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Coastal Land Loss And Hypoxia: The 'Outwelling' Hypothesis Revisited

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Coastal land loss and hypoxia: the 'outwelling' hypothesis revisited

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Abstract

It is generally believed that interannual variability in the areal extent of the Gulf of Mexico hypoxia is driven primarily by the magnitude of the Mississippi River freshwater and nutrient fluxes. It has recently been proposed that outwelling of carbon from deteriorating coastal wetlands into the surrounding Gulf of Mexico could be an important mechanism promoting the development of hypoxia. We used a coupled hydrology–hydrodynamics model of the Barataria estuary, a site of massive wetland loss, to calculate the fluxes of nitrogen, chlorophyll a and carbon at the estuary–ocean interface. The hydrology model calculates runoff from rainfall and evaporation data, and then feeds it into the high-resolution (100 m × 100 m grid, 1.3 million elements), two-dimensional depth-integrated hydrodynamic model. Model results show substantial outwelling of total organic carbon (TOC, 110×10^6 kg yr⁻¹), dissolved organic carbon (DOC, 94.3×10^6 kg yr⁻¹), particulate organic carbon (POC, 15.7×10^6 kg yr⁻¹) and chlorophyll a (Chl a, 0.3×10^6 kg yr⁻¹) from the estuary to the coastal waters and an import of nitrate (N–NO₃, 6.9×10^6 kg yr⁻¹) from the nutrient-rich coastal waters into the estuary. Estuarine fluxes of TOC, DOC, POC, Chl a and N–NO₃, account for 2.8%, 2.7%, 3.4%, 7.5% and 1%, respectively, of the annual fluxes carried by the lower Mississippi River. The flux of total nitrogen was not statistically significant. Overall, this study supports the conclusion of the previous modeling study (Das *et al* 2010 *Ecol. Modeling* **221** 978–85), suggesting that the Barataria estuary supplies a relatively small amount of the carbon consumed in the Gulf's hypoxic zone. Importantly, our results indicate that import of nitrate from the coastal waters and its assimilation within the estuary could account for 38% and 208%, respectively, of the calculated TOC and Chl a exports, demonstrating the pervasive control of the Mississippi River on the productivity of this shelf.

Keywords: coastal ecosystems, ecological modeling, wetlands, carbon budgets, hypoxia, Gulf of Mexico

1. Introduction

Widespread hypoxia has been documented in the northern Gulf of Mexico for >25 years, with a present areal extent of up to 22 000 km² (figure 1). Hypoxia develops from a suite of biological and physical factors, two of which are

the most important: (1) nutrient-enhanced surface primary productivity, which is also manifested in a high carbon flux to sediments, and (2) high water column stability, which controls vertical diffusive oxygen flux (Rabalais *et al* 2001, Justic *et al* 2007). The strong decadal association between the magnitude of the Mississippi River nutrient fluxes and the areal extent of

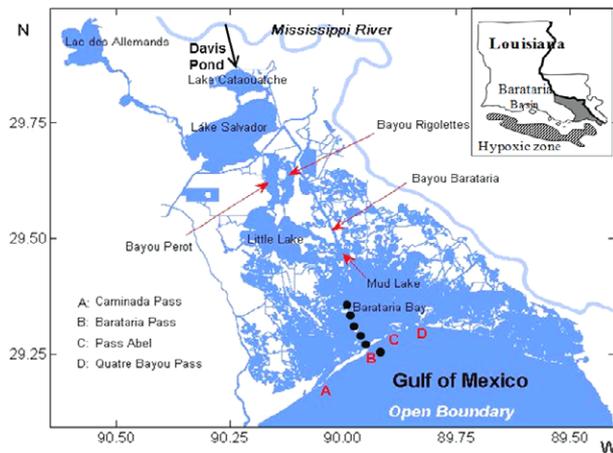


Figure 1. Model domain of the 2D model of the Barataria estuary depicting major water bodies, the Davis Pond freshwater diversion, and locations of the sampling stations (black dots). The inset map shows approximate extent of the Gulf’s hypoxic zone during July 1993.

hypoxia indicate that riverine nutrients control the magnitude of primary productivity that ultimately fuels hypoxia (Rabalais et al 2007, Turner et al 2008). It has recently been proposed that deteriorating coastal wetlands provide an additional source of carbon for the Gulf’s hypoxia region (Dagg et al 2007, Bianchi et al 2008, 2010a, 2010b). The Louisiana coastal zone has been the site of massive wetland loss amounting to about a quarter of the nearly 1.9×10^{10} m² of wetlands existing at the beginning of the 20th century, and a loss of 3.5×10^9 m² from 1956 to 2006 (Barras et al 2008, Turner 2010). The majority of wetland loss occurred from marsh edge erosion and vegetated wetlands becoming open water (Dahl and Johnson 1991). This loss is attributed to a complex interaction of factors, including altered wetland hydrology, channelization, sea level rise, and elimination of riverine sediment input to coastal wetlands due to flood control levees on the Mississippi River (e.g. Day et al 1997, Turner 1997). Eroding coastal wetlands have the potential to release appreciable amounts of nutrients and carbon into the surrounding bays and estuaries (the ‘outwelling hypothesis’, Odum 1980). Using a simple box model Das et al (2010) showed that the Barataria estuary exports total organic carbon (109×10^6 kg TOC yr⁻¹) and imports nitrate (7×10^6 kg N–NO₃ yr⁻¹) from the coastal waters, but cautioned that these fluxes are small compared to the Mississippi River TOC and N–NO₃ fluxes.

This study uses a high-resolution two-dimensional (2D) model and a large water quality database (1994–2010, Turner 2010) to quantify the estuarine-shelf exchanges of carbon and nutrients in the Barataria estuary. Our objectives are threefold: (1) to estimate the fluxes of water, nitrate (N–NO₃ + N–NO₂, herein referred to as N–NO₃), total nitrogen (TN), total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC) and chlorophyll a (Chl a) through the Barataria passes; (2) to compare and cross-check the fluxes obtained from a 2D model with those obtained from a simple box model (Das et al 2010) and field studies; and (3) to estimate the importance of estuarine outwelling for the overall carbon budget in the Gulf’s hypoxic zone.

2. Methods

2.1. The study site

The Barataria estuary is a 120 km long estuary located in the north-central Gulf of Mexico, just to the west of the Mississippi River Delta (figure 1). The northern half of the estuary contains several large lakes. The southern half of the estuary contains tidally influenced marshes interconnected by ponds, lakes, and channels that finally empty into a large bay system behind the barrier islands. The average depth of the estuary is about 2 m. The estuary is connected to the Gulf of Mexico through four tidal passes (Barataria, Caminada, Abel and Quatre Bayou). The tropic diurnal tide range is approximately 0.35 m at the coastal endpoint, but decreases by an order of magnitude as tide progresses up the estuary. Salinities range from near zero in the upper reaches of the estuary to about 25 in the southernmost section of the estuary. Freshwater enters the Barataria estuary mainly from four sources: rainfall, stream runoff, man-made diversions and siphons, and from the Gulf Intracoastal Waterway. Due to its proximity to the Mississippi River Delta, the southern sections of the estuary are influenced by discharges from the Mississippi River.

2.2. Approach to modeling

The 2D model is a high-resolution (100 m × 100 m grid, 1.3 million elements), coupled hydrology–hydrodynamic model of the Barataria estuary (figure 1). The model was originally developed by Inoue et al (2008) and further refined in this study.

Runoff from the drainage basins is the major source of fresh water for the Barataria estuary (Marmer 1954, Kjerfve 1973, Light et al 1973). The hydrology model calculates runoff from rainfall and evaporation data, and then feeds it into the hydrodynamic model (Inoue et al 2008). The hydrology model is based on the unit hydrograph, i.e., the difference between actual local precipitation and evaporation integrated over the model domain that was used to calculate runoff. Groundwater flow is not considered significant because of the shallow depth of the Barataria estuary and the fact that most of the land is covered by wetlands that are saturated with water (Gagliano 1973). In order to estimate local runoff, the Barataria estuary was divided into eight sub-basins. Each of the eight runoff hydrographs included a specific time-delayed function to mimic marsh drainage.

The hydrodynamic part of 2D model of the estuary is a depth-integrated two-dimensional model of estuarine circulation. Depth-integrated equations were used because the water column in this shallow estuary is generally well-mixed due to winds and tides (Inoue et al 1998). The equations of conservation of mass and momentum, including baroclinic pressure gradient, are written in Cartesian coordinates in terms of depth-integrated transport:

$$\frac{\partial U}{\partial t} + \frac{\partial U^2}{\partial x} + \frac{\partial UV}{\partial y} - fV = -gH \frac{\partial \zeta}{\partial x} - \frac{1}{2}gH^2 \frac{\partial \rho}{\partial x} - g \frac{U}{c^2} \left\{ \left(\frac{U}{H} \right)^2 + \left(\frac{V}{H} \right)^2 \right\}^{1/2} + \frac{\tau_x}{\rho} + A \nabla^2 U \quad (1)$$

$$\frac{\partial V}{\partial t} + \frac{\partial UV^2}{\partial x H} + \frac{\partial U^2}{\partial y H} - fU = -gH \frac{\partial \zeta}{\partial y} - \frac{1}{2}gH^2 \frac{\partial \rho}{\partial y} - g \frac{\frac{V}{H} \{ (\frac{U}{H})^2 + (\frac{V}{H})^2 \}^{1/2}}{c^2} + \frac{\tau_y}{\rho} + A \nabla^2 V \quad (2)$$

$$\frac{\partial \zeta}{\partial t} + \frac{\partial U}{\partial x} + \frac{\partial V}{\partial y} = 0 \quad (3)$$

$$\frac{\partial HS}{\partial t} + \frac{\partial US}{\partial x} + \frac{\partial VS}{\partial y} = D_S \left(\frac{\partial H \frac{\partial S}{\partial x}}{\partial x} + \frac{\partial H \frac{\partial S}{\partial y}}{\partial y} \right) \quad (4)$$

$$\frac{\partial HT}{\partial t} + \frac{\partial UT}{\partial x} + \frac{\partial VT}{\partial y} = D_{ST} \left(\frac{\partial H \frac{\partial T}{\partial x}}{\partial x} + \frac{\partial H \frac{\partial T}{\partial y}}{\partial y} \right), \quad (5)$$

where $U = \int_{-h}^{\zeta} u dz$, $V = \int_{-h}^{\zeta} v dz$, $H = h + \zeta$, $S = (1/H) \int_{-h}^{\zeta} s(z) dz$, and $T = (1/H) \int_{-h}^{\zeta} t(z) dz$.

In the above equations, t denotes time, x , y , and z are Cartesian coordinates, u and v denote velocity components in the direction of x and y , respectively, z is elevation of the free surface above mean sea level, h is the undisturbed depth of the water, f is the Coriolis parameter (assumed to be a constant), g is the acceleration due to gravity, τ_x and τ_y are the x and y components of wind stress, respectively, ρ is the density of water, $s(z)$ and $t(z)$ are depth-dependent salinity and temperature, respectively, A is the horizontal eddy viscosity, S is depth-averaged salinity, T is depth-averaged temperature, D_S and D_T are the horizontal eddy diffusivities for S and T , respectively, and C is the Chezy coefficient which is depth-dependent. The bottom roughness is represented through Manning's n coefficient, such that the Chezy coefficient is evaluated as

$$C = \frac{1}{n} H^{1/6}. \quad (6)$$

The model equations are finite-difference equations on a staggered mesh grid C of Arakawa (Mesinger and Arakawa 1976). The conservation of mass and total energy is done by using the Grammeltvedt C scheme (Grammeltvedt 1969). The centered-difference Leapfrog scheme is used for time integration, interspersed at regular intervals with the Euler scheme to remove the computational mode due to central time differencing. The advection scheme of Hsu and Arakawa (1990) based on Takacs scheme (Takacs 1985) is used because this is an accurate upstream scheme with very little numerical dispersion, which is usually seen in centered-difference schemes.

The forcing functions used in this depth-integrated two-dimensional model are tides coming in from the Gulf of Mexico, rainfall and evaporation over the model domain, local runoff, salinity, water temperature, wind, and freshwater diversions from the Mississippi River (Davis Pond, West Pointe a la Hache, Naomi).

2.3. Model parameterization

2.3.1. Evaporation. Because evaporation data were available from one station, an empirical formula developed by Roll (1965), suitable for the Gulf coastal regions, was used to estimate evaporation:

$$E = C_E \rho (q_{\text{sea}} - q_{\text{air}}) U_{10},$$

where E is the evaporation rate, C_E is the transfer coefficient, ρ is the air density, q_{sea} and q_{air} are the specific humidity for the sea and air, respectively, and U_{10} is wind speed at the 10 m reference height. Hourly measurements of the parameters used to calculate evaporation (such as atmospheric pressure, wind speed, sea surface temperature, and dew-point temperature) were obtained from the NOAA monitoring station at Grand Isle (Inoue *et al* 2008).

2.3.2. Precipitation and runoff. Precipitation records were obtained from the US Weather Service site at New Orleans Airport (MSY), because it best represents the dominant upstream region (61% of the total land). Also, rainfall is measured at MSY at hourly intervals, which is important given the small estuarine catchment area. Because the small drainage areas of the Barataria Basin result in relatively rapid runoff, evapotranspiration was not considered in this model. Accordingly, the runoff from any of the 8 drainage sub-basins was calculated using the simple model:

$$\text{Runoff (m}^3 \text{ hr}^{-1}) = (\text{rainfall} - \text{evaporation}) (\text{m hr}^{-1}) \times \text{area (m}^2).$$

The Barataria estuary was divided into 22 watershed management units using a pre-existing watershed chart (a digital map of Louisiana) to estimate the discharge rate via a network of 64 known and 522 unknown and ungauged streams (for details, see Inoue *et al* 2008). A persistence time for each stream was estimated by a simple linear interpolation based on the longest stream, Bayou Chevreuil, which had a persistence time of 72 h. The persistence time varied from 3 to 72 h in the estuary. Total volume of runoff entering through a sub-basin is calculated by multiplying the amount of precipitation by area of the sub-basin. So there are eight hydrographs for runoff data, each having a certain number of hours it takes to enter the basin. A one-sided filter is used to calculate rainfall per unit time per unit area for each sub-basin (Inoue *et al* 2008):

$$y(t_i) = a_1 \times (t_{i-1}) + a_2 x(t_{i-2}) + \dots + a_j x(t_{i-j}),$$

where j is the filter width and $a_1 \dots a_j$ are filter coefficients. The filter width for each sub-basin is chosen to be equal to the persistence time of the water within the sub-basin so that the effective runoff time is less than, or equal to, the persistence time.

2.3.3. Water level. Hourly water level data were obtained from recording gages (41 stations) maintained by the Louisiana Department of Wildlife and Fisheries (LDWF), the United States Geological Survey (USGS) and the LA DNR. Hourly water levels at a coastal station at Grand Isle obtained from the National Ocean Service (NOS) were used to represent conditions at the open boundary.

2.3.4. Wind. Wind speed was converted to wind stress using an empirical relationship derived for the Barataria estuary (Inoue *et al* 2008):

$$\tau = \rho_a U_*^2 \quad \text{and} \quad U_* = 0.037 U_{10} - 0.03,$$

where τ is the wind stress and ρ_a is the air density and U_* is the shear velocity.

2.3.5. Salinity. Hourly salinity records for the station at Grand Isle (the mouth of the Barataria Bay) were used as a forcing function at the open boundary.

2.4. Model simulations

The model was run on Tezpur, a supercomputer at Louisiana State University. A typical run of the 2D model used 32 Tezpur nodes (64 processors) and required 72 h of computing time to simulate hydrology and hydrodynamics over a nine-month period, from March 20 to December 31, 2002. This period was chosen because it provided a good reference data set for model calibration and validation. The Davis Pond diversion into Lake Cataouatche started operating in July 2002 and so we were able to examine system responses with and without river diversion. Further, during 2002, coastal Louisiana experienced frequent frontal passages that increased the amplitude of sea level variations significantly above the mean tropical diurnal tide range of 0.35 m. Also, tropical storm Isidore and hurricane Lili affected the area during September and October 2002. These storms had similar water level responses, but significantly different rainfall amounts that provided a unique opportunity to test model responses to simultaneous variations in rainfall and water level at the open boundary. Finally, between October and December 2002, Acoustic Doppler Current Profiler (ADCP) measurements were carried out in all four tidal passes (Moffatt and Nichol 2005), and this particular data set was used in model validation.

2.5. Estimates of fluxes at the estuary–ocean interface

Because the passes are not in a straight line, the direction of u (velocity in x direction) and v (velocity in y direction) components had to be determined for every model cell in the four tidal passes. This was done by plotting the boundary on a Cartesian coordinate graph and determining the direction of flow in each cell. After the model simulation was completed, the values of u and v were extracted as separate files and then used to compute the total flux of water at the estuary–ocean interface. Based on the direction of flow, the flux were separated into ebb and flood cycles and, integrated over the entire simulation period (20 March–29 December 2002), and then prorated to the entire year (365 days).

The model estimates of flow through the tidal passes were compared with flow measurements carried out by Moffatt and Nichol (2005) between 24 October and 7 December 2002. Moffatt and Nichol (2005) positioned the ADCP at the bottom of the Barataria Pass where it measured currents throughout the water column. For this particular comparison, we used the data collected in the middle of the water column (15 m depth). A Nash–Sutcliffe model efficiency coefficient (Nash and Sutcliffe 1970) was calculated to compare measured and modeled fluxes for the period from 24 October to 7 December 2002. Such a coefficient is generally used to determine the predictive power of hydrological models. The range of coefficients can range

Table 1. Average concentrations of nitrate (N–NO₃), total nitrogen (TN), chlorophyll a (Chl a), total organic carbon (TOC), dissolved organic carbon (DOC), and particulate organic carbon (POC) in the lower Barataria estuary and in the coastal Gulf of Mexico for 1994–2010 (Turner 2010). TOC was partitioned into DOC and POC fractions by assuming a DOC:POC ratio of 6:1, based on the monthly measurements conducted from September 2008 until September 2010 (Turner 2010). The Barataria Bay average was computed from the monthly data collected at five inshore stations depicted in figure 1. The offshore sampling station was located approximately 2 km from the entrance into the estuary. * denotes a significant difference ($\alpha = 0.05$) based on the result of Duncan’s Multiple Range test.

Constituent	Barataria estuary	Gulf of Mexico	Difference	<i>n</i>
N–NO ₃ (μM)	6.96	11.80	4.84*	1120
TN (μM)	36.61	36.41	–0.20	784
Chl a (mg m^{-3})	18.10	16.05	–2.05*	1165
TOC (mg l^{-1})	4.49	3.63	–0.86*	757
DOC (mg l^{-1})	3.84	3.11	–0.73	—
POC (mg l^{-1})	0.65	0.52	–0.13	—

from $-\infty$ to 1 with values closer to 1 indicating better accuracy of the model.

The fluxes of different constituents, total organic carbon (TOC), particulate organic carbon (POC), dissolved organic carbon (DOC), nitrate (N–NO₃), total nitrogen (TN) and chlorophyll a (Chl a) were estimated by multiplying the ebb and flood fluxes of water with the average constituent concentrations measured in the lower Barataria estuary and the coastal Gulf of Mexico, and then subtracting them to obtain the net flux (tables 1 and 2). The nitrate and TOC data were obtained from monthly water quality transects conducted by researchers at Louisiana State University (Turner 2010). TOC was partitioned into DOC and POC fractions by assuming a DOC:POC ratio of 6:1, based on the measurements conducted from September 2008 until September 2010 (Turner 2010). Chlorophyll a (Chl a) concentrations were determined using a modification of EPA method 445.0 (Arar and Collins 1992) in which DMSO is used in lieu of grinding for extraction of the pigments. TOC was measured by employing High Temperature Catalytic Oxidation (HTCO) using a Shimadzu® TOC-5000A analyzer (Singh *et al* 2010). TOC analyses were run on the whole water samples, and DOC analyses were run on samples that had been filtered through a pre-combusted (at 450 °C) glass fiber filter (Whatman® GF/F). POC was obtained by subtracting the DOC value from the TOC value. Total nitrogen (TN) was measured using wet oxidation and colorimetry (Raimbault *et al* 1999).

3. Results

The simulated annual ebb and flood fluxes of water through the Barataria passes (Q) are $111 \times 10^9 \text{ m}^3$ and $107 \times 10^9 \text{ m}^3$, respectively (table 2). The difference between the ebb and flood fluxes is $4 \times 10^9 \text{ m}^3$, corresponding to a net outflow of $127 \text{ m}^3 \text{ s}^{-1}$. The instantaneous modeled Q values in 2002 ranged from near zero to over $\pm 25\,000 \text{ m}^3 \text{ s}^{-1}$ (figure 2). The average hourly Q value is $6951 \text{ m}^3 \text{ s}^{-1}$, or about 43% of the average discharge of the lower Mississippi River.

Table 2. Estimates of the annual fluxes of water (Q), nitrate (N-NO₃), total nitrogen (TN), total organic carbon (TOC), dissolved organic carbon (DOC), particulate organic carbon (POC), and chlorophyll a (Chl a) for the lower Mississippi river (MR) and the Barataria estuary (BE). The Barataria estuary fluxes are calculated from the 2D model. Negative sign denotes that a constituent is exported from the estuary.

Constituent	Mississippi river fluxes	Barataria estuary fluxes			BE _{Net} :MR (%)
		Ebb	Flood	Net	
Q (10 ⁹ m ³)	504.6 ^a	-111.1 ^b	107.1 ^b	-4.0 ^b	0.8
N-NO ₃ (10 ⁶ kg N yr ⁻¹)	724 ^a	-10.8 ^b	17.7 ^b	6.9 ^b	1.0
TN (10 ⁶ kg N yr ⁻¹)	1030 ^c	-56.9 ^b	54.6 ^b	-2.3 ^b	0.2
Chl a (10 ⁶ kg yr ⁻¹)	4.0 ^d	-2.0 ^b	1.7 ^b	-0.3 ^b	7.5
TOC (10 ⁶ kg yr ⁻¹)	4000 ^e	-498.8 ^b	388.8 ^b	-110.0 ^b	2.8
DOC (10 ⁶ kg yr ⁻¹)	3520 ^f	-427.5 ^b	333.3 ^b	-94.3 ^b	2.7
POC (10 ⁶ kg yr ⁻¹)	480 ^f	-71.3 ^b	55.5 ^b	-15.7 ^b	3.4

^aTurner *et al* (2007). ^bThis study. ^c1983–2000 (Justic *et al* 2003). ^dBased on the Chl a value of 8 mg m⁻³ in the Mississippi River for February 1997–November 2010 (Turner 2010). ^eBianchi *et al* (2007).

^fBased on the POC:TOC ratio of 12% in the Mississippi River for April 2009–May 2010 (Turner 2010).

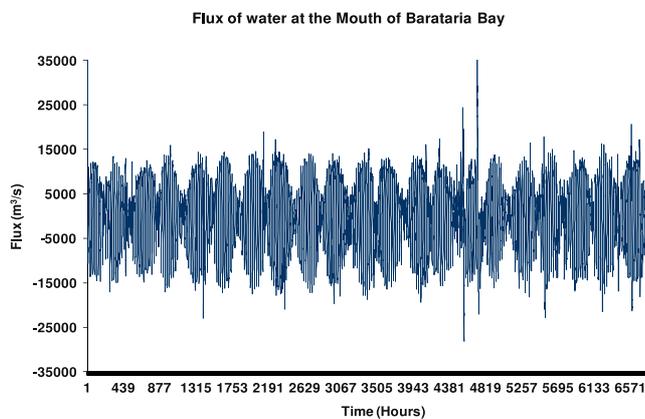


Figure 2. Simulated flux of water through the Barataria passes for 20 March–29 December 2002.

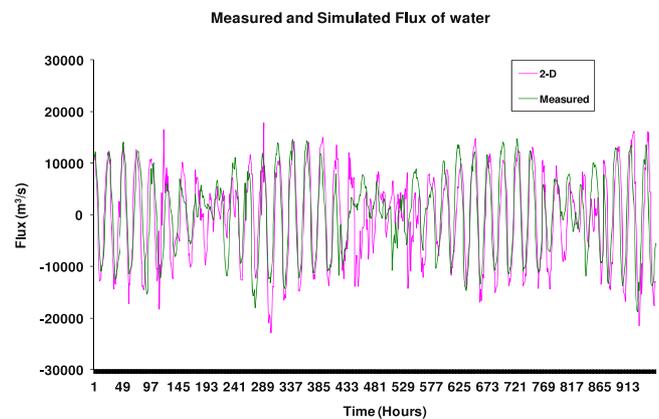


Figure 3. Measured and simulated (2D model) fluxes of water through the Barataria passes for 24 October–7 December 2002.

The predicted flows through the Barataria passes agree very well with the available observations. The average Q value obtained from the ADCP measurements conducted during the period 24 October–7 December 2002 (Moffatt and Nichol 2005) was 6609 m³ s⁻¹, which compares favorably to the model estimate of 6775 m³ s⁻¹ for the same period (figure 3). The Nash–Sutcliffe model efficiency coefficient calculated based on the modeled and observed Q values is 0.99, indicating a very good agreement between the model and the data. However, the modeled ebb flows are consistently higher than measured (figure 3) and the reason for this discrepancy is unknown. It is possible that the 2D model could not fully reproduce dynamics of water in the estuary because it does not take into account flooding and drying of adjacent marshes. It is also likely that because of complex flow conditions in multiple tidal passes there are inherent errors in the ADCP flux estimates.

The estimated fluxes of various constituents (table 2) show that the Barataria estuary annually exports 110 × 10⁶ kg TOC, 94.3 × 10⁶ kg DOC, 15.7 × 10⁶ kg POC and 0.3 × 10⁶ kg Chl a to the coastal Gulf of Mexico, while importing 6.9 × 10⁶ kg N-NO₃ (table 2). Estuarine fluxes of TOC, DOC, POC,

Chl a and N-NO₃, account for 2.8%, 2.7%, 3.4%, 7.5% and 1%, respectively, of the annual fluxes carried by the lower Mississippi River. Total nitrogen (TN) flux was not statistically significant because of small differences between inshore and offshore TN concentrations (table 1). The overall error in these export and import terms could not be adequately assessed because samples for TOC, N-NO₃, TN and Chl a were collected as single monthly discrete samples, which did not allow for the determination of flood and ebb concentrations of these constituents. Nevertheless, by combining the uncertainty in the modeled fluxes of water and the uncertainty in the measured N-NO₃ and TOC concentrations, Das *et al* (2010) estimated that errors ranged from 26% in case of N-NO₃, to 29% for TOC.

4. Discussion and conclusions

4.1. Estuarine outwelling of carbon and nutrients

The significance of carbon and nutrient fluxes at the estuary–ocean interface has been debated for decades (Nixon 1980, Childers *et al* 2000). At the heart of the debate is the

'outwelling' hypothesis which states that marsh–estuarine systems produce more material than can be degraded or stored within the systems. The excess material is exported to the coastal ocean where it supports coastal ocean productivity (Odum 1980). For example, Dame *et al* (1986) found that carbon, nitrogen and phosphorous were exported both seasonally and annually from the North Inlet, South Carolina. Moran *et al* (1991) studied the dynamics of lignin oxidation products, a proxy for terrestrially derived carbon, in the waters of the continental shelf of the southeastern US. They concluded that a contribution of terrestrially derived carbon (as represented by lignin) was highly variable on both weekly and seasonal timescales. Winter *et al* (1996) integrated carbon concentrations with water flow rates obtained from a one-dimensional numerical hydrodynamic model and found that, over a year, there was a net export of carbon from the Swartkops estuary, South Africa, to the Indian Ocean. Ayukai *et al* (1998) used two different methods, a Eulerian method and a variation of the salt balance method, to calculate the fluxes of POC, DOC, nitrates, silicates over tidal cycles during different times of the year in two mangroves (Coral and Conn Creek) with differing salinities and freshwater inputs in northeastern Australia. They found that DOC and silicate were usually exported to the coastal waters while there was a fine balance between the export and import of nitrate, phosphate, and POC.

Cai *et al* (1999) measured dissolved oxygen concentrations and $p\text{CO}_2$ values in five southeastern estuaries in the US. They found that the estuarine export of organic matter was very small compared to the amount of dissolved inorganic carbon being exported from the estuaries. In a study of the Satilla River–estuarine complex in Georgia, Cai *et al* (2000) used a 10-box model of the Satilla River and concluded that all the nitrates that enter the estuary from the Satilla River and that are generated within the estuary (water and marsh) are removed by the time the estuarine waters entered the sea. Jickells *et al* (2000) showed that the Humber estuary in England exported phosphorous. Pomeroy *et al* (2000) studied a decade-long data set (1990–1999) collected in five Georgia estuaries and concluded that the amount of dissolved and particulate organic carbon entering the coastal ocean from these estuaries contribute the equivalent of <1% of the overall primary production in the coastal waters. Cunha *et al* (2003) found that carbon is exported to the coastal ocean during the summer when the freshwater supply to the Ria de Aveiro estuary in Portugal is low.

Sylaios *et al* (2006) studied the Vassova Lagoon, a microtidal, well-mixed lagoon in northern Greece. They used a tidal prism model and found that during the ebb phase of autumn and winter tidal cycles nutrients and chlorophyll a are exported to the coastal ocean while in spring and early summer nutrients enter the lagoon during the flood phase. McGuirk Flynn (2008) showed that the Mullica River–Great Bay estuary in New Jersey was a net exporter of carbon, nitrogen and phosphorous. Bianchi *et al* (2009) looked at marsh exchanges with the inner shelf in the Terrebonne–Timbalier Bay estuary by studying the changes in DOC and lignin concentrations and compositions. They did not find any significant difference in DOC concentrations between the inner bay and shelf stations

but found a decreasing gradient of syringyl/vanillyl lignin phenols from the upper marshes to the shelf. They suggested that this could be indicative of additional organic carbon sources from the marshes to the coastal waters for microbial food webs. Falco *et al* (2010) used a mass balance approach to study the Ebro estuary in Spain and found that there was a net export of nitrogen and phosphorous from the estuary to the sea.

From the review presented above, it is clear that the recent research has not settled the debate on the 'outwelling' hypothesis. While there are estuaries that export appreciable amounts of carbon and nutrients, numerous studies pointed out that fluxes are often very nearly balanced and the net fluxes are only small fractions (e.g., <5%) of the total estuarine-shelf exchanges.

4.2. Estuarine-shelf exchanges in the Barataria estuary

While there is a large body of work of estuarine export of large amounts of nutrients and carbon, few studies have attempted to estimate the importance of estuarine sources for the coastal carbon budgets in river-dominated coastal ecosystems like the Barataria estuary. This estuary has been the site of a massive wetland loss (Barras *et al* 2008, Turner 2010) and the fate of carbon from eroded wetlands remains incompletely known. Our results show (table 2) that the Barataria estuary annually exports 110×10^6 kg TOC, 94.3×10^6 kg DOC, 15.7×10^6 kg POC and 0.3×10^6 kg Chl a to the coastal Gulf of Mexico, while importing 6.9×10^6 kg N–NO₃. Interestingly, assuming C:N ratio of 5.7:1 by weight (mol. C:N = 106:16, Redfield *et al* 1963), and a C:Chl a ratio of 63:1 (Malone *et al* 1988), the N–NO₃ import from the coastal ocean could account for 38% and 208% of the calculated TOC and Chl a exports, respectively. The fact that the Barataria estuary receives N–NO₃ from the coastal Gulf of Mexico is not surprising given the proximity of the Mississippi River Delta, high riverine N–NO₃ load (Turner *et al* 2007, 2008), and circulation in the Louisiana Bight (Wang and Justic 2009, Das *et al* 2010, Li *et al* 2011). Regardless of the cause, it appears that eroding coastal wetlands are not the only source of carbon for the Barataria estuary. In fact, Wissel *et al* (2005) found that POM in the lower Barataria estuary was primarily of phytoplankton origin.

In a related study, Wilson and Allison (2008) used a conceptual model to study wave-induced subaqueous platform erosion due to retreat of marsh shoreline in the Barataria estuary and the yield of sediments and POC to the estuary. Their estimated annual POC yield (37×10^6 kg yr⁻¹) is of the same order of magnitude as our estimate of POC export (15.7×10^6 kg yr⁻¹, table 2), potentially suggesting that about 40% of POC released from eroding marshes is exported to the coastal Gulf of Mexico.

Li *et al* (2011) conducted a 24 h continuous survey across the Barataria Pass during 31 July–1 August 2008. The net fluxes of water and total suspended sediments (TSS) out of the estuary were 2.7×10^7 m³ d⁻¹ and 8.8×10^6 kg d⁻¹, respectively. The measured TSS concentrations were several times higher than the long-term TSS averages for stations in the lower Barataria Bay (1994–2001, Turner 2010). This

discrepancy points to the need to supplement the long-term monitoring data with continuous estuarine flux studies. Storm events which cause stirring and resuspension of estuarine sediments are likely to increase the export of estuarine carbon into the coastal Gulf of Mexico (Sampere *et al* 2008). Also, inundation of marshes due to cold fronts and their subsequent drainage could increase the export of carbon due to marsh flushing. In Fourleague Bay, Louisiana, flushing time decreased four-fold (from about eight days to less than two days) in response to northerly winds associated with a passage of a strong cold-front (Perez *et al* 2003). Similarly, a study of the Atchafalaya/Vermillion Bays, Terrebonne/Timbalier Bays and Barataria Bay, Louisiana, concluded that strong cold fronts may flush more than 40% of the bay waters out onto the continental shelf within a less than 40 h period (Feng and Li 2010). Nevertheless, it is also likely that substantial imports of offshore sediment, nutrients and carbon take place during the inundation phase of cold-front related flushing.

4.3. Importance of riverine and estuarine nutrient and carbon sources as controls of hypoxia

Our modeled fluxes of water, N–NO₃ and TOC (table 2) are nearly identical to those predicted by a simple box model using the same driving variables (Das *et al* 2010). Das *et al* (2010) calculated that the Barataria estuary annually exports 109×10^6 kg TOC and imports 7×10^6 kg N–NO₃ from the coastal waters. They estimated that the TOC export from the Barataria estuary, when prorated to the total water area of the estuary (19×10^8 m²), averages $57 \text{ gC m}^2 \text{ yr}^{-1}$. Das *et al* (2010) further pointed out that the Barataria estuary appears to be a very small source of TOC compared to the lower Mississippi River (2.7% of riverine TOC). Under the most liberal assumptions, TOC export from the Barataria Bay can account for only 10% of the oxygen demand within the entire (16 000 km², Rabalais *et al* 2007) Gulf's hypoxic zone. This finding was criticized by Bianchi *et al* (2010b) on the grounds that the estimate of TOC export ($57 \text{ gC m}^2 \text{ yr}^{-1}$) is much lower than $150 \text{ gC m}^2 \text{ yr}^{-1}$ calculated by Happ *et al* (1977) and that Das *et al* (2010) did not include stored marsh-derived carbon in the shelf sediments. The differences between the TOC export calculated by Happ *et al* (1977) and Das *et al* (2010) are likely due to the differences in the locations of sampling stations between the two studies. The stations occupied by Happ *et al* (1977) were inshore near the marsh edge, while Das *et al* (2010) used the data collected at stations in the lower Barataria Bay, where estuarine-shelf exchanges take place. Das *et al* (2010) assumed that all estuarine-derived carbon would be respired outside the estuary and that no sediment storage would take place. If it is assumed that a fraction of estuarine-derived carbon is stored in the shelf sediments, then the calculated oxygen demand would be proportionally lower. Further, in evaluating the marsh contribution to the overall estuarine carbon flux, it is important to consider the lability of carbon to microbial use. Degradation experiments for Barataria estuary POM (Fry 2011) have revealed that 'material lost' after 28 days has the C/N of phytoplankton, with very little apparent activity from the residue. This residue would

include the hypothetical wetland carbon. Freshly produced organic matter (e.g., phytoplankton) is typically several times more labile than old marsh soil. When the lability factor is considered, the possible importance of marsh carbon export from the Barataria estuary for hypoxia in the northern Gulf of Mexico decreases even further.

In conclusion, our results support the findings of the previous modeling study (Das *et al* 2010), reinforcing the conclusion that carbon export from the Barataria estuary is small compared to the carbon flux of the Mississippi River and the overall carbon demand in the Gulf's hypoxic zone. Our results further indicate that import of N–NO₃ from the coastal waters and its assimilation within the estuarine proper could account for 38% and 208%, respectively, of the calculated TOC and Chl *a* exports. These findings reinforce the conclusion that the Mississippi River is the largest influence controlling the productivity and carbon budgets in the vicinity of the Mississippi River delta. Nevertheless, we note that the role of episodic storm events on carbon export could not have been fully evaluated in this study due to the lack of continuous measurements in the Barataria Bay passes. We call for more measurements to supplement the long-term monitoring data with continuous estuarine flux studies.

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