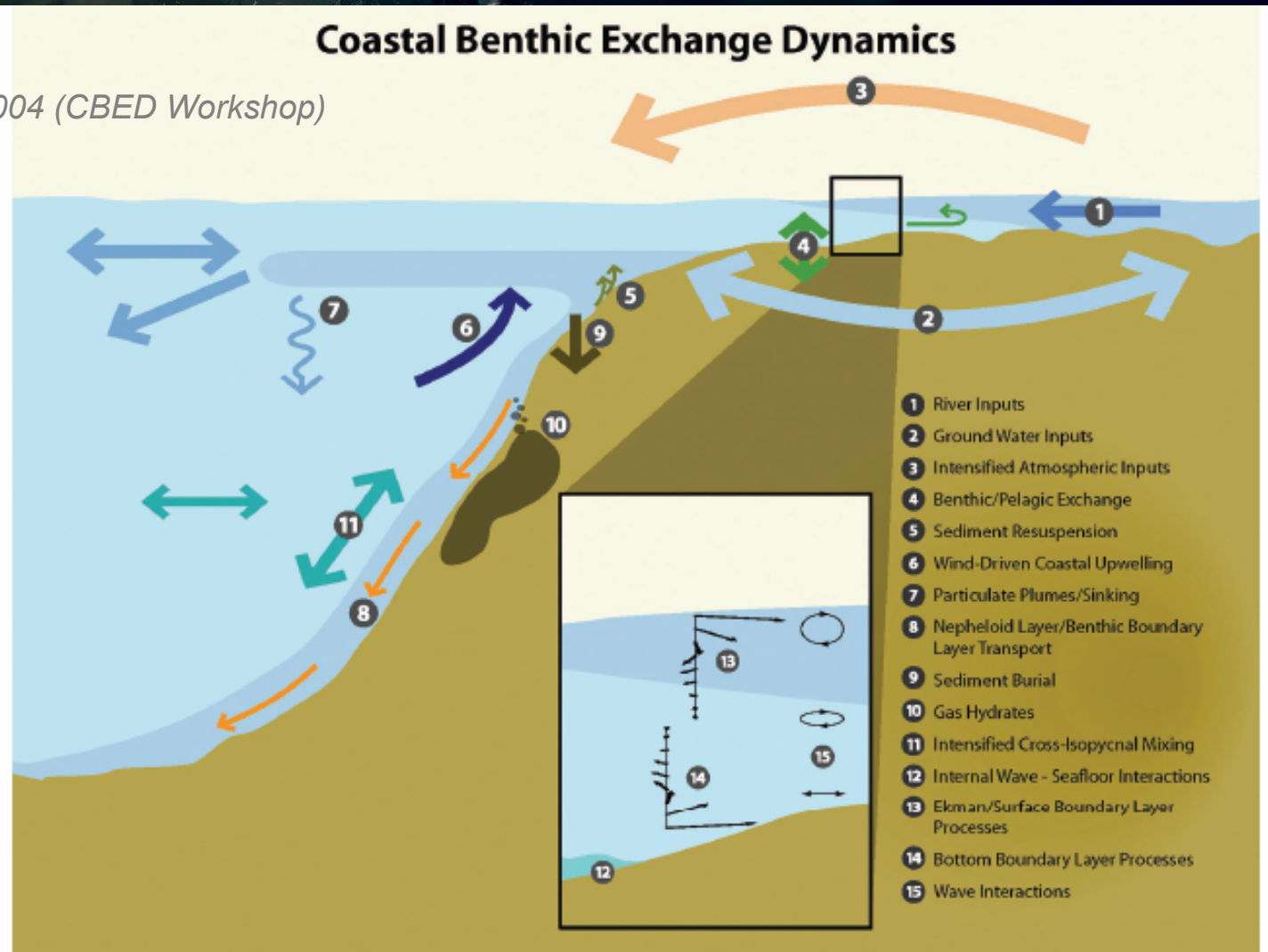
Remineralization/Biogeochemical Cycling

- **Nitrogen fixation**
 - *“Cascade of diazotrophic communities along gradients of salinity and nutrients” (Foster et al., 2007)*
 - *Low slope inputs of nitrogen on west Florida shelf -- nitrogen fixation may represent important source in frontal aggregations (Lenes et al., 2001; Walsh et al. 2003, 2006)*

Vertical Flux, Sinking, Burial

Reimers et al., 2004 (CBED Workshop)

Figure II.A.1. Schematic of selected transport processes that are either unique to or intensified at the ocean - continental margin boundary as described in the text. In response to complex interactions between physical forces and local topography, it is important to recognize that these exchanges vary significantly spatially and temporally.



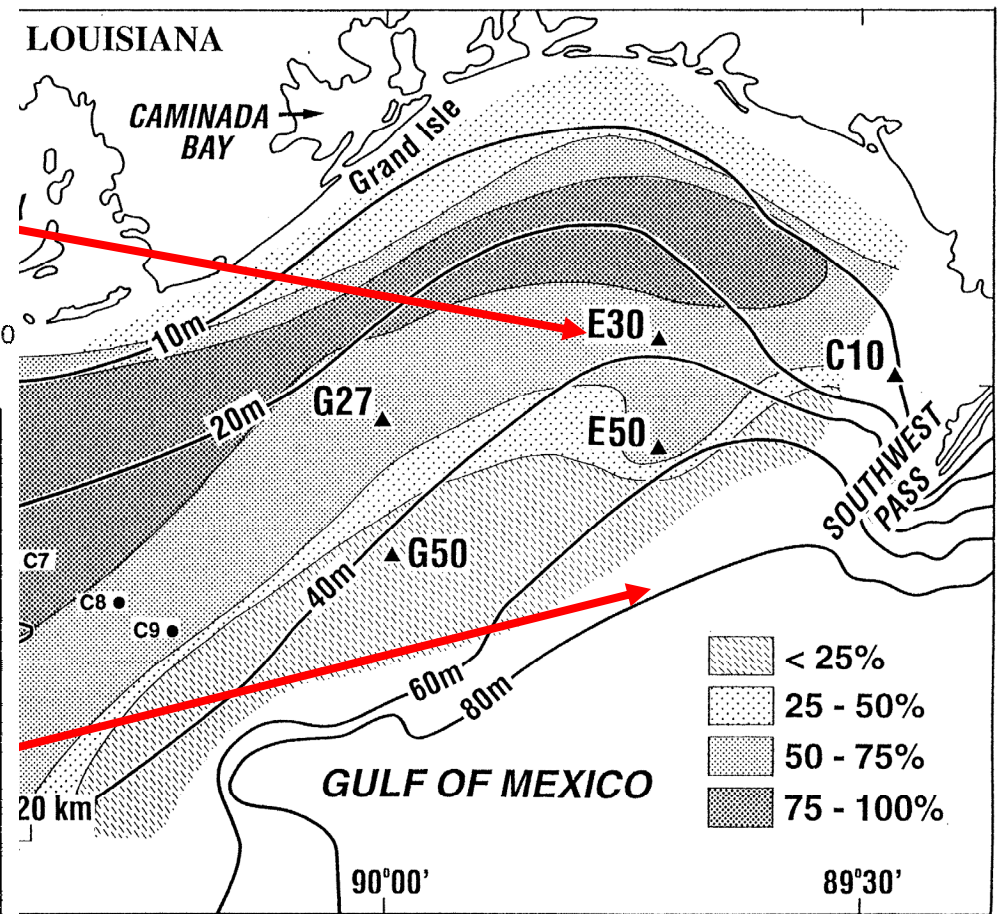
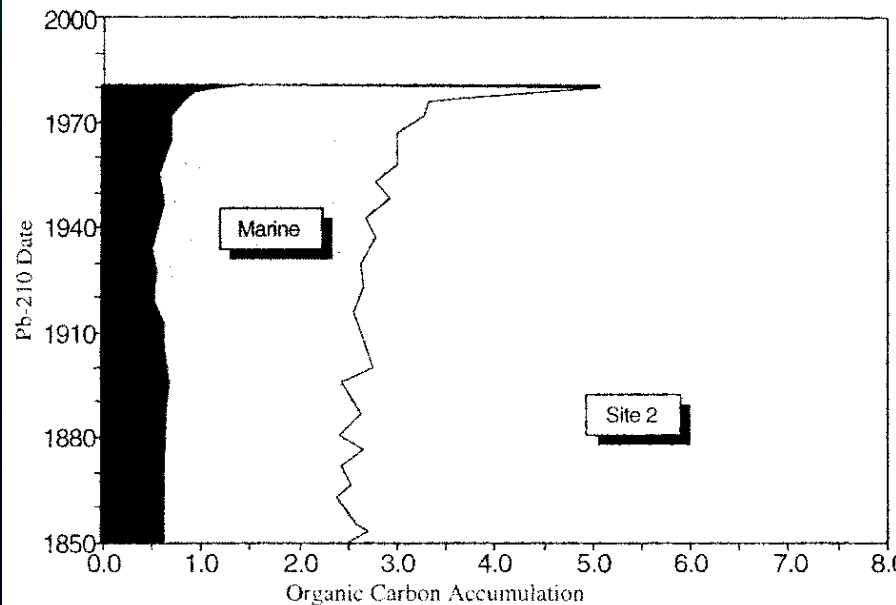
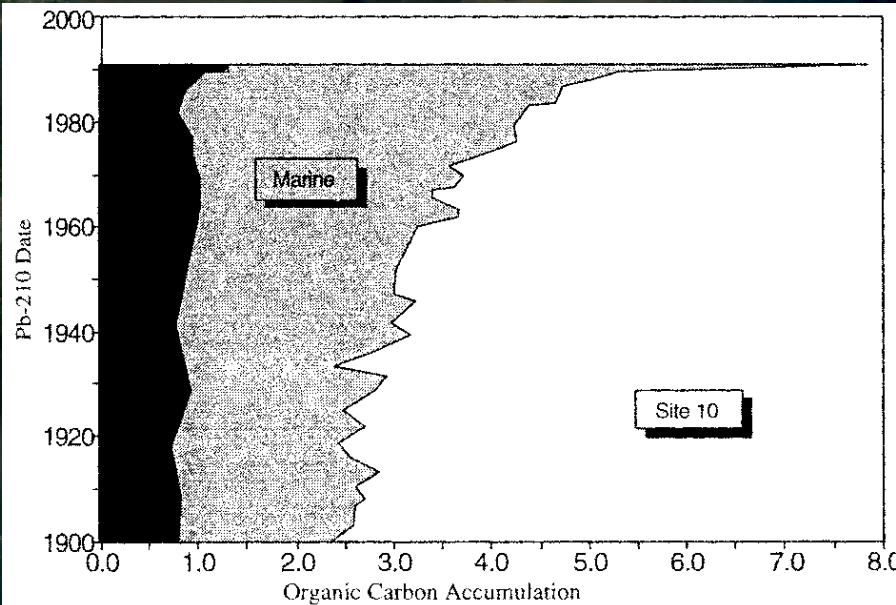


