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Key Points:

- Sources and dynamics of carbon species were examined for the Mississippi River
- C speciation and isotopic composition were largely regulated by hydrologic conditions
- Export fluxes of all C species from the Mississippi River during 2006–2008 were quantified

Supporting Information:

- Supporting Information S1

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Abundance, stable isotopic composition, and export fluxes of DOC, POC, and DIC from the Lower Mississippi River during 2006–2008

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Abstract Sources, abundance, isotopic compositions, and export fluxes of dissolved inorganic carbon (DIC), dissolved and colloidal organic carbon (DOC and COC), and particulate organic carbon (POC), and their response to hydrologic regimes were examined through monthly sampling from the Lower Mississippi River during 2006–2008. DIC was the most abundant carbon species, followed by POC and DOC. Concentration and δ^{13}C of DIC decreased with increasing river discharge, while those of DOC remained fairly stable. COC comprised 61 ± 3% of the bulk DOC with similar δ^{13}C abundances but higher percentages of hydrophobic organic acids than DOC, suggesting its aromatic and diagenetically younger status. POC showed peak concentrations during medium flooding events and at the rising limb of large flooding events. While δ^{13}C-POC increased, δ^{15}N of particulate nitrogen decreased with increasing discharge. Overall, the differences in δ^{13}C between DOC or DIC and POC show an inverse correlation with river discharge. The higher input of soil organic matter and respired CO_2 during wet seasons was likely the main driver for the convergence of δ^{13}C between DIC and DOC or POC, whereas enhanced in situ primary production and respiration during dry seasons might be responsible for their isotopic divergence. Carbon export fluxes from the Mississippi River were estimated to be 13.6 Tg C yr^{-1} for DIC, 1.88 Tg C yr^{-1} for DOC, and 2.30 Tg C yr^{-1} for POC during 2006–2008. The discharge-normalized DIC yield decreased during wet seasons, while those of POC and DOC increased and remained constant, respectively, implying variable responses in carbon export to the increasing discharge.

1. Introduction

River transport is a major pathway for exporting terrestrially derived materials and associated carbon to marine environments. Global riverine carbon exports have been estimated to be 0.25–0.36 Pg C yr^{-1} for dissolved organic carbon (DOC), 0.20 Pg C yr^{-1} for particulate organic carbon (POC) and 0.41 Pg C yr^{-1} for dissolved inorganic carbon (DIC [*Meybeck*, 1982; *Hedges and Keil*, 1995; *Aitkenhead and McDowell*, 2000; *W.-J. Cai et al.*, 2008]). While riverine organic carbon can be rapidly respired or degraded in estuarine and coastal waters, photosynthetic fixation of riverine DIC can occur simultaneously along with the utilization of macronutrients in productive coastal regions [*Hedges et al.*, 1997; *Cai*, 2003; *Mayorga et al.*, 2005; *Bianchi et al.*, 2013]. The large amounts of riverine carbon export and active transformation of carbon species between dissolved and particulate, and between inorganic and organic phases can dominate the carbon input, alter the organic carbon reactivity, promote the exchange of CO_2 with the atmosphere, and modify the autotrophic-heterotrophic balance in the coastal oceans [*Bauer et al.*, 2013]. These processes are prominent in river-dominated ocean margins, such as the Mississippi River plume [*Bianchi et al.*, 2013; *Fichot and Benner*, 2014].

As one of the world's largest rivers, the Mississippi River drains 41% of the contiguous United States with an increasing trend of water discharge over the past century from 494 to 578 km^3 yr^{-1} [*Milliman*, 1991; *Raymond et al.*, 2008]. Water chemistry in the Mississippi River has been heavily influenced by agricultural activities (58% cropland coverage in the entire basin) and the presence of hydraulic infrastructures (dams and flood control levees) on the primary tributaries and the main river channel. Along with the enormous annual river discharge, the Mississippi River delivers large amounts of terrestrially derived materials, including nutrients and carbon, to the Gulf of Mexico [*Bianchi et al.*, 2007; *W.-J. Cai et al.*, 2008; *Raymond et al.*, 2008;

Shen et al., 2012]. The extensive exports of nutrients and organic matter from the Mississippi River have led to severe environmental concerns, such as eutrophication, seasonal hypoxia, and acidification [*Lohrenz et al*., 1997; *Rabalais et al*., 2002; *Cai et al*., 2012].

Agricultural practices in the river drainage have been implicated as a cause of increasing bicarbonate concentrations in the Mississippi River through lime addition and enhanced weathering rates [*W.-J. Cai et al*., 2008; *Raymond et al*., 2008]. Intensive human activities in the Mississippi River Basin have also been proposed to limit the supply of DOC from the watershed and to strengthen in-river processing and degradation of terrestrial DOC [*Duan et al*., 2007a, 2007b]. Furthermore, damming and channelization of the Mississippi River change the organic carbon composition in the Lower Mississippi River Basin by dramatically decreasing its sediment load and allochthonous POC concentration [*Meade and Moody*, 2010], favoring the growth of phytoplankton, and enhancing photodegradation of terrestrial dissolved organic matter (DOM). While most studies of carbon dynamics in the Mississippi River have tried to constrain the interannual or decadal variations in water chemistry, the seasonal effects of changing hydrographic and biogeochemical processes on carbon isotopic composition and export fluxes of different carbon species remain poorly quantified [*Bianchi et al*., 2004, 2007; *Dubois et al*., 2010].

Although carbon transformations and interactions between different chemical and size fractions are important in influencing carbon chemistry and cycling in aquatic environments, most studies focus on single carbon species or discrete sampling, preventing comprehensive understanding of carbon dynamics and export fluxes from the Mississippi River Basin to the northern Gulf of Mexico. *W.-J. Cai et al*. [2008] and *Raymond et al*. [2008] estimated DIC export and discussed its controlling factors and potential sources without linkages with organic carbon pools. On the other hand, concentrations and compositions of DOC and POC were reported without considering DIC [*Trefry et al*., 1994; *Duan et al*., 2007b; *Shen et al*., 2012; *Bianchi et al*., 2007, 2013; *Duan et al*., 2013], which is the largest carbon pool in Mississippi River waters. Further, reports on colloidal organic carbon (COC), which comprises a major part of the bulk DOC pool and has high chemical and biological reactivity [*Guo et al*., 2009], and isotopic composition of all carbon species are even scarce. Overall, studies on carbon biogeochemistry in the Mississippi River based on simultaneous sampling of all carbon species (DIC, DOC, COC, and POC) are still inadequate for the purpose of integration.

Stable carbon isotopes are useful tracers for constraining carbon sources and cycling in aquatic ecosystems [*Schulte et al*., 2011]. So far, δ^{13}C values have been reported for both POC and COC in the Mississippi River, but very few isotopic data are available for DIC and the bulk DOC pools [*Onstad et al*., 2000; *Bianchi et al*., 2004, 2007; *Duan et al*., 2007b; *Guo et al*., 2009; *Dubois et al*., 2010]. Simultaneous measurements of stable isotopic composition in both organic and inorganic carbon are still very few but should allow a more complete understanding of source, transport, and transformation of different carbon species in the river basin. Furthermore, studies on organic acid compositions of riverine DOM derived from both ultrafiltration, a physical size fractionation, and XAD resin column chromatography, a chemical separation technique, should provide detailed information on the quality and transformation of size-fractionated DOM. Thus far, there exist no reports on the application of XAD chromatography to the characterization of high molecular weight, or colloidal, DOM in the Mississippi River although individual separation techniques have been widely applied [e.g., *Aiken et al*., 1992; *Guo et al*., 2009; *Cai and Guo*, 2009; *Butman et al*., 2012; *Bianchi et al*., 2013; *Wang et al*., 2013].

Our objectives were to investigate temporal variations in abundance, chemical and isotopic compositions, and export fluxes of different carbon species, including inorganic and organic carbon in particulate and dissolved phases, from the Mississippi River Basin to determine their interrelationship with hydrologic and biogeochemical processes, and to provide new insights into the dynamic cycling pathways of carbon in the Mississippi River. To accomplish these objectives, monthly water samples were collected during 2006–2008 from the Lower Mississippi River to quantify the concentrations and stable isotopic composition of DIC, DOC, COC, and POC. The bulk DOC was further characterized by size partitioning and organic acid composition. Our hypothesis is that active transformation processes between carbon species are important in the river basin and should be manifested in changes in abundance, composition, and isotopic signatures of the different carbon species.

