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Floodplain influence on dissolved organic matter composition and export from the Mississippi–Atchafalaya River system to the Gulf of Mexico

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Abstract

Comparisons of the concentrations and compositions of dissolved organic matter (DOM) between the lower Mississippi River (MR) and its distributary, the Atchafalaya River (AR), indicated a strong influence of floodplains on DOM in the AR. Concentrations of dissolved organic carbon (DOC), lignin phenols, amino acids, neutral sugars, and chromophoric DOM (CDOM) absorption coefficients were higher in the AR than in the MR. Significantly lower syringyl to vanillyl phenol ratios (S : V) in the AR indicated substantial contributions from gymnosperms (e.g., *Taxodium distichum*). The lowest S : V values in the AR were measured during maximal litterfall in October–November when yields of lignin phenols were highest. Lower spectral slope coefficients ($S_{275–295}$) in the AR were indicative of relatively high-molecular-weight CDOM. Yields and compositions of amino acids and neutral sugars indicated DOM in the AR was more bioavailable than in the MR. Nitrogen removal in the floodplain was in part responsible for the significantly lower concentrations of total dissolved nitrogen (TDN) in the AR. Seasonal variability in DOM composition was greater in the AR. About 35% of the DOC and $>$ 44% of the lignin phenols, amino acids, and neutral sugars exported from the Mississippi–Atchafalaya River system was carried by the AR, thereby revealing the important role of the AR in DOM export from the river system. DOC export from rivers was predominantly controlled by water discharge. The long-term (1996–2010) average DOC export from the Mississippi–Atchafalaya River system was 2.70 Tg yr^{-1} (MR: 1.75 Tg yr^{-1}; AR: 0.95 Tg yr^{-1}), accounting for 0.8–1.1% of global riverine DOC export.

Riverine dissolved organic matter (DOM) influences biological productivity, community structure, microbial metabolism, and air–sea carbon dioxide fluxes in river-influenced ocean margins (Gattuso et al. 1998). Those influences are largely determined by the chemical composition of DOM, which is shaped by source and biogeochemical processing (Hedges et al. 1994, 2000). River floodplains are highly productive environments with diverse biogeochemical processes and organic matter sources, so interactions between rivers and their floodplains can have a large effect on the concentrations of dissolved organic carbon (DOC) in rivers (Tockner et al. 1999). Rapid organic matter accumulation occurs in floodplains, which are considered sinks of particulate organic matter and sources of DOM (Tockner et al. 1999).

Many of the characteristics of organic matter found in floodplain-influenced rivers are believed to result from floodplain contributions, but they can also be due to variations in upstream water sources, hydrological and climatic conditions, and river size (Battin 1998; Hedges et al. 2000). Direct evidence demonstrating the effects of floodplains on the composition of riverine DOM based on comparisons of rivers having similar climatologies and water sources but distinct floodplain interactions is scarce. The Mississippi (MR) and Atchafalaya (AR) Rivers form the largest river system in North America. The two rivers have similar water sources, but the reaches of the MR and AR from the Old River Control Structure to the Gulf of Mexico are very different. The MR is channelized by artificial levees and has little interaction with its floodplains, whereas the AR floods its alluvial system annually for long time periods and has substantial interactions with its floodplain (Lambou and Hern 1983). The sharp contrast in geomorphology and floodplain interaction between the two rivers together with similar climatic and hydrologic conditions provide a unique opportunity to investigate the influence of floodplains on the concentration and composition of DOM from the Mississippi–Atchafalaya River system.

The northern Gulf of Mexico receives large amounts of DOM from the Mississippi–Atchafalaya River system (Malcolm and Durum 1976). Estimates of DOC export from the MR range from 1.7–3.5 Tg yr^{-1} (Malcolm and Durum 1976; Leenheer 1982; Bianchi et al. 2004), but these estimates do not include the export of DOC from the AR, which accounts for $\sim$ 30% of the water discharge in the Mississippi–Atchafalaya River system (Kammerter 1990). The AR flows through the largest swamp wilderness in the United States (Atchafalaya Basin Program 2009) and carries higher concentrations of DOC than the MR (Chen and Gardner 2004). Thus, the export of DOC from the AR to the northern Gulf of Mexico is likely large and should therefore be considered.

In the present study, the concentrations and compositions of DOM from the MR and AR were determined and compared at various stages of the hydrograph during 2009–2010. DOC, chromophoric dissolved organic matter (CDOM), total dissolved lignin phenols (TDLP), amino acids (TDAA), neutral sugars (TDNS), and nitrogen (TDN) from the two rivers were characterized. In addition, long-term (1996–2010) estimates of DOC export from the MR and AR were examined.