Vertical Flux, Sinking, Burial

- Export fluxes (Dagg et al., 2007)
 - *Sediment trap-derived estimates*
 - › Redalje et al., 1994: $1.80 \text{ g C m}^{-2} \text{ d}^{-1}$ in spring, but lower during other seasons ($0.29\text{--}0.95 \text{ g C m}^{-2} \text{ d}^{-1}$) and away from the plume ($0.18\text{--}0.40 \text{ g C m}^{-2} \text{ d}^{-1}$)
 - › Qureshi, 1995: 0.50 and $0.60 \text{ g C m}^{-2} \text{ d}^{-1}$

Vertical Flux, Sinking, Burial

Eadie et al., 1994; Rabalais et al., 1996



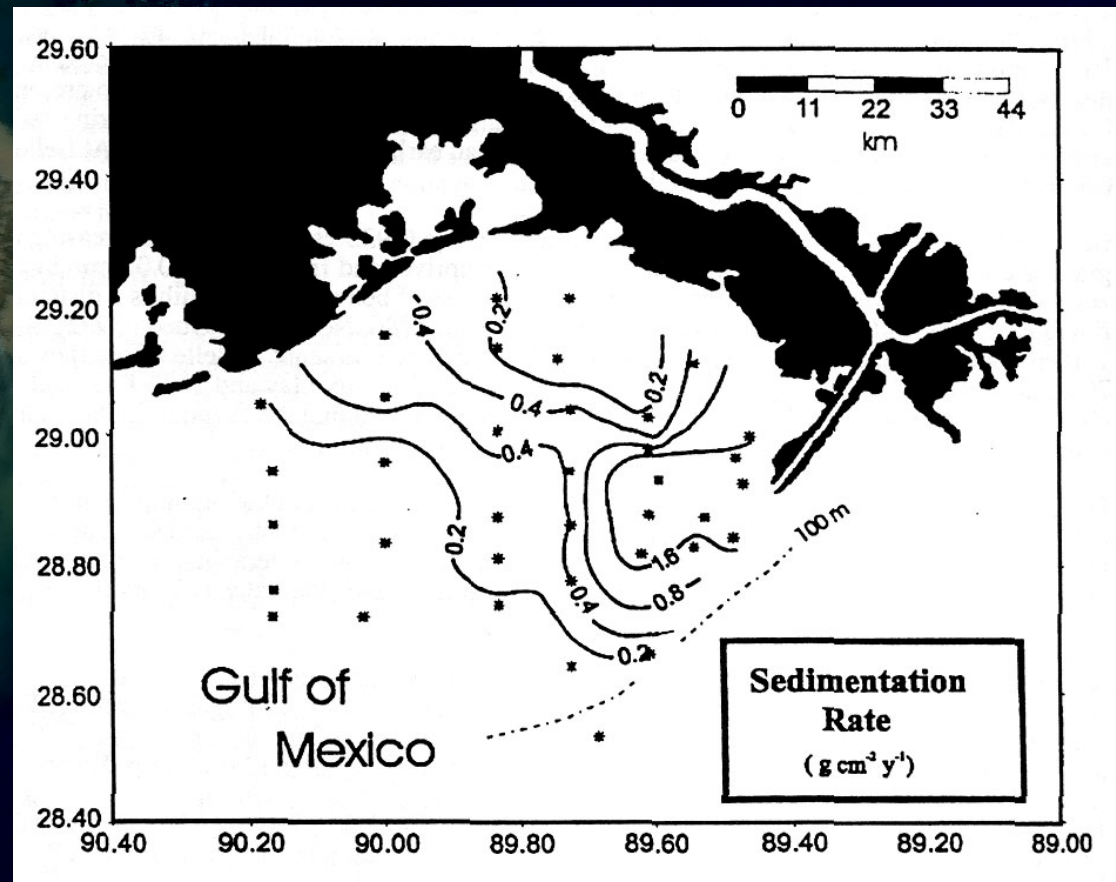
An aerial photograph of a coastal area showing a large, turbid plume of water extending from a river or estuary into the ocean. The plume is a mix of brown and green, indicating suspended sediments and organic matter. The surrounding ocean is a deep blue, and the coastline is visible with some green land areas.