2. Materials and Methods

2.1. Site Description

The Mississippi River is one of the world's largest rivers, draining about 41% of the contiguous United States and a small part of Canada [*Milliman*, 1991]. The Mississippi River ranks third in drainage basin area among the world's

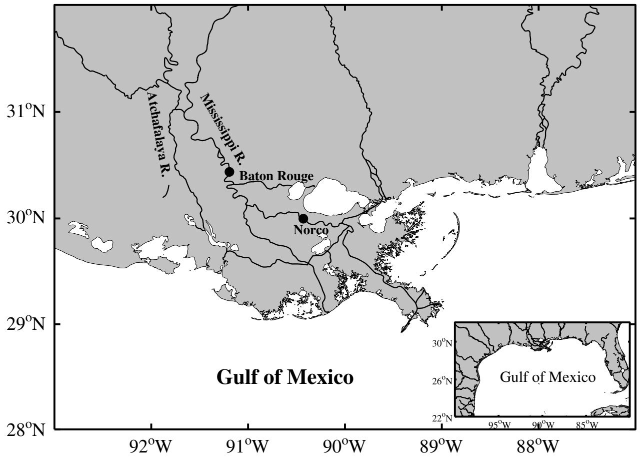

Figure 1. Map showing sampling locations in the Lower Mississippi River.

major rivers, seventh in freshwater discharge, and fifth in sediment discharge [*Meade*, 1995; *Horowitz*, 2010]. C_3 vascular plants account for 73% of the vegetation in the Mississippi River Basin, leaving 27% for C_4 plants [*Lee and Veizer*, 2003]. The Lower Mississippi River is conventionally assigned to the Mississippi River below its confluence with the Ohio River [*Meade*, 1995].

2.2. Sample Collection and DOM Size Fractionation

Surface water samples from the Lower Mississippi River were collected monthly at Baton Rouge, Louisiana (30.4380°N, 91.1926°W), from September 2006 to May 2008 (Figure 1). On 14 April 2008, one additional large volume surface water sample was collected from Norco, Louisiana (29.9979°N, 90.4302°W), during a major flooding event for the ultrafiltration and subsequent determination of organic acid compositions. Previous investigations suggested that chemical compositions of DOM remained quite stable along the main channel [*Meade*, 1995; *Duan et al.*, 2007b]. Therefore, we assume that this sample is similar to those collected at Baton Rouge. The Mississippi River daily discharge was obtained from the U.S. Geological Survey (USGS) hydrological station at Baton Rouge, Louisiana (http://waterdata.usgs.gov/la/nwis/uv/?site_no=07374000).

About 20 L of filtered water samples were collected by directly pumping through an in-line prerinsed Memtrex polycarbonate cartridge (Osmonics, 0.45 μm) and transported in an ice-filled cooler to Stennis Space Center, Mississippi, for further ultrafiltration using the cross-flow ultrafiltration technique [*Cai and Guo*, 2009]. Aliquots of filtrates were also sampled for measurements of DOC and DIC concentrations and their stable isotopic compositions (δ^{13}C-DOC and δ^{13}C-DIC [*Y. Cai et al.*, 2008, 2012]). Immediately, after the sample collection, $HgCl_2$ was added to the DIC samples in the fully-filled 125 mL amber glass bottles before they were sealed.

Meanwhile, separate whole water samples were collected with a peristaltic pump into clean, 2 L high-density polyethylene bottles. Known volumes (50–200 mL) of whole water samples were filtered in the laboratory through either preweighed 0.45 μm polycarbonate filters (Millipore) for the determination of suspended particulate matter (SPM) concentration or precombusted 0.7 μm glass fiber filters (Whatman) for the measurements of POC and particulate nitrogen (PN) concentrations and stable isotopic compositions (δ^{13}C-POC and δ^{15}N-PN).

In the laboratory, the large volume (20 L), prefiltered water samples were ultrafiltered to quantify the abundance and isotopic composition of COC (1 kDa–0.4 μm [*Guo and Macdonald*, 2006]). The ultrafiltration system was equipped with a spiral-wound 1 kDa cartridge (Amicon S10Y1), and colloids were operationally defined here as the fraction between 1 kDa and 0.4 μm. Time series permeate samples (<1 kDa) were collected at different concentration factors. The resulting retentate was then freeze-dried for the measurements of stable isotopic composition of COC (δ^{13}C-COC).

2.3. Measurements of Carbon Species and Their Stable Isotopic Composition

Concentrations of total dissolved carbon (TDC, including DOC and DIC) and DOC in filtrate were measured on a Shimadzu TOC-V high-temperature combustion total organic carbon analyzer. For DOC measurements, the samples were acidified with concentrated HCl to pH <2 before analysis. Samples were not acidified for TDC measurements. The total DOC blank (including Milli-Q water, acid for sample acidification, and the instrument blank) was usually <2–3 μmol/L^{-1}. Consensus reference material, a deep-sea water reference material produced by the Hansell Consensus Reference Material Program (http://www.rsmas.miami.edu/groups/biogeochem/CRM.html), was used as an external DOC standard during sample analysis. Precision and accuracy were within 2% and 1%, respectively, for DOC, while precision for TDC was better than 1%

due to its higher concentration [*Y. Cai et al.*, 2008]. Concentrations of DIC were calculated from the difference between TDC and DOC concentrations.

Concentrations of DOC in the discrete time series permeate samples ($<$1 kDa) were also measured to calculate the COC abundance. The results showed a constant permeation behavior of low molecular weight (LMW) DOC, as expected from the ultrafiltration permeation model [*Guo and Santschi*, 1996]. Quantification of COC abundance using the ultrafiltration permeation model can quantitatively correct the retention of LMW DOC by the ultrafilter and therefore eliminate COC overestimation [*Guo and Santschi*, 1996; *Cai and Guo*, 2009].

The glass fiber filter samples were acid-fumed to remove carbonate and then measured for the concentrations of POC and PN as well as their stable isotopic compositions (δ^{13}C-POC and δ^{15}N-PN) on a PDZ Europa ANCA-GSL elemental analyzer interfaced with a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd.) at the UC-Davis Stable Isotope Facility. DOC samples were also measured for δ^{13}C-DOC after removing inorganic carbon through acidification and subsequent persulfate oxidation. COC samples were freeze-dried and acid-fumed before the analysis of δ^{13}C-COC. δ^{13}C-DIC was also measured on a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd.) interfacing with an O.I. Analytical Model 1010 TOC Analyzer (OI Analytical) at the UC-Davis Stable Isotope Facility. DIC samples were acidified with H_3PO_4 to convert DIC into gaseous CO_2. The released CO_2 was purified, and its δ^{13}C was measured by the mass spectrometer. The analytical precision (2σ) was typically $<$0.20‰, and the sample reproducibility was 0.10–0.35‰ [*St-Jean*, 2003].

