Floodplain influence on carbon speciation and fluxes from the lower Pearl River, Mississippi

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Abstract

To investigate the floodplain influence on carbon speciation and export to the northern Gulf of Mexico, water samples were collected monthly from two sites in the East Pearl River (EPR) basin during 2006-2008. Additionally, four spatial surveys in the river basin between those two sites were also conducted. Compared with the upstream sampling site at Bogalusa, MS, dissolved inorganic carbon (DIC) and particulate organic carbon (POC) concentrations were 36% and 55% lower, respectively, and dissolved organic carbon (DOC) concentration was 49% higher at the downstream Stennis Space Center (SSC) site. In addition, the bulk DOC pool at SSC had a higher colloidal fraction than at Bogalusa (75% vs. 68%). Detailed spatial surveys revealed the differences between the upstream and downstream stations resulted both from input from Hobolochitto Creek, a tributary of the EPR, and from influence of the swamp-rich floodplain. The contributions from Hobolochitto Creek to the carbon pool in the EPR basin were lowest during a high flow event and reached a maximum during the dry season. Meanwhile, the floodplain in the EPR basin acted as a significant sink for DOC, POC and particulate nitrogen during summer and for suspended sediment during a high flow event. However, the floodplain was converted into a source of suspended sediment, DOC, and POC to the EPR during winter, revealing a dynamic nature and seasonality in the floodplain influence. Consistent with its dominant forest coverage, abundant wetlands along the river corridor, and mild anthropogenic disturbance, the Pearl River basin above Bogalusa generally had higher yields of DOC and POC (1903 and 1386 kg-C km^{-2} yr^{-1}, respectively), but a lower yield of DIC (2126 kg-C km^{-2} yr^{-1}) compared to other North American rivers. An estimation based on a mass balance approach suggests the interactions between

floodplain and the main river stem could reduce the annual DIC and POC export fluxes from downstream of the EPR by 24% and 40%, respectively, but enhance the annual riverine DOC export by 25%. Similar scenarios likely occur in other wetland-rich coastal rivers and are capable of significantly altering the current estimation of riverine carbon export.

1. Introduction

Rivers are major pathways for the transfer of terrigenous materials into coastal marine environments. The global riverine carbon flux is as high as 250-360×10^9 kg-C yr^{-1} for dissolved organic carbon (DOC), 200×10^9 kg-C yr^{-1} for particulate organic carbon (POC), and 407×10^9 kg-C yr^{-1} for dissolved inorganic carbon (DIC; Hedges and Keil, 1995; Aitkenhead and McDowell, 2000; Cai et al., 2008). World rivers also discharge 15×10^{12} kg sediment annually into the coastal ocean (Milliman, 1991). This terrestrially derived carbon is actively involved in biogeochemical cycles in coastal environments (Hedges et al., 1997; Dagg et al., 2004; Hernes and Benner, 2006; Tank et al., 2012; Bianchi et al., 2013). As a result, the carbon cycle, biological productivity, ecological status, and community metabolism in the river-dominated coastal ocean can be extensively altered in response to the riverine carbon inputs (Gattuso et al., 1998; Hernes and Benner, 2003; Wysochi et al., 2006; Bianchi et al., 2008; Bauer et al., 2013). Riverine sediment supply is also an important source for coastal restoration and affects the light availability in coastal regions, thereby having a profound influence on biological productivity (Lohrenz et al., 1999, 2008; Allison et al., 2013). The organic matter and nutrients associated with riverine sediment can also play an important role in regulating the primary productivity and community metabolism (Goni et al., 2006; Turner et al., 2007; Zhang et al., 2010).

It has been demonstrated that human activities, such as damming, land use, and water control structures, can significantly alter riverine export fluxes of carbon and sediment (Raymond et al., 2008; Meade and Moody, 2010; Gao et al., 2012; Zhang et al., 2014). Climatic variability and associated extreme events also have huge impacts on terrigenous

material export (Raymond and Cole, 2003; Striegl et al., 2005; Allison et al., 2012; Bianchi et al., 2013; Cai et al., 2013). However, most riverine flux estimates, including the Mississippi, Amazon, and Yangtze Rivers, are based on measurements tens to hundreds kilometers upstream of the river mouth due to sampling constraints and limitations in determining water discharge in tidal reaches and floodplains in lower river basins as well as due to difficulties in obtaining representative river end-member samples (e.g., Emmerton et al., 2008; Allison et al., 2012; Gao et al., 2012; Cai et al., 2013; Seidal et al., 2015; Ward et al., 2015). These constraints can result in a large uncertainty in riverine flux estimation and hinder the understanding of the role of rivers and their floodplains as the connection between terrestrial and marine systems (Meade, 1996).

Lower river wetlands, consisting of river swamps, salt marshes, lakes, and other water bodies, are widespread in river deltas and lowermost river floodplains with extended coastal plains. It is well acknowledged that wetland-rich river deltas and floodplains are productive and their dynamic biogeochemical processes have a large capacity to significantly alter the concentrations, chemical composition and riverine loads of carbon, nutrients and suspended sediment in the main river channel. For example, Cai et al. (2000) suggested that metabolic processes in salt marshes could result in a tenfold increase of riverine DIC export. For the Atchafalaya River, the swamps also enhance the riverine DOC export by up to 25% although its sediment load to the coastal ocean was reduced by 30% (Allison et al., 2012; Shen et al., 2012). The floodplain and river delta in the Danube and Mackenzie Rivers have been shown to reduce the riverine POC load by 7% and 15%, respectively (Tockner et al., 1999; Emmerton et al., 2008). In the Amazon River, which represents 16% of the global freshwater discharge, the flooded forests

supported a large amount of riverine carbon export as DOC and dissolved CO_2 through their primary production (Richey et al., 2002; Abril et al., 2014). Recent observations in the lower reach of the Amazon River further revealed about a 50% decrease of POC concentration and 8% increase of DOC concentration during riverine transport as well as a decreasing reactivity of the organic matter (Seidal et al., 2015; Ward et al., 2015). In river basins with significant influences from floodplains and wetlands, fluvial flux estimates from the continents could significantly deviate from the actual riverine carbon and sediment fluxes. Nevertheless, the interaction between floodplains and rivers could be an important process in altering riverine material export in addition to anthropogenic and extreme climatic events, such as hurricanes and major flooding and drought events (Cai et al., 2008, 2013; Raymond et al., 2008; Meade and Moody et al., 2010; Bianchi et al., 2013).

There have been extensive efforts to direct investigations on the floodplain-river interactions in wetland-rich river systems, such as the Atchafalaya and Amazon Rivers. Observations have shown a great variation in the influence of floodplains on the riverine material export (Tockner et al., 1999; Cai et al., 2000; Richey et al., 2002; Emmerton et al., 2008; Allison et al., 2012; Shen et al., 2012; Abril et al., 2014; Ward et al., 2015). Due to their dynamic nature, the same floodplain can show contradictory roles based on different field observations (e.g., Xu, 2006; Shen et al., 2012; BryantMason et al., 2013; Scott et al., 2014). Although the floodplain's capacity to change the riverine material export fluxes is likely linked to the differences of geomorphologic, ecologic and hydrologic conditions among various floodplains, the controlling mechanisms and

subsequent variations in the quantity and quality of riverine chemical species remain largely unknown.

To better understand the effects of lower river floodplains in altering carbon speciation and export, a comprehensive study was executed in the East Pearl River (EPR) floodplain in southern Mississippi, which has widespread swamps and wetlands. Monthly water samples from upstream and downstream stations in the EPR floodplain were collected during 2006-2008. In addition, four spatial surveys on the floodplain and tributaries were carried out in different seasons throughout the 2007-2008 water year. Concentrations of three carbon species (DIC, DOC and POC) and suspended sediment and their stable carbon and nitrogen isotopic composition were quantified to examine the roles of floodplain and tributaries and their influence on the EPR water chemistry as well as their relationship to watershed geographic and ecological characteristics and possible controlling factors.

2. Materials and methods

2.1. Site description

The Pearl River originates in the east–central portion of the state of Mississippi and discharges into the Gulf of Mexico via the Mississippi Sound (Fig. 1). It is a small, forested, blackwater river with a drainage basin of 22,690 km^2 and a length of approximately 790 km. The Pearl River Basin covers southeastern Louisiana and southwestern Mississippi and is dominated by forest (69%), followed by agricultural land (27%) and wetland and water area (3%; Mississippi Department of Environmental Quality, 2007). Between Bogalusa, LA, and Picayune, MS, the lower Pearl River divides

into the East Pearl River and (West) Pearl River. The watershed area gauged by the U.S. Geological Survey hydrological station near Bogalusa, LA (http://waterdata.usgs.gov/nwis/uv?02489500) is 17024 km^2, leaving approximately 5,600 km^2 for the downstream watersheds.

The EPR has several possible freshwater and carbon and sediment sources, including the upper Pearl River from Bogalusa, Hobolochitto Creek, and wetlands in the floodplain. During low flow, most of the upper Pearl River discharge flows into the West Pearl River while the upper and East Pearl Rivers are better connected during flooding. The fraction of upper Pearl River discharge flowing into the EPR promptly increases during high flow events compared to dry seasons (Shiller et al., 2012). In contrast to the whole Pearl River Basin, the EPR sub-basin is dominated by marsh and swamp (Gosslink, 1990), both of which are subject to annual flooding. Hobolochitto Creek is the main source of water to the EPR during low discharge.

2.2. Sample collection and size fractionation of dissolved organic matter

Ten sampling stations were set out in the study area (Fig. 1). The lower Pearl River main stem was sampled near Bogalusa (Station ID: PRB), LA. The EPR Basin was sampled at several locations from Walkiah Bluff (PRW), immediately after the split of the Pearl River into the East and West Pearl River, to Stennis Space Center (PRS) to trace the river flow as it receives water from tributaries and interacts with the floodplain wetlands. Samples were also collected from a tributary (Hobolochitto Creek, PRHC) and wetland channels in the floodplain, including Indian Bayou (PRIB), Mike's Bayou (PRMB), Mike's River (PRMR) and English Bayou (PREB; Fig. 1). Another two

stations in the EPR main stem were located under Interstate Highway 59 (PRI59) and about 2 km before the Stennis Space Center (PRTS), respectively. Station PRI59 provides an good opportunity to monitor the effect of Hobolochitto Creek on the EPR water chemistry while Station PRTS is a time series station which has been monitored at various times for a decade (Duan et al., 2007a, b; Shiller et al., 2012; Cai et al., 2013).

River water was collected monthly at Stations PRB and PRS from August 2006 to September 2008. Additionally, four basin-wide sampling campaigns were conducted to collect water samples from all 10 stations on November 8 and February 27, 2007 and June 25 and September 26, 2008. Small volume surface water samples were hand grabbed with an acid cleaned 1 L high density polyethylene bottle mounted on a 2-m long pole sampler while facing upstream (Shim et al., 2016). The bottle was rinsed with the river water three times before collecting samples. Water samples were stored in an ice-filled cooler and transported to the lab for further processing within 2-3 h. Aliquots of water samples were filtered through 0.4 μm Millipore polycarbonate filters. Filter samples were then freeze-dried for the analysis of suspended particulate matter (SPM). For POC and particulate nitrogen (PN) analysis, an aliquot of water was filtered through pre-combusted 0.7 μm GF/F filters (Whatman). Filters were freeze-dried, acid fumed for three days and freeze-dried again before the analysis of POC and PN concentrations and their isotopic compositions, while filtrates were collected for analysis of total dissolved nitrogen (TDN), DOC and DIC concentrations and their stable carbon isotopic composition (Cai et al., 2008*a, b*).

On selected sampling events, large volume water samples were collected from both stations PRB and PRS for the quantification of colloidal (1 kDa-0.45 μm) organic carbon

(COC) concentration and isotopic composition (n=5 and 7 for PRB and PRS, respectively). Surface water samples were filtered through a pre-rinsed in-line 0.45-μm polycarbonate cartridge (Osmonics) and about 25 liters of filtrate were collected for ultrafiltration (Cai and Guo, 2009). An ultrafiltration system equipped with a spiral-wound 1 kDa cartridge (Amicon S10Y1) and Teflon pump head and tubing was used for sample processing. Details of the cartridge calibration, cleaning and ultrafiltration procedure have been previously described (Guo and Santschi 1996; Guo et al. 2000; Cai and Guo, 2009). Discrete permeate samples were collected for DOC measurement at different concentration factors and for fitting the ultrafiltration permeation model to quantify the low molecular weight (LMW, <1 kDa) and colloidal or high molecular weight (HMW, >1 kDa) fractions (Cai and Guo, 2009).

2.3. Sample analysis

Concentrations of DOC, DIC and TDN were measured on a Shimadzu TOC analyzer (TOC-V) interfaced to a nitrogen detector (TNM-1; Cai et al., 2008a). Samples were acidified with concentrated HCl to pH < 2 before DOC analysis while samples remained unacidified for total dissolved carbon (TDC) measurements. DIC concentration was calculated from the difference between DOC and TDC concentrations. The total DOC blank (including Milli-Q water, acid for sample acidification, and the instrument blank) was generally less than 2-6 μM. Precision was better than 2% and accuracy was within 1% based on the analysis of DOC standards (Cai et al., 2013). Dissolved organic nitrogen (DON) concentrations were calculated from the difference between TDN and available dissolved inorganic nitrogen concentrations in the same samples during the

spatial surveys (Shim, 2011). $\delta^{13}C$ of DOC ($\delta^{13}C$-DOC) and DIC ($\delta^{13}C$-DIC) were measured on a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd.) interfaced to an O.I. Analytical Model 1010 TOC Analyzer (OI Analytical) at University of California Davis Stable Isotope Facility (St-Jean, 2003). Concentrations of POC and PN as well as their $\delta^{13}C$ ($\delta^{13}C$-POC) and $\delta^{15}N$ ($\delta^{15}N$-PN) values were also measured at University of California Davis Stable Isotope Facility on a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd.). Samples were acid-fumed to remove inorganic carbon before the analysis of POC and $\delta^{13}C$-POC. The stable carbon isotopic composition of COC ($\delta^{13}C$-COC) was measured with freeze-dried COC samples as described in Guo et al. (2003b).

2.4. Flow separation and flux estimation

The river discharge of the Pearl River main stem (Q-Bogalusa) was recorded by the US Geological Survey near Bogalusa, Louisiana (http://waterdata.usgs.gov/nwis/uv?02489500), while the river discharge of Hobolochitto Creek (Q-Hobolochitto Creek) was estimated from the sum of the West and East Hobolochitto Creek flow rates (http://waterdata.usgs.gov/nwis/uv?02492343 and http://waterdata.usgs.gov/nwis/uv?02492360). However, the river flow of the EPR after the split of the main stem of the Pearl River is not gauged. Using dissolved Na as a conservative tracer, Shiller et al. (2012) established a flow separation formula in the EPR to estimate the contribution of Hobolochitto Creek flow (%Hobolochitto Creek):

$$\%\text{Hobolochitto Creek} = 1.602 - 0.1819*\ln(\text{Q-Bogalusa}) \quad \text{(Eq 1)}$$

Where Q is in m^3/s. So the EPR discharge (Q-EPR) is:

$$\text{Q-EPR} = \text{Q-Hobolochitto Creek} / \%\text{Hobolochitto Creek} \quad \text{(Eq 2)}$$

The discharge of the upper Pearl River into the EPR is the difference between Q-EPR and Q-Hobolochitto Creek. The flow separation estimates suggest that Hobolochitto Creek contributed 30-90% of the EPR flow during the investigation period, and the relative contribution of Hobolochitto Creek to the EPR increased with decreasing discharge at Station PRB.

Annual riverine export fluxes of carbon species from the Pearl River near Bogalusa (Flux-PRB), Louisiana, and the EPR at Stennis Space Center (Flux-PRS), Mississippi, were estimated using the USGS LOADEST program (Cai et al., 2015; http://water.usgs.gov/software/loadest/). Since only four samples each were obtained in Hobolochitto Creek (PRHC) and the upper EPR at Walkiah Bluff (PRW), the flow-weighted mean solute concentrations are applied together with the annual river discharge to estimate the annual carbon export from these two locations (Flux-PRHC and Flux-PRW). The instantaneous carbon and sediment fluxes show a linear correlation with river discharge, suggesting the reliability of results obtained with the flow-weighted mean solute method (Warnken and Santschi, 2004). The material supply of the floodplain to the EPR (Flux-Floodplain) is defined as the difference between Flux-PRS and the sum of Flux-PRW and Flux-PRHC. A comparison in fluxes estimated by both LOADEST and the flow-weighted mean solute methods showed a difference of <10% in the export fluxes from the pristine Yukon River for carbon and nitrogen species (Guo et al., 2012). Therefore, a 10% relative contribution of floodplain input to the Flux-PRS is selected to test the significance of floodplain contribution in the study area considering the uncertainties of both flux estimates. The instantaneous riverine carbon fluxes from the

upper EPR at Walkiah Bluff, Hobolochitto Creek and lower EPR at Stennis Space Center were further estimated for each season (November, February, June and September) by multiplying the instantaneous river discharge and solute concentrations. By comparing the input and output of carbon in the EPR basin, the seasonal contributions from the floodplain to river carbon fluxes were obtained. The seasonal variations of the relative contributions of the floodplain and Hobolochitto Creek to the carbon export from the EPR were then examined.

2.5. Statistical analysis

The SigmaPlot 11.0 program was used to run paired t-test to examine the statistical difference in data between two or more groups. The average values and their 1σ standard deviations of measured parameters were estimated with the Microsoft Excel 2010 program.

3. Results

3.1. Variations in hydrological settings

Generally, the river discharge of the Pearl River near Bogalusa, Louisiana, exhibited a typical hydrological pattern with a dry summer and wet winter (Table S1; Fig. 2a). This discharge pattern was attributed to the local rainstorm events, which are the major water supplier to the basin (Duan et al., 2007a). Water temperature also varied seasonally at both Stations PRB and PRS. It reached a maximum of 33ºC in August and decreased to a minimum of 10ºC during late January (Tables S1, S2; Fig. 2a). Generally, the pH at both Stations PRB and PRS followed an inverse relationship with river discharge though it

remained weakly acidic at Station PRS where pH was lower than that at PRB. Some exceptions were observed at Station PRS with the most acidic condition during a small increase of river discharge in the dry period, indicating the effect of local hydrological processes and associated possible input from floodplains (Tables S1, S2; Fig. 2b). Specific conductivity at both sampling sites was inversely correlated with river discharge (Tables S1, S2; Fig. 2c). However, specific conductivity up to 200 times higher than normal river water was measured during August-December, 2008, due to the intrusion of Gulf of Mexico seawater under the extreme low river discharge (Cai et al., 2013). Other than this period, specific conductivity at Station PRS was lower than PRB. SPM had a lower concentration at Station PRS than Station PRB, but correlated positively with river discharge at both sites (Tables S1, S2; Fig. 2d), suggesting its major terrestrial source and hydrological control in the EPR.

The carbon chemistry was monitored in the Pearl River near Bogalusa, Louisiana, and lower EPR at Stennis Space Center, Mississippi, for two years. As revealed by the flow separation estimates, the Pearl River main stem contributed 10-60% of the water in the EPR with the rest coming from Hobolochitto Creek. Therefore, the difference of carbon chemistry, if any, between the Pearl River main stem and lower EPR likely resulted both from interactions with the floodplain and input from Hobolochitto Creek.

3.2. Abundance and temporal variations of DIC and DOC

DIC concentrations in the Pearl River at Bogalusa ranged from 366 to 1032 μmol L^{-1} with an average of 691±199 μmol L^{-1}, while it ranged from 243 to 918 μmol L^{-1} with an average of 441±127μmol L^{-1} at Station PRS (Tables 1, S1, S2; Fig. 2e). DIC

concentration at both stations varied inversely with river discharge with minimum concentrations during peak flow events and elevated concentrations during dry seasons. The inverse correlation between DIC concentration and river flow has been observed in numerous rivers due to simple dilution effect, carbon source variation and seawater intrusion in coastal rivers (e.g., Cai, 2003; Cai et al., 2008a; Guo et al., 2012; Cai et al., 2013). Unlike DIC concentration, stable isotopic composition of DIC at Stations PRB and PRS did not show clear seasonal variations or significant difference (p=0.23). Values of δ^{13}C-DIC ranged from -14.57‰ to -4.14‰ with a mean value of -7.45±2.61‰ at Station PRB, and from -12.42‰ to -5.91‰ with a mean value of -8.08±2.07‰ at Station PRS (Tables 2, S1, S2; Fig. 2f). The δ^{13}C-DIC in the Lower Pearl River was generally inside the range of chemical weathering input whereas some minimum values could imply the contribution of sources with depleted δ^{13}C, most likely from the respiration of soil organic matter (Raymond et al., 2004; Cai et al., 2015).

DOC concentrations at both Stations PRB and PRS increased with river discharge, showing a hydrological control. Duan et al. (2007*b*) also observed a positive correlation between DOC concentration and river flow at Station PRTS during their 2001-2003 investigation. However, a peak DOC concentration was observed at Station PRS along with a small increase of river discharge in the middle of the 2007 dry season while DOC concentration at Station PRB remained below 400 μmol L^{-1} (Tables S1, S2; Fig. 2g). This could be attributed to a temporary connection between the river channel and floodplain which resulted in a pulsed input of accumulated swamp materials as evidenced by the more depleted δ^{13}C-DOC values at PRS compared to PRB (Fry and Sherr et al., 1984; Cai et al., 2013) and further implies the contribution of the floodplain to riverine

DOC in the lower Pearl River basin. For comparison, the mean concentration of DOC at Station PRB was 406±135 μmol L^{-1}, which was about 2/3 of that (606±208 μmol L^{-1}) at Station PRS (Tables 1, S1, S2). Similarly, the average TDN concentration at PRS was 10.3 μmol L^{-1} or nearly 40% higher than that at PRB (Tables 1, S1, S2; Fig. 2i). Since PRS is generally more depleted in dissolved inorganic nitrogen than PRB (Shim, 2011), higher TDN concentration at PRS suggests an intensive increase of DON concentration at PRS relative to PRB. Furthermore, DOC at PRS had a higher COC percentage (75±2%) than that at PRB (68±3%) (p<0.001; Table 1). Similar to DIC, stable carbon isotopic composition of DOC at both sites did not show a clear seasonal trend during the investigation period. However, a small, but statistically significant difference was observed in δ^{13}C-DOC values between PRB and PRS (-27.66±0.55‰ vs. -28.23±0.44‰, p<0.001; Tables 2, S1, S2; Fig. 2h). In contrast, δ^{13}C-COC was almost identical between the two sites (-27.94±0.51‰ at PRB and -27.66±0.13‰ at PRS, p=0.38; Table 2, S1, S2), suggesting a similar source for COC.

3.3. Abundance and temporal variations in particulate organic matter

POC concentrations ranged from 241 to 531μmol L^{-1} at station PRB and from 20 to 316 μmol L^{-1} at station PRS, respectively. Similar to SPM, POC concentrations at PRB were consistently higher than those at PRS (359±91μmol L^{-1} vs. 160±69 μmol L^{-1}, p<0.001; Tables 1, S3, S4; Fig. 3a). Similarly, PN concentrations (19.0-52.4 μmol L^{-1}) at PRB were also higher than those of PRS (4.28-23.0 μmol L^{-1}), with 210% higher in the average PN concentration (33.5±10.4μmol L^{-1} vs. 10.8±4.6μmol L^{-1}, p<0.001; Tables 1, S3, S4; Fig. 3b). Although concentrations of SPM, POC and PN decreased from PRB to

PRS, POC content in suspended particles (in mg-C/g-particle) showed little difference between sites (p=0.22; Table 2), while PN contents (in mg-N/g-particle) at PRB was nearly 40% higher than those at PRS (p=0.007; Tables 2, S3, S4; Figs. 3c, d). While POC quality or sources are similar at both sampling sites, PN is subjected to a dilution effect by N-depleted terrestrial particulate organic matter (POM) from tributary input and/or preferential decomposition of N-containing POM during its transport from PRB to PRS along the Pearl River.

Values of δ^{13}C-POC at PRB varied from -31.55‰ to -26.12‰ with an average of -29.58±1.38‰ while δ^{13}C-POC at PRS varied from -32.67‰ to -26.79‰ with an average of -29.28±1.42‰ (Tables S3, S4; Figs. 3e, f), with no significant difference in δ^{13}C-POC between the two sampling stations (p=0.46; Table 2). In contrast, average δ^{15}N-PN values were 5.48±1.41‰ and 2.18±1.98‰ for samples at PRB and PRS, respectively, showing a distinct difference in δ^{15}N-PN between the two sampling stations (p<0.001; Table 2). The difference in both the PN content and isotopic composition between PRB and PRS suggests a change in nitrogen sources between the upstream and downstream sites, which could be derived from the river-floodplain interaction, degradation processes in the lower Pearl River, and the input from Hobolochitto Creek. However, similar POC contents (in µmol-C/g) and stable carbon isotopic composition between PRB and PRS implies that the influence of the floodplain and tributaries was only limited to POC abundance in the water.

The large decrease in PN concentrations (µmol-N/L and µmol-N/g-particles) at PRS also resulted in a higher average POC/PN ratio (15.3±4.5) compared to PRB (11.0±1.8;

p<0.001, Tables 2, S3, S4; Fig. 3g), suggesting more degraded POM or more terrestrial organic matter at the downstream PRS station.

3.4. Spatial variations in carbon species

The concentrations of carbon species showed extensive spatial variability below the confluence with Hobolochitto Creek, the most important tributary and water source in the EPR. This is not surprising since flow separation estimates suggest that the water supplied by Hobolochitto Creek contributes 30-90% of the EPR flow, with the higher fraction during dry seasons. For comparison, we divide the EPR into upper and lower river sections at Hobolochitto Creek.

DIC concentration decreased from 1000 μmol L^{-1} in the upper river section to 400 μmol L^{-1} in the lower section during the dry season, although it remained somewhat constant at 400 μmol L^{-1} at both stations during high flow. The lowest DIC concentration in the EPR basin was observed in Hobolochitto Creek throughout the four samplings (Table S5; Fig. 4a). DOC and DON concentrations, however, increased from the upper to lower section of the EPR, regardless of the river flow. Both DOC and DON concentrations at PRHC were generally higher than the immediately adjoining upstream and downstream stations. Meanwhile, the floodplain stations in the lower section had variable DOC and DON concentrations compared to the main stem (Table S5; Figs. 4b,c). The difference in SPM concentration between the upper and lower EPR appears to be hydrologically controlled. The greatest SPM difference (of nearly 200 mg L^{-1}) was observed during February 2008, when a high flow event of 1031 m^3 s^{-1} was observed at Bogalusa, Louisiana. The difference in SPM concentrations was only 20 mg L^{-1} as the

river flow remained in the range of 50-150 m^3 s^{-1}. During the driest time in November 2007, no significant difference could be observed (Table S5; Fig. 4d). Overall, POC and PN had lower concentrations in the lower section than the upper section (Table S6; Figs. 4e,f).

Though there were distinct spatial distribution patterns for different carbon species in the EPR basin, their stable isotopic composition, C/N ratios, and POC and PN contents, in contrast, were similar between the upper and lower sections (Tables S5, S6; Figs. 4 and 5). The δ^{13}C-DIC in the EPR basin was in the range of -14.57‰ to -5.39‰, which was consistent with previously reported values in North American rivers and suggests its major source is from carbonate weathering (Raymond et al., 2004; Striegl et al., 2007; Cai et al., 2015). The δ^{13}C-DOC and δ^{13}C-POC varied from -29.45‰ to -27.11‰ and from -34.67‰ to -26.12‰, respectively. These carbon isotopic compositions are generally similar to those of typical C_3 plants except for one sample with a value of -34.67‰, suggesting potential microbial and other autochthonous sources (Fry and Sherr, 1984; Goni et al., 2005; Cai et al., 2013). The DOC/DON ratio ranged from 11.8 to 45.7 and was consistently higher than the POC/PN ratio (8.42-23.9) in the same samples. Higher C/N ratio of dissolved organic matter (DOM) than POM is frequently attributed to its more intensive degradation and the preferential loss of N-containing compounds during degradation, and further implies a general diagenetic pathway from POM to DOM in the Pearl River (Guo et al., 2003a; Cai et al., 2015). Due to simultaneous spatiotemporal variations in POC, PN and SPM concentrations in the EPR, the POC/SPM and PN/SPM ratios were relatively stable throughout all floodplain surveys.

4. Discussion

4.1. Difference in carbon speciation between PRB and PRS

As revealed by the flow separation estimates, Hobolochitto Creek contributed significant amounts of water to the EPR, ranging from 30% during the high flow events to 90% during the driest period, which should result in differences in organic matter quantity and quality between PRB and PRS. Therefore, an alteration in the carbon speciation and biogeochemistry between Stations PRB and PRS is expected during the sampling period with the input from Hobolochitto Creek and the superimposing effects of the floodplain in the EPR basin. Consistent with this expectation, our time-series sampling over two-years at both Stations PRB and PRS clearly shows a distinct difference in water chemistry between the EPR and the Pearl River main stem (Table 1). The river water in the lower reach of the EPR tended to be more acidic and lower in SPM concentration than Station PRB. Lower SPM concentrations, on the other hand, were accompanied by lower POC and PN concentrations at Station PRS. Together with 36% lower DIC concentration at Station PRS compared with PRB, carbon speciation was distinctly different between the lower reach of the EPR and the main stem of the Pearl River (Fig. S1). At Station PRB, DIC was the most abundant carbon species, accounting for 47% of total carbon (i.e., DIC + DOC + POC), followed by DOC (28%) and POC (27%). Meanwhile, DOC was the dominant carbon species and accounted for half of the total carbon pool, leaving 37% and 13% partitioned in DIC and POC, respectively, in the lower EPR section. The variation of carbon speciation in the EPR basin indicates the retention and dilution of DIC and POC, but significant addition of DOC by the floodplain and/or Hobolochitto Creek. COC was the dominant fraction of the bulk DOC at both

Stations PRB and PRS, but its abundance increased from 68% at Station PRB to 75% at Station PRS, due to a 65% increase in the average COC concentration from 276 μM at Station PRB to 455 μM at Station PRS. Apparently, the EPR received significant input of DOM from fresh soil and terrestrial organic materials or in situ production in the river basin, both being major sources of colloidal organic matter in river waters (Duan et al., 2007a; Guo and Santschi, 2007; Cai et al., 2008b; Cai et al., 2015). An increased COC fraction was also observed in the swamp-dominant Atchafalaya River basin due to floodplain input (Shen et al., 2012). However, the somewhat constant stable isotopic composition, which is identical to that of vascular plants, between DOC and COC excludes any significant autochthonous contribution to the EPR (Duan et al., 2007a).

Even though carbon concentrations and speciation displayed distinct variations between lower reaches of the EPR and the main stem of the Pearl River over the two years of monitoring, the stable isotopic compositions of all carbon species and SPM-normalized POC showed little or insignificant difference (Table 2). The spatial surveys further revealed a consistent fluctuation of carbon concentrations, but not for isotopic compositions and SPM contents, below the confluence of Hobolochitto Creek in the EPR basin (Figs. 4, 5). Therefore, the influences of the floodplain and Hobolochitto Creek were limited to the alteration of carbon speciation and export fluxes. In contrast, the quality of individual carbon species remained relatively stable, suggesting constant carbon provenance and reactivity in the floodplain. On the other hand, both concentrations and compositions of nitrogen species (TDN and PN) varied significantly between PRB and PRS and therefore resulted in contrasting differences in sedimentary nitrogen content and C/N ratio (Tables 1, 2). This implies the mixing of nitrogen sources

with distinct isotopic and elemental signatures and/or more intensive transformation of nitrogen phases and chemical speciation in the EPR basin than organic carbon. Recent investigations also suggested an active role of floodplains and/or river deltas in regulating the riverine nitrogen speciation and reactivity (Xu et al., 2006; Emmerton et al., 2008; Shen et al., 2012; BryantMason et al., 2013; Scott et al., 2014).

4.2. Relative contributions from floodplain and Hobolochitto Creek

Besides the upstream input from the main stem of the Pearl River, other sources of water and associated materials to the EPR include Hobolochitto Creek and the floodplain in the EPR basin, the latter being dominated by marshes and swamps (Gosslink, 1990). Wetland-rich floodplains frequently serve as reactors retaining biogeochemically active chemical species through sedimentation, river processing and biological assimilation as well as serving as a source (Pellerin et al., 2004; Emmerton et al., 2008; Allison et al., 2012; Shen et al., 2012; Scott et al., 2014). To better understand the role of tributaries and the floodplain in altering the riverine constituents and their transport, relative contributions of different carbon species and their seasonal variations from Hobolochitto Creek and the floodplain to the lower reach of the EPR were estimated using the aforementioned flow separation and flux estimation methods. The instantaneous contribution from Hobolochitto Creek to riverine export fluxes from the lower reach of the EPR ranged from 15% to 130%, while the instantaneous contribution from the floodplain ranged from -100% to 50%, depending on specific carbon species and sampling season (Fig. 6). Note that uncertainties of instantaneous carbon fluxes mostly depend on the analytical precision of carbon species, which is usually less than 2%.

Relative contributions of both Hobolochitto Creek and the floodplain showed distinct seasonality (Fig. 6). Hobolochitto Creek supplied the least for all chemical species measured, including DOC, DON, POC, PN, SPM and DIC, to the EPR during February when a large flood occurred. Peak contributions from Hobolochitto Creek were observed in June and November, concurrent with the driest time periods in the Pearl River basin. The flow separation had suggested a disproportionate decrease in water contribution from Hobolochitto Creek to the EPR with increasing river discharge (Shiller et al., 2012). Consistent with the hydrologic conditions and relative water supply from the Pearl River main stem and Hobolochitto Creek, material contribution from Hobolochitto Creek also decreased with increasing Pearl River discharge.

Floodplain effects on the riverine constituents varied among different chemical species. DOC, POC and PN showed the most intensive (40-100%) removal in the floodplain during summer dry season, while the floodplain acted as a weak source for the same species during the winter dry season (Fig. 6). The floodplain effects on these species during spring flooding and autumn seasons were intermediate compared to summer and winter dry seasons. Summertime intensive removal of organic carbon and nitrogen by the floodplain was likely due to extensive photodegradation. A 20-day photo-oxidation experiment revealed that DOC and chromophoric DOM in lower EPR waters were reduced by 20-40% under the spring natural light cycle (Shiller et al., 2006). However, this reduction in DOC and chromophoric DOM quantity might be a lower limit due to frequent cloudy conditions during their incubation experiments (Shiller et al., 2006). Duan and Bianchi (2007) also attributed the decrease in dissolved combined amino acids in the downstream EPR to photodegradation during their summer sampling

campaign along the main stem. Superimposed on the photochemical degradation is the bacterial consumption of bioactive organic compounds, such as carbohydrates, due to the summer high water temperature and prolonged water residence time during dry seasons (Fig. 2a). Carbohydrates comprised, on average, 35% of the bulk DOC in our samples and should be subjected to rapid and intensive microbial degradation (Wang et al., 2010; 2013). A previous study on a Texas river also observed an enhanced carbohydrate degradation under higher water temperature (Hung et al., 2005). On the other hand, the river floodplain did not retain significant amounts of suspended particles during the summer dry season, thus excluding the sedimentation of organic matter in the floodplain. However, the decreased POC/SPM and PN/SPM ratios along the EPR channel support the preferential removal of POM compared to bulk SPM (Fig. 5). Based on the observations during sample filtration, SPM was in a finer size range during the dry season than the wet season in the EPR, which could promote the microbial decomposition and photo-oxidation of terrestrial POM (Keil et al., 1998; Bianchi et al., 2007; Tesi et al., 2007).

The bulk suspended particles (in terms of SPM) in the floodplain showed a behavior distinct from POM (Fig. 6). SPM was strongly retained in the floodplain during a February major flooding event, which amounted to as much as 84% of the export flux at PRS. However, the floodplain became a source of SPM to the EPR during other seasons, contributing up to half of SPM exported from PRS. Although the floodplain contributed half of the SPM to the lower EPR during the dry season, its export flux was not significantly elevated due to the low river discharge, which resulted in less connection between floodplain and river channel. Since SPM concentration increased with

increasing river discharge at both PRB and PRS, the EPR floodplain acted as a buffer zone to level off the SPM concentration in the river through seasonal cycling of storage and supply in correspondence with the hydrological conditions and to maintain a balance between inflow and outflow. This is different from some other wetland-rich or lake-rich rivers, such as the Mississippi and Mackenzie River deltas, where sediment can be significantly retained (Emmerton et al., 2008; Allison et al., 2012; Nittrouer and Viparelli, 2014). The swamp-dominant Atchafalaya floodplain also retained more than 30% of annual sediment load though overbank storage and channel bed aggradation (Allison et al., 2012). Nevertheless, the storage of sediment in the EPR floodplain only occurred during high flow events when riverine sediment might be dominated by coarse materials, while reworking or resuspension of fine particles likely happened during the dry season. Allison et al. (2012) also revealed that muds could be reworked in the lower Atchafalaya River basin while net sedimentation of sand was simultaneously observed. The annual hydrological flooding-dry cycles thus, might exert a regulatory role on the sediment quality and dynamics in the EPR floodplain. Further observations are needed to quantify the hydrology-sediment interactions and the role of swamp-rich river floodplains.

For both DIC and DON, floodplain effects on their river export from PRS only varied slightly (<±20%) without a clear seasonal trend (Fig. 6). The EPR might have elevated primary production during the summer dry season (Duan and Bianchi, 2006). However, the maximal removal of DIC was observed during early fall in the present study. Our companion monitoring also revealed slightly higher chlorophyll-*a* concentration in September compared to June, but lower than in November and February during the sampling period (Shim, 2011). The high chromophoric DOM concentration in

the Pearl River limited light availability and resulted in lower primary production than the highly turbid Mississippi River (Duan and Bianchi, 2006; Duan et al., 2007b; Cai et al., 2013). Thus, the carbon fixation by phytoplankton might only account for a small fraction of floodplain DIC removal. One other possible pathway to retain a major part of the DIC could be the carbon fixation by the swamp plants in the flooded EPR floodplain. The presence of terrestrial C_3 plants dominated organic matter in the EPR throughout the investigation period further supporting the dominant role of swamp plants in regulating the carbon cycles in the EPR floodplain (Figs. 2, 3). Flooded inland wetland vegetation has been shown to be productive and its carbon fixation supports extensive riverine CO_2 outgassing (Mayorga et al., 2005; Abril et al., 2014). Schilling et al. (1999) also suggested that the hardwood community dominant in the Pearl River floodplain was productive.

Unlike DOC, DON did not shown significant removal in the EPR floodplain during the whole water year (Fig. 6). That might imply either a refractory characteristic of DON or an additional input of DON compensating its photo-oxidation and biodegradation. Numerous studies have concluded a high turnover of N-containing organic matter in aquatic environments and, therefore, oppose the dominance of a refractory DON pool in the EPR (Bronk, 2002; Zou et al., 2006; Duan and Bianchi, 2007; Cai et al., 2012). The productive terrestrial ecosystems in the EPR floodplain might be a major DON source substantially covering its loss (Schilling et al, 1999). Considering the much lower DON concentration than DOC and low C/N ratio of algal biomass, riverine algal growth could also supply riverine DON although the autochthonous supply of DOC in the main stem was negligible in the total DOC pool as discussed above. Indeed, Duan and Bianchi

(2007) observed an in situ contribution of amino acids in the EPR during the summer dry period with enhanced chlorophyll-*a* concentrations. Again, different behaviors of DON and DOC support the dynamic nature of N-rich organic compounds in the EPR floodplain.

4.3. Carbon yields and floodplain influence

The carbon export fluxes from the Pearl River at Bogalusa, Mississippi, were estimated to be 36.2×10^6 kg-C yr^{-1} for DIC, 32.4×10^6 kg-C yr^{-1} for DOC and 23.6×10^6 kg-C yr^{-1} for POC (Table 3). When normalized to drainage basin area, they corresponded to annual carbon yields of 2126, 1903 and 1386 kg-C km^{-2} yr^{-1} for DIC, DOC and POC, respectively (Table 4). As a whole, the annual export flux and yield of total carbon, including DIC, DOC and POC, was 92.2×10^6 kg-C yr^{-1} and 5415 kg-C km^{-2} yr^{-1}, respectively, from the Pearl River. Although the carbon export flux is relatively small compared to other world large rivers, the carbon yield from the swamp-rich Pearl River, on the other hand, is comparable or higher than selected world rivers, especially for the DOC yields (Table 4 and references therein). The carbon flux transported by the Pearl River was dominated by organic carbon, leaving 39% of total carbon flux and yield as DIC. This is quite different from large rivers, including the Amazon, Yangtze, Mississippi, Columbia and Yukon Rivers, which have much higher DIC yields than DOC (Dahm et al., 1981; Guo et al., 2012; Cai et al., 2015). The low DIC yield in the Pearl River is consistent with its low limestone distribution and basin geographic characteristics, which is dominated by forests and has widespread riparian swamps and limited agriculture land usage (Duan et al., 2007b; Mississippi Department of Environmental Quality, 2007; Cai et al., 2013). On the other hand, DOC and POC yields

from the Pearl River are among the highest of the selected world rivers and were 2-3 times higher than that of the Mississippi River basin although the Amazon and Hudson Rivers have the highest DOC yield (Table 4). However, DOC and POC yields from the Pearl River are similar to those in more pristine Yukon and Colville Rivers, which receive large amounts of organic carbon through surface soil and plant litters (Guo and Macdonald, 2006; Guo et al., 2012; McClelland et al., 2014), indicating less anthropogenic influences on the Pearl River basin compared to the Mississippi River.

Extensive anthropogenic activities have been found to substantially decrease the sediment load, limit the organic material input and intensify the decomposition of organic compounds in human-altered rivers, such as the Mississippi River (Bianchi et al., 2007; Duan et al., 2007a; Meade and Moody, 2010; Cai et al., 2015). In contrast, the input from its productive forest and swamp ecosystems and the lower physiochemical and biological degradation of its organic matter support the high organic carbon yield in the Pearl River basin (Schilling et al., 1999; Duan and Bianchi, 2006, 2007; Duan et al., 2007a, b; Cai and Guo, 2009). The Trinity River, another small semi-natural river discharging into the northern Gulf of Mexico, also had almost twice the organic carbon yield as the Mississippi River (Warnken and Santschi, 2004). Therefore, the export of organic matter from small coastal rivers around the northern Gulf of Mexico could have a significant regional influence on coastal carbon budget and ecosystem as a whole.

The annual material input from the upstream EPR and Hobolochitto Creek to the EPR and the annual outflow from the lower EPR are listed in Table 3. The imbalance between the annual input and outflow is defined as the influence of the EPR floodplain on individual chemical species during a complete water year. As shown in Table 3, the EPR

floodplain significantly altered the riverine carbon and nitrogen export fluxes. The EPR floodplain retained 0.52×10^6 kg-C yr^{-1} DIC and 0.38×10^6 kg-C yr^{-1} POC, or 24% of DIC and 40% of POC export fluxes while it contributed 1.37×10^6 kg-C yr^{-1} or 40% of the DOC export flux from the lower EPR. Similar to POC, the EPR floodplain also retained 0.036×10^6 kg-N yr^{-1} PN, which corresponds to 39% reduction of riverine PN export flux. However, little influence of EPR floodplain on the riverine DON and SPM transport was observed (Table 3).

The retention of DIC in the floodplain seems mostly to occur in fall as suggested by its maximum removal rate at that time (Fig. 6). The retention of DIC in the floodplain was consistent with our simultaneous monitoring of nutrient concentrations which showed the reduction of dissolved inorganic nitrogen and phosphate concentrations between the upper and lower EPR (Shim, 2011). River swamps and wetlands have been widely demonstrated to be able to remove the inorganic nutrients (Lane et al., 2004; Vohla et al., 2007; Emmerton et al., 2008; Noe and Hupp, 2009; Scott et al., 2014), largely due to the assimilation by the highly productive terrestrial ecosystems and riverine algal mass (Mayorga et al., 2005; Duan and Bianchi, 2007; Abril et al., 2014). Apparently, river floodplains with widespread flooded swamps and wetlands also have the capacity to assimilate riverine DIC as suggested by our data.

Compared with the Atchafalaya River, the EPR has a much smaller size, shorter river channel and, as a result, much shorter water residence time. However, the floodplain contribution to the DOC yield in the EPR was comparable to that observed in the Atchafalaya River basin but higher than the lake-rich Mackenzie River delta (Emmerton et al., 2008; Shen et al., 2012), suggesting the more intensive river-floodplain interaction

in the EPR in terms of DOC production in the floodplain. This is consistent with its highly productive environment (Schilling et al., 1999) and the remarkable DIC retention by the assimilation of terrestrial ecosystems in the EPR floodplain with widespread swamps. However, the lack of direct investigation on the influence of the floodplain on the riverine DOC export restricts further comparisons between different studies and between different river-floodplain systems.

In contrast to DOC, the EPR only received a small amount of DON (5%) from the floodplain. This is also contrary to a study of northeastern U.S. watersheds which showed that wetlands enhance the riverine DON concentration (Pellerin et al., 2004). Considering the large amount of DOC input from the EPR floodplain, this lack of influence on DON might imply a strong removal counteracting the DON input from nitrogen assimilation. Previous studies also suggested a large fraction of dissolved inorganic nitrogen and DON could be removed in the swamp-rich Atchafalaya River basin (Xu et al., 2006; Shen et al., 2012). However, an apparent production of DON was observed in the lake-rich Mackenzie River, in which low water temperature could limit DON removal processes (Emmerton et al., 2008).

Insignificant (3%) annual retention of SPM in the EPR floodplain (Table 3) indicated the balance of production of SPM during dry seasons and retention of SPM during flood periods. This observation contradicts the general viewpoint that flooded or lake-rich floodplains usually act as effective sinks of riverine sediment. For example, the Atchafalaya River basin, which has widespread swamps as well, retained 32% of the suspended sediment load from the upstream river (Allison et al., 2012). Likewise, the lake-rich Mackenzie River delta can reduce the suspended sediment concentration as

much as 18% (Emmerton et al., 2008). The accumulation rate of sediment in the coastal floodplains of the Chesapeake Bay watershed can be comparable to its riverine load (Noe and Hupp, 2009). However, POC and PN were significantly removed from the EPR floodplain, resulting in a 40% reduction in riverine POC and PN loads. Together with constant riverine SPM load, these observations suggest that the riverine sediment discharged into the northern Gulf of Mexico is depleted in organic matter relative to the data from upstream river monitoring stations beyond the coastal floodplains. Previous investigations also revealed that the Atchafalaya River basin would retain 27% of riverine organic nitrogen load while the lake-rich Mackenzie River delta would increase the sedimentary organic content through autochthonous input (Xu et al., 2006; Emmerton et al., 2008). Nevertheless, the alteration in the quality of river-exported sediment can affect its physiochemical and biological reactivity, transport and fate. Such variations of carbon cycling pathways would have a potential impact on coastal environmental issues such as hypoxia in the northern Gulf of Mexico (Bianchi et al., 2008; Dagg et al., 2008).

A regional carbon mass balance model in the EPR floodplain is further developed based on the above results (Fig. 7). The mass balance estimation indicates the EPR floodplain retained up to 24% and 40% of the annual DIC and POC export fluxes, respectively, from the lowermost EPR, but enhanced the annual riverine DOC export by 25% during 2006-2008. These results imply that riverine carbon export fluxes could be significantly underestimated or overestimated depending on specific carbon species when the floodplain contributions and/or retention are ignored. Within the EPR basin, the floodplain acted as a significant sink for DOC and POC during the summer dry season whereas the maximum DIC removal rate was observed during fall. Although the

floodplain did not exhibit significant removal or addition for SPM on an annual basis, a 84% retention and a 48% production of SPM was observed during a spring high flow event and the winter dry season, respectively.

5. Conclusion

Monthly monitoring of concentrations and isotopic compositions of various carbon species (DIC, DOC and POC) was conducted at both upstream (Bogalusa, MS) and downstream (Stennis Space Center, MS) sites in the wetland-rich EPR basin with a tributary (Hobolochitto Creek) input during 2006-2008. On average, DIC and POC concentrations decreased 36% and 55%, respectively, during downstream transport in the EPR, while DOC concentration increased 49%. This resulted in a change of the carbon speciation from upstream DIC dominance to downstream DOC dominance. However, a small but statistically significant different $\delta^{13}C$ value between the upstream and downstream sites was only observed for DOC along with its increasing colloidal fraction (75% vs. 68%). Results of four spatial surveys covering the river basin between these two sites further revealed a seasonal variation in the relative contributions from the wetland-rich floodplain and the Hobolochitto Creek tributary in the EPR basin. The relative contributions from the tributary to the EPR basin were consistently low during flood period and peaked during dry periods. Contrastingly, a large seasonality switching between sources and sinks was shown for the floodplain contributions to various carbon species. DOC and POC were intensively removed in the floodplain during the summer dry season (42% and 97% of export fluxes from the basin, respectively) while DIC was moderately removed during fall (-22%). However, the floodplain could also contribute

part of the DOC (up to 17%) and POC (13%) to the basin during fall and winter. Overall, the wetland-rich floodplain could reduce 24% and 40% of the annual DIC and POC export fluxes, respectively, from downstream of the EPR but enhance the annual riverine DOC export by 25%. These results provide new insights into our understanding of floodplain-river interactions and their effect on altering riverine carbon export.

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Figure captions

Fig. 1. Map of the lower Pearl River, including the East Pearl River (EPR) and West Pearl River (WPR), and monitoring stations in the main stem and floodplain. The EPR and WPR are the eastern and western branches, respectively, downstream of Bogalusa after the Pearl River divides. The East and West Hobolochitto Creeks (HC) are the major tributaries joining the EPR. The main stem stations at Bogalusa (PRB), Walkiah Bluff (PRW), Interstate Highway 59 (PRI59), a previous time-series station (PRTS) and Stennis Space Center (PRS) are denoted with solid circle and the floodplain and tributary stations at Hobolochitto Creek (PRHC), Indian Bayou (PRIB), Mike's Bayou (PRMB), Mike's River (PRMR) and English Bayou (PREB) are denoted with open circles. The station PRHC is located downstream of the convergence of the West and East HCs for an estimate of the sum of both tributaries.

Fig. 2. Seasonal variations in discharge, concentrations and isotopic composition of DIC and DOC in the Pearl River at Bogalusa and Stennis Space Center. River discharge for the Bogalusa station was obtained from the USGS and is shown as the grey area in all plots: (a) River discharge and water temperature; (b) pH; (c) Specific conductivity; (d) SPM; (e) DIC; (f) δ^{13}C-DIC; (g) DOC; (h) δ^{13}C-DOC; and (i) TDN.

Fig. 3. Seasonal variations in concentrations and isotopic compositions of particulate organic matter in the Pearl River at Bogalusa and Stennis Space Center. River discharge for the Bogalusa hydrologic station was obtained from the USGS and is indicated as grey area graph in all plots: (a) River discharge and POC; (b) PN; (c) POC content in SPM; (d) PN content in SPM; (e) δ^{13}C-POC; (f) δ^{15}N-PN; and (g) POC/PN ratio.

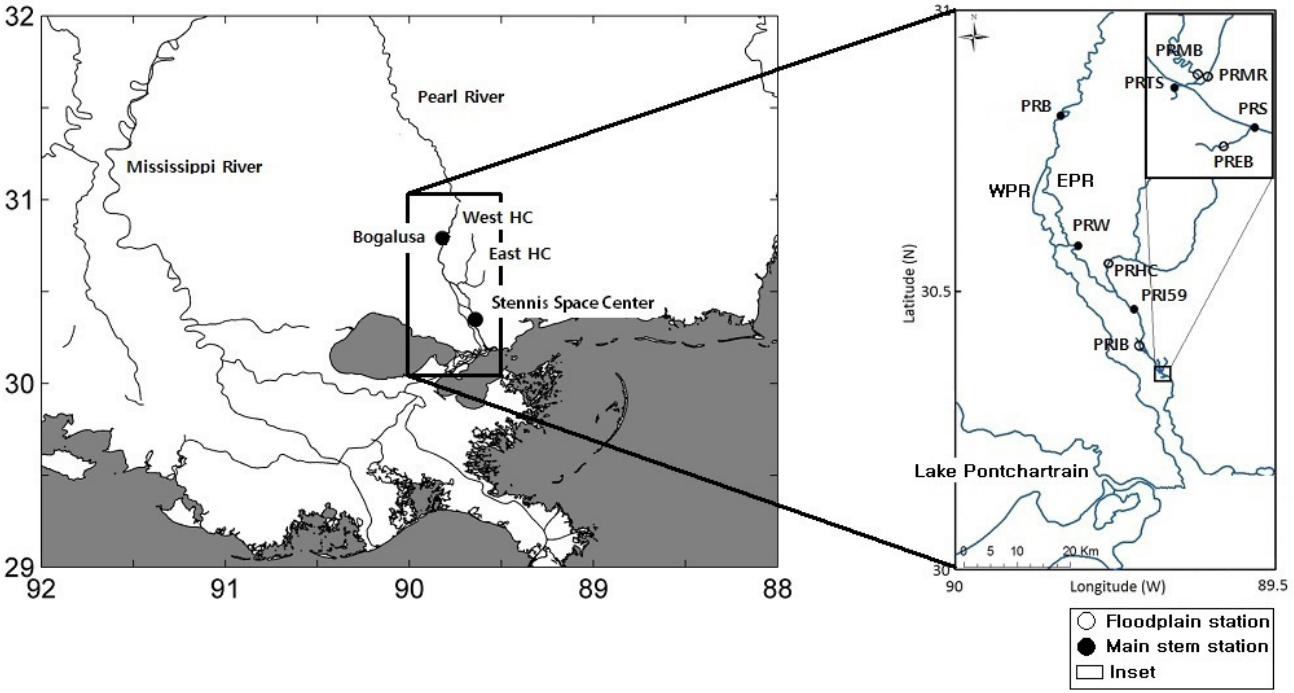
Fig. 4. Spatial variations in concentrations of carbon, nitrogen and suspended particulate materials in the East Pearl River floodplain. (a) DIC; (b) DOC; (c) DON; (d) SPM; (e) POC; and (f) PN. The main stem stations are denoted with bold.

Fig. 5. Spatial variations of isotopic and elemental composition of carbon and nitrogen in the East Pearl River floodplain: (a) δ^{13}C-DIC; (b) δ^{13}C-DOC; (c) DOC/DON ratio;

(d) δ^{13}C-POC; (e) δ^{15}N-PN; (f) POC content in SPM; (g) PN content in SPM; and (h) POC/PN ratio. The main stem stations are denoted with bold.

Fig. 6. Seasonal variations in the relative contributions of Hobolochitto Creek and floodplain. The arrows in the plots denote the seasonal cycles (November to February to June and to September) of both relative contributions to the carbon pool in the East Pearl River Basin.

Fig. 7. A schematic demonstrating carbon and SPM mass balances in the East Pearl River basin and the role of the floodplain in altering the annual and seasonal carbon and SPM export fluxes. The numbers in the figure denote the carbon and SPM fluxes from the individual sources in the East Pearl River basin with a unit of kg yr^{-1} whereas the percentages denote the capacity of the East Pearl River Basin to alter the annual and seasonal export fluxes of carbon species and SPM.


Pearl River
Mississippi River
West HC
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WPR
EPR
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PRHC
PRI59
PRIB
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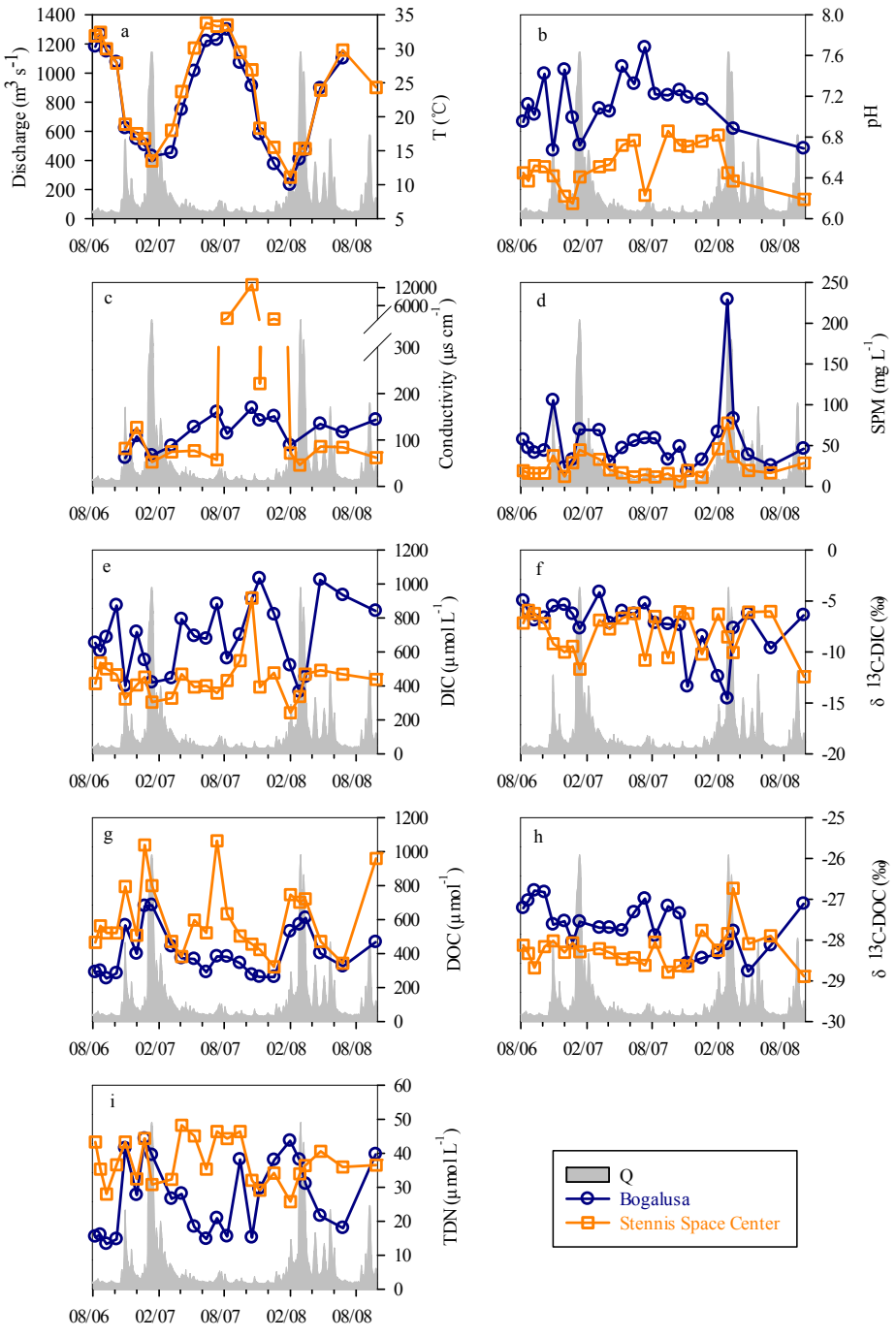
Floodplain station
Main stem station
Inset

Fig. 1


a
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Discharge (m3 s-1)
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δ 13C-DOC (‰)
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Fig. 2

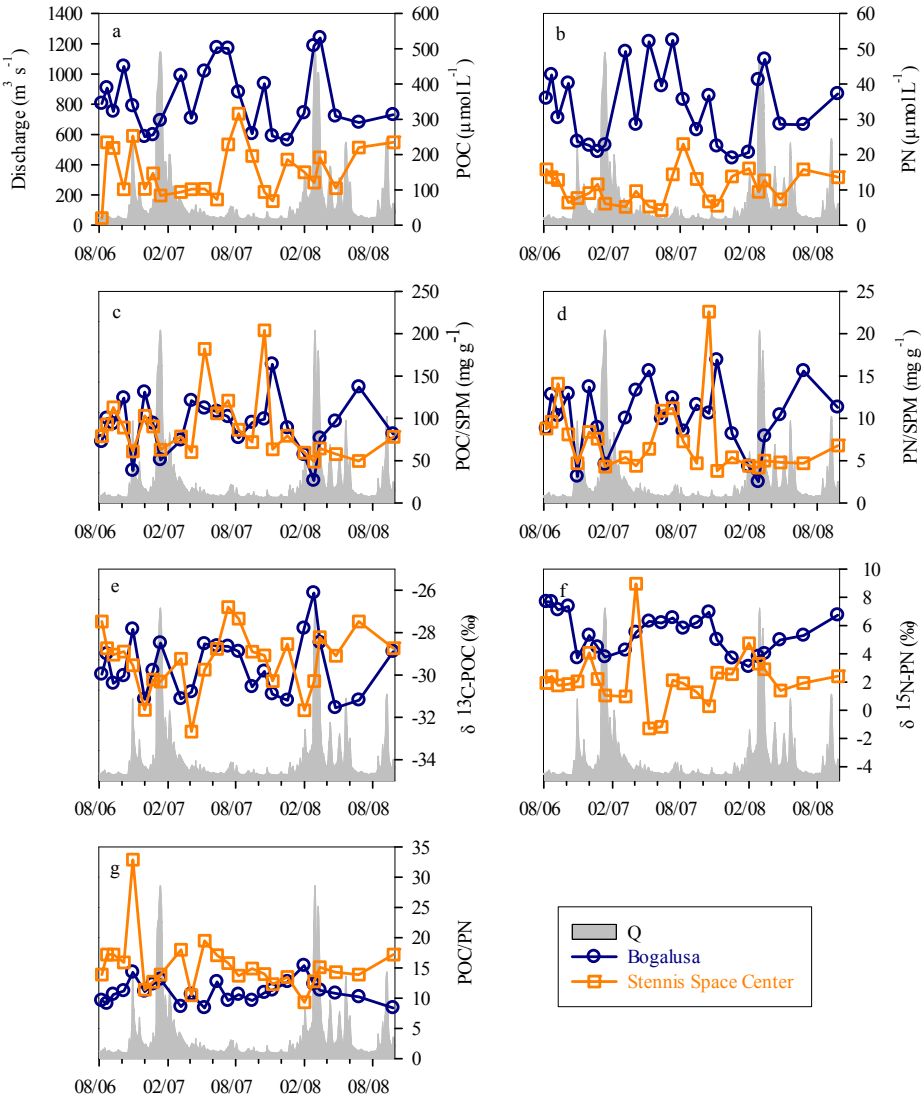
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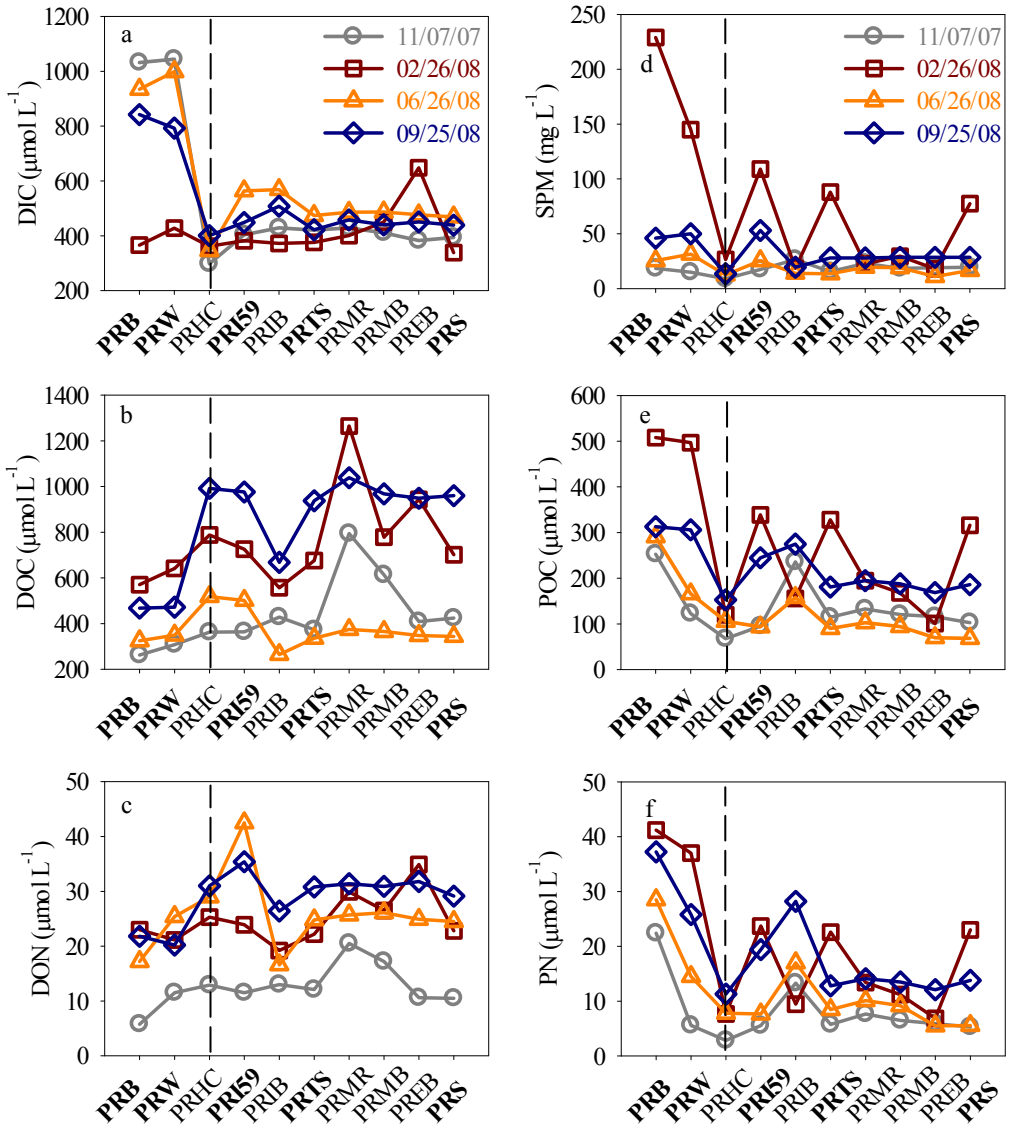
Fig. 3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DIC (µmol L-1)
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DON (µmol L-1)
SPM (mg L-1)
POC (µmol L-1)
PN (µmol L-1)
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PREB
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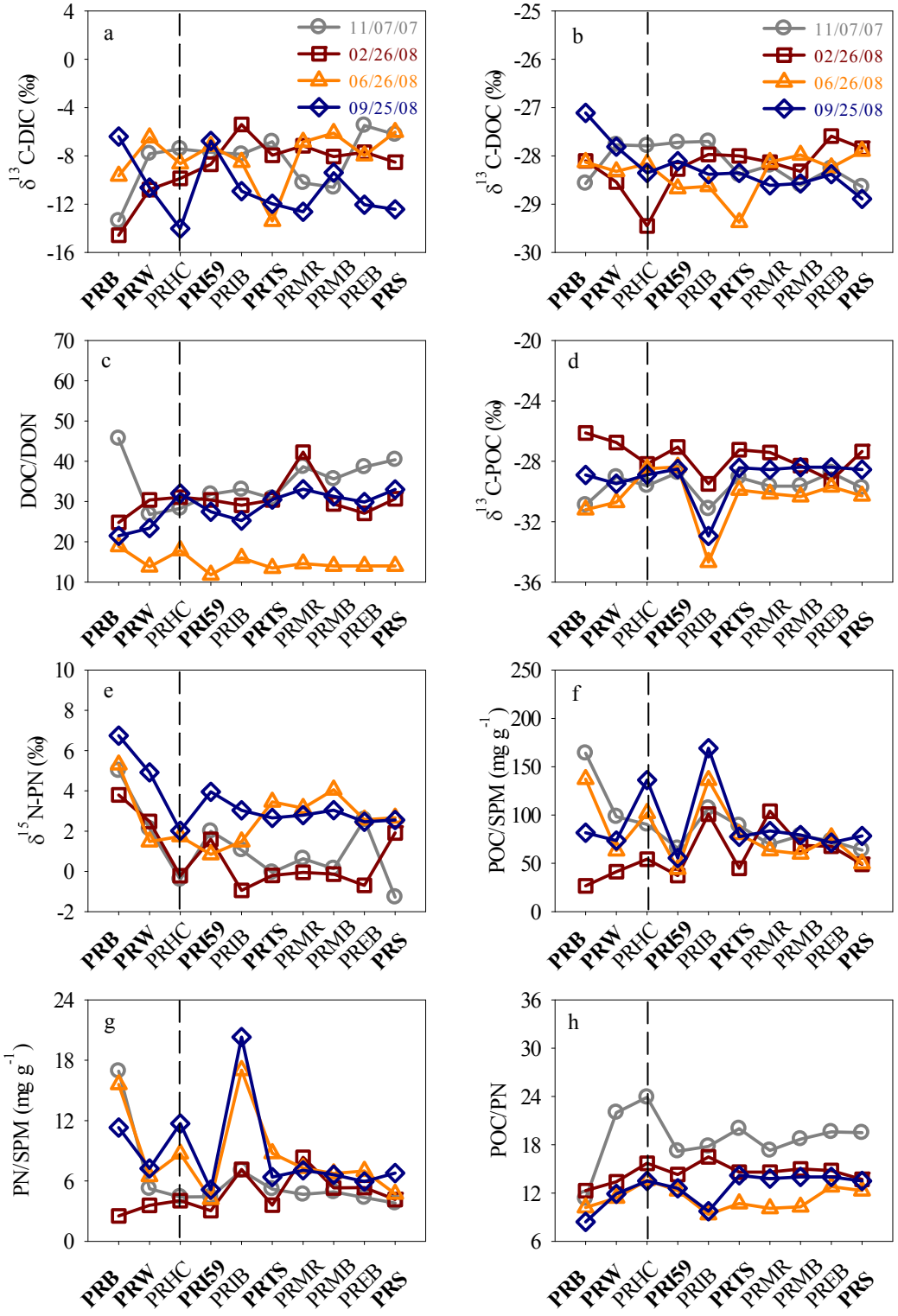
Fig. 4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δ13C-DIC (‰)
δ13C-DOC (‰)
DOC/DON
δ13C-POC (‰)
δ15N-PN (‰)
POC/SPM (mg g-1)
PN/SPM (mg g-1)
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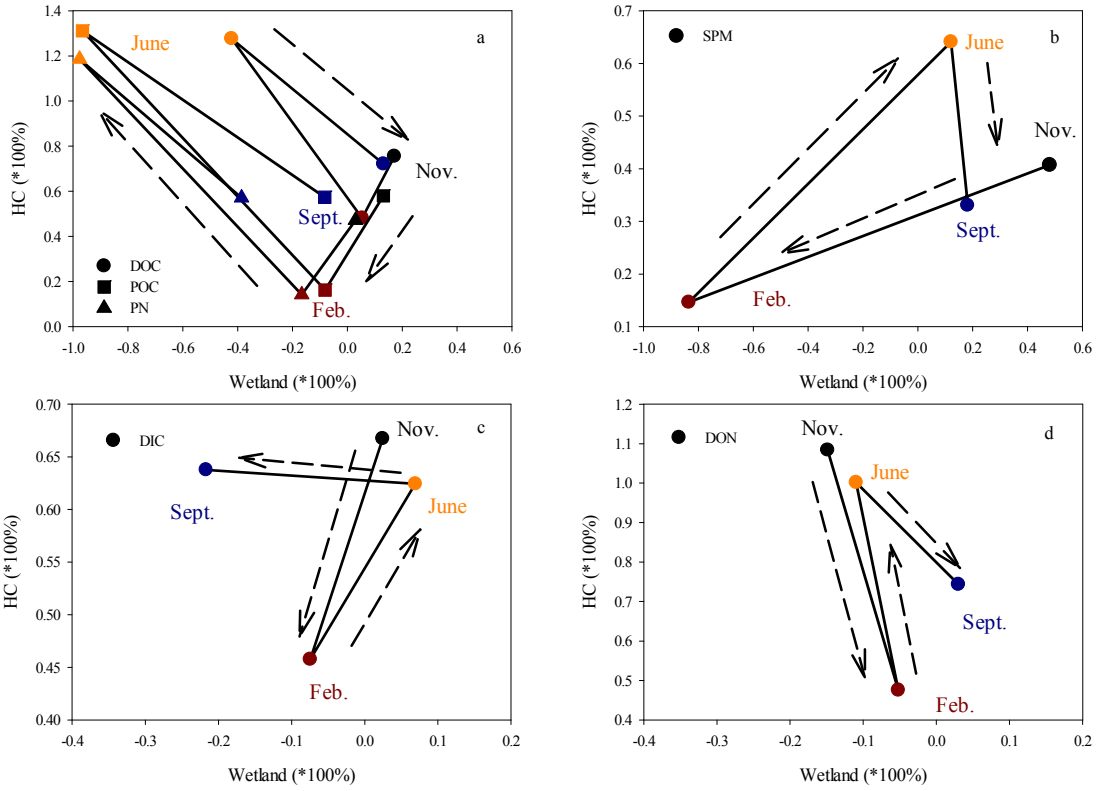
Fig. 5


a
June
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Sept.
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DOC
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PN
HC (*100%)
Wetland (*100%)
b
SPM
June
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HC (*100%)
Wetland (*100%)
c
DIC
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Wetland (*100%)
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DON
Nov.
June
Sept.
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HC (*100%)
Wetland (*100%)

Fig. 6

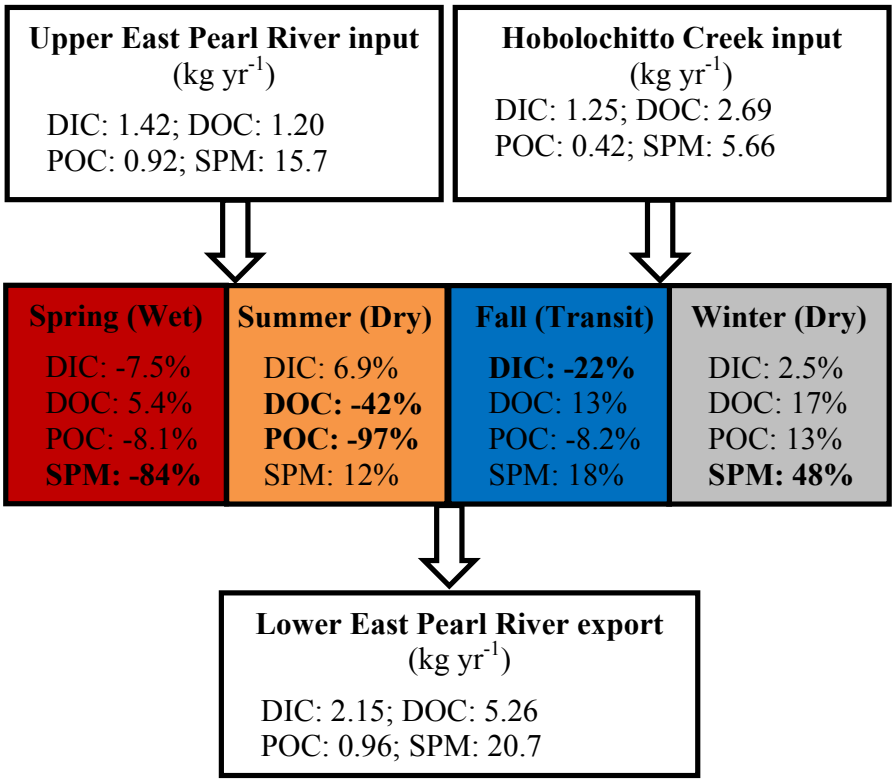
Upper East Pearl River input
(kg yr-1)
DIC: 1.42; DOC: 1.20
POC: 0.92; SPM: 15.7
Hobolochitto Creek input
(kg yr-1)
DIC: 1.25; DOC: 2.69
POC: 0.42; SPM: 5.66
Spring (Wet)
DIC: -7.5%
DOC: 5.4%
POC: -8.1%
SPM: -84%
Summer (Dry)
DIC: 6.9%
DOC: -42%
POC: -97%
SPM: 12%
Fall (Transit)
DIC: -22%
DOC: 13%
POC: -8.2%
SPM: 18%
Winter (Dry)
DIC: 2.5%
DOC: 17%
POC: 13%
SPM: 48%
Lower East Pearl River export
(kg yr-1)
DIC: 2.15; DOC: 5.26
POC: 0.96; SPM: 20.7

Fig. 7

Table 1. Differences in carbon concentrations between stations at Bogalusa (PRB) and Stennis Space Center (PRS) in the lower Pearl River

	T (ºC)	pH	SPM (mg L^{-1})	DIC (µmol L^{-1})	DOC (µmol L^{-1})	TDN (µmol L^{-1})	POC (µmol L^{-1})	PN (µmol L^{-1})	COC (%)
Bogalusa	22.5±7.4	7.13±0.27	56.6±41.9	691±199	406±135	27.0±10.9	359±91	33.5±10.4	68±3
Stennis Space Center	23.8±7.4	6.51±0.22	24.0±15.8	441±127	606±208	37.3±6.5	160±69	10.8±4.6	75±2
Difference (%)	5.8	-8.7	-58	-36	49	38	-55	-68	10
p value	0.45	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	<0.001	<0.001

Table 2. Differences in carbon content and isotopic composition between stations at Bogalusa (PRB) and Stennis Space Center (PRS) in the lower Pearl River

	δ^{13}C-DIC (‰)	δ^{13}C-DOC (‰)	δ^{13}C-COC (‰)	δ^{13}C-POC (‰)	δ^{15}N-PN (‰)	POC/SPM (mg g^{-1})	PN/SPM (mg g^{-1})	POC/PN
Bogalusa	-7.45±2.61	-27.66±0.55	-27.94±0.51	-29.58±1.38	5.48±1.41	92.6±31.5	10.2±3.8	11.0±1.8
Stennis Space Center	-8.08±2.07	-28.23±0.44	-27.66±0.13	-29.28±1.42	2.18±1.98	87.7±37.9	7.4±4.2	15.3±4.5
Difference (%)	8.5	2.1	-1.0	-1.0	-60	-5.3	-27	39
p value	0.23	<0.001	0.38	0.46	<0.001	0.22	0.007	<0.001

Table 3. Annual fluxes and yields of different carbon species from the Pearl River at Bogalusa (PRB), Mississippi, and floodplain influence on carbon export in the East Pearl River (EPR)

	DIC	DOC	POC	TC	DON	PN	TON	SPM
Flux-PRB (10^6 kg yr^{-1})	36.2	32.4	23.6	92.2	1.29	2.45	3.74	401
Yield-PRB (kg km^{-2} yr^{-1})	2126	1903	1386	5415	75.8	144	220	23554
Flux-PRW (10^6 kg yr^{-1})	1.42	1.20	0.92	3.54	0.059	0.096	0.155	15.7
Flux-PRHC (10^6 kg yr^{-1})	1.25	2.69	0.42	4.36	0.105	0.033	0.138	5.66
Flux-PRS (10^6 kg yr^{-1})	2.15	5.26	0.96	8.37	0.156	0.093	0.249	20.7
Flux-Floodplain (10^6 kg yr^{-1})	-0.52	1.37	-0.38	0.47	-0.008	-0.036	-0.044	-0.66
Contribution-Floodplain (%)	**-24**	**26**	**-40**	6	-5	**-39**	**-18**	-3

Fluxes from the upper EPR (PRW) were estimated with the flow-weighted method, DON flux was calculated with only four sample points. Fluxes from the Hobolochitto Creek (PRHC) were estimated with the flow-weighted method with four sample points for all solutes. Fluxes from the Pearl River at Bogalusa (PRB) and the lower EPR (PRS) were estimated with the USGS-LOADEST program other than DON which only had four data points in each sampling site and solely allows the flow weighted estimation. The error of the fluxes estimation is usually less than 10%.

Table 4. Comparisons of annual carbon yields (kg km^{-2} yr^{-1}) among selected world rivers

Rivers	DIC	DOC	POC	TC	Reference
Pearl River	2126	1903	1386	5415	This Study
Mississippi River	4664	645	789	6098	Cai et al. (2015)
Trinity River	-	1696	818	-	Warnken and Santschi (2004)
Columbia River	4298	781	97.0	5716	Dahm et al. (1981)
Hudson River	-	3500	400	-	Findlay et al. (1991); Findlay (2005)
Amazon River	8000	5000	3200	16200	Richey et al. (1990)
Yangtze River	9389	778	730	10897	Gao et al. (2012); Zhang et al. (2014); Bao et al. (2015)
Chena River	4332	1596	324	6252	Cai et al. (2008)
Yukon River	5292	1949	1070	8311	Guo et al. (2012)
Sagavanirktok River	-	398	211	-	McClelland et al. (2014)
Kuparuk River	-	1342	186	-	McClelland et al. (2014)
Colville River	-	2002	2635	-	McClelland et al. (2014)
Mackenzie River	-	301	248	-	Emmerton et al. (2008)