Vertical Flux, Sinking, Burial

- Large fluxes in near-field plume
 - *Sinking of large lithogenic particles and particulate organic material (Trefry et al. 1994)*
 - *Flocculation and aggregation processes also stimulate sinking of materials (Dagg et al., 1996)*
 - *Coupling between surface plume organic production and supply of organic carbon to sediments (Wysocki et al., 2006)*
 - *Mineral association may enhance preservation of organic matter (Mead et al., 2007; Gordon and Goni et al., 2004)*

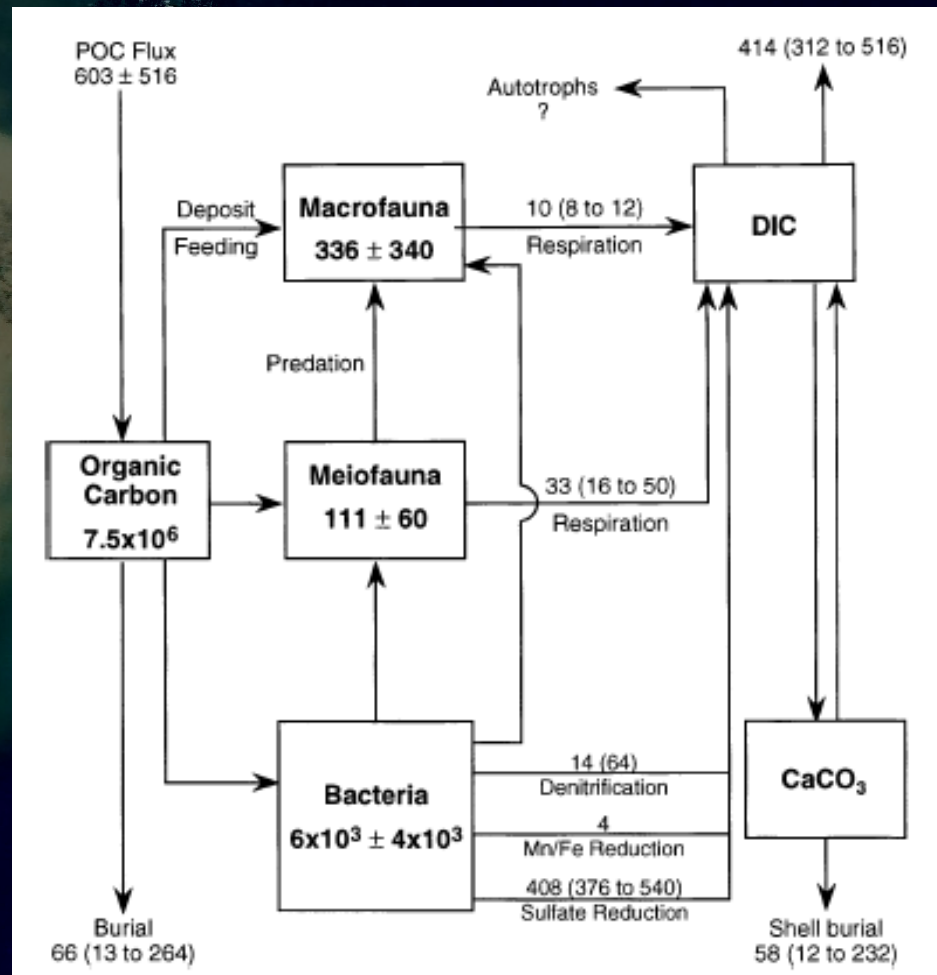
Vertical Flux, Sinking, Burial

- Benthic Processes
 - *Rapid sedimentation enhances preservation of material (Wiseman et al., 1999)*



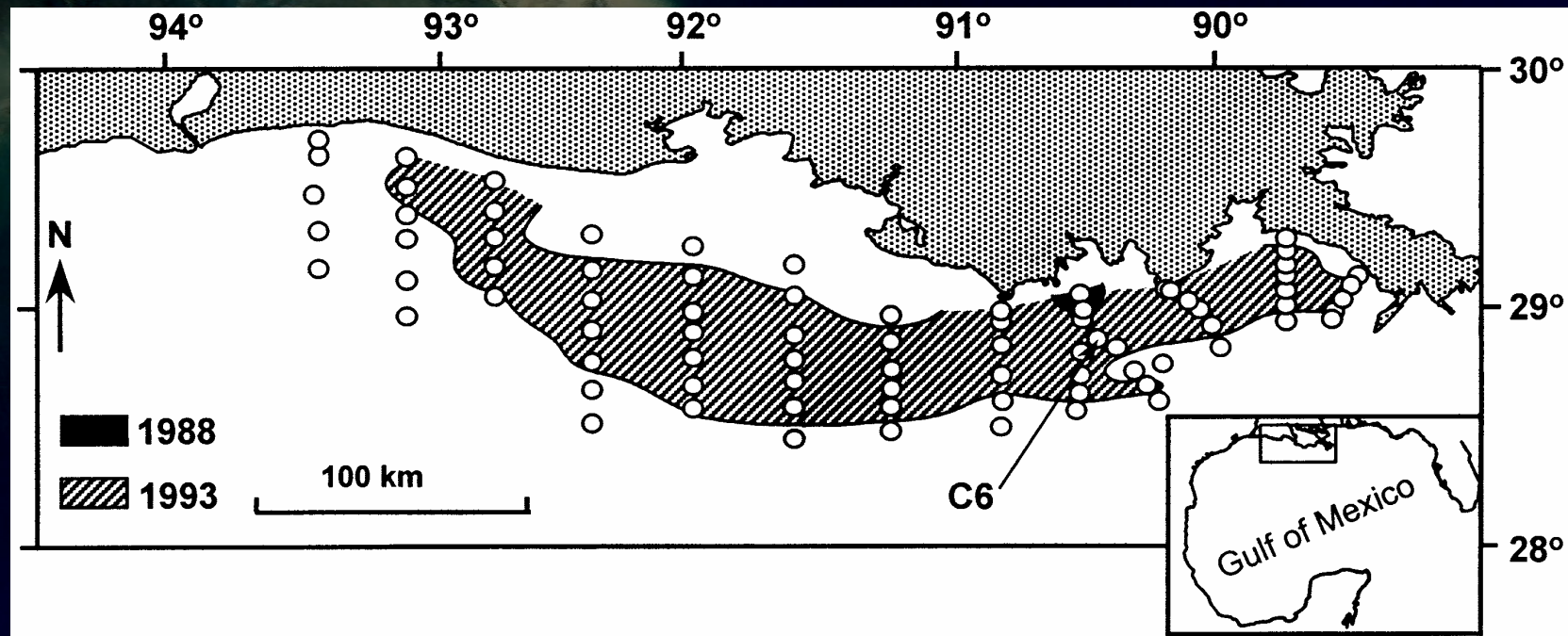
Vertical Flux, Sinking, Burial

- Sediment Metabolism Model (Rowe et al., 2002)



Vertical Flux, Sinking, Burial

- High sedimentary oxygen demand driven by sustained high nutrient loading (Turner et al., 2008)



