

# A 1000-year sediment record of recurring hypoxia off the Mississippi River: The potential role of terrestrially-derived organic matter inputs

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## Abstract

A suite of inorganic and organic geochemical tracers and a low-oxygen tolerant benthic faunal index ('PEB') were measured in a <sup>14</sup>C-dated 2+ m long gravity core collected on the Louisiana shelf adjacent to the Mississippi River delta to study potential millennium-scale low-oxygen events. Periodic down-core excursions in the PEB index throughout the core suggest recurring, natural bottom water low-oxygen events that extend back ~1000 <sup>14</sup>C years. Select trace element and biomarker distributions in these same sediments were examined as potential tracers of past hypoxic events and to help distinguish between marine versus terrestrial processes involved in organic carbon production. In discrete sediment horizons where the PEB index was elevated, redox-sensitive vanadium concentrations were consistently depleted, excursions in sedimentary  $\delta^{13}\text{C}$  suggest periodic, preferential terrestrial inputs, and the concentrations of two sterol biomarkers (sitosterol and  $\beta$ -stigmaterol) also showed concurrent enrichments.

If the PEB index successfully records ~1000 <sup>14</sup>C year-scale low-oxygen events, then the distribution of these geochemical tracers can be interpreted to corroborate the view that naturally occurring low-oxygen bottom water conditions have existed on the inner Louisiana continental shelf, not only in recent times, but also over at least the last 1000 <sup>14</sup>C years. These data support the general hypothesis that historic, low-oxygen bottom water conditions on the Louisiana shelf are likely tied to periods of increased fluvial discharge and associated wetland export in the absence of modern river levees. Enhanced river discharge and associated material export would both stimulate enhanced *in situ* organic carbon production and foster water column stratification. Such periodic elevated river flows during the last millennium can be linked to climate fluctuations and tropical storm activity.

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## 1. Introduction

The combined Mississippi–Atchafalaya Rivers drain not quite half of the conterminous United States and

annually deliver about 200 Tg of suspended material and 580 km<sup>3</sup> of fresh water to the northern Gulf of Mexico (Milliman and Meade, 1983; Meade, 1995, 1996). This river system therefore is also the primary nutrient source (more than 90% of the annual load of N and P, respectively) to this area (Dunn, 1996), and for about the last 30 years, the riverine nitrate N loads have approximately tripled in response to basin-wide fertilizer

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use (Rabalais and Turner, 2001; Goolsby et al., 2001; Turner et al., 2006). These recent nutrient load increases, in particular nitrate N, have been attributed at least in part, to the *in situ* production of organic carbon that can lead to eutrophication and summertime hypoxic conditions (Turner and Allen, 1982; Lohrenz et al., 1994; Rabalais et al., 1996; Goolsby, 2000; Green et al., 2006).

Hypoxia was first observed in the northern Gulf in the early 1970s (Harper et al., 1981) and since 1985 a large area west of the Mississippi River delta has been systematically surveyed for low dissolved oxygen and its varied driving processes (Rabalais et al., 1991; Rabalais and Turner, 2001, 2006; Chen et al., 2001). Today, the magnitude and recurrence of hypoxia off the Louisiana — Texas coast is one the world's largest examples of coastal eutrophication, with associated complex management implications (Malakof, 1998; CENR, 2000; NRC, 2000; Cloern, 2001; Boesch, 2002). As the Mississippi River discharge directly affects both nutrient loading estimates and the degree of water column stratification, fluctuations in climate and the frequency and intensity of tropical storms will likely impact the magnitude and severity of offshore hypoxia (Justič et al., 2003, 2005; Turner and Rabalais, 2003; Goñi et al., 2007).

Oxygen-depleted natural waters have been documented in many modern and ancient marine systems (Emerson and Husted, 1991; Calvert and Pedersen, 1993; Diaz, 2001), and a suite of specific geochemical and biological tracers have been developed to aid in the interpretation of these events (cf. Eadie et al., 1994; Crusius et al., 1996; Morse et al., 2002; Rickard and Morse, 2005; Tribouillard et al., 2006; Morse and Eldridge, 2007). For example, select redox-sensitive trace elements (e.g., V, Re, U), biomarkers (e.g., lignin phenols, thiophenes), and low-oxygen tolerant foraminifera indices have been utilized as proxies for redox shifts or hypoxia/anoxia. The sedimentary record of a select suite of trace elements, including V, can record relevant information on the changing redox state of the marine depositional environment over time (Morse and Rowe, 1999; Rowe et al., 2002). Previous studies have shown, for example, that V is typically highly enriched in the sulfide-bearing sediments underlying the world's anoxic basins due to the formation of sulfide complexes (Calvert and Pedersen, 1993). In natural systems, V may occur in two or three oxidation states; pentavalent V prevails in oxygenated seawater, forming the vanadate oxo-anion  $H_xVO_4^{3+x}$ . It has been shown that vanadates, like phosphates, can readily form surface complexes with either Fe- or Mn-hydroxides (Hastings, 1994). Under moderately reducing conditions, such as those that exist ephemerally on the Louisiana shelf, the

tetravalent vanadyl cation  $VO^{2+}$  likely dominates, which may either hydrolyse to  $VO(OH)_3^-$  in seawater, or may diffuse outward across the sediment/water interface into bottom waters (Emerson and Husted, 1991). In contrast, under prevailing anoxic conditions, reduced V species would be irreversibly scavenged in anoxic sediments (Morford and Emerson, 1999).