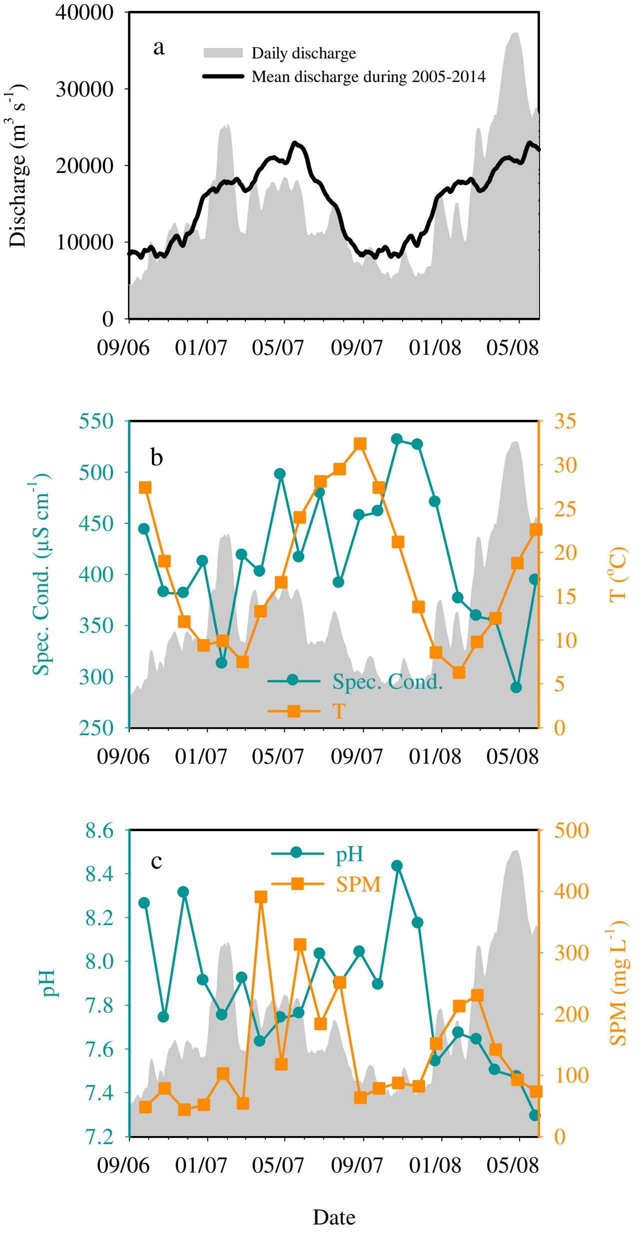

Figure 2. Seasonal variations in (a) real time water discharge and mean daily discharge during 2005–2014 (b) specific conductivity and water temperature, and (c) pH and suspended particulate materials in the Lower Mississippi River at Baton Rouge during 2006–2008.

2.4. Measurements of Organic Acid Components

Selected DOM samples, including the $<$1 kDa permeate, colloidal, and bulk DOM samples, were fractionated using XAD4 and XAD8 columns into hydrophobic organic acid (HPOA), transphilic acid (TPIA), and LMW hydrophilic compound fractions (HPI) [*Aiken et al.*, 1992]. The organic carbon contents of HPOA, TPIA, and HPI were measured to quantify each fraction's abundance [*Aiken et al.*, 1992]. The absorption coefficients at 254 nm, 350 nm, and 412 nm were spectrophotometrically analyzed with 1 cm quartz cuvettes. Specific UV absorbance (SUVA$_{254}$) at 254 nm, an index of DOM aromaticity [*Weishaar et al.*, 2003], was calculated from

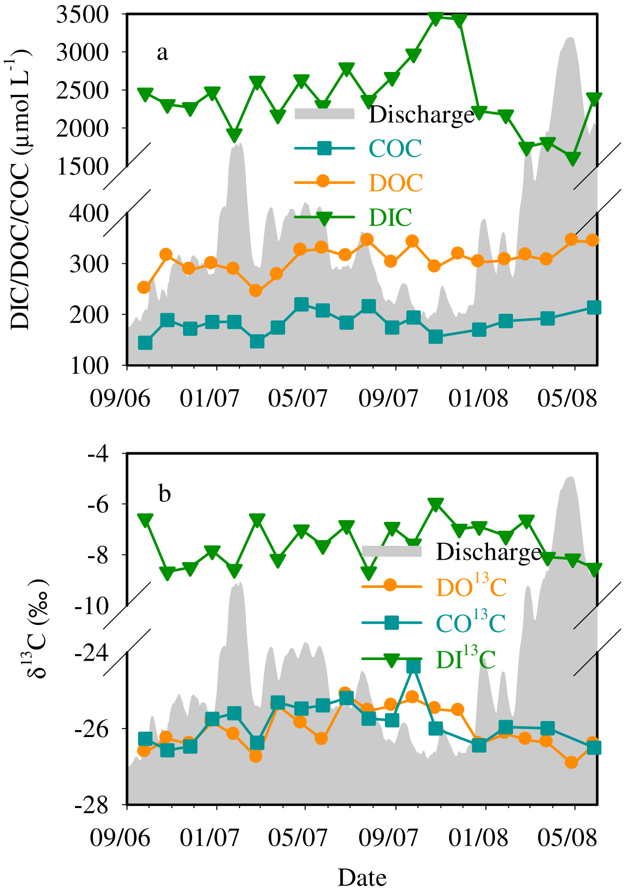

Figure 3. Seasonal variations in concentrations and stable isotopic compositions of dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in the Lower Mississippi River at Baton Rouge during 2006–2008. (a) Concentrations of DOC, DIC and colloidal organic carbon (COC); (b) δ^{13}C of DOC DIC and COC.

the ratio of absorbance at 254 nm to DOC concentration and expressed in units of L mgC^{-1} m^{-1}. The ratio of the absorption coefficients of 254 nm and 350 nm ($R_{254/350}$), a parameter similar to E2:E3 that is related to DOM molecular size, was also calculated [*Helms et al.*, 2008].

2.5. Statistical Analysis

Pearson correlation analysis with a two-tailed test of significance was performed using the SigmaPlot 11.0 program to study the relationships between the measured parameters. The equations and statistical significance of the correlations between measured parameters are listed in Table S1 in the supporting information. The SigmaPlot 11.0 program was also used to run paired *t* test to examine the statistical differences 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 Water Temperature, Conductivity, pH, and SPM Concentrations

August to December was the dry season in the Mississippi River during 2006–2008, with a discharge <10,000 m^3 s^{-1} at Baton Rouge, whereas the wet season was from January to July with a discharge >10,000 m^3 s^{-1} (Table S2 in the supporting information and Figure 2a). This definition of wet and dry seasons is consistent with the 10 year mean river discharge variation during 2005–2014.

Water temperature in the Mississippi River at Baton Rouge was in the range of 6–32°C and showed strong seasonal variability (Table S2 and Figure 2b). Specific conductivity ranged from 288 to 531 µS cm^{-1}, with an average of 417 ± 64 µS cm^{-1} (Table S2). Generally, it varied inversely with river discharge ($p = 0.0007$) and showed peak values during dry seasons and minima during high flow seasons (Figure 2b).

SPM concentrations in the Lower Mississippi River at Baton Rouge varied from 44 to 390 mg L^{-1}, with an average of 136 ± 95 mg L^{-1} (Table S2 and Figure 2c). It generally had higher concentrations in the wet season and lower in the dry season. However, the maximal SPM concentrations were not associated with the peak river flow (Figure 2c). Mississippi River at Baton Rouge was normally slightly alkaline, with an average pH of 7.84 ± 0.29 (Table S2 and Figure 2c). Higher pH was measured during dry seasons and lower pH during wet seasons, resulting in a significant inverse correlation between pH and river discharge and significant positive correlations between pH and both specific conductivity and DIC concentration ($p < 0.01$).

3.2. Dissolved Inorganic Carbon (DIC)

Concentrations of DIC in the Lower Mississippi River at Baton Rouge ranged from 1600 to 3450 µmol L^{-1}, with an average of 2421 ± 480 µmol L^{-1} (Table S2). The highest DIC concentration (>3400 µmol L^{-1}) appeared during the 2007 dry season (October to November), whereas the lowest concentration (<2000 µmol L^{-1})

Table 1. Dissolved Organic Matter Optical ($SUVA_{254}$) and Fractionation Data as Percent of COC, HPOA, HPI, and TPIA for Select Samples in the Mississippi River

Sampling site	Date	Discharge ($m^3\ s^{-1}$)	Size	$SUVA_{254}$ ($L\ mg^{-1}\ m^{-1}$)	$R_{254/350}$	$R_{254/412}$	COC (%)	HPOA ($SUVA_{254}$)	HPI ($SUVA_{254}$)	TPIA ($SUVA_{254}$)	Recovery
Baton Rouge	23/12/2007	13196	<0.45 μm	2.6	4.12	10.5	56	42% (3.6)	19% (1.3)	18% (2.2)	79%
Baton Rouge	28/01/2008	12063	<0.45 μm	2.8	4.01	10.9	61	46% (3.6)	23% (1.3)	17% (1.7)	86%
			<1 kDa	1.9	4.16	9.5		27% (2.7)			
			1 kDa-0.45 μm μM	3.2	3.91	11.2		58% (4.2)[a]			
Baton Rouge	25/03/2008	25656	<0.45 μm	2.7	4.10	11.5	63	44% (3.6)	22% (1.4)	18% (1.8)	84%
			<1 kDa	1.8	4.70	14.1		31% (2.6)			
			1 kDa–0.45 μm	3.1	4.03	11.6		52% (4.2)[a]			
Norco	14/04/2008	29733	<0.45 μm	2.9	4.18	12.6	63	48% (3.7)	19% (1.3)	19% (2.1)	86%
			<1 kDa	2.1	4.73	13.7		31% (3.0			
			1 kDa–0.45 μm μM	3.3	3.98	11.4		58% (4.1)[a]			

[a] Values were estimated from the mass balance between bulk (<0.45 μm) DOM and low molecular weight (<1 kDa) DOM.
$R_{254/350}$ and $R_{254/412}$ refer to the ratios between absorption coefficients at 254, 350, and 412 nm, respectively.

was observed during the high river flow periods (Figure 3a). Values of δ^{13}C-DIC in the Lower Mississippi River varied from −8.67‰ to −5.96‰ and averaged −7.53 ± 0.83‰ (Table S2).