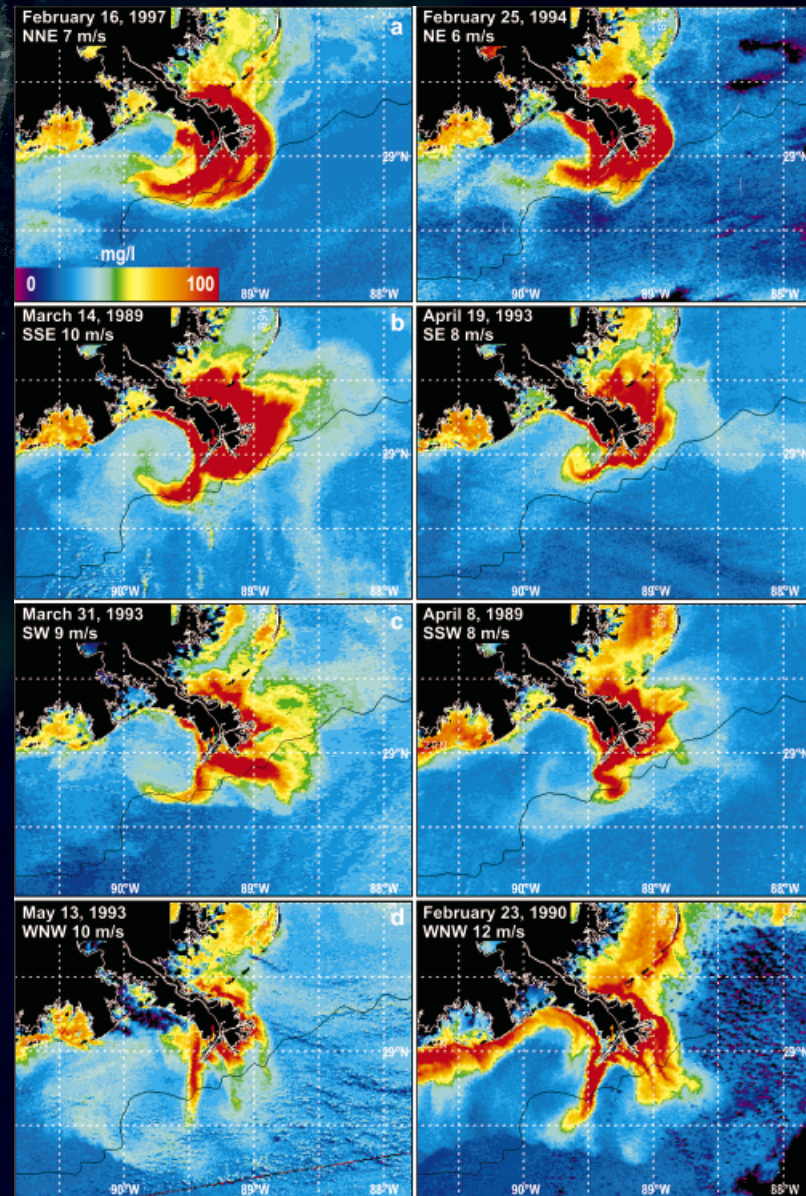
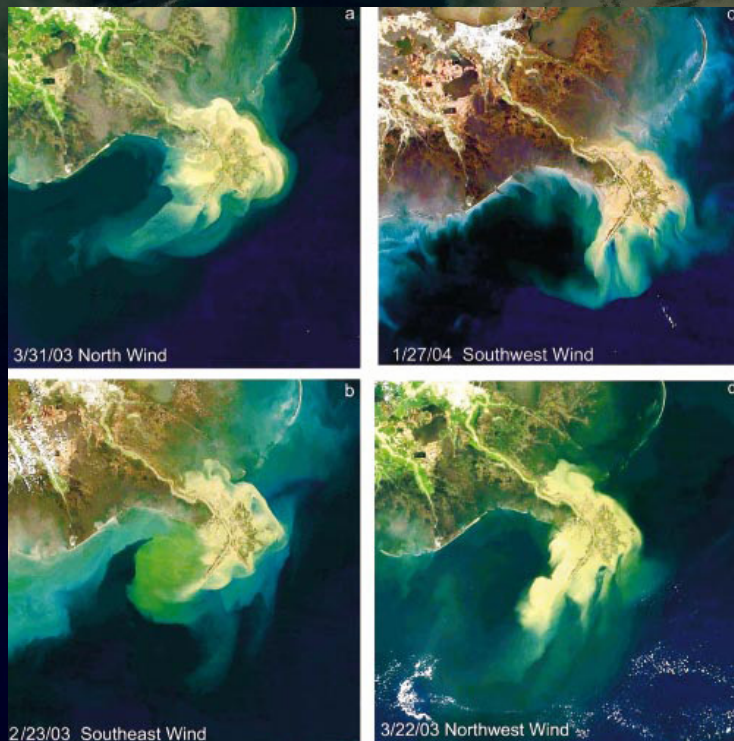
A satellite image of a coastal region, likely the Mississippi River delta, showing a complex network of waterways and land. The text is overlaid on the right side of the image.

Shelf/Ocean Exchange

- Eddy Interactions/wind driven upwelling
 - *Nowlin et al., 2000; Muller-Karger et al., 2000*
- Baroclinic eddies (Sutyrin et al., 2003)
- Barotropic intrusions (DeSoto Canyon, Yuan, 2002)
- In vicinity of Mississippi River, shelf exchanges generally thought to result in net export of inorganic nutrients and organic matter due to high gradients (Dagg and Breed, 2004)
- Significance to overall carbon and nutrient budgets not well quantified

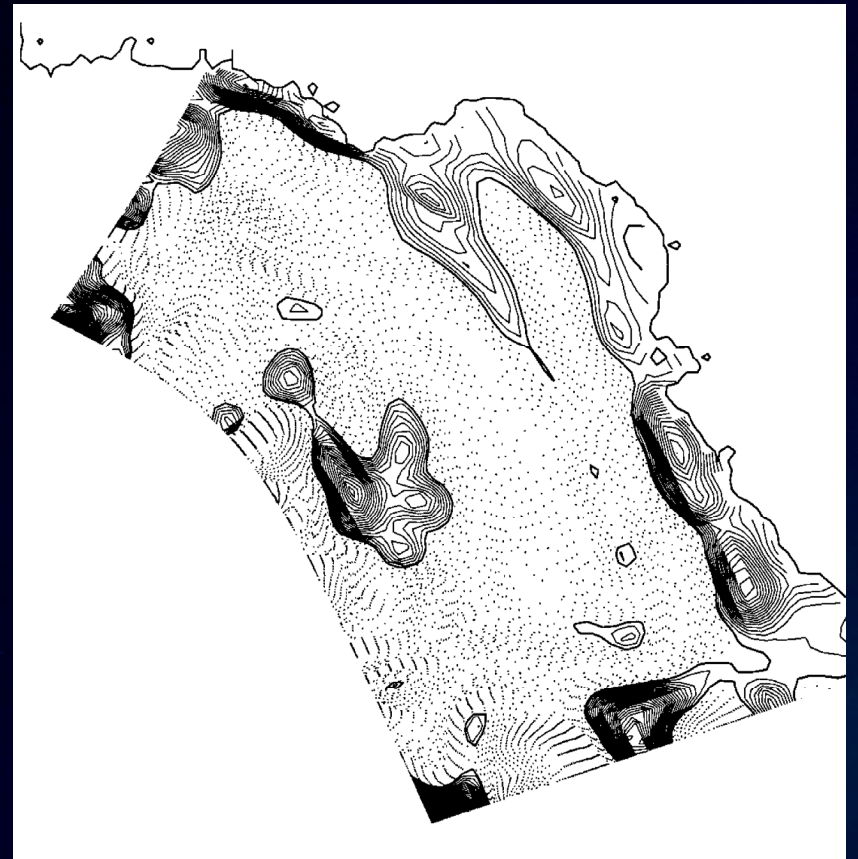
Shelf/Ocean Exchange

- Differences in TSS transport as a function of wind forcing (Walker et al., 2005)



Shelf/Ocean Exchange

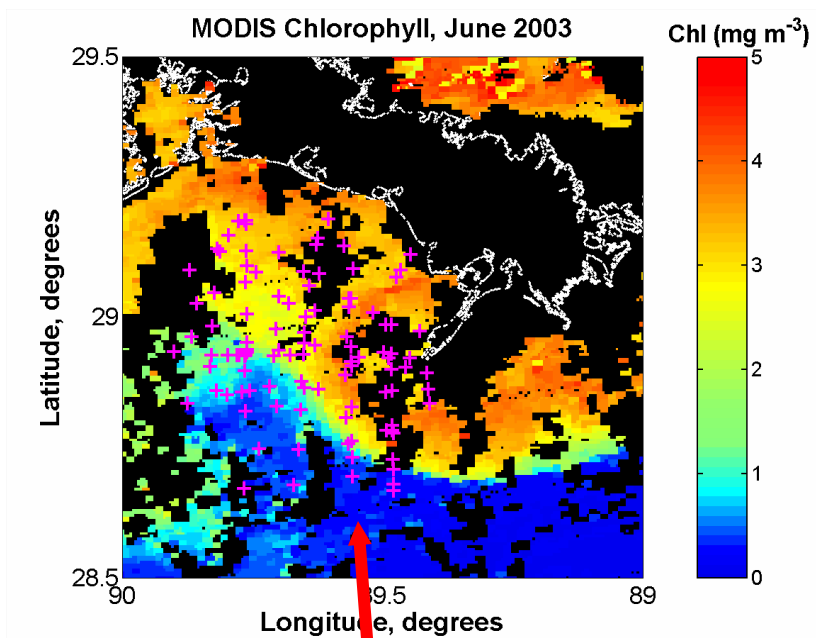
- Coastal Circulation/Upwelling
 - *Weisberg et al., 2000 – importance of bottom bathymetry to pattern of upwelling*