Sterols are a class of lipid biomarkers often used in reconstruction of past environmental conditions. They are utilized to assess sources of organic carbon and to distinguish among specific organismal inputs (e.g., diatoms, dinoflagellates, zooplankton, mammals), marine phytoplankton, and terrestrial inputs (i.e., vascular plants). Specific sterols such as stigmasterol (24-ethylcholest-5, 22E-dien-3 $\beta$ -ol) and  $\beta$ -sitosterol (244-ethylcholest-5-en-3 $\beta$ -ol) have been used to infer inputs to sedimentary material from terrestrial organic matter (i.e., vascular, higher plant material). Carbon isotopes ( $\delta^{13}C$ ) can be utilized to distinguish between marine and terrestrial source material of sedimentary organic matter (Sackett, 1989; Eadie et al. 1994; Goñi et al., 1997, 1998). The Great Plains of America, which form a vast majority of the Mississippi River drainage basin, contain a mixture of natural grasslands composed of C4 and C3 species that exhibit a strong latitudinal gradient in the C4/C3 species composition (Teeri and Stowe, 1976; Goñi et al., 1997, 1998). From the work off the Mississippi and Atchafalaya Rivers, Goñi and colleagues have been able to confirm a natural source of isotopically heavy carbon being discharged from the Mississippi River that is independent of recent (100+ years) agricultural change (i.e., corn and soybean production). Stable carbon isotopes, when used in conjunction with biomarker analyses, can thus provide a powerful tool in the reconstruction of past environmental conditions (cf. Jasper and Gagosian, 1993).

While Sen Gupta et al. (1996) and Brunner et al. (2006) utilized an index of *Ammonium* and *Elphidium* ('A–E' index) as a specific micro-fossil proxy of hypoxic conditions in the northern Gulf of Mexico, Blackwelder et al. (1996) examined the response of various benthic foraminifera to external stressors such as hypoxia. Osterman (2003) utilized the cumulative percentage of three foraminifera species (*Protonionia atlanticum*, *Epistominella vitrea*, *Buliminella morgani*, 'PEB' index), as an indicator of past low-oxygen bottom waters on the Louisiana shelf. These PEB species are epifaunal opportunists that are generally tolerant of low-oxygen conditions and are documented to occur most abundantly in waters that are 13–70 m deep within the Louisiana hypoxia zone.

From a series of five box cores collected over ~ 3000 km<sup>2</sup> on the Louisiana shelf, a consistent trend

of decreasing PEB with increasing sediment depth (i.e., ‘age’) was observed (Osterman et al., 2005, 2007a,b), which agrees with the generally accepted paradigm of recent anthropogenically-enhanced hypoxia (Goolsby, 2000; Rabalais et al., 2002a,b). Additional linkages were also made between PEB excursions in a gravity core to long-term Mississippi River discharge records (Osterman et al., 2005) and from those records it was suggested that the historic (pre-anthropogenic) hypoxic events in that core must be related to periods of increased river flow. From such work, it is evident that a combination of natural processes, such as increased river discharge and associated enhanced export of wetland-derived organic material, as well as anthropogenic activities (e.g., land clearing, agriculture) may have had an impact in the development of low-oxygen bottom waters on the Louisiana continental shelf prior to 1900 (cf. Turner and Rabalais, 2003).

This paper reports on the distribution of PEB and select sediment geochemical tracers, including sterol biomarkers, stable carbon isotopes, and particulate vanadium, from a new radiocarbon-dated gravity core collected in the hypoxic zone near the Mississippi River

delta (Fig. 1). This new long record confirms previous results and provides evidence that periodic low-oxygen conditions likely formed on the Louisiana Shelf over the last 1000  $^{14}\text{C}$  years. Using a multi-proxy geochemical tracer approach, we reason that the striking PEB excursions in this core may reflect recurring low-oxygen events that are tied to periods of increased river discharge and associated wetland export.

## 2. Methods

### 2.1. Shipboard

In addition to multiple box cores, a gravity core (MRD05-04GC; Lat: 28.9319° N, Long: 89.8961° W) was collected in 38 m water depth on the inner Louisiana shelf aboard the R/V Pelican in May 2005 (Fig. 1). This location had been previously sampled as part of a larger network of coring sites initiated in 2003 and reoccupied at least yearly (Swarzenski et al., 2006, 2007; Osterman et al., 2007b). Sediment from plastic core liners was extruded and sectioned shortly after collection to ensure minimal cross-contamination. Each

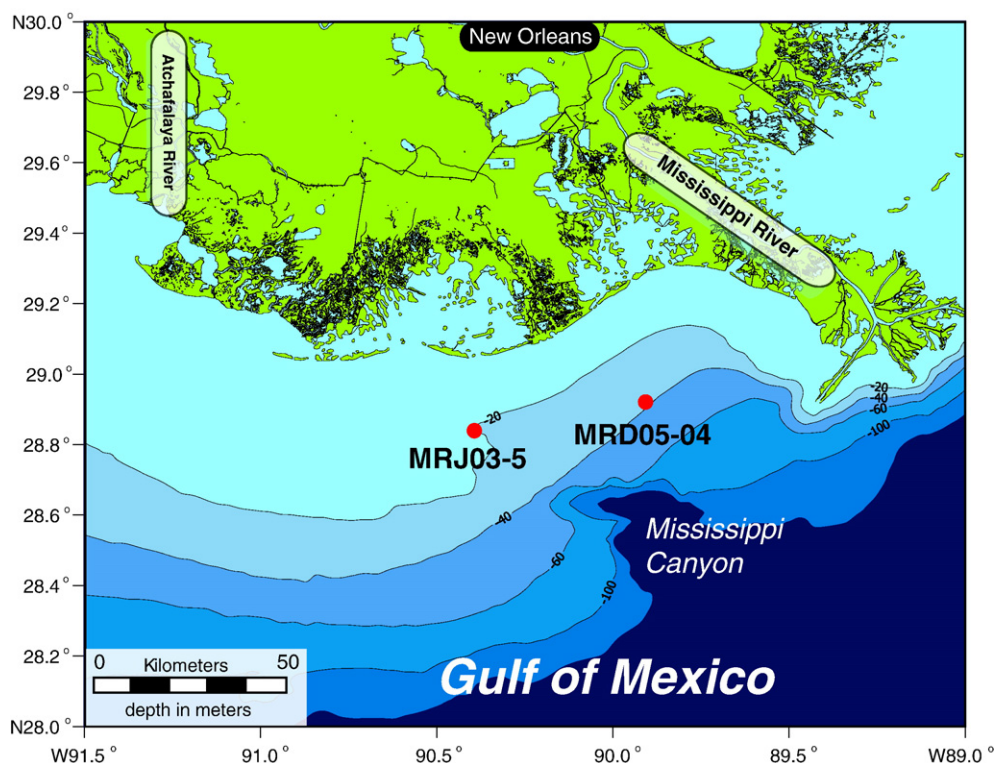


Fig. 1. Map showing the sampling site of gravity core MRD05-04 (Lat: 28.9319° N, Long: 89.8961° W) collected in 38 m water depth in the zone of recent hypoxia on the Louisiana continental shelf in May 2005. Also shown is the station location (MRJ03-5) of the pore water V and Mn(II) profile (see Fig. 4).