3.3. Dissolved Organic Matter

DOC concentrations in the Lower Mississippi River at Baton Rouge varied between 244 and 344 μmol L^{-1}, with an average of 307 ± 28 μmol L^{-1} during 2006–2008 (Table S3 in the supporting informationand Figure 3a). Similar to the bulk DOC pool, concentrations of COC in the Lower Mississippi River also showed small temporal variability, ranging between 144 and 220 μmol L^{-1} (Figure 3a). The average COC concentration was 184 ± 22 μmol L^{-1} in the Lower Mississippi River. The COC fraction accounted for 53–68% of the bulk DOC (average of 61 ± 3%).

Values of δ^{13}C-DOC in the Lower Mississippi River at Baton Rouge ranged from −26.94‰ to −25.12‰, with an average of −26.03 ± 0.53‰ (Table S3 and Figure 3b). As a major fraction of DOC, δ^{13}C-COC in the Mississippi River averaged −25.85 ± 0.57‰ and was not significantly different from δ^{13}C-DOC ($p > 0.05$).

3.4. Dissolved Organic Carbon Fractionation

The composition and optical properties of bulk DOM (<0.45 μm) in Mississippi River samples fractionated with the XAD resins are given in Table 1. Organic acids, including HPOA, HPI, and TPIA fractions, accounted for 79–86% of the bulk DOM. Among these three fractions, the HPOA fraction was the most abundant, comprising 42–48% of the bulk DOM, followed by HPI and TPIA (19–23% and 17–19%, respectively). In terms of aromaticity, the HPOA had the highest $SUVA_{254}$ value (3.6 L mgC^{-1} m^{-1}), followed by TPIA and HPI (1.9 and 1.3 L mgC^{-1} m^{-1}, respectively). The $SUVA_{254}$ value of the HPOA fraction was higher than the bulk DOM (2.6–2.9 L mgC^{-1} m^{-1}), while $SUVA_{254}$ values of the TPIA and HPI fractions were only two thirds and one half of that of the bulk DOM, respectively. Compared with the bulk DOM, the 1 kDa–0.45 μm colloidal DOM fraction had higher $SUVA_{254}$ values but lower $R_{254/350}$ values (ratio between absorbance at 254 nm and 350 nm). In contrast, the LMW-DOM (<1 kDa) had lower $SUVA_{254}$ and higher $R_{254/350}$ values than the bulk DOM. Across a large range of discharge in the Mississippi River (12,063–29,733 $m^3\ s^{-1}$), the percentage of DOC represented by the HPOA fraction increased in the order of LMW-DOM < bulk DOM < colloidal DOM.

3.5. Particulate Organic Matter

POC and PN concentrations in the Lower Mississippi River at Baton Rouge were in the range of 160–805 (average of 361 ± 184) μmol C L^{-1} and 11.9–57.3 (24.6 ± 13.2) μmol N L^{-1}, respectively (Table S3). In general,

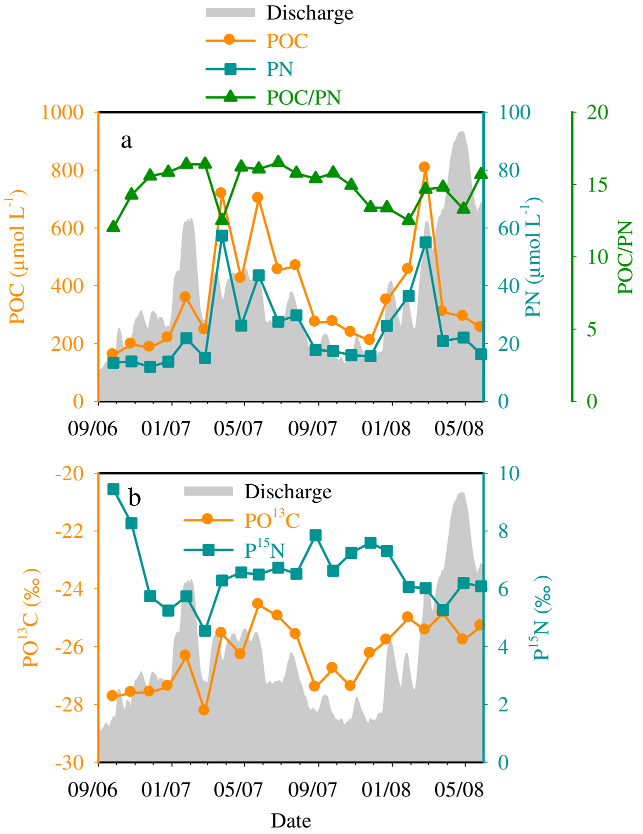

Figure 4. Seasonal variation in concentrations and C/N ratio of (a) particulate organic matter (POM) and (b) δ^{13}C and δ^{15}N of POM in the Lower Mississippi River at Baton Rouge during 2006–2008.

both POC and PN remained at lower concentrations during dry seasons and increased during high flows (Figure 4a). Similar to SPM, all peak POC and PN concentrations occurred during wet seasons though POC and PN concentrations dropped significantly during June 2008 flooding (Figure 4a). Both POC and PN concentrations showed similar seasonal variation and the POC/PN ratios had a narrow range of 12.0–16.5, with an average of 14.8 ± 1.4 (Figure 4a).

δ^{13}C-POC in the Lower Mississippi River averaged −26.28 ± 1.12‰, ranging from −28.24‰ to −24.56‰ and was not significantly different from δ^{13}C-DOC (Table S3). Seasonally, δ^{13}C-POC was near −27.5‰ during low flow seasons and increased to around −25‰ at peak flow (Figure 4b). δ^{15}N-PN values varied between 4.54 and 9.44‰, with an average of 6.56 ± 1.11‰ (Table S3). δ^{15}N-PN showed the opposite trend, low during high flow seasons and relatively high during base flows (Figure 4b).

4. Discussion

4.1. Abundance and Seasonality of Different Carbon Species

The average DIC concentration in the Mississippi River (2421 ± 480 μmol L^{-1}) is among the highest of major world rivers, only second to the Yellow River [*W.-J. Cai et al.*, 2008]. This DIC concentration is even higher than those of deep ocean water [*Broecker and Peng*, 1982]. During 2006–2008, DIC concentration was inversely correlated to the river discharge ($p < 0.05$; Figure 5a), suggesting the major role of surface runoff in regulating DIC concentrations in the Mississippi River through dilution by precipitation [*Cai*, 2003] and changes in carbon sources, as suggested by its isotopic composition (Figure 5a).

In contrast to the DIC data, DOC concentrations in the Lower Mississippi River were less variable with an average of 307 ± 28 μmol L^{-1} over the entire 21 month sampling period. Variability of DOC abundance was rather small in the Lower Mississippi River, with a standard deviation of ~9% (versus 16% and 51% for DIC and POC, respectively). In addition, DOC concentration was not significantly correlated to river discharge (Figure 6), indicating weak hydrologic control on riverine DOC concentration in the Lower Mississippi River, which is different from less impacted river systems [e.g., *Duan et al.*, 2007a, 2007b; *Y. Cai et al.*, 2008; *Guo et al.*, 2012; *Hanley et al.*, 2013]. Little variation in DOC concentration in the Mississippi River and a poor correlation between DOC and river discharge were likely the result of mixing of tributaries with different DOC concentrations and the presence of numerous impoundments along the upper-middle mainstream and in the major tributaries which increase water residence times [*Duan et al.*, 2007b; *Meade*, 1995] and average event driven changes in constituent concentrations. A previous study showed that only 10% of the outflow from the heavily dammed Missouri River was derived from precipitation supported surface flows [*Michel*, 2004]. Prolonged water residence times can also result in increased in situ microbial and photochemical decomposition of terrestrially derived DOC, while stimulating autochthonous production of DOC [*Bianchi et al.*, 2004; *Duan et al.*, 2007b]. These processes would further reduce the DOC variation [*Duan et al.*, 2007b].