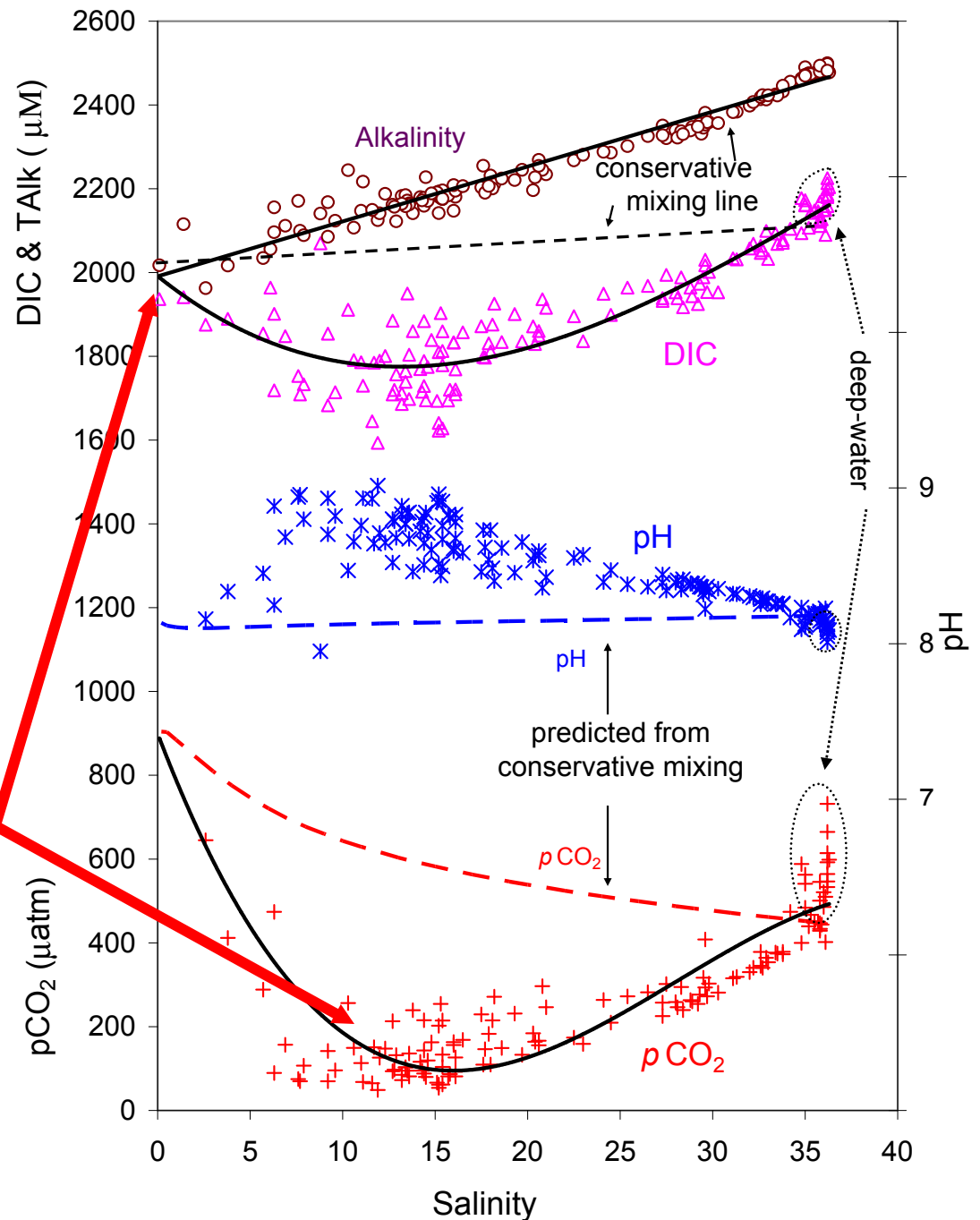
An aerial photograph of a coastal region, likely the Gulf of Mexico near Louisiana. A large, turbid, brownish plume of water extends from the coast into the darker blue ocean. The plume has a complex, branching shape. The coastline is visible with some green land and marshes. The title 'Air-Sea Flux' is overlaid in white text on the upper part of the image.

Air-Sea Flux

- Evidence that river-influenced Louisiana coastal waters are a local net sink for atmospheric carbon
 - *Nutrient enhanced productivity approximately balanced by nutrient flux (Lohrenz et al., 1997)*
 - *Justic et al. (1996) estimated 47% of net organic production was respired in lower waters*
 - *Areal integrated biological uptake rates of 130–190 mmol m⁻² d⁻¹ in plume (Cai, 2003)*

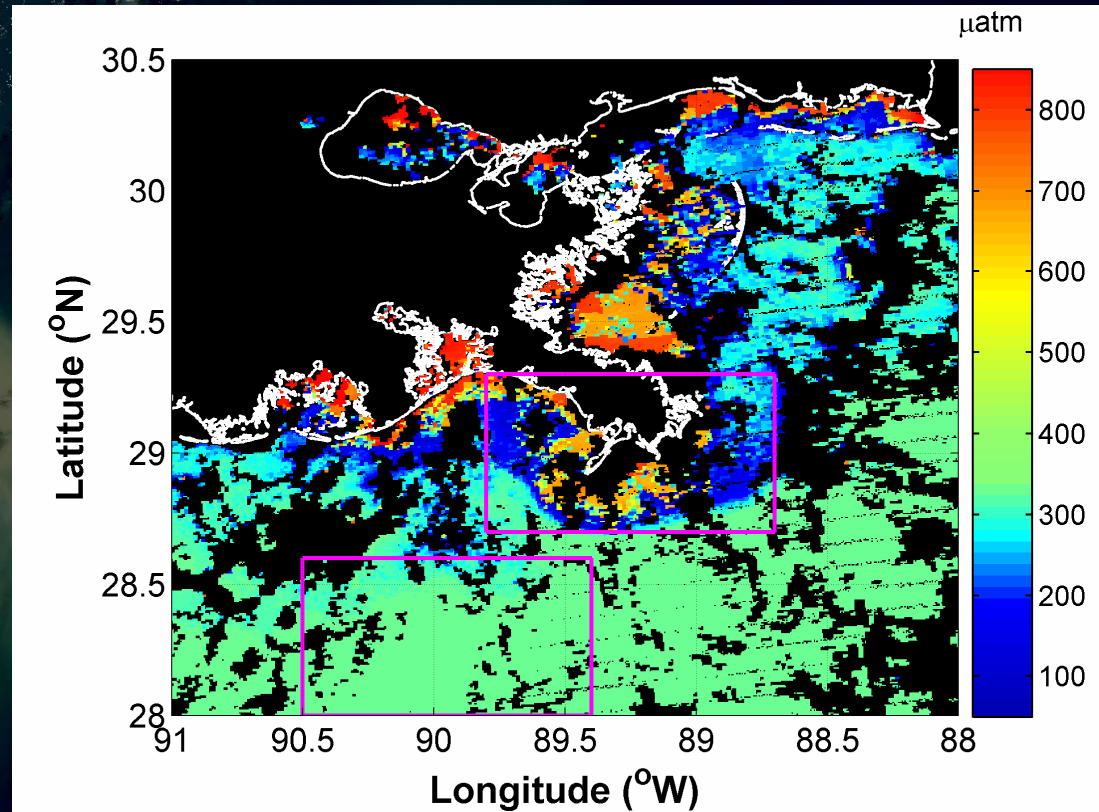


- Surface mapping (June 24-31, 2003) of the Mississippi plume and surrounding shelf
- High biological uptake of CO_2 and great variability in this system
- High alkalinity of Mississippi River imparts a strong buffering capacity to outflow waters



Air-Sea Flux

- Using a satellite based approach, Lohrenz and Cai (2006) estimated net CO₂ uptake during summer of 2.0–4.2 mmol C m⁻² d⁻¹



