Anthropogenic and Natural Effects on the Biogeochemistry of Organic Carbon Cycling in a River-Dominated Margin: The Mississippi River System

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Seminar Outline

•Brief overview the global importance of river-dominated margins (RiOMar)

•Controls of the temporal and spatial dynamics of POM and DOM in the upper and lower Mississippi River (MR)

•Sources and transport of terrestrially-derived organic carbon along the LA coast

Important Questions for Workshop

Collaborators

- Brent McKee (UNC) radionuclides
- Mead Allison (UT) seismic analysis and sedimentology
- Martha Sutula and Rebecca Green (ONR) nutrients and carbon cycling
- •Sid Mitra (ECU) organics
- •Nianhong Chen (postdoc at ODU), Shuiwang Duan (potsdoc at TAMUG), Bryan Grace, Troy Sampere, Laura Wysocki, - (Tulane, EES, graduate students) - chemical biomarkers (pigments, lignin), and bulk C, N, measurements

The Mississippi-Atchafalaya River System and Louisiana Shelf: A River-Dominated Margin (RiOMar)



River-Dominated Ocean Margins (**RiOMars**)



Most of the terrestrial materials (organic carbon, macronutrients, micronutrients, major/minor elements, mineral matter) transported to the oceans enter via these margin environments







The World's Twelve Largest Rivers

Sediment Discharge

Water Discharge

	River	Discharge (10^6 t y^{-1})	River	Discharge $(10^9 \text{ m}^3 \text{ y}^{-1})$
1.	Amazon	1000-1300	1. Amazon	6300
2.	Yellow (Huanghe)	1100	2. Zaire	1250
3.	Ganges/Brahmaputra	900-1200	3. Orinoco	1200
4.	Yangtze (Changjiang)	480	4. Ganges/Brahmaputra	970
5.	Irrawaddy	260	5. Yangtze (Changijang)	900
6.	Magdalena	220	6. Yenisev	630
7.	Mississippi	210	7 Mississinni	530
8.	Godavari	170		510
9.	Red (Hunghe)	160	o. Lena	310
9.	Mekong	160	9. Mekong	4/0
10	. Orinoco	150	9. Parana/Uruguay	470
11	Purari/Flv	110	10. St. Lawrence	450
12	MacKenzie	100	11. Irrawaddy	430
14	. 111011011210	100	12. Ob	400

The Mississippi River and its Tributary Drainage Basins





Day et al. (2007), as modified from Boyd and Penland (1988)



Figure 5: Modelled surface salinity showing the freshwater plumes from the Atchafalaya and Mississippi Rivers during upwelling favorable winds (top panel) and during downwelling favorable winds 8 days later (bottom panel). Adapted from Hetland and DiMarco (2007).

Hetland and DiMarco (2008)

Regional Distinctions



Figure 7: An illustration depicting different zones (Zones 1-4, numbered above) in the NGOM during the period when hypoxia can occur. These zones are controlled by differing physical, chemical, and biological processes, are variable in size, and move temporally and spatially. Diagram created by D. Gilbert.

Modified from Rowe and Chapman (2002)

Historical Changes in the Suspended Particulate Matter and Nitrate Concentration in the Lower MR



SPM concentrations decreased from 800 mg L^{-1} in 1950s to 250 mg L^{-1} in 1990s due to dam construction in the upper river. Average nitrate concentrations increased from 0.6 to 0.7 mg L⁻¹ in 1950s to the present level of about 1.5 mg L⁻¹ because of utilization of chemical fertilizers.