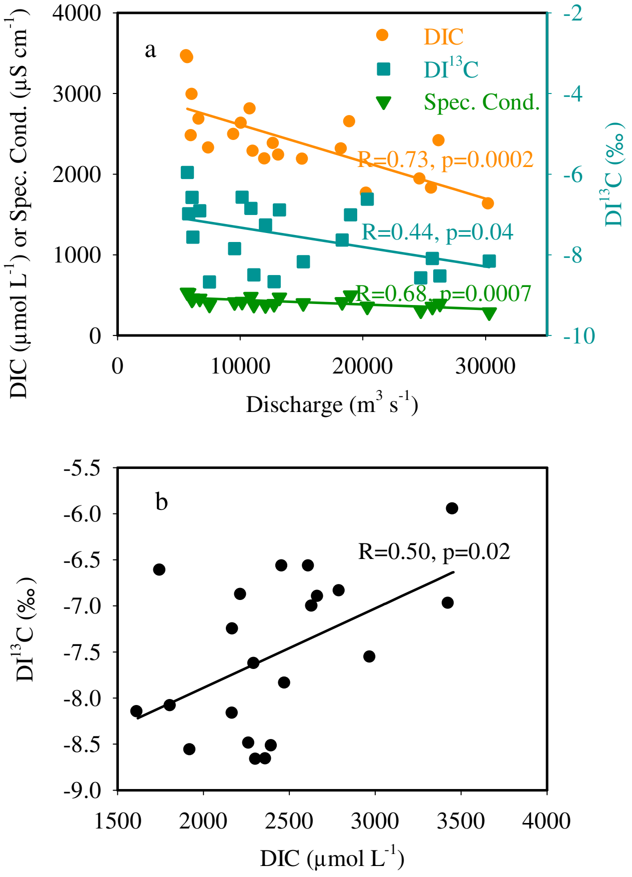

Figure 5. (a) The relationships between river discharge and concentrations of DIC and specific conductivity and δ^{13}C of DIC, and (b) the relationship between concentration versus δ^{13}C of DIC in the Lower Mississippi River at Baton Rouge.

Stable carbon isotopic composition of the bulk DOC pool changed little with an average of -26.03 ± 0.53‰, indicating constant DOC sources in the Lower Mississippi River (see also discussion below). Moreover, the percentages and the optical properties of organic acids (HPOA, HPI, and TPIA) in different size fractions of the bulk DOM also showed little variation even though the river discharge varied in a wide range of 12,063–29,733 $\mathrm{m^3\,s^{-1}}$ (Table 1). Together with stable DOC concentrations, constant isotopic and organic acid compositions point to somewhat constant DOM sources and inputs in the river without a clear connection to hydrological conditions.

The peak concentrations of both SPM and associated POC and PN occurred during medium flooding events and at the rising limb of large flooding events when the river discharge was around 20,000 $\mathrm{m^3\,s^{-1}}$ (Figure 7a). This might be caused by the limited sediment supply in the Mississippi River Basin during large magnitude flooding events. This observation is supported by some previous investigations. For example, *Duan and Bianchi* [2006] observed the peak concentrations of SPM and particulate organic matter (POM) in the Mississippi River in the transition period from low to high flow during 2001–2003. In 2011, a large flooding event occurred in the Mississippi River during which the highest sediment load appeared at a discharge of around 20,000 $\mathrm{m^3\,s^{-1}}$ on the rising limb of the flood [*Allison et al*., 2013]. A comparative study compiled by *Allison et al*. [2012] further showed that daily sediment loads in the Mississippi River during the last four decades reached a plateau when discharge was greater than 20,000 $\mathrm{m^3\,s^{-1}}$. The threshold of sediment supply during a large flooding period might be an important factor responsible for the historical decline of suspended sediment load transported by the Mississippi River while river discharge continues to increase. In contrast to 2008, in which the peak POC and PN concentrations were observed before the peak flow event, the peak concentrations of POC and PN appeared after the peak flow event in 2007 (Figure 4a). This was most likely due to lower sediment input caused by a smaller magnitude and shorter duration peak flow event in 2007 compared to 2008. The reservoirs and lock dams along the river channels might gradually retain the sediment during its transport and only small increases of POC and PN concentrations were thus observed.

Overall, DIC was the dominant carbon species in the Mississippi River, accounting for 60–90% of total carbon. The dominance of DIC in the total carbon pool was likely supported by the wide distribution of limestone [*Epstein et al*., 2002] and the high weathering intensity in the Mississippi River Basin. The percent of total carbon accounted for by DOC remained fairly constant around 10%, while POC accounted for 5–30% (Figure 8a). In general, DIC was a larger percent of total carbon during dry seasons, whereas the percent POC increased from dry to wet seasons.

4.2. Size Partitioning and Organic Acid Composition of the Bulk DOC

On average, COC comprised 61 ± 3% of the bulk DOC in the Lower Mississippi River, leaving about 40% as LMW-DOC. The COC abundance in the Mississippi River is lower than those observed for the adjacent Pearl

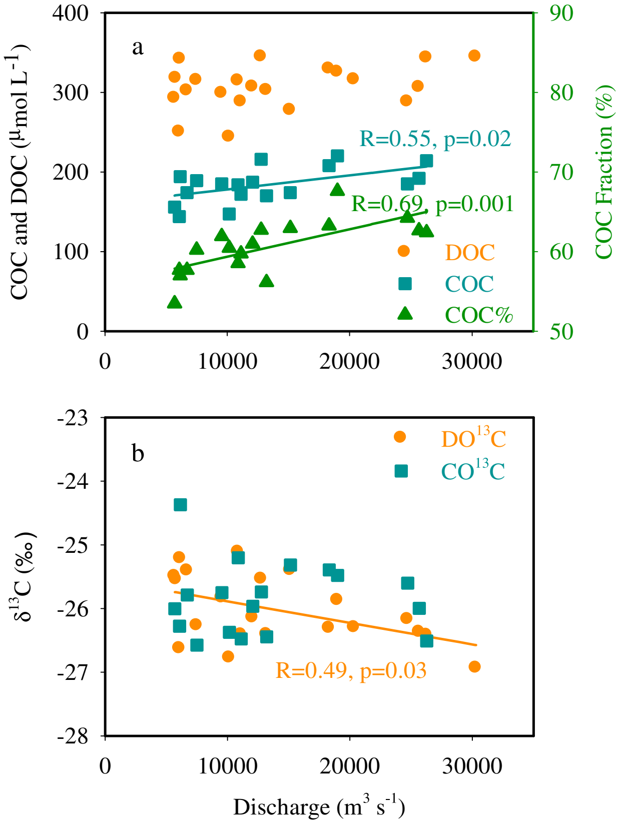

Figure 6. (a) The relationships between the concentrations of DOC and COC and the percentage COC versus discharge, and (b) the relationships between δ^{13}C of DOC and COC versus discharge in the Lower Mississippi River at Baton Rouge.

River (Mississippi; ~71%) and the Trinity River (Texas; 68%), both small subtropical rivers undergoing less human alteration (Cai et al., unpublished results; *Guo and Santschi*, 1997), high latitude Alaska rivers (>70% for the Yukon and Chena Rivers; *Guo and Macdonald*, 2006; *Y. Cai et al.*, 2008), and the Amazon River [76%; *Benner and Hedges*, 1993]. Lower COC abundance in the Mississippi River is consistent with more intensive photochemical and microbial degradation of DOM due to the prolonged water residence time in the river [*Guo and Santschi*, 1997; *Guo et al.*, 2009; *Stolpe et al.*, 2010; *Duan et al.*, 2013].

Previously reported percentages of the HPOA fraction of the bulk DOM during 2008–2011 remained fairly constant regardless of variations in discharge, even during a major flood in 2011 [*Spencer et al.*, 2012; *Bianchi et al.*, 2013; *Hanley et al.*, 2013]. These results agree well with the constant DOC concentrations we observed in the Lower Mississippi River and suggest that the dissolved organic acid compositions of selected size-fractionated samples in this study could well represent the whole sampling period. The observed constant HPOA fraction and its SUVA$_{254}$ values across a wide range of discharge (12,063–29,733 m^3 s^{-1}) further support a consistent DOC source and constant organic acid composition in the river (Table 1). To the best of our knowledge, the percentage HPOA (HPOA%) of the size fractionated COC samples reported in this study is the first data comparing the difference of organic acid composition between colloidal and LMW-DOM fractions.