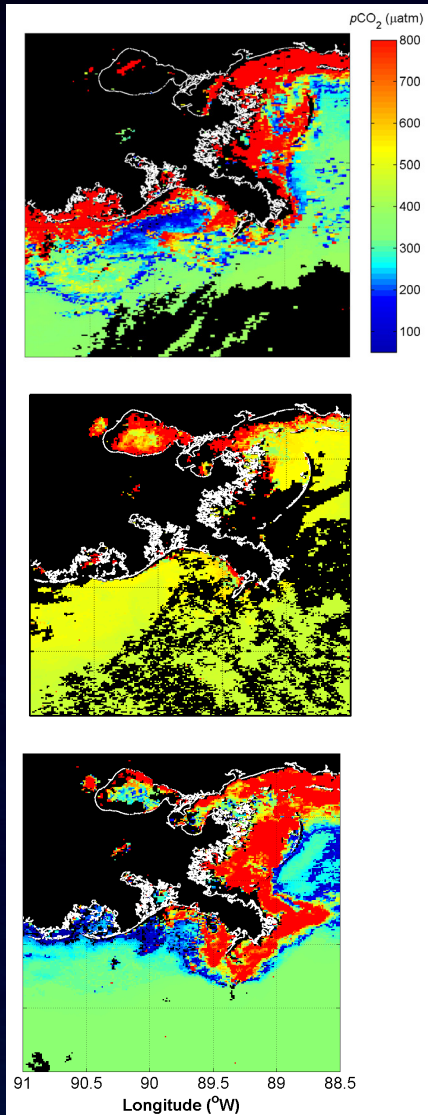
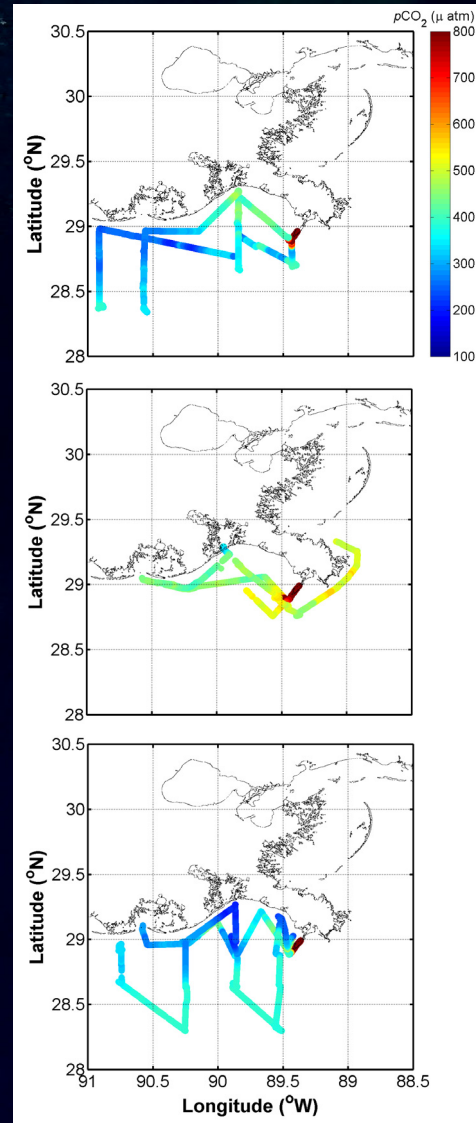
Air-Sea Flux

- Subsequent studies have revealed high variability related to discharge and seasonal conditions (Cai et al.; Lohrenz et al., in prep)
- High inshore values represent a potentially important and variable signal
- Estimated fluxes vary from -3.7 - > 100 $\text{mmol C m}^{-2} \text{ d}^{-1}$

Aug 2004

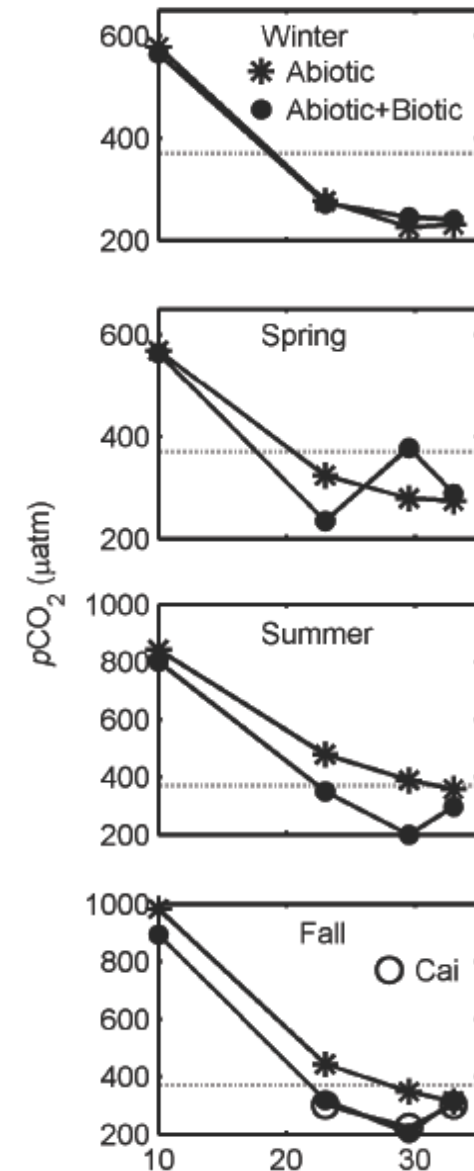
Oct 2005

Apr 2006



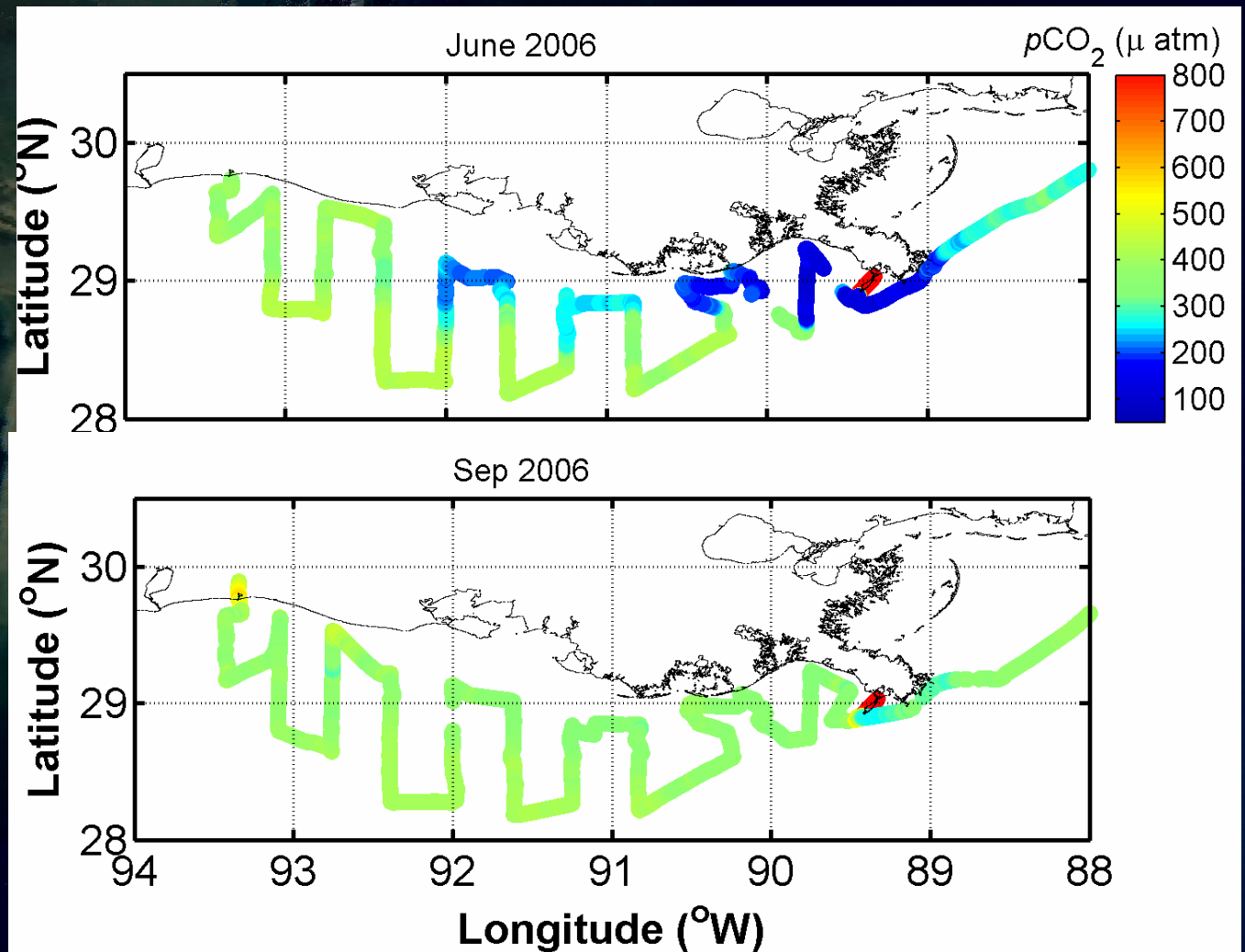
Air-Sea CO₂ Flux

- Modeled $p\text{CO}_2$ along the salinity gradient of the Mississippi River for different seasons as influenced by abiotic mixing along versus including biotic transformations of carbon (from Green et al., 2006).