Discharge Patterns of Mississippi, Ohio, and Missouri Rivers



USGS data from Duan and Bianchi (2006)

Particulate Organic Carbon and Chlorophyll-a



Table 1 Comparation of Chl-a concentration in MR, PR with other aquatic systems				
	Range (uM)	Average(uM)	Source	
Lower Mississippi	0.8 - 23.6	7.1	This study	
Pearl	0.8 - 10.7	3.4	This study	
Columbia (USA)	1.1 - 22.2		Sullivan et al. 2001	
Ohio (USA)	1.1 - 17.7		Sellers and Bukaveckas, 2003	
MR Plume	0.44 - 31.1	3.2/6.9	Wysocki, et al., 2005	
Lake Pontchartrain (U	0.3 - 7.7	2.6	Bianchi and Argyrou, 1997	
Plumes in Baltic Sea		6.5-13.1	Wasmund et al., 1999	
Suwannee (USA)	< 0.1			
Amazon	0.17-2.38		Saliot et al., 2001	

Phytoplankton Abundance in Primary Tributaries of the MR

(EPA-EMAP, 2004)

Likely due to export of phytoplankton biomass from backwater reservoirs, navigation locks, and wetlands of tributaries during high-flow periods. Duan and Bianchi (2006)



Controls on Temporal and Spatial Dynamics of POM and DOM in the Upper and Lower Mississippi River (MR)

Temporal Sampling

Major river systems in the United States

The Mississippi is the Nation's most important waterway



Source: Prepared by the Economic Research Service.



Mississippi River Sampling : Sept.2001-August 2003 Duan and Bianchi (2006)

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Phytoplankton Composition

Mississippi River



High-Molecular Weight (> 1 kDa) (colloidal) and Low Molecular (< 1 kDa) Organic Carbon



HMW DOC: 82 ± 26 μM; 25 ± 6%; LMW DOC: 236 ± 45 μM; 75 ± 7 %

Duan et al. (2007)

Mean molecular weight in the MR was lower than expected based on other studies. However, this is consistent with size continuum concept (Amon and Benner, 1996) whereby *in-situ* processing decreases OM size. Tilling activity in agricultural watershed blocks formation of large molecules (e.g. humic substances) producing more LMW DOM in runoff (Dalzell et al., 2005).

¹³C-NMR and Lignin Analysis of HMW DOM





Duan and Bianchi (2006); Duan et al. 2007)

Amino Acids and Bacterial Activity





Spatial Sampling



June 20-24, 2003

During June 2003, a period of mid-level discharge (17,400 m⁻³ s⁻¹), a parcel of water in the lower Mississippi River was sampled every 2 h during its 4 d transit from river-mile 225 near Baton Rouge, Louisiana, USA to river-mile 0 at Head of Passes, Louisiana, USA.



Dagg et al. (2006)

Transect of Chlorophyll-*a* and Dominant Carotenoids in lower MR





Dagg et al. (2006)

DOC in the Mississippi River From Headwater to Head of Passes



Duan et al. (2007)

- DOC gradually decreases, most of the decrease occurred in upper MR (by 30-48%), very little (6-8%) in lower river
- Large decrease in DOC below the confluence of the Missouri River and Ohio River, likely from dilution effect and *in-situ* processing

Are dissolved and particulate constituents transformed in lower MR in the presence of the salt wedge during low discharge stages? Recharge of dissolved porewater constituents in lower Mississippi River sediments



Porewater concentrations of diagenetic products at a lower river location collected before (May) and during (November) a depositional period



Biogeochemical Dynamics at the Salt Wedge



ITBL – Intensely turbulent boundary layer

Photochemical Breakdown of Lignin



Opsahl and Benner (1998)

Mean Global Fluvial Loadings of Organic Carbon to the Oceans

Reference	DOC	POC	TOC	
Smith and Hollibaugh (1993)	164	197	386	
	Uni	$its = 10^{11} mol C$	yr-1	
Mean Annual Fluvial Loadings of Organic Carbon from the Mississippi River				
the	Mississippi Riv	er		
the	Mississippi Riv	er POC	ТОС	
the	Mississippi Riv DOC 3.0 (62%)	er <u>POC</u> 1.8 (38%)	TOC 4.8	

Units = 10^{11} mol C yr⁻¹

Bianchi et al. (2004, 2007)

Diversity and Magnitude of Organic Matter Sources and Loading



Nearshore diatom sources?