1-cm sediment slice was divided into three sub-samples and stored either frozen in pre-combusted glass jars (organics), refrigerated in pre-weighed plastic cups (trace elements and radionuclides), or in plastic bags (foraminifers) for further processing. Briefly, for the analyses of the following radionuclides, 1-cm intervals of dried, powdered sediment were counted in a calibrated high-purity Ge well-type gamma detector using the 46.52 keV ( $^{210}\text{Pb}$ ), 351.87 and 609.31 keV ( $^{226}\text{Ra}$ ) and the 661.6 keV ( $^{137}\text{Cs}$ ) energies. Precision in the activities  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ , and  $^{137}\text{Cs}$  were <5%. Excess  $^{210}\text{Pb}$  derived geochronologies were calculated as per methods described in Swarzenski et al. (2006).

## 2.2. Benthic foraminiferal analysis

The benthic foraminifers in every 1-cm sample were counted for the relative percentage of the three PEB species (% *P. atlanticum*, + % *E. vitrea*, + % *B. morgani*). Further information about core collection, sample processing, taxonomic notes, and total benthic foraminifer counts are reported elsewhere (Osterman et al., 2007a,b).

## 2.3. Organic and inorganic geochemical tracers

Sediment samples were combined from two 1-cm intervals for molecular analysis. Approximately 50 g of each frozen sample were Soxhlet-extracted with a methylene chloride and methanol (2:1) solvent mixture. Total extracts were concentrated to ~1.0 ml using rotary evaporators. Compound classes were separated on silica gel (Biorad, 70–230 mesh, 5% deactivated) using solvents of increasing polarity: 25 ml of hexane (hydrocarbons), a mixture of 10 ml of hexane and 20 ml of 25% of toluene in hexane (polycyclic aromatic hydrocarbons), 20 ml of 50% toluene in hexane (wax esters), 20 ml each of 5% and 20 ml of 10% ethyl acetate in hexane (alkenones), 20 ml of 15% of ethyl acetate in hexane (alcohols), 20 ml of 20% of ethyl acetate in hexane (sterols), finally 30 ml of 100% ethyl acetate and 30 ml of methanol (polars). The sterol fractions were concentrated, transferred to vials and evaporated under a nitrogen stream to 0.5 ml. Sterols were converted into trimethylsilyl ether derivatives using bis(trimethylsilyl)trifluoroacetamide (BSTFA) in 10% trimethylchlorosilane (TMCS) prior to analysis by gas chromatography. Sterol derivatives were analyzed with an Agilent 6890 gas chromatograph and a Hewlett-Packard 5973 mass selective detector equipped with a fused silica DB5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). The oven temperature was programmed from 80 °C to 300 °C at 4 °C min<sup>-1</sup>. Helium was used as a carrier gas. Sterols were

quantified using 5α-cholestane as an internal standard and final concentrations were normalized to organic carbon. Recoveries for sterols were on average ~90%; the detection limit was ~1 ng. Compounds were quantified using Agilent PC-based chromatographic software.

Frozen sediment samples for total carbon and  $\delta^{13}\text{C}$  analyses were dried at 60 °C for 24 h and then ground and homogenized to a fine powder using a mortar and pestle. From a 1.0 g split, organic and inorganic carbon concentrations were determined using a Shimadzu TOC 5000A analyzer with a relative standard deviation of ±1% (0.01% at 1.0% TOC). Weighed aliquots (~100 mg) of dried sediment were transferred to Costech silver capsules, vapor acidified with concentrated hydrochloric acid for 24 h, dried at 60 °C for 24 h, crimp-sealed, and stored in a desiccator until analyzed. Samples were analyzed for  $\delta^{13}\text{C}$  using a Micromass (now VG) Optima continuous-flow mass spectrometer. Stable isotope ratios were calculated as follows,

$$\delta^{13}\text{C}(\text{‰}) = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000$$

where  $R = {}^{13}\text{C}/{}^{12}\text{C}$  and expressed in per mil (‰) relative to Vienna Pee Dee belemnite (VPDB) standard (Kendall and McDonnell, 1998). The analytical precision ( $1\sigma$ ) for triplicate analyses of split samples was <0.15‰ and similar in magnitude to replication of standards. Blanks were generally <0.6‰.

Sediment sub-samples for trace metal analyses were dried, powdered, homogenized, and digested in a mixture of HCl, HNO<sub>3</sub>, HClO<sub>4</sub>, and HF acids. The concentrations of V and Mn were quantified by ICP-MS (Nameroff et al., 2002) and instrument calibration was performed using digested standard rock reference material, multi-element solution standards, as well as internal standards. The trace element concentration in standard reference samples and duplicates yielded an analytical precision of <10%.

## 3. Results

### 3.1. Age models

Sediment geochronologies, in terms of both mass accumulation and linear sedimentation rates, were derived from box core sediment samples collected at the same site and time using excess  $^{210}\text{Pb}$  ( $t_{1/2} = 22.3$  years) and  $^{137}\text{Cs}$  ( $t_{1/2} = 30.1$  years) (cf. Swarzenski et al., 2006). A companion box core record at the site MRD05-04 (Fig. 2) yielded a robust ( $r^2 = 96$ ) sedimentation rate at this site of 0.31 cm year<sup>-1</sup> that corresponded to a mass accumulation rate of 0.18 g cm<sup>-2</sup> year<sup>-1</sup>.

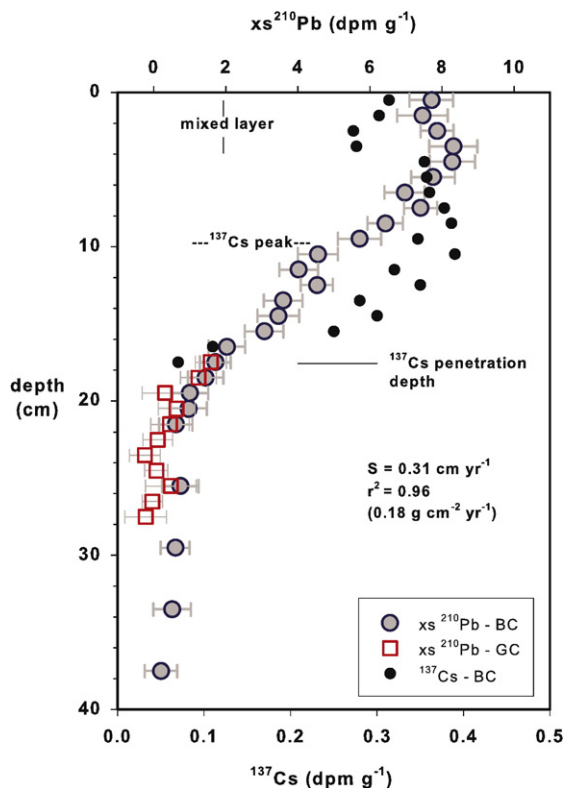


Fig. 2. A companion box core, collected at the same site and time, is used to derive 100-year sedimentation rates at MRD05-04 from excess  $xs^{210}\text{Pb}$  (shaded symbols) and  $^{137}\text{Cs}$  (filled symbols) activities. A direct comparison of  $xs^{210}\text{Pb}$  in the box core and the gravity core (square symbols) yields information on the integrity of the gravity core top;  $\sim 17$  cm ( $\sim 55$  years) of the most recent record are missing from the gravity core.

While the  $^{137}\text{Cs}$  profile does not show a clear maximum related to the 1963 fallout peak, the first appearance of  $^{137}\text{Cs}$  should relate to  $\sim 1954$ , which would also yield a rate of about  $0.3 \text{ cm year}^{-1}$ . Such box core accumulation rates indicate that the last 100 years are represented by approximately the upper 35 cm. Extrapolating an age-date on sediments much older than 100 years is obviously tenuous, as we must assume a constant mass accumulation rate. For example, a comparison of  $xs^{210}\text{Pb}$  inventories from one site pre- and post hurricane Katrina (Swarzenski et al., 2007) illustrates the sensitivity of the uppermost sediment layer to storm-induced resuspension and shear (cf. Goñi et al., 2006, 2007; Corbett et al., 2006; Mead and Goñi, 2006; Dail et al., 2007). To evaluate the integrity of the top of the gravity core, we also measured the distribution of  $xs^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in the uppermost sediments by gamma spectroscopy. An examination of  $xs^{210}\text{Pb}$  in the gravity core and

box core (Fig. 2) indicates that  $\sim 17$  cm of the gravity core top were lost during core collection. This implies that the most recent  $\sim 55$  years are missing from the gravity core record.

Two AMS  $^{14}\text{C}$  dates were also obtained on mixed foraminifers from the base of the gravity core (226.5 cm:  $1400 \pm 140$  years BP; 228.5 cm:  $1630 \pm 45$  years BP; BP = before present). The reported ages are in radiocarbon years (BP) using the Libby  $^{14}\text{C}$  half-life of 5568 years. As the core was collected in 38 m of water, a surface water reservoir correction of 400 years was applied (Poore et al., 2004) to obtain an average age of about 1100  $^{14}\text{C}$  years before present for the base of the gravity core. Such corrected dates yield a corresponding ‘whole core’ sediment accumulation rate of  $0.2 \text{ cm year}^{-1}$  — a value not dissimilar from the  $xs^{210}\text{Pb}$  or  $^{137}\text{Cs}$  derived rate of  $0.3 \text{ cm year}^{-1}$  calculated from the upper 38 cm of the companion box core.

### 3.2. Benthic foraminiferal analysis

The gravity core recorded a trend of increasing PEB in the uppermost sediments of the core and this distribution is associated with the recent increase in the occurrence and intensity of hypoxia (cf. Blackwelder et al., 1996; Sen Gupta et al., 1996; Platon et al., 2005; Osterman, 2003, Osterman et al., 2005). The recent PEB record in surface sediments from a companion box core collected at this same site (Osterman et al., 2007b) extended to  $>80\%$ , further confirming that the top of the gravity core was lost during collection. However, at depth there are notable additional PEB excursions that reach or exceed one standard deviation above the mean value for the gravity core record (55–60 cm, 104–111 cm, 130–132 cm, 156–159 cm, and 186–189 cm) (Fig. 3). It is these periodic excursions that imply millennium-scale historic low-oxygen events and that warrant more in-depth investigation using complementary geochemical tracers.

### 3.3. Particulate vanadium (V)

At the top (0–20 cm) of the gravity core, the sediment V concentration ranges from about  $136\text{--}146 \mu\text{g g}^{-1}$  (Fig. 3). Similar values were generally observed down-core except at several notable depth intervals (22.5 cm, 60.5 cm, 110–111 cm, 130–135 cm, 158.5 cm, and 188.5 cm) where pronounced depletions, to  $\sim 100 \mu\text{g g}^{-1}$ , were observed. The mean V concentration of the 111 analyses was  $142.3 \pm 10.2 \mu\text{g g}^{-1}$ ; a number close to the crustal abundance value of  $135 \mu\text{g g}^{-1}$  reported in Turekian and Wedepohl (1961).

### 3.4. TOC and $\delta^{13}\text{C}$

Total organic carbon (TOC) concentrations ranged from 0.92% to 1.45%, with a mean value of 1.18% (Fig. 3). In general, highest TOC values were observed in the upper 20 cm; yet below 20 cm there were several intervals where TOC concentrations extended above this mean value. Such values are similar to previous results for the Louisiana shelf (Eadie et al., 1994; Santschi et al., 2007).

The sedimentary organic carbon isotope ratio ( $\delta^{13}\text{C}$ ) record is also shown in Fig. 3. In general,  $\delta^{13}\text{C}$  values fall into a narrow range ( $-23.6\text{‰}$  to  $-21.2\text{‰}$ ) with a mean value of  $-22.3\text{‰}$  ( $n=144$ ). This range in  $\delta^{13}\text{C}$  is consistent with other reported values (Eadie et al., 1994; Bianchi et al., 2002, 2007; Santschi et al., 2007) for the northern Gulf of Mexico. Surface sediments are isotopically heavier (more marine) while the rest of the sediment column shows both lighter ( $-23.6$ ) and heavier ( $-21.1$ ) excursions, depending on the depth.

### 3.5. Sterol analyses

Stigmasterol and  $\beta$ -sitosterol concentrations were generally low ( $\sim 2 \mu\text{g g}^{-1}$ ; Fig. 3) yet large (up to 10-fold) excursions from background concentrations were observed at 53–67 cm, 104–108 cm, 151–157 cm, and 166 cm. Notably, the marine phytoplankton sterols (i.e., desmosterol, brassicasterol) were either close to the limits of detection or absent. The proximity of this core to the Mississippi River delta and adjacent wetlands, as well as the presence of long chain n-alkanes (i.e., C27, C29) that indicate a higher plant source, suggests that these sterols record a variable terrestrial signature (Volkman, 1986; Mead and Goñi, 2006).

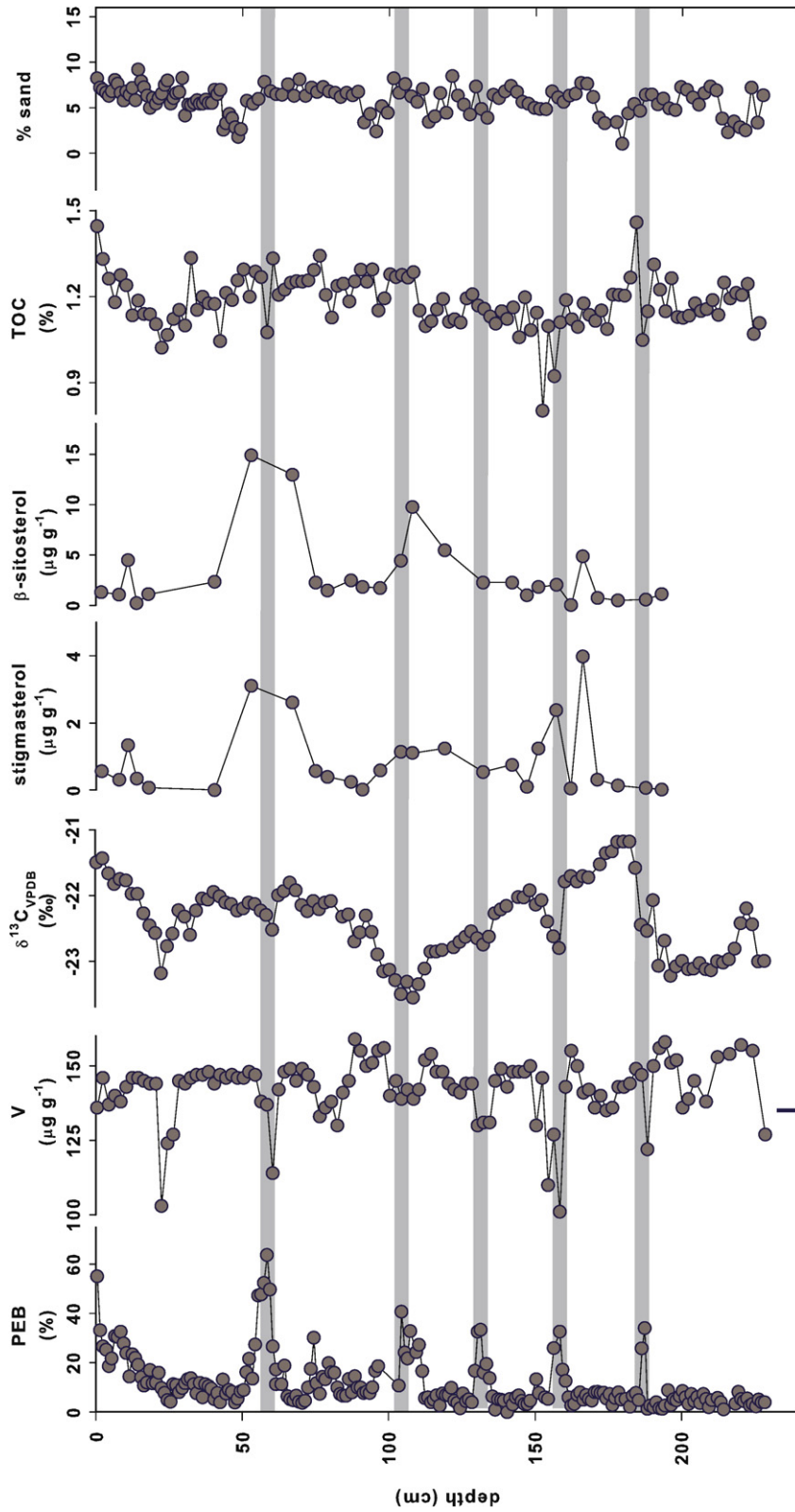
## 4. Discussion

The forensic reconstruction of a sedimentary record for potential evidence of past low-oxygen conditions relies on several assumptions. An important concern is the integrity of gravity core sediment structure itself. While we can reasonably well evaluate the loss of surface sediment due to core collection (Fig. 2) and make appropriate adjustments in our interpretations, an assessment of deeper sediments can best be made only using X-ray photography or coulometry. Examination of X-radiographs from a companion gravity core at the same site (Swarzenski, unpublished data) reveals no obvious sediment discontinuities throughout the entire core record. Similarly, the range in the sand-sized particle distribution (Fig. 3), measured using an automatic Coulter LS 200 particle-size analyzer, fluctuated little from an average value of 5.9% in

the gravity core, and any deviations were not observed at those same depth intervals identified by the PEB index maxima. The sand-sized fraction was used as a likely proxy for the foraminifers and should result in a reasonably close correlation if some external sedimentary process (i.e., benthic mud flows, tropical storm-induced shear and resuspension; Walsh et al., 2006; Goñi et al., 2007) were responsible for defining these profiles. Instead, Fig. 3 clearly shows that PEB and % sand are poorly correlated and that these two profiles thus are most likely generated by different processes. An upward fining silt/clay ratio can reveal episodic storm-induced sediment transport and associated sorting (e.g., Walsh et al., 2006; Goñi et al., 2007), but such trends were not observed in this sediment record. Furthermore, if the sediments in the gravity core were in fact transported in from other depths via a sediment or gravity flow, the foraminifer assemblage would be diluted with increased numbers of shallow-water species (Osterman et al., 2007b). In contrast, the PEB peaks contained elevated numbers of species indigenous to the water depth at the site.

A second assumption is that the PEB index correctly tracks low-oxygen events in sediments that are up to 1000  $^{14}\text{C}$  years old. While this assumption is almost impossible to verify, we now know that specific foraminifers exhibit unique low-oxygen tolerance and that various species ratios or indices have been developed as reliable proxies of modern hypoxia (Blackwelder et al., 1996; Sen Gupta et al., 1996; Osterman, 2003; Osterman et al., 2005; Brunner et al., 2006). Osterman et al. (2005) further interpreted PEB results from a gravity core on the Louisiana shelf as likely evidence of pre-anthropogenic hypoxia and from this record inferred that these low-oxygen bottom water intervals were likely related to increased discharge periods of the Mississippi River. Based on these microfossil studies and the general integrity (i.e., X-ray image and chronology) of the entire gravity core sediment structure of MRD05-04, it is not unreasonable to extend the interpretation of the observed PEB maxima in the gravity core as recurring low-oxygen events.

The V record in the gravity core can be used to bolster the PEB-based interpretation of historic recurring low-oxygen events. Sedimentary V is a function of the deposition and accumulation of terrigenous materials, surface adsorption/desorption reactions, and diffusion processes across the sediment/water interface (Morford and Emerson, 1999). The kinetics of these processes is controlled, in part, by the dynamic redox state of the sediments and the overlying water column (Rue et al., 1997) as well as by fluctuating terrigenous and marine V inputs. A strong relation between the down-core concentration of TOC and V would yield



information on the fluvial controls on V geochemistry, rather than on the environmental redox state. Clearly, here the V concentrations are not related directly to TOC but to some other process(es) (Fig. 3). If these sediments were under a truly anoxic water column, V enrichment would be tied irreversibly to the formation of immobile  $S^-$  complexes (Nameroff et al., 2002). In contrast, Rabalais and Turner (2001) observe an ephemerally suboxic (dissolved oxygen  $\leq 2 \text{ mg L}^{-1}$ ) modern water column. The redox chemistry of V must therefore be examined under such moderately reducing conditions, not anoxia, and under such conditions, V depletions are likely to occur (Shiller and Mao, 1999). Fig. 4 shows the down-core distribution of pore water V and Mn(II) from a box core record (MRJ03-5) collected at a location slightly further west than where the gravity core for this study was collected (see Fig. 1 for localities). As expected, the pore water V appears to anti-correlate with the Mn(II) record; under more oxidizing conditions one would expect V loss and Mn(II) enrichment, while under more reducing conditions one would expect Mn(II) loss and V enrichment. Furthermore, Fig. 5 presents the combined, adjusted (17 cm offset accounted for) box core and gravity core solid-phase vanadium (A) and Mn(IV) (B) records, as well as a ratio of V/Mn(IV) (C) as a function of the cumulative mass depth. Under strongly reducing conditions, this V/manganese ratio may be a more sensitive paleo-redox proxy. The observed recurring V depletions that extend also to the surface sediments as recorded in the box core record (Fig. 5A), could thus record either fluctuating V inputs (elevated V observed in Mississippi River/offshore waters and lower V observed in nearshore waters; Shiller and Mao, 1999) or a coupled redox response (Tribouillard et al., 2006). Because these V depletions appear at similar depth intervals where PEB maxima,  $\delta^{13}\text{C}$  depletions, and increased sterol concentrations are also often observed, it is likely that a coupled process, such as increased runoff into a stratified water column, may control the distribution of these tracers.

To evaluate the variable role of the Mississippi River discharge in defining low-oxygen or hypoxia-related signals, marine and terrestrial organic matter was examined using  $\delta^{13}\text{C}$  in sediment and two sterol biomarkers. An increased fluvial discharge would promote increased productivity (Lohrenz et al., 1994) and preferential frac-

tionation pathways would subsequently remove more  $^{12}\text{C}$  relative to  $^{13}\text{C}$  from the surface waters by sinking organic matter (Fry and Sherr, 1984; Killops and Killops, 2005). This organic matter may deposit on the seabed as the bottom waters become depleted in oxygen. A study of the  $\delta^{13}\text{C}$  systematics in accumulating marine sediments may therefore contain a record of the paleo-productivity and/or anoxia/hypoxia (Eadie et al., 1994; Canuel and Martens, 1996). In general, terrestrially-derived organic matter is much more refractory than marine organic matter (Goñi et al., 1997, 1998; Gordon et al., 2001), and so in the absence of significant post-depositional diagenetic alterations, the accumulation of riverine materials in shelf sediments may be tied to river discharge fluctuations. Using the marine and fresh water endmember stable isotope values of Eadie et al. (1994), the observed  $\delta^{13}\text{C}$  values in the gravity core top suggest that the vast majority of recent organic carbon deposited is of marine origin. Down-core excursions to less negative  $\delta^{13}\text{C}$  (heavier) values, however, suggest periods of heightened terrestrial inputs from peat or marsh residues (cf. Santschi et al., 2007).

On the Louisiana shelf, there are many competing factors that can either enhance or hinder summertime hypoxia. These processes operate over a broad range of spatial (10s of cm to 10s of km) and temporal (hours to years) scales that can also be regionally unique. For example, in terms of forcing factors for hypoxia, it has been shown that closest to the Mississippi River delta, riverine loading takes precedence over water column stratification, while on the broad, shallow shelf off the Atchafalaya River, stratification appears to dominate riverine loading (Hetland and DiMarco, 2008). Chen et al. (2001) and Bianchi et al. (2002) proposed that hydraulic forcing may effectively fractionate C3 (nearshore) from C4 (offshore) plants during deposition and accumulation. Santschi et al. (2007) used carbon isotope data and iodine concentrations to evaluate the different contributions of organic carbon in an undisturbed, dated core collected from a similar region of the Louisiana shelf. These authors were able to link their  $\delta^{13}\text{C}$  data to recent anthropogenic hydrologic modifications of the main-stem Mississippi River.

Variable inputs of organic matter from C4 plants and other terrestrial sources, as well as anaerobic microbial recycling, may also contribute to the observed down-

Fig. 3. The distribution of % PEB (low-oxygen tolerant benthic foraminifers), particulate vanadium ( $\mu\text{g g}^{-1}$ ),  $\delta^{13}\text{C}$  values (‰), two sterol concentrations ( $\mu\text{g g}^{-1}$ ), total organic carbon (TOC, %), and % sand in the gravity core (MRD05-04), as a function of depth. Based on multiple proxies, the surface  $\sim 17 \text{ cm}$  of the gravity core are missing. The base of the gravity core was  $^{14}\text{C}$  dated using mixed foraminifers to  $\sim 1100 \text{ }^{14}\text{C}$  years. Shaded horizontal bars identify periods of recurring, historic low-oxygen, as defined solely by the PEB index. The modern record of PEB in MRD05-04 is discussed in detail in Osterman et al., 2007b. The vertical line at the base of the V plot indicates the crustal abundance value of Turkian and Wedepohl (1961).



core fluctuations in  $\delta^{13}\text{C}$  values (Eadie et al., 1994; Sun and Wakeham, 1998; Bianchi et al., 2004; Gordon and Goñi, 2003, 2004; Allison et al., 2007). Periods of increased river discharge can similarly explain the stigmaterol and  $\beta$ -sitosterol distributions that showed pronounced increases at select depth intervals where PEB also spiked (~60 cm, 106 cm, 154 cm, and 166 cm). The general absence of marine phytoplankton sterols and the presence of long chain n-alkanes (i.e., C27, C29) at these depth intervals suggest more of a terrestrial rather than a marine source. Compound specific isotope analyses may provide additional information towards a more quantitative distinction between marine and terrestrial carbon sources. For example, Wysocki et al. (2005) used lignin-specific isotope analyses to show that up to 60% of total organic carbon in Louisiana shelf sediments is derived from both riverine and marsh (i.e., terrestrial) origins. The implication of these observations is that during times of increased precipitation, rates of surface water runoff and even groundwater discharge (Krest et al., 1999) will also increase and deliver greater concentrations of terrestrial constituents into a stratified coastal water column that may contribute towards ephemeral low-oxygen conditions. This is in line with recent evidence that suggests that autochthonous organic matter production within the Mississippi plume alone was vastly insufficient (<25%) to sustain regional hypoxia (Green et al., 2006).

Not all geochemical and biological proxies of hypoxia will trace a low-oxygen event equally. From recent observations (cf. Rabalais and Turner, 2001), we know that each yearly hypoxia event is unique in its size and intensity and a product of the driving physico-chemical and biological processes. The timing of a flood event is also critical; an early spring flood will not yield a similarly sized hypoxic area as a late-spring/summer flood. The duration and intensity of a hypoxic event will impact the geochemical signatures in the water column and across the sediment/water interface, and will also eventually impact the non-mobile pelagic and benthic biota. It is expected that the PEB or A–E species respond to pronounced periods of hypoxia (Blackwelder et al., 1996; Osterman et al., 2005; Brunner et al., 2006), rather than short-term low-oxygen events. It is possible that a highly ephemeral but intense period of hypoxia may thus be preserved in the geochemical record, but not using the PEB index (i.e., 22.5 cm). The size of the Mississippi River watershed and the dynamic nature of coastal mixing off the Mississippi River delta (Corbett et al., 2004; McKee et al., 2004) thus require a multi-proxy approach in examining historic hypoxia.

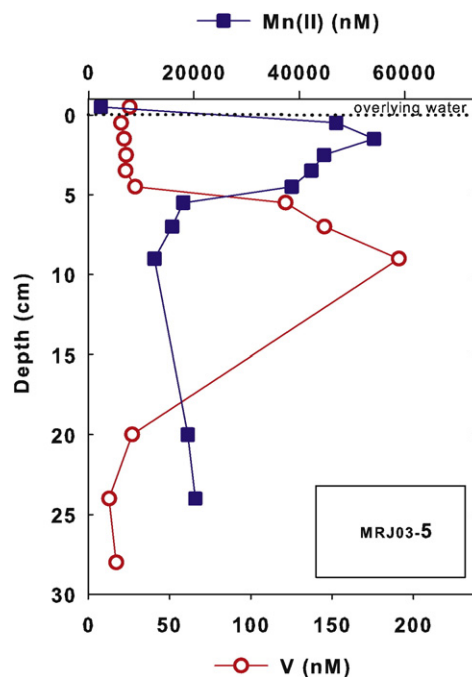


Fig. 4. Pore water (A) profiles of Mn(II) (closed symbols) and V (open symbols) as a function of depth from a box core (MRJ03-5) record collected in 20 m of water, ~45 km west of MRD05-04. Pore waters were collected by whole core squeezing and *in situ* filtration. For site location of MRJ03-5 see Fig. 1; for further details on the geochemistry of core MRJ03-5 see Swarzenski et al. (2006).

Prior to wide-spread canalization and dam construction, periods of increased river discharge would have been expressed also in the adjacent wetlands as intervals of increased material exchange and export. Periods of heightened runoff would thus facilitate organic carbon transport to the coastal ocean (Allison et al., 2007) where higher productivity could contribute towards the development of low-oxygen conditions. Results from this gravity core suggest that low-oxygen events occurred periodically on the Louisiana shelf, over at least the last ~1000  $^{14}\text{C}$  years, as a result of episodes of increased Mississippi River discharge and wetland export. While tropical storms can impact the coastal ocean both in terms of heightened terrestrial material export and episodic sediment transport, such as resuspension, and sorting, detailed grain-size analyses (e.g., silt/clay ratios) of core MRD05-04 do not indicate that the observed PEB and geochemical tracer distributions are solely storm-induced. Because each sediment sample likely integrates environmental conditions over many years, we infer that the high PEB excursions mark intervals when seasonal hypoxia developed intermittently over a number of years, rather than

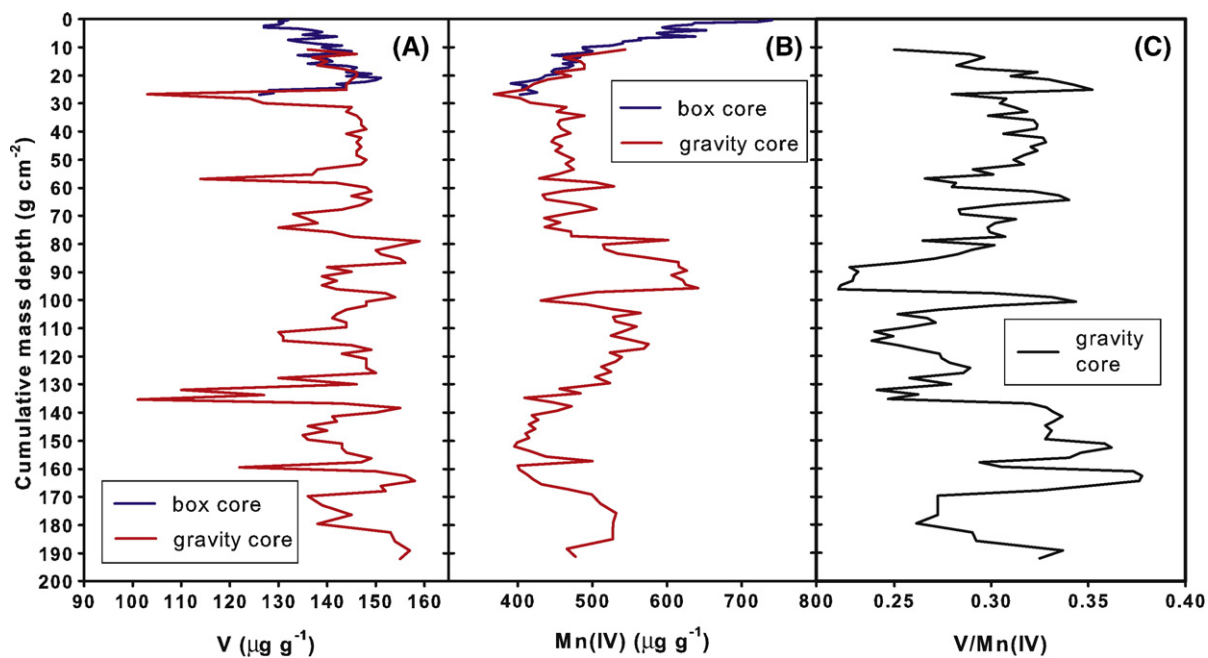


Fig. 5. Combined (box core + gravity core), adjusted (accounting for the 17 cm offset — see Section 3.1 for details), solid-phase profiles of (A) V ( $\mu\text{g g}^{-1}$ ), (B) Mn(IV) ( $\mu\text{g g}^{-1}$ ), and (C) the V/Mn(IV) ratio, as a function of the cumulative mass depth ( $\text{g cm}^{-2}$ ) at MRD05-04.

long uninterrupted intervals of low-oxygen subsurface water.

## 5. Conclusions

Inorganic and organic geochemical tracer and foraminifer data from a  $^{14}\text{C}$ -dated 229-cm long gravity core collected near the Mississippi River delta suggest that episodic low-oxygen bottom water conditions may have occurred on the Louisiana shelf during the last 1000  $^{14}\text{C}$  years. These low-oxygen intervals in the sediment record are characterized by increases in the relative abundance of low-oxygen tolerant benthic foraminifers (high PEB index values), decreases in the sediment V concentration, and excursions in  $\delta^{13}\text{C}$  and two sterol concentrations. The down-core distributions of  $\delta^{13}\text{C}$ , stigmasterol, and  $\beta$ -sitosterol are consistent with the interpretation that periodic increases in the Mississippi River discharge would have delivered more terrigenous material to the coastal shelf to enhance both water column organic carbon production and stratification. Our results suggest that the development of periodic low-oxygen waters on the Louisiana shelf have likely occurred for at least the last 1000  $^{14}\text{C}$  years, and that this historic record has most recently been amplified by human activities in the watershed.

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