Air-Sea Flux

- Larger surveys reveal consistent pattern of reduce $p\text{CO}_2$ in late spring and early summer

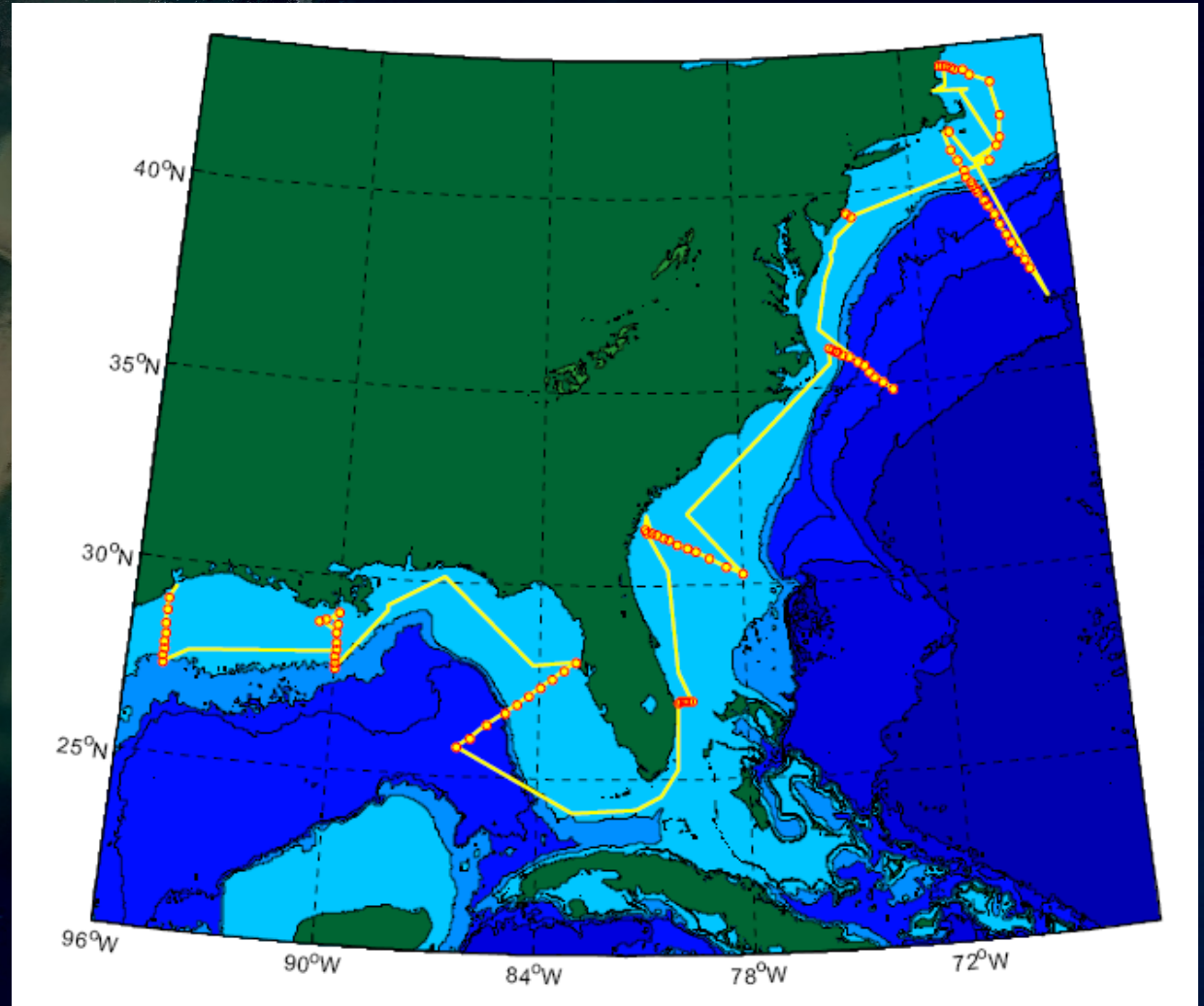


Air-Sea Flux

- West Florida shelf
 - *Lagrangian study in April 1996 showed remineralization exceeded primary production based on increases in DIC (Wanninkhof et al., 1997)*
 - *Community respiration rates from the tracer patch provided evidence that heterotrophs dominated the community following an episodic bloom (Hitchcock et al., 2000)*
 - *Walsh et al. (2003) model generated net source of CO₂ during spring and summer and net sink in fall*

Air-Sea Flux

- Gulf of Mexico and East Coast Carbon Cruise (GOMECC)



Air-Sea Flux

- **MAGMIX**

<http://www.stpt.usf.edu/coas/espg/magmix/home.asp>



Emerging Research Topics

- Understanding of the fate of the large input of organic carbon and associated carbon and nutrient cycling remains limited
 - *Comparisons of Atchafalaya and Mississippi and other major river systems such as the Mobile, Suwannee, etc. might be appropriate (relatively little is known about the Atchafalaya and its impact on the shelf ecosystem, cf. Dagg et al., 2007)*
- Role of coastal wetlands as a source of OM export (i.e., outwelling) as observed in SAB remains limited
- Role of denitrification, nitrification, DNRA, and N fixation rates in nutrient cycling and impact on C processes
- Understanding of benthic processes, including mechanisms related to sediment transport, mineral preservation, and reworking of organic matter
- General importance of changes in calcification and carbonate preservation in the overall inorganic carbon cycle
- Better constraints on air-sea flux of carbon dioxide and its variability in different regions
- Better understanding of the physical dynamics of coastal circulation contributing to coastal-ocean exchange and ventilation of sub-pycnocline waters is needed
- Understanding of linkages of freshwater constituent concentrations and composition to watershed properties remains limited
- Effects of climate change on sea level, precipitation, and river discharge will require integrated study



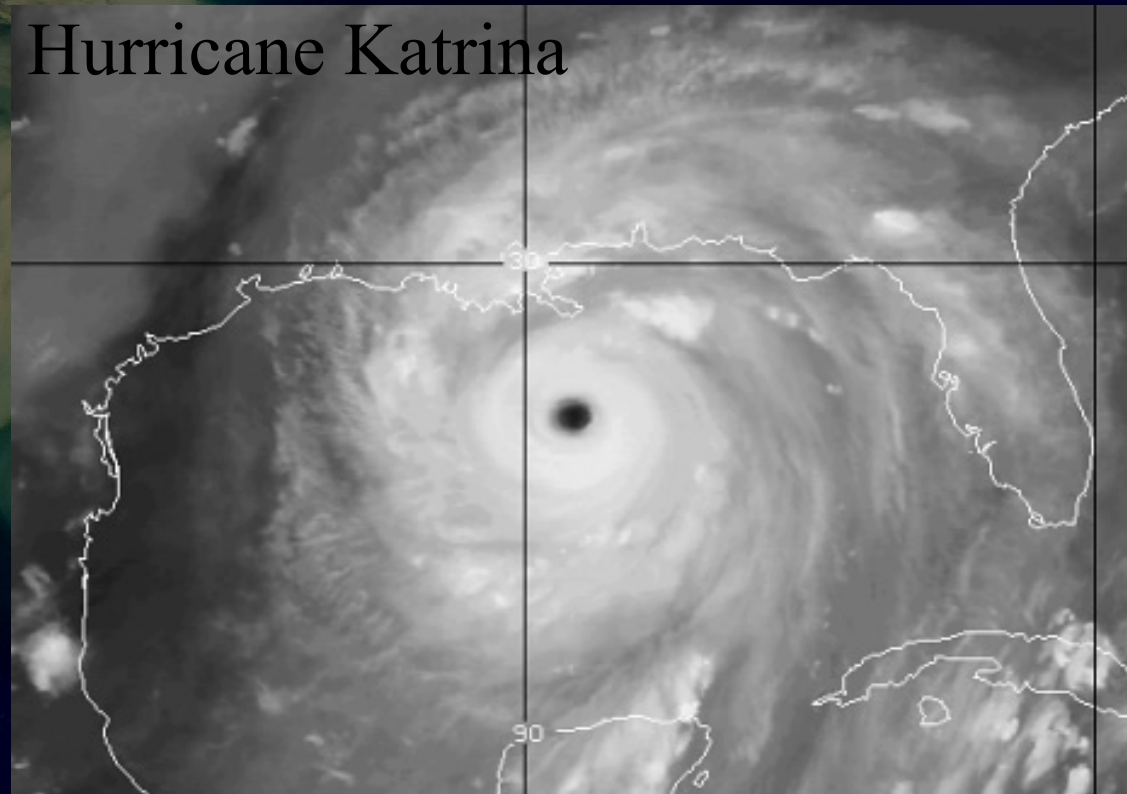
Acknowledgements

- Funding for this work was provided by NASA (NNG05GD22G and NNS04AB84H) and NSF (OCE-0752254)
- Thanks to the many colleagues who provided material for this presentation