Chlorophyll-a



Fucoxanthin



Wysocki et al. (2006)

Coastal Wetland Inputs





Note: With the projected gain, the net loss from year 1956 to 2050 is estimated to be 2,038 sq mi (5,278 sq km) whereas without the projected gain, the estimated total loss amounts to 2,199 sq mi (5,695 sq km).

Barras et al. (2003)

Chen and Gardner (2004) reported significant outwelling of chromophoric dissolved organic matter (CDOM) from wetlands

Deposition Across the Shelf/Slope Margin



Gordon and Goni (2004)



Gordon and Goni (2003)

Using three parameters to define each end-member – total lignin as Λ (mg lignin 100mg OC⁻¹), N/C ratio, and $\delta^{13}C$ – the proportional contributions were calculated as follows:

$$\delta^{13}C \text{ sample} = (\delta^{13}C_{mar}*OC_{mar}) + (\delta^{13}C_{marsh}*OC_{marsh}) + (\delta^{13}C_{river}*OC_{river})$$
(Eq. 1)

$$\Lambda \text{ sample} = (\Lambda_{mar}*OC_{mar}) + (\Lambda_{marsh}*OC_{marsh}) + (\Lambda_{river}*OC_{river})$$
(Eq. 2)

$$N/C \text{ sample} = (N/C_{mar}*OC_{mar}) + (N/C_{marsh}*OC_{marsh}) + (0.033*OC_{river})$$
(Eq. 3)

	$\delta^{13}C$	Λ	N/C
marine	-19.50‰ ¹	0.00	0.15^{2}
marsh	-17.89‰ ³	4.30 ⁴	0.06^{4}
mean river	-24.78‰ ⁵	1.35 ⁵	0.105
spring river	-25.13‰ ⁵	1.405	0.105
fall river	-24.06‰ ⁵	1.195	0.115
¹ Eadie et al, 1	994		

² Redfield values; C/N = 6.6

³ J. Willis, LSU; personal communiction

⁴ samples analyzed for this study

⁵ Bianchi et al, 2007b

Wysocki et al. (submitted)

where,

 OC_{mar} is the proportion of OC that is derived from marine organic matter, OC_{marsh} is the proportion derived from marsh OM, and OC_{river} is the proportion that is derived from riverine OM.











Wysocki et al. (submitted)



Radiocarbon ages of this peat material ranged from 2,140 to 4,210 yr BP in to 32,580 yr BP in Pleistocene clay layers below.

Galler et al. (2003)



Decreases in the extent of relict outcropping downstream is due to the seaward dip of the layer caused by it overlaying the dipping continental shelf.

Galler et al. (2003)

Rates and Efficiency Organic Matter Diagenesis in Mobile Muds





Diagenesis in Mobile Muds

Aller (1998)



Aller and Blair (2006)





Transport of Mobile Muds



Chen et al. (2005)



(Aller, unpublished)





Heterotrophy in Mobile Muds



Aller and Aller (1994, 2006); Aller andn Stupekoff (1996)

Louisiana Shelf Benthos

Sites and Dates	$\begin{array}{c} Macrofauna \\ (g \ C \ m^{-2}) \end{array}$	$\begin{array}{c} \text{Meiofauna} \\ \text{(g C } m^{-2}) \end{array}$	Bacteria (g C m ⁻² 8 cm depth)	Total Biomass $(g C m^{-2})$
July 1991				
Č6A (1)	0.68	1.1	2.67	4.45
C6B (1)	0.16	0.43	7.12	7.71
C7 (1)	0.56	0.76	30.49	31.81
D2 (1)	0.11	0.21	22.22	22.54
Mean biomass	0.38 ± 0.29	0.66 ± 0.34	15.6 ± 12.9	16.7 ± 12.9
April 1991				
GC1	0.23 ± 0.62 (4)	0.37 ± 0.08 (2)	1.67	2.3
4	0.01 ± 0.01 (3)	0.55 ± 0.51 (2)	4.18	4.7
C6A	1.24 ± 0.7 (3)	0.55 ± 0.3 (2)	1.72	3.5
D2	0.49 (1)	0.07 ± 0.03 (2)	1.85	2.4
Mean biomass	0.49 ± 0.54	0.38 ± 0.23	2.36 ± 1.22	2.81 ± 0.99
August 1994				
1	0.19 ± 0.18 (3)	_	2.81 ± 1.1 (3)	3.4
2	0.20 ± 0.18 (3)	_	3.41 ± 1.1 (3)	3.7
3	0.11 ± 0.07 (3)	_	3.8 ± 1.1 (8)	4.0
4	0.12 ± 0.1 (3)	_	2.6 ± 1.3 (8)	2.8
C6B	0.04 ± 0.01 (3)		1.7 (1)	1.8
Mean biomass	0.15 ± 0.1	0.09 ± 0.1	3.1 ± 0.9	3.1 ± 0.9





Rowe et al. (2002)

Fig. 1. Map of northern Gulf of Mexico showing the location of the sites studied.

Benthic Macrofaunal Succession



Zajac (2001)



April range: $0 - 2 \mu g/g$ mean: 0.44 ± 0.09

October range: $0-12 \mu g/g$ mean: 1.75 ± 0.67

Wysocki et al. (2006)

Co-metabolism: the set of processes whereby refractory organic material (e.g. terrestrial OC) is broken down more efficiently when mixed with labile material (e.g. marine OC), via higher microbial turnover rates

Lohnis (1926); Canfield (1993); Aller (1998)



Diagenetic Models and Pyrite Storage



Fig. 11. Relationship between pyrice-S and organic carbon in sediments (Mississippi River delta-shelf-slope (\blacksquare), recarbon (\square), south-western (\square), and southern (\square) Gulf of Mexico sediments. The dashed lines represent a C/S ratio envelope of 2.8 ± 0.8.

Lin and Morse (1991)

Of the total pyrite deposition in the study are (ca. $6 \ge 10^{11} \ge y^{-1}$), about 81% is deposited in Texas-Louisiana continental shelf sediments and about 15% in the Mississippi River delta sediments.



Eldridge and Morse (2006); Morse and Eldridge (2008) Rapid Transport of Labile Shelf-Derived Organic Matter to the Mississippi River Canyon



Spatial Variability of Surface Depositional Processes



Fig. 6. Spatial distribution of the ⁷Be inventory demonstrates the importance of the river as its source and the potential of sediment remobilization during the winter. Inventories are shown for MiRIR I (A) and II (B) in dpm cm⁻². The apparent bull's eye in the near river contour during both cruises is due to exceedingly high inventories (>10 dpm cm⁻²) in several near river stations.

Corbett et al. (2004)

D. Reide Corbett et al. / Marine Geology 209 (2004) 91-112

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Gulf of Mexico Basin



Rapid Export of Organic Matter from the shelf to the Mississippi Canyon







Bianchi et al. (2006)

Transport of Terrestrial-Derived Organic Matter along Primary Depositional Pathways



Sampere et al. (2008)





B. Fatty Acid Methyl Esters

Waterson and Canuel (2008)

Historical Records of Hurricane in Louisiana Shelf Sediments



Sampere et al., submitted (JGR)

Effects Hurricane Lili on Organic Matter Distribution



Goni et al. (2006)

Important Issues for Workshop

Need a better understanding of the following:

- Importance of autochthonous production in the river, below the confluence, relative to inputs from tributaries and watershed
- Relative importance of the adsorption/desorption processes in the saltwedge on sedimentation and river fluxes to the coast
- Role of photochemical processes on net autotrophic/heterotrophic processes in the plume and in shallow-shelf regions, as related to overall carbon sequestration
- Fate and transport of river, wetland, and plume-derived organic matter across the shelf/slope to the canyon