Based on the correlation between the HPOA% and chromophoric DOM spectral slope values in U.S. rivers, *Spencer et al.* [2012] suggested HPOA% as an indicator of DOM molecular weight and diagenetic status; however, DOM size distribution data were not determined. In the present study, our results, showing a decreasing order of HPOA% and its SUVA$_{254}$ value from colloidal DOM to bulk DOM and to LMW-DOM, provided direct evidence to support the use of HPOA as proxy for DOM size and quality in river waters. In addition, our results also indicated the greater aromaticity and potentially diagenetically younger status of colloidal DOM than LMW-DOM in the Lower Mississippi River. Since δ^{13}C signatures between COC and DOC are indistinguishable, the organic acid composition might be a more sensitive indicator for the quality and bioavailability of DOM of different classes in the Lower Mississippi River (Figure 6).

4.3. Carbon Isotopic Composition and Sources

The δ^{13}C-DIC values in the Mississippi River are similar to those reported for other northeast U.S. rivers and are in the range of chemical weathering signatures, consistent with carbonate dissolution as a major DIC source in the river basin [*Raymond et al.*, 2004], which includes groundwater transport as a transfer pathway of chemical weathering derived DIC into the Mississippi River. Our data are also similar to previously reported δ^{13}C-DIC (−7.0‰ to −11.5‰) across the Lower Mississippi River Basin, including sampling sites from the Arkansas, Atchafalaya, and Lower Mississippi Rivers, while a wide spatial variation of δ^{13}C-DIC (−3.3‰ to −12.2‰) existed across the major subbasins (the Missouri, Ohio, Upper Mississippi, and Lower Mississippi

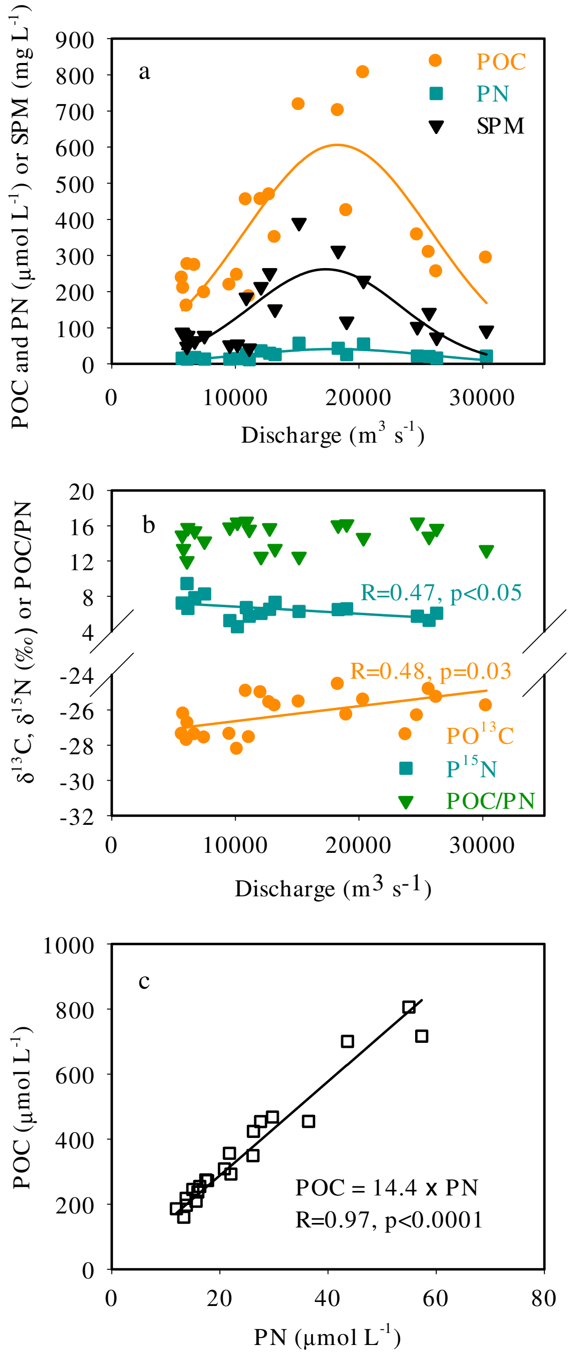

Figure 7. (a) The relationships between the concentrations of POC, PN and SPM concentrations versus discharge, (b) the relationships between the δ^{13}C, δ^{15}N, contents and C/N ratio of POM versus discharge, and (c) POC concentration versus PN concentrations in the Lower Mississippi River at Baton Rouge.

River Basins) of the Mississippi River watershed due to isotopic fractionation caused by photosynthesis, respiration, and possible degassing processes [*Dubois et al.*, 2010]. *Dubois et al.* [2010] also estimated the chemical weathering derived δ^{13}C-DIC (−7.0‰ to −7.9‰) in the Mississippi River Basin with an isotopic mass balance approach. The similarity between our data and chemical weathering derived δ^{13}C-DIC in the Mississippi River further supports carbonate dissolution as a major DIC source. Based on a global relationship between riverine bicarbonate fluxes and watershed carbonate mineral contents, *W.-J. Cai et al.* [2008] also suggested that DIC in the Mississippi River was mostly supplied by carbonate weathering. However, the narrow δ^{13}C-DIC range obtained in this study also reflected the effect of extensive impoundment in the Mississippi River Basin, which strongly mixed the isotopic signals of DIC from upper tributaries and other sources, resulting in the rather constant ^{13}C isotopic composition of DIC (Figure 5b).

Although δ^{13}C-DIC in the Mississippi River varied over a narrow range (−5.96 to −8.67‰), a statistically significant, but weak, inverse correlation between δ^{13}C-DIC and discharge ($R = 0.44$, $p = 0.04$) was observed (Figure 5a), indicating some changes in DIC sources. The positive correlation between DIC concentration and its isotopic composition also suggested the mixing of variable DIC sources with distinct isotopic signatures in the Mississippi River ($R = 0.50$, $p = 0.02$; Figure 5b). High DIC concentrations were generally accompanied by relatively enriched δ^{13}C signatures, consistent with carbonate dissolution as a major source of DIC to the river. On the other hand, the lower δ^{13}C signature accompanying the low DIC concentration indicated the input of DIC with depleted δ^{13}C composition, most likely from the respiration of soil organic matter. To better demonstrate the hydrological control on the carbon source variability, a two end-member isotopic mixing model is adopted in this study [*Raymond et al.*, 2004; *Goñi et al.*, 2005]. Given the stable carbon isotopic signatures of carbonate rock (δ^{13}C = 0‰) and soil organic matter (δ^{13}C = −26‰), the contribution of respired soil and terrigenous organic carbon to the DIC pool increased from ~23% during dry seasons to ~33% during wet seasons. Since the instantaneous DIC load during wet seasons increased four times compared to dry seasons, the quantity of respired soil organic carbon contributing to the DIC pool in the Mississippi River during wet seasons could be near six times that during dry seasons considering a 40% increase of its contribution (from ~23% to ~33%). Although the contribution of soil organic

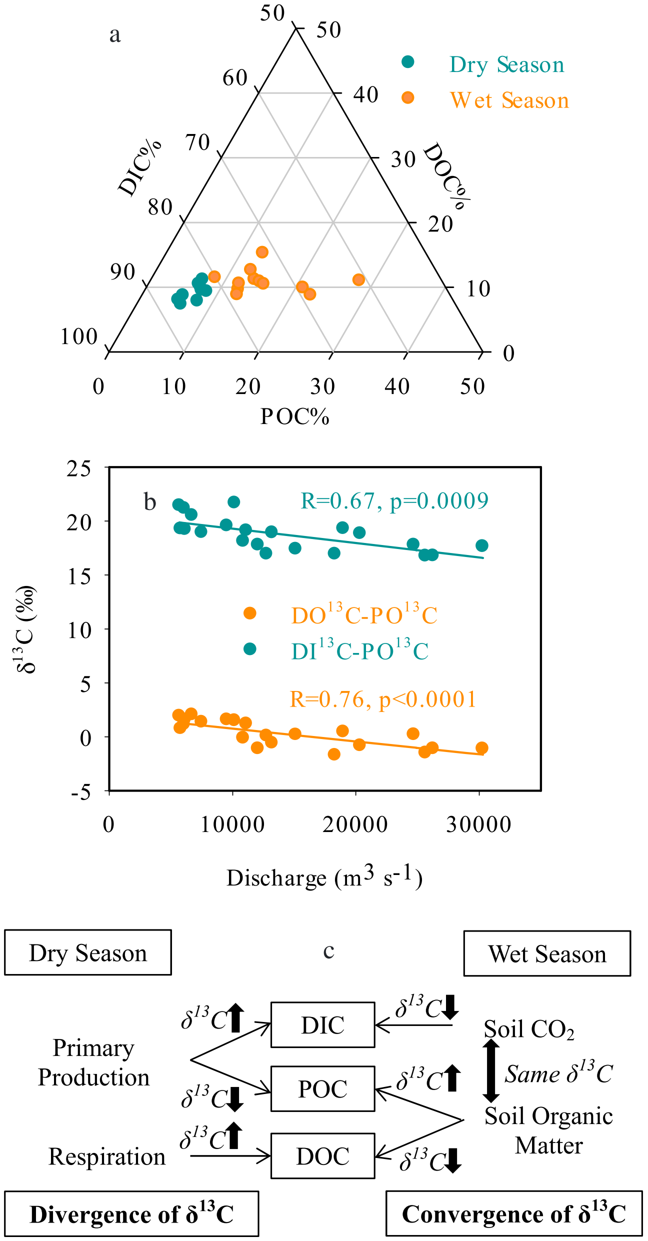

Figure 8. (a) A ternary diagram of percentage of the total carbon pool represented by DOC, DIC, and POC fractions, (b) the relationships between the differences of δ^{13}C content between DIC and POC and between DOC and POC in the Lower Mississippi River at Baton Rouge, and (c) a conceptual model of potential controls on δ^{13}C of individual carbon species in dry and wet seasons.

carbon would be overestimated due to the involvement of atmospheric CO_2 in carbonate rock dissolution, the higher input from soil organic carbon could still be validated during wet seasons. Meanwhile, phytoplankton DIC uptake in the river, as supported by high productivity [*Duan and Bianchi*, 2006], could increase ^{13}C isotopic composition of residual riverine DIC. Nevertheless, the simultaneous influences of carbonate weathering, DOM degradation, biological utilization, and anthropogenic sources may obscure the transition of δ^{13}C-DIC between wet and dry seasons in the Mississippi River.

The δ^{13}C-DOC in the Lower Mississippi River is higher than that of the algae materials but lower than that of C_4 plants (Delong and Thorp, 2005 [*Goñi et al.*, 2005]). Nevertheless, the similarity in δ^{13}C values between DOC in the Lower Mississippi River and C_3 plants suggests C_3 plants are major sources of the DOC, consistent with the dominance of C_3 plants over C_4 plants (73% versus 27%) in the Mississippi River Basin [*Lee and Veizer*, 2003; *Goñi et al.*, 2005]. The δ^{13}C value of COC, which was indistinct from that of DOC ($p < 0.05$; Figure 6b), also indicated that COC was mostly derived from C_3 plants, and the contribution to DOC from C_4 material was limited in the Lower Mississippi River [*Bianchi et al.*, 2004; *Duan et al.*, 2007a].

Although concentrations and organic acid compositions of DOM generally remained constant during the sampling period, increasing COC concentrations and its proportion of the bulk DOC with increasing discharge were observed (Figure 6), indicative of enhanced input of fresh DOM during the high flow regime [*Stolpe et al.*, 2010]. In addition, a companion study by *Wang et al.* [2013] and previous investigations by *Duan et al.* [2007a] and *Duan and Bianchi* [2007] observed greater amounts of labile organic compounds, such as carbohydrates, amino acids, and terrestrially derived lignin phenols, contributing to the DOC pool during wet seasons compared to dry seasons. These results further attested a fresher, less altered DOM pool during wet seasons. The higher fraction of fresher DOM was likely an important factor resulting in the decreasing δ^{13}C-DOC during high flow periods. Meanwhile, more extensive degradation of DOM during dry seasons would further strengthen the inverse correlation between δ^{13}C-DOC and discharge. This is consistent with studies showing that natural DOM depleted in ^{13}C was preferentially photooxidized, resulting in more positive ^{13}C in the residual DOM

Table 2. Seasonal and Annual Carbon Fluxes From the Lower Mississippi River at Baton Rouge During 2006–2008[a]

Species	Average Concentration (μmol L^{-1})	n	$Flux_A$	$Flux_D$	$Flux_W$	$R_{W/D}$
Water	-	-	457	108	349	
DOC	307	21	1.88	0.43	1.45	1.04
COC	184	21	1.16	0.25	0.91	1.13
POC	361	21	2.30	0.37	1.93	1.61
DIC	2421	21	13.6	3.75	9.85	0.81
TOC	668	21	4.18	0.80	3.38	1.31
TC	3089	21	17.8	4.55	13.2	0.90

[a] $Flux_A$, $Flux_D$ and $Flux_W$ denote annual flux, dry season flux, and wet season flux, respectively. The units for the carbon and water flux are Tg C yr^{-1} and km^3 yr^{-1}, respectively. $R_{W/D}$ is the ratio of discharge-normalized fluxes between wet and dry seasons.

[*Opsahl and Zepp*, 2001; *Lalonde et al.*, 2014]. Nevertheless, hydrologic control of DOM quantity and quality in the Mississippi River seemed much weaker compared to more pristine, less managed rivers [*Duan et al.*, 2007a, 2007b; *Striegl et al.*, 2007; *Y. Cai et al.*, 2008; *Butman et al.*, 2012; *Guo et al.*, 2013].

δ^{13}C-POC values ranged from −28.24‰ to −24.56‰, with an average of −26.28 ± 1.12‰ (Figure 7b). Similar to DOC, these values are close to the typical δ^{13}C value of C_3 vascular plants, suggesting major contributions of POC from C_3 plants in the Mississippi River Basin [*Lee and Veizer*, 2003; *Goñi et al.*, 2005]. Although the C/N ratio of POM remained fairly constant at 14.8 ± 1.4 with a good correlation between POC and PN concentration ($R = 0.97$, $p < 0.0001$; Figure 7c), increasing δ^{13}C-POC but decreasing δ^{15}N-PN was observed simultaneously with increasing river discharge (Figure 7b). This may suggest the alteration of POM sources with distinct isotopic signatures but similar elemental compositions. Higher autochthonous contributions with depleted ^{13}C and enriched ^{15}N abundances during dry periods and the rising limbs of high flow events, as suggested by Chl-*a* concentrations, would result in the observed change in isotopic composition of the POM in the Lower Mississippi River [*Delong and Thorp*, 2006; *Duan and Bianchi*, 2006]. Depleted ^{13}C and enriched ^{15}N abundances have also been reported for freshwater phytoplankton in Texas streams [*Duan et al.*, 2014], further supporting the above explanation. Meanwhile, the variation in suspended sediment size fractions and resuspension of bed sediment between different hydrologic conditions could further change the isotopic composition of POM without significantly disturbing the elemental stoichiometry [*Meade*, 1995; *Allison et al.*, 2012].

The differences in stable carbon isotopic composition between DOC and POC or between DIC and POC show an inverse correlation with river discharge (Figure 8b), indicating seasonal variations in the contributions of various sources for these carbon species. The convergence of δ^{13}C of DOC and POC during wet seasons suggests the same source inputs, while the smaller difference between δ^{13}C of DIC and POC during wet seasons indicates an increasing contribution of DIC from soil CO_2 and respiration of soil organic matter (Figure 8c). During dry seasons, the higher contributions of autochthonous production to the POC with depleted δ^{13}C, prolonged river processing of DOM which increases the δ^{13}C of remaining DOM, and less DIC from soil organic matter would be the main causes of the increased differences in δ^{13}C between POC and DOC and between DIC and POC (Figure 8c).

4.4. Export Fluxes of Carbon Species

Based on monthly data collected during 2006–2008, annual export fluxes from the Mississippi River were estimated using the USGS LOADEST program [*Runkel et al.*, 2004] for DOC, COC, POC, and DIC. The carbon fluxes were 1.88 Tg C yr^{-1} for DOC (of which 1.16 Tg C yr^{-1} was COC), 2.30 Tg C yr^{-1} for POC, and 13.6 Tg C yr^{-1} for DIC during 2006–2008 (Table 2). This is the first data set providing riverine export fluxes simultaneously for all the carbon species. Within the bulk DOC flux, 62% was exported as COC in the Mississippi River. Taken as a whole, the annual carbon export from the Lower Mississippi River during 2006–2008 was 17.8 Tg C yr^{-1}. Similar to carbon speciation in the Lower Mississippi River, DIC export accounted for 76% of the total carbon flux, followed by POC (13%) and DOC (11%). More than 70% of total carbon was exported during wet seasons from January to July although the different carbon species had different seasonal patterns. As indicated by ratios between wet and dry season discharge-normalized carbon export fluxes, DOC export efficiency showed no difference between wet and dry seasons after being normalized by river discharge due to its stable concentrations. Meanwhile, discharge-normalized POC flux was 60% higher and that of DIC was 20% less during wet seasons than dry seasons (Table 2).

Our multiple-year DOC export flux is consistent with most previous flux estimates with discrete or short-term sampling [e.g., *Malcolm and Durum*, 1976; *Trefry et al.*, 1994; *Shen et al.*, 2012; *Duan et al.*, 2013; *Spencer et al.*, 2013]. DOC export fluxes from the Mississippi River for the 2006–2008 period were surprisingly similar to the results during 2008–2010 (1.92 Tg C yr^{-1} [*Hanley et al.*, 2013]), further indicating the less variable feature in both DOC concentration and export flux from the Mississippi River. Because the instantaneous daily DOC flux was significantly correlated with discharge in the Mississippi River (plot not shown), DOC fluxes from the Mississippi River can be well predicted from river discharge due to the near-constant DOC concentration shown in this study. The similar discharge-normalized DOC export during wet and dry seasons further supports the control of river discharge on the DOC export (Table 2). Due to the limited data and some questionable data sets in early studies [*Hanley et al.*, 2013], long-term changes in DOC concentrations and flux for the last 50 years cannot be precisely established yet and hinder the projection of its future variation in the context of increasing discharge [*Tao et al.*, 2014]. However, the average annual DOC concentration (293 ± 62 μmol L^{-1}) and flux (1.72 Tg C yr^{-1}) data reported for samples collected in 1969 by *Malcolm and Durum* [1976], who employed similar methods to ours, are comparable to those reported here. These results suggest that DOC concentrations and flux in the lower Mississippi River have been relatively stable or have increased only slightly over the last four decades.

The POC fluxes estimated by previous studies showed large variability ranging from 0.85 to 3.78 Tg C yr^{-1} without clear temporal patterns, possibly due to inconsistent sampling protocols and few data points [*Duan et al.*, 2013, and references therein]. Our estimated POC flux is in the middle of this range and is comparable to the DOC export flux from the Mississippi River even though sediment loads have decreased since 1950. Although $>$80% of POC was transported during wet seasons, decreased POC concentrations at discharges greater than 20,000 m^3 s^{-1} reduces the usefulness of instantaneous POC fluxes during major flooding events. Therefore, unlike the case for DOC, the capacity of a major flooding event in the Mississippi River to deliver terrestrial POC is not proportional to the river discharge. Similar to the case of DOC, in spite of the deceasing trend of riverine sediment load, the POC export slightly increased over the last 40 years compared to the estimation (2.00 Tg C yr^{-1}) of *Malcolm and Durum* [1976].

DIC fluxes in the Mississippi River have been generally increasing over the last 100 years [*Cai*, 2003; *Raymond and Cole*, 2003; *Raymond et al.*, 2008]. The DIC flux data reported here for 2006–2008 are similar to previous estimates for the 1990–2005 period [*Raymond et al.*, 2008] and consistent with the increasing trend of DIC export from the Mississippi River. As pointed out in previous studies, increasing DIC fluxes are thought to be due largely to enhanced chemical weathering and changes in agricultural practices and land use [*W.-J. Cai et al.*, 2008; *Raymond et al.*, 2008]. In this study, a decreasing discharge-normalized DIC flux from dry to wet seasons was observed, although higher DIC instantaneous export occurred during wet seasons. Thus, the annual discharge-normalized mean DIC flux would decrease with projected increasing discharge.

Overall, 76% of annual water discharge, 72% of annual riverine DIC flux, and 81% of annual total OC flux occurred during the wet seasons in the Mississippi River, revealing the importance of high flow and major flooding events on the riverine and coastal carbon cycles in the northern Gulf of Mexico [*Cai*, 2003; *Bianchi et al.*, 2013; *Fichot et al.*, 2014]. The export efficiencies for different carbon species varied with hydrology as shown by the ratios of discharge-normalized carbon fluxes between wet and dry seasons (Table 2). Discharge-normalized DOC export was near constant while discharge-normalized POC export increased 60% from dry to wet seasons. In total, discharge-normalized OC export increased 30% during wet seasons. However, the discharge-normalized DIC and total carbon (TC) fluxes in the Mississippi River during wet seasons were lower than those during dry seasons (Table 2). The discharge of the Mississippi River has increased for the past century and is anticipated to continue increasing for the next century [*Raymond and Cole*, 2003; *Tao et al.*, 2014]. In accordance with increasing discharge, disproportional increases in organic carbon exports are expected based on the higher OC export efficiency during wet seasons. In contrast, lower DIC and TC export efficiencies in the wet seasons will result in the 8–48% and 9–54% increase of DIC and TC, respectively, assuming a 10–60% increase of discharge in the 21st century [*Tao et al.*, 2014]. The projection of DIC export based on its response to the river hydrology is supported by a recent model simulation with slightly higher estimation (35–65%) of increased DIC export flux [*Ren et al.*, 2015].

The contrasting responses of DOC, POC, and DIC export efficiencies to the hydrology in the Mississippi River Basin will likely alter carbon speciation, transformation, and transport. Previous estimations of carbon export from the Mississippi River mostly focused on interannual variabilities and the effects of sporadic major flooding events [*Raymond et al.*, 2008; *Bianchi et al.*, 2013; *Fichot et al.*, 2014]. In contrast, the seasonal variability of inorganic and organic carbon export was not well addressed, hindering the projection of future carbon export in the Mississippi River. Furthermore, long-term changes of both DOC and POC exports remain uncertain due to the lack of reliable data sets for earlier periods. Carbon flux estimates in this study thus provide not only recent reliable data sets for the establishment of long-term variability but also useful information on seasonal variability of carbon speciation and transport for the assessment of future carbon export trends in the Mississippi River.

5. Conclusions

Seasonal variations in the concentrations, isotopic compositions and export fluxes of DOC, COC, POC, and DIC in response to hydrologic regimes in the Lower Mississippi River during 2006–2008 were investigated in this study. The size partitioning and organic acid composition of DOM were also obtained with the application of cross-flow ultrafiltration and XAD column chromatography. DIC was the dominant species in the TC pool (including DIC, DOC, and POC), followed by POC and DOC. The COC (1 kDa–0.45 μm) comprised, on average, 61% of the bulk DOC. Compared to the bulk DOC, COC showed higher HPOA fraction and $SUVA_{254}$ value, indicating its high aromaticity and diagenetically younger status. Analyses of stable carbon isotopic compositions revealed that carbonate dissolution is a major source for DIC in the Mississippi River, and that COC, DOC, and POC are likely derived primarily from terrestrial C_3 plants. Generally, δ^{13}C-DIC and δ^{13}C-DOC were inversely correlated with discharge, whereas δ^{13}C-POC increased and δ^{15}N-PN slightly decreased with increasing discharge. The convergence of δ^{13}C between DIC or DOC and POC during wet seasons could be caused by the enhanced contribution of terrigenous organic matter and soil CO_2 with similar carbon isotopic composition. In contrast, aquatic photosynthesis and microbial and photooxidation processes might be the main drivers for the divergence of δ^{13}C between DIC or DOC and POC during dry seasons. Carbon export fluxes from the Mississippi River were estimated to be 13.6 Tg C yr^{-1} for DIC, 1.88 Tg C yr^{-1} for DOC, and 2.30 Tg C yr^{-1} for POC. The discharge-normalized DIC and POC fluxes were 20% less and 60% higher, respectively, during wet seasons than dry seasons while the discharge-normalized DOC flux remained quite stable. Correspondingly, the POC export flux from the Mississippi River will likely increase the most, follow by the DOC and DIC export fluxes in responses to future increasing discharge. The carbon speciation and transformation pathways would therefore be altered as suggested by the variable responses of isotopic compositions and export fluxes of individual carbon species to the hydrologic regimes.

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