Dominant Forcings

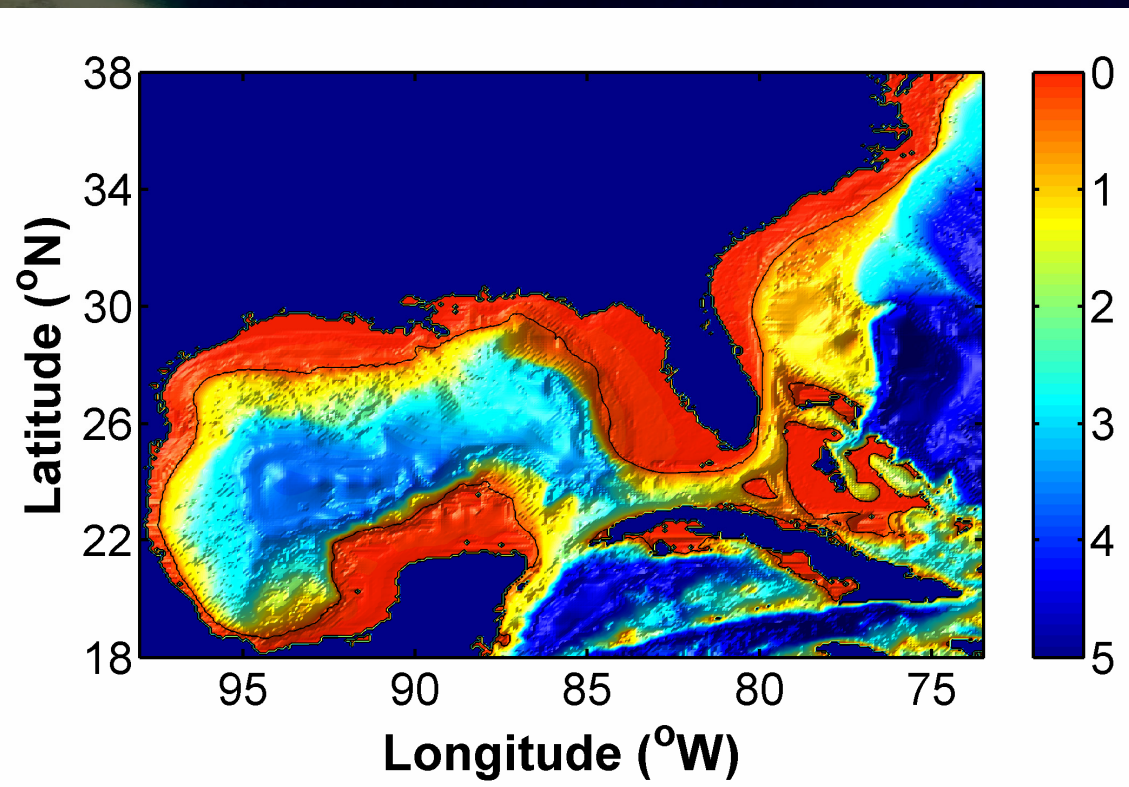
- Tropical Storm Events/Other Extreme Weather Events

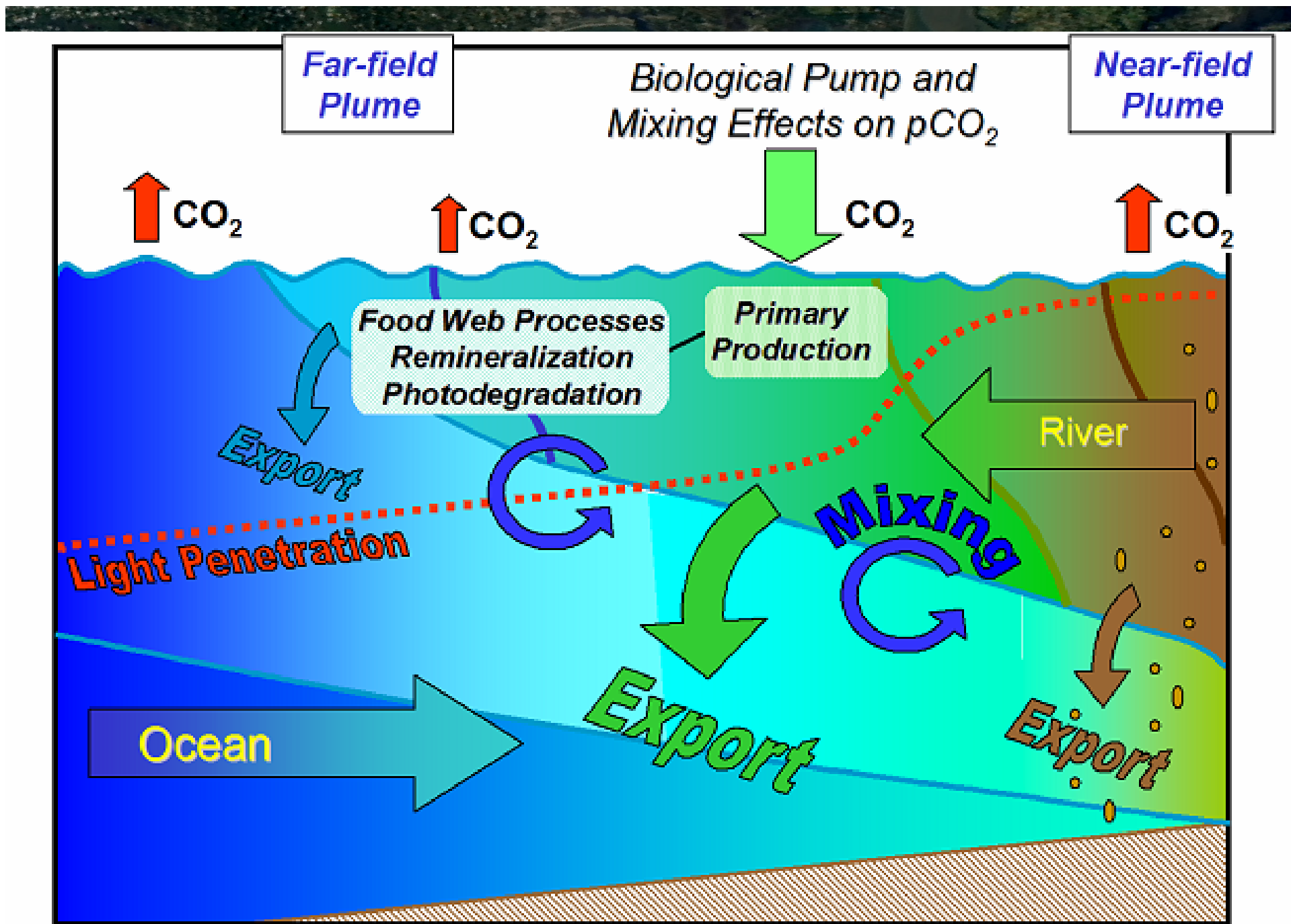
Hurricane Katrina



Gulf of Mexico

- Semi-enclosed basin (U.S. portion of coastline, about 2600 km or roughly one third of the conterminus U.S.)





Reimers et al., 2004 (CBED Workshop)

