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>
<thead>
<tr>
<th>C flux (Tg/yr)</th>
<th>Range (Tg C yr(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Riverine Carbon Input to the Ocean</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolved Inorganic Carbon (DIC)</td>
<td>450</td>
<td>381-410</td>
</tr>
<tr>
<td>Total Organic Carbon (TOC)</td>
<td>450</td>
<td>200-530</td>
</tr>
<tr>
<td>Particulate Organic Carbon (POC)</td>
<td>200</td>
<td>138-288</td>
</tr>
<tr>
<td>Dissolved Organic Carbon (DOC)</td>
<td>250</td>
<td>214-360</td>
</tr>
<tr>
<td><strong>Terrestrial Storage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>600-1500</td>
</tr>
<tr>
<td><strong>Burial in Marine Sediments</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terrestrial</td>
<td>130</td>
<td>98-138</td>
</tr>
<tr>
<td>Marine</td>
<td></td>
<td>43-104</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
</tr>
</tbody>
</table>

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\(^1\)Meybeck, 1993  
\(^2\)Meybeck and Vörösmarty, 1999  
\(^3\)Degens et al., 1991  
\(^4\)Spitzy and Ittekkot, 1991  
\(^5\)Schlunz and Schneider, 2000  
\(^6\)Lyons et al., 2002 (and references within)  
\(^7\)Ittekkot and Laane, 1991  
\(^8\)Spitzy and Leenheer, 1991  
\(^9\)Aitkenhead and McDowell, 2000  
\(^10\)Hedges et al, 1997  
\(^11\)Stallard, 1998  
\(^12\)Berner, 1982  
\(^13\)Hedges and Keil, 1995  
\(^14\)Berger et al., 1989  

RiOMar report, (McKee et al., 2003)
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 CO₂ 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
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
Terrestrial Inputs:
- 5.5 OC Tg a\(^{-1}\)
- 0.3 PIC Tg a\(^{-1}\)
- 21 DIC Tg a\(^{-1}\)

OC Burial: 0.5-1.0 Tg a\(^{-1}\)

Shelf Area (US GOM): 1.56 x 10\(^5\) km\(^2\)

PP=30-550 (~150) g m\(^{-2}\) a\(^{-1}\)
=23 Tg a\(^{-1}\)

R=~11-? Tg a\(^{-1}\)

Air-Sea Flux of CO2: -2 - >70 Tg a\(^{-1}\)

Shelf/Ocean Exchange: ?
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)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration (mM)</th>
<th>Annual Flux Tg y(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSM</td>
<td>---</td>
<td>210(^3)</td>
<td>Meade and Parker (1985)</td>
</tr>
<tr>
<td>POC</td>
<td>1.6% of TSM</td>
<td>3.4</td>
<td>Trefry et al. (1994)</td>
</tr>
<tr>
<td>DOC</td>
<td>0.28</td>
<td>1.2(&amp;)</td>
<td>Duan and Bianchi 2006</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>2.1</td>
<td>Trefry et al. (1994)</td>
</tr>
<tr>
<td></td>
<td>0.49</td>
<td>3.1</td>
<td>Benner and Opsahl 2001</td>
</tr>
<tr>
<td></td>
<td>0.15% of TSM</td>
<td>0.31</td>
<td>Bianchi et al. 2004</td>
</tr>
<tr>
<td>PIC</td>
<td>0.219</td>
<td>21*</td>
<td>Trefry et al. (1994)</td>
</tr>
<tr>
<td>DIC</td>
<td>0.216</td>
<td>1.57</td>
<td>Cai (2003); Raymond and Cole (2003)</td>
</tr>
<tr>
<td></td>
<td>0.219</td>
<td>21*</td>
<td>Goolsby et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>0.219</td>
<td>21*</td>
<td>Goolsby et al. (1999)</td>
</tr>
<tr>
<td>TAlk</td>
<td>0.216</td>
<td>1.57</td>
<td>Cai (2003); Raymond and Cole (2003)</td>
</tr>
<tr>
<td></td>
<td>Total Nitrogen (N)</td>
<td>1.57</td>
<td>Goolsby et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>NO(_3^+) NO(_2^-)</td>
<td>0.95</td>
<td>Goolsby et al. (1999); Howarth et al. (1996)</td>
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<td></td>
<td>Ammonium</td>
<td>0.03</td>
<td>Goolsby et al. (1999)</td>
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<tr>
<td></td>
<td>Dissolved Org. N</td>
<td>0.38</td>
<td>Goolsby et al. (1999)</td>
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<tr>
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<td>Particulate Org. N</td>
<td>0.20</td>
<td>Goolsby et al. (1999)</td>
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<td>Particulate Org. N</td>
<td>0.45*</td>
<td>Trefry et al. (1994)</td>
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<tr>
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<td>Total Phosphorus (P)</td>
<td>0.136</td>
<td>Goolsby et al. (1999)</td>
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<tr>
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<td>PO(_4^-)</td>
<td>0.042</td>
<td>Goolsby et al. (1999)</td>
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<td>Particulate P</td>
<td>0.095</td>
<td>Goolsby et al. (1999)</td>
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<td></td>
<td>Si-dissolved</td>
<td>2.32</td>
<td>Goolsby et al. (1999)</td>
</tr>
</tbody>
</table>
Mississippi nutrient fluxes (Cai and Lohrenz, 2007)
- Increase in NOx flux, especially during 1970s
- NOx: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)
Terrestrial Inputs