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Methods

Study area—The MR and its distributary, the AR, are defined herein as the Mississippi–Atchafalaya River system. It is the largest river system in North America and flows 3732 km from its headwater source in Lake Itasca (Minnesota) to the northern Gulf of Mexico, draining about 41% of the conterminous United States. The Red River joins the MR and diverts ~ 30% of the combined water flow into the AR at the Old River Control Structure, and the remaining ~ 70% flows down the lower MR main channel, which is restricted by flood-control levees. Water in the lower MR travels about 520 km in 5–6 d from the control structure to the Gulf of Mexico. Water discharge from the Mississippi–Atchafalaya River system averaged 5.8×10^{11} m^3 yr^{-1} between 1951 and 1979 (Kammerter 1990), supplying about 80% of total riverine discharge to the Gulf of Mexico.

The AR, a distributary of the MR, is located in south-central Louisiana and is characterized by extensive floodplains (Lambou and Hern 1983). The AR combines water from the Red River with water diverted from the MR near Simmesport (Louisiana) and flows 275 km in a southeasterly direction to the Gulf of Mexico. The water transit time from the control structure to the Gulf of Mexico is about 7 d. In the upper 84 km of the AR, water flow is confined by guide (Hern et al. 1980). The flow subsequently enters the Atchafalaya Basin Floodway, where it enters the bayous system and floods the basin (Lambou and Hern 1983). The Atchafalaya Basin Floodway comprises 2129 km^2 and experiences extensive flooding (> 1619 km^2 during normal years; Lambou and Hern 1983). Hydrological patterns in Buffalo Cove and Fordoche (both are within the floodway) reveal prolonged overbank flooding throughout the entire year. The maximal depth of flooding in these areas varies from < 0.1 m to > 1.1 m (Lambou and Hern 1983). Most (60–70%) of the AR discharge enters Atchafalaya Bay through the main channel from Morgan City, and the rest passes through the Wax Lake Outlet (Fig. 1). The river basin is predominantly forest, cypress (*Taxodium distichum*)–tupelo (*Nyssa aquatica*) swamp, and freshwater marsh (Atchafalaya Basin Program 2009).

Sample collection—Water samples were collected during five cruises to the northern Gulf of Mexico on the R/V *Cape Hatteras* and the R/V *Hugh Sharp* between January 2009 and March 2010. Sampling sites in the two rivers were located downstream of the Head of Passes in the MR delta (29.0465°N, 89.3169°W) and in Atchafalaya Bay (29.3824°N, 91.3747°W) (Fig. 1). Average salinity of the MR and AR samples was 0.31 (0.08–0.83) and 0.55 (0.15–1.36), respectively. Water samples were collected near the surface (1–3 m) with Niskin bottles mounted on a conductivity-temperature-depth (CTD) rosette. Immediately following collection, samples were filtered through pre-combusted (450°C, 4 h) GF/F filters and stored frozen (−20°C) in high-density polyethylene screw-cap bottles until analysis of DOC, TDN, amino acids, and neutral sugars in the home laboratory. Water samples for optical characterization were passed through 0.2-μm-pore-size cartridge filters (Whatman Polycap AS) and stored in the dark at 4°C in clean glass vials. Dissolved lignin was isolated by solid-phase extraction from filtered (0.2-μm-pore-size) water samples, which were acidified to pH 2.8 with sulfuric acid (Louchouarn et al. 2000).

Chemical analyses—DOC and TDN concentrations were measured using high-temperature combustion via a Shimadzu total organic carbon–V analyzer equipped with an inline chemiluminescence nitrogen detector. TDAA were measured as *o*-phthaldialdehyde derivatives using an Agilent 1100 high-performance liquid chromatography system with a fluorescence detector (Kaiser and Benner 2005). Asparagine and glutamine were converted to aspartic acid and glutamic acid, respectively, during acid hydrolysis. Sixteen amino acids were quantified: aspartic acid + asparagine (Asx), glutamic acid + glutamine (Glx), serine (Ser), glycine (Gly), threonine (Thr), β-alanine (β-Ala), arginine (Arg), alanine (Ala), γ-aminobutyric acid (γ-Aba), tyrosine (Tyr), valine (Val), phenylalanine (Phe), isoleucine (Ile), and lysine (Lys). Hydrolyzable neutral sugars were determined as TDNS using a Dionex 500 high-performance liquid chromatography system with a pulsed amperometric detector (Kaiser and Benner 2009). Seven neutral sugars were quantified: fucose (Fuc), rhamnose (Rