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## Carbon burial on river-dominated continental shelves: Impact of historical changes in sediment loading adjacent to the Mississippi River

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[1] Seabed cores collected on the continental shelf adjacent to the Mississippi River show a direct temporal correlation between decreases in mass accumulation rate (factor of 2–3) and suspended sediment loads in the river. This mid 20th century decline is not apparent shelf-wide due to sediment focusing and biological seabed mixing. Total organic carbon diagenetic loss rate across this sediment age interval is relatively uninterrupted when corrected for the non-steady state mass flux. This suggests that organic carbon burial rates in oxic bottom water settings on river-dominated continental margins are directly proportional to lithogenic flux. Variations in OM remineralization rates due to changes in the composition (marine vs. terrestrial) of the particulate OM flux at the sediment surface are a second-order effect that cannot be distinguished in the bulk carbon sediment record at these oxic sites; although they may significantly alter the OM degradation-induced CO<sub>2</sub> flux to the overlying water column. **Citation:** Allison, M. A., T. S. Bianchi, B. A. McKee, and T. P. Sampere (2007), Carbon burial on river-dominated continental shelves: Impact of historical changes in sediment loading adjacent to the Mississippi River, *Geophys. Res. Lett.*, 34, L01606, doi:10.1029/2006GL028362.

### 1. Introduction

[2] Recent climate change models [*Intergovernmental Panel on Climate Change*, 1996] suggest that continued global warming will likely induce latitudinal changes in precipitation and storm intensity, with associated alterations in continental weathering rates. These models also predict runoff will increase for 75% of the world's major rivers but decrease for some low latitude systems [*Miller and Russell*, 1992], which will likely result in changes to oceanic inputs of mineral particles and dissolved and particulate organic matter (OM). Large rivers are particularly important in this scenario as they carry an inordinate percentage of freshwater and particulates to the oceans (the top 25 rivers supply approximately 50% of the freshwater and 40% of the fluvial sediment [*Milliman and Meade*, 1983; *Meade*, 1996]) and changes in loading will be more readily recognizable in large drainage basins that integrate precipitation and weathering on a continental scale. Large point source inputs of

water and sediment to continental margins are also important loci for carbon production, remineralization and burial (continental margins are the site for 80–85% of global carbon burial [*Berner*, 1982; *Hedges and Keil*, 1997]), although their net effect on the global carbon budget remains unresolved [*McKee*, 2003]. The uncertainties about carbon cycling on these margins presently do not allow us to adequately predict their response to climate-induced changes in carbon loading and quantities of mineral particles that are responsible for particulate organic carbon (POC) burial. One avenue to examine this issue and gain further insight into carbon cycling on river-dominated continental margins is to document the effect of historical changes in river water and sediment (mineral and POC) input. In particular, anthropogenic effects such as drainage basin land use changes and damming have had dramatic, and sometimes opposing, impacts on suspended sediment load in many rivers in the past 1 to 2 centuries. In this study we examine the effects of declining Mississippi River (3rd largest drainage basin on Earth) sediment discharge on burial rates and carbon cycling on the adjacent Gulf of Mexico continental margin. The timing and magnitude of changes in suspended sediment load carried by the Mississippi are relatively well-constrained over the last ~150 years [*Keown et al.*, 1986; *Kesel*, 1988] and the spatial geometry of the modern margin depocenter has been defined [*Corbett et al.*, 2006]. The Mississippi, like many other river basins in the last half century, has also experienced huge increases in dissolved nitrogen and phosphorous flux associated with agricultural development and the use of artificial fertilizers that fuels coastal eutrophication. The present study examines the interplay between these two influences on the bulk carbon signal.

### 2. Materials and Methods

[3] Field and laboratory methods are outlined in the auxiliary materials and methods section.<sup>1</sup>

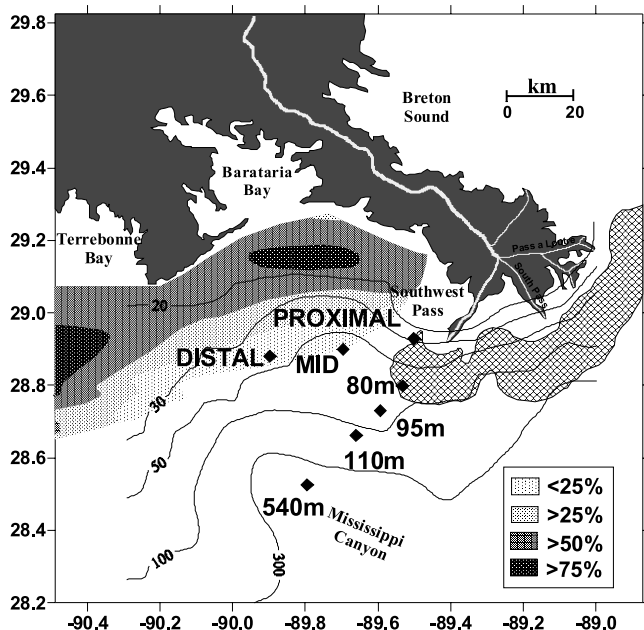
### 3. Mineral and Carbon Burial Rates

[4] Box and gravity cores from two (of 7) sites (95 m, Mid at 50m) along shelf transects adjacent to the main Southwest Pass distributary of the Mississippi deltaic mouth (Figure 1) exhibit a sharp decrease in exponential decay rate with depth (Figure 2 and Table 1) of the particle-reactive radiotracer <sup>210</sup>Pb (T<sub>1/2</sub> = 22.3 yr). We interpret this as a decline in mass accumulation rate (MAR in g/cm<sup>2</sup>/yr) of 235 and 273% at the two sites. The linear regression age model for these two sites, which are at an intermediate

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**Figure 1.** Map of the core sites on the continental shelf west of the Mississippi River mouth. The cross-hatched area surrounding the river mouths is the mapped limits (using side-scan sonar) of mass movement along the delta front [Coleman *et al.*, 1998]. The inner shelf contours represent the limits of hypoxia as observed in summer survey cruises between 1985–1997 [Rabalais *et al.*, 1999]. These are the percentage of years when the hypoxia was observed.

distance from Southwest Pass, indicates that the decline in MAR occurred in  $1946 \pm 8$  years.  $^{137}\text{Cs}$  penetration depths in the cores confirm this timing. The rate of total organic carbon (TOC) decrease with depth also declines markedly at this core depth (Figure 1) in both cores. The rate of porosity decrease with depth is consistent with a normally compacting sediment, with little evidence of grain size variability sufficient to generate measurable changes in  $^{210}\text{Pb}$  activity. Bioturbation-induced disruption of primary sedimentary layers is observed to decrease below the inflection point in core x-radiographs, which indicates these areas were more densely colonized by soft-bodied benthic macrofauna following the decrease in MAR.

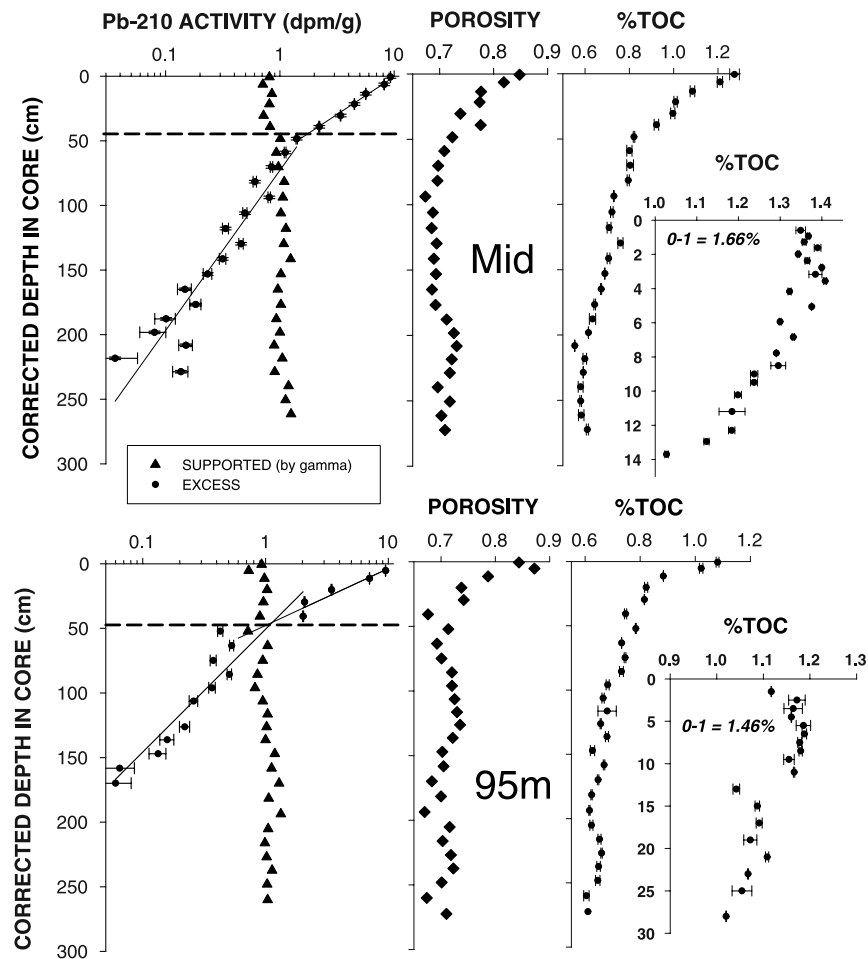
[5] Historical sediment data in the lower Mississippi River indicates suspended sediment load has been declining since perhaps as far back as 1900, but that the largest decrease (62%) occurred immediately after 1952 [Kesel, 1988]. The decline has been attributed to dam construction on the Upper Mississippi (pre-1941), Missouri (1952–3) and Arkansas (1962–3) tributaries, soil conservation practices instituted beginning in the 1930's, and elimination of overbank flooding and bank caving by artificial levee construction and channel shortening (1928–1942 [Keown *et al.*, 1986; Kesel, 1988, 2003]). Although annual variations in lower Mississippi water discharge (at Vicksburg, Mississippi) show no net trend since 1815 [Poore *et al.*, 2001], water and sediment discharge entering the Gulf through the main Mississippi passes has decreased further due to an increase in water capture by the Atchafalaya distributary from 5% in 1920 to >20% in 1960 [Mossa,

1996]. However, any net loss in water at gauging stations below the Atchafalaya off-take is obscured by annual and decadal episodicity [Rabalais *et al.*, 1999]. We conclude that the timing of decreasing MAR's in these two shelf stations closely follows the timing of decreasing river particulate loads established from historical river records.

[6]  $^{210}\text{Pb}$ -derived MAR's at our seven core sites decrease with distance from the river mouth and in greater water depths (Table 1). This explains, in part, why the mid-century change in MAR is not apparent at our other five sites and in previous studies of this region. The two nearest sites to Southwest Pass have high MAR's and  $^{137}\text{Cs}$  penetration rates that place the inflection point either below the cored interval (Proximal site) or near the core base (80 m site). Further, the geochronology is obscured by proximity to the riverine particle source, which results in low  $^{210}\text{Pb}_{\text{xs}}$  activity (5–10 dpm/g) on particles and downcore-variable porosities (i.e., grain sizes). Most of the published MAR's near the Southwest Pass distributary were collected in relatively short box cores that also do not capture the entire  $^{210}\text{Pb}_{\text{xs}}$  interval [Corbett *et al.*, 2006]. We have identified only one core collected in 1982 with a similar MAR near our two non-steady state sites that measured a steady-state  $^{210}\text{Pb}$  MAR (Site 10 [Eadie *et al.*, 1994]). These alpha spectrometry results are discounted because  $^{210}\text{Pb}$  supported levels were estimated in this 92 cm core: an increase of only 0.2 to 0.3 dpm/g in supported levels in our non-steady state sites would eliminate enough of the deeper points from the regression to make identification of the more rapid pre-1946 MAR difficult.

[7] The absence of evidence for declining MAR's in the three sites distal from Southwest Pass (2 shelf, 1 in Mississippi Canyon) is likely a function of bioturbation and sediment delivery mechanisms. Skeletal biogenic particle dilution is not a major factor even in these distal sites (bulk carbonate mass <1%), however, MAR's are the lowest observed (0.02–0.23 g/cm<sup>2</sup>/yr), reducing vertical resolution significantly.  $^{210}\text{Pb}_{\text{xs}}$  surface mixed layers (SML) are thickest (5–7 cm) and X-radiographs of the ~150 year depth interval of measurable  $^{210}\text{Pb}_{\text{xs}}$  activity display a massive stratigraphy overprinted by modern macrofaunal burrows. These factors suggest that bioturbation may have played a role by smoothing the distinct inflection in MAR's. We also do not observe an inflection in TOC in any of the three distal sites at the depth that  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  geochronology indicates was deposited in the years around 1946. Bioturbation does not fully explain the absence of evidence for declining MAR's, particularly on the inner shelf where benthic biological activity has been suppressed by the seasonal hypoxia [Rabalais *et al.*, 1999].

[8] Studies of the Southwest Pass buoyant plume show that the limits of the turbid zone (>25 mg/l suspended sediment concentration) extend outward from the mouth a distance of 4 to 23 km, controlled by river discharge and wind direction [Walker *et al.*, 2005]. This agrees with short-period radiotracer ( $^{234}\text{Th}$ ,  $^7\text{Be}$ ) deposition rates that indicate river-borne particulates are deposited within 30 km of the Pass [Corbett *et al.*, 2004]. It can be concluded that much of the river-derived sediment and associated terrestrial organic matter (OM) delivered to our distal sites are remobilized after initial deposition in shallow areas subject to resuspension adjacent to the Pass. Winter and cyclonic storms are the



**Figure 2.** Downcore  $^{210}\text{Pb}$  activity, porosity, and total organic carbon (TOC) content for the two non-steady state mass accumulation rate (MAR) sites.  $^{137}\text{Cs}$  penetration depths are shown by the dashed line on the  $^{210}\text{Pb}$  plots. The timing of the decrease in MAR at the Mid and 95m site observed in  $^{210}\text{Pb}_{\text{xs}}$  decay trends is closely associated with declining suspended sediment loads observed in the Mississippi River. Data for the sites was obtained from the kasten cores. TOC data is shown for both the gravity core and the box core (inset).  $^{210}\text{Pb}$  data were collected by alpha (total and excess) and gamma counting (supported) methods.

primary drivers in resuspending this material, and can be expected to produce a pattern of offshore-decreasing sediment supply and grain size—a contention borne out by a progressive decline in bulk sediment lignin contents offshore attributed to hydrodynamic sorting of terrestrial POC [Gordon and Goni, 2004]. Hurricanes have also been shown to deposit sediment layers shelf-wide in this region and in

the upper Mississippi Canyon [Walsh *et al.*, 2006]. Although the supply of readily resuspendable sediment to the inner shelf might be expected to have decreased after 1946–52, it is unlikely that this would produce the sharp declines observed at the Mid and 95 m sites. This is particularly true since the 1950’s–1970’s was the period of extreme wetland loss (up to  $73 \text{ km}^2/\text{yr}$ ) in coastal Louisiana [Britsch and

**Table 1.** Summary of Particle-Reactive Radiotracer Data From the Core Sites

Site	Latitude	Longitude	Surface $\text{Pb}_{\text{xs}}$ , dpm/g	LSR, cm/yr	MAR ( $r^2$ ), $\text{g}/\text{cm}^2/\text{yr}$	SML, cm	$^{137}\text{Cs}$ LSR, cm/yr
80 m	28.8001	-89.5369	$9.8 \pm 0.9$	$3.3 \pm 0.4$	$2.3 \pm 0.3$ (0.91)	2.5	$3.1 \pm 0.08$
90 m	28.7323	-89.5974	$13.1 \pm 1.8$			4.5	$0.85 \pm 0.08$
Upper				$0.72 \pm 0.08$	$0.36 \pm 0.06$ (0.88)		
Lower				$1.4 \pm 0.3$	$0.99 \pm 0.19$ (0.87)		
110 m	28.6628	-89.6641	$21.0 \pm 3.0$	$0.56 \pm 0.19^a$	$0.02 \pm 0.01$ (0.60) <sup>a</sup>	5	$0.40 \pm 0.08$
540 m	28.5280	-89.7985	$69.7 \pm 14.0$	$0.39 \pm 0.08^a$	$0.23 \pm 0.05$ (0.88) <sup>a</sup>	6.5	$0.29 \pm 0.01^a$
Proximal	28.9294	-89.5053	$5.7 \pm 1.4$	$5.9 \pm 1.2$	$4.5 \pm 0.9$ (0.87)	2	>5.7
Mid	28.9005	-89.6996	$11.3 \pm 1.6$			2.5	$1.1 \pm 0.08$
Upper				$1.0 \pm 0.04$	$0.54 \pm 0.02$ (0.99)		
Lower				$1.7 \pm 0.34$	$1.3 \pm 0.25$ (0.88)		
Distal	28.8816	-89.9004	$7.1 \pm 0.7$	$0.19 \pm 0.06^a$	$0.07 \pm 0.01$ (0.80) <sup>a</sup>	7	$0.27 \pm 0.01^a$

<sup>a</sup>Calculations from the box core data.

Kemp, 1990], which might have provided an additional sediment supply to the inner shelf from erosion of marsh edges and subsiding (subaqueous) platforms. Another possible factor is sediment focusing to the prodelta zone immediately seaward of the base of the deltaic front. The relatively steeply dipping delta front is an active zone of muddy submarine debris flows (Figure 1), generated by rapid topset sediment loading. The topset deposits are weakened by pore pressurization and methanogenesis and move downslope as slumps, slides and growth faults [Coleman *et al.*, 1998]. Although CHIRP seismic profiling (see auxiliary materials and methods) establishes that our core sites are beyond the disturbed zone, benthic suspensions, triggered by debris flows, could deliver sediment beyond the toe of the delta front. The two sites immediately seaward of the delta front toe (Proximal and 80 m) exhibit step-wise profiles of declining  $^{210}\text{Pb}_{\text{xs}}$  activity with depth, supportive of episodic input, either by benthic nepheloid layers or hyperpycnal flows (e.g., fluid muds) associated with extreme floods [Wright *et al.*, 1990]. Time-series studies by benthic tripods are necessary to identify the exact benthic transport mechanism(s) at work. Regardless of the operative process, hyperpycnal transport would not deliver sediment upslope against gravity to the seasonally hypoxic inner shelf zone (see Figure 1).

#### 4. Impact of Declining Burial Rates on Shelf Carbon Dynamics

[9] The well-constrained timing of declining MARs and TOC at the Mid and 95 m sites predates by more than a decade changes in nutrient flux from the Mississippi River plume due to increased fertilizer use in the drainage basin. Although artificial fertilizer use began in the 1930's, river records indicate that between 1964 and 1980 nitrate concentrations tripled, silicate declined by 40% and total phosphorous doubled (estimated) before values stabilized [Rabalais *et al.*, 1999]. Historical sediment records [Eadie *et al.*, 1994; Chen *et al.*, 2001] support the link between increased nutrient loading and the onset of bottom-water hypoxia on the inner shelf, which reaches a maximum extent in summer when stratification is strongest. The Mid station is at the seaward limit of the hypoxic zone (Figure 1) and the 95 m station is even further seaward. These stations are located at least part of the year in the most productive intermediate area of the plume where primary productivity is enhanced by the riverine nutrients but not light limited by turbidity [Lohrenz *et al.*, 1999]. This suggests that they may have experienced an increase in marine POC input post-1964.

[10] The degradation of sedimentary OM is often modeled using the Berner [1964, 1980] first-order G-model, where metabolizable TOC ( $G_m$ ) is remineralized at a constant rate ( $k$ ), such that:

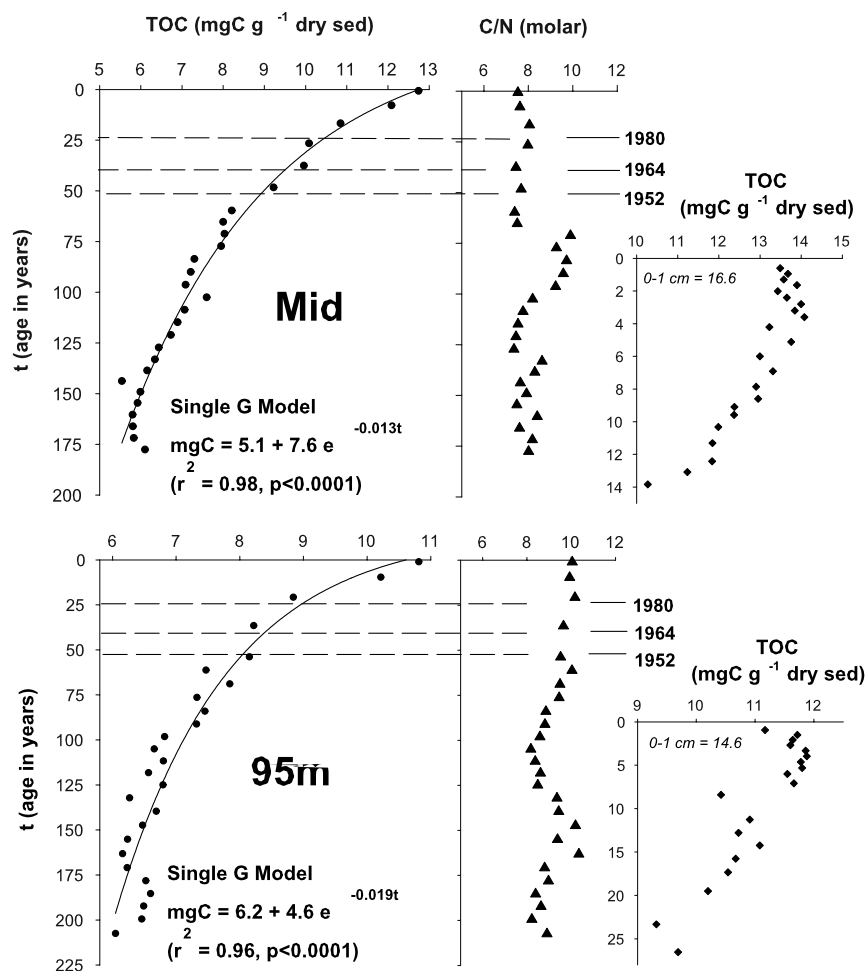
$$G_m = G_{m0} e^{-kt} + G_{\infty} \quad (1)$$

where,  $G_{m0}$  is the metabolizable TOC at the sediment surface,  $t$  is the time at any depth, and  $G_{\infty}$  is the non-metabolizable TOC, measured from the asymptotic decrease at depth in the sediments. Sediment studies [Zimmerman and Canuel, 2000] in hypoxic settings when plotted using

this model show sharp downcore offsets and patterns in the residuals relative to an exponential function that correlates with the timing of increased marine TOC input. We find no such patterns (Figure 3) from our two non-hypoxic sites when corrected for the non-steady state MAR (using an  $^{210}\text{Pb}$  age-depth relationship segmented into the depth intervals showing the two MAR's in Table 1) in the period between 1952 and 1980:  $r^2 = 0.96$  and  $0.98$ ,  $p < 0.0001$ . C/N ratios also show no consistent change across the time interval of interest (Figure 3). We conclude that there is no evidence of a change in bulk OM diagenesis in the cores when corrected for the non-steady state MAR.

[11] The analysis outlined above suggests that POC burial at both stations is closely tied to the riverine lithogenic influx. Significantly, no inflection or offset of the TOC trend with depth is apparent after the MAR decline, such as might be associated with the documented increase in marine organic productivity that led to the onset of hypoxia on the inner shelf, or associated with the peak in wetland loss along the adjacent coastline. The cause of the TOC inflection at the time of MAR reduction can be explained as the product of a change in remineralization rate or in %TOC input at the seafloor. This can be illustrated (not shown) if a single MAR rate equivalent to the upper or lower MAR is assumed throughout the core. Single-G Berner diagenetic trends either do not fit TOC values at the base of the core using the rapid MAR, suggesting a change in remineralization rate, or do not fit TOC values in the upper core using the slow MAR, suggesting a change in %TOC input. Our lignin biomarker data (T. Sampere *et al.*, Reconstruction of land-use changes and flooding events in the Mississippi River watershed using terrestrial biomarkers preserved in Louisiana shelf sediments, submitted to *Geochimica Cosmochimica Acta*, 2006) (hereinafter referred to as Sampere *et al.*, submitted manuscript, 2006) indicates that while degradation indices (acid:aldehyde ratio of the vanillyl phenols) at the two sites before and after the MAR reduction show only minor changes, there is an increase in the syringyl:vanillyl and cinnamyl:vanillyl phenol ratios (1.16 to 1.41 and 0.075 to 0.139 for the mid site and 1.05 to 1.27 and 0.095 to 0.14 for the 95 m site) post-MAR reduction. The increase in these ratios is interpreted as an increase in the abundance of grassy angiosperm material delivered to these sites post-MAR reduction. An increase in sediment lignin concentration was also noted from 53.7 ng/g dry sed to 96.6 at the 95 m station and from 40.5 to 86.0 at the mid-site.

[12] While an increase in terrigenous-sourced lignin seems counter-intuitive to a reduction in the riverine particle load, it could be explained by 1) a reduced woody:grassy lignin content due to an increased fraction of the larger, woody particles associated with the sand load possibly being trapped hydrodynamically behind dams and/or 2) an increase in marsh grass input from wetland loss. Recent work has shown that average lignin concentrations in sands containing these woody particles ( $3.6 \pm 2.6 \text{ mg gOC}^{-1}$ ), was actually higher than in muds ( $1.4 \pm 1.1 \text{ mg gOC}^{-1}$ ) in the lower river [Bianchi *et al.*, 2002]. The shallower, Mid site adjacent to the hypoxic zone also shows steadily increasing %N from 0.08 pre-1950's to 0.12 at the sediment surface and a low correlation between lignin content normalized to OC ( $\text{Lambda-8}$ ) and concentration by mass (ng



**Figure 3.** Downcore profiles of single-G Berner model results for TOC [Berner, 1964, 1980] plotted against age depths corrected for non-steady state MAR's in the Mid (upper) and 95 m (lower) kasten cores and against molar C:N ratios. Boxcore TOC data is also shown for both cores (inset) presented as mgC per gram of dry sediment. This widely utilized method of examining diagenetic loss of carbon with depth shows no evidence of changing preservation rates resulting from potential increases in marine:terrestrial ratio with declining terrestrial OM input, or increasing OM input from other sources (marine or marsh), supplied to the sites.

lignin/mgOC) at this site ( $r^2 = 0.29$  versus  $r^2 = 0.89$  at the 95 meter site) (Sampere et al., submitted manuscript, 2006); evidence of an increased marine component post-MAR reduction. While these data are not definitive in determining the balance of remineralization versus sourcing in causing the TOC inflection, particularly since lignin is only a small fraction of the TOC, they are sufficient to allow us to say that significant changes in the character of the OM reaching the sites occurred post-MAR reduction. Despite this, we do not observe %TOC offsets at the inflection point, as has been observed in hypoxic areas [Zimmerman and Canuel, 2000]. We conclude that, in the shelf region characterized by high lithogenic sediment input, the bulk of the OM flux arrives complexed with mineral particles of river origin, as has been previously suggested in this system [Cai, 2003]. This serves to overwhelm second-order source effects that are visible in biomarkers, such that normal diagenetic trends can be reconstructed by correcting for MAR changes. That is, the overall mineral:OM ratio reaching the sediment-water interface remains relatively constant as MAR varies. Other recent work has shown that despite the frequency of

occurrences of bottom water hypoxia on the Louisiana shelf, sediment accumulation rate and lability of organic matter are more important in controlling the preservation of organic carbon [Chen et al., 2005].

[13] The relative importance of  $O_2$  and MAR in OM preservation on the seafloor is a subject of community debate [Keil et al., 1994]. Our results suggest that, within the limited range observed ( $0.7\text{--}1.7\text{ g/cm}^2/\text{yr}$ ), the MAR in this river-dominated shelf setting is the key factor determining POC burial rate in oxic areas (but not in adjacent hypoxic areas), despite increasing flux of nutrients in many systems from anthropogenic sourcing and accelerated deltaic wetland loss associated with rising sea level. As suggested by Hartnett et al. [1998], reduced MAR does also result in increased  $O_2$  time exposure for OM prior to burial. Our results also suggest that climate-induced changes in terrestrial POC flux to large-river dominated continental margins will likely also result in changes in the quantity of organic carbon buried in these settings, which can be easily modeled. These results do not, however, rule out that changes in OM loading from other sources men-

tioned above may significantly change seafloor OM remineralization rates in these oxic settings, and hence, potential CO<sub>2</sub> fluxes to the water column and atmosphere.

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