- CDOM/DOC

DelCastillo and Miller, 2007
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

- Mobile Bay
  - Average of >2,245 m³ s⁻¹ daily freshwater inflow
  - Dissolved inorganic nutrient concentrations closely related to freshwater discharge (predominantly the Alabama and Tombigbee Rivers) (Pennock et al. 1992)
  - Average DIN is about 14 μM (Pennock et al., 1999), lower during low flow months
  - DON makes up 40% of the total nitrogen; particulate phosphorus comprises 75% of the total phosphorus (Pennock et al., 1999)
  - Association between watershed agricultural activities and streams in drainage basin (Harned et al., 2004)
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)
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

Next we consider transformation and fate of carbon and associated elements:

- Primary production
- Remineralization
- Photodegradation
Transformation and Fate

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

![Graph showing the relationship between Integrated PP (mol C m⁻² d⁻¹) and NO₃ + NO₂ Flux at SW Pass (10⁶ mol N d⁻¹), with the equation PP = 0.0026(N flux) + 0.0083 and r² = 0.411.](image-url)
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 gC m\(^{-2}\) y\(^{-1}\) (Lohrenz and Verity, 2004)
- In the northwestern Gulf of Mexico, primary production was lower, averaging 160 gC m\(^{-2}\) 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 gC m\(^{-2}\) 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)
Carbon Cycling

Modified from EDOCC Report, 2001
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 \((136-159 \times 10^9 \text{ mol y}^{-1})\), 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)
• 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)
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 g C m\(^{-2}\) d\(^{-1}\) in spring, but lower during other seasons (0.29–0.95 g C m\(^{-2}\) d\(^{-1}\)) and away from the plume (0.18–0.40 g C m\(^{-2}\) d\(^{-1}\))
    › Qureshi, 1995: 0.50 and 0.60 g C m\(^{-2}\) d\(^{-1}\)
Vertical Flux, Sinking, Burial

Eadie et al., 1994; Rabalais et al., 1996
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)
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
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 CO₂ 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 CO$_2$ uptake during summer of 2.0–4.2 mmol C m$^{-2}$ d$^{-1}$. 
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 mmol C m² d⁻¹.
Air-Sea CO2 Flux

- Modeled $pCO_2$ 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).
Larger surveys reveal consistent pattern of reduced $pCO_2$ 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

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• 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 conterminous U.S.)
From Gruber et al., 2004; Sabine et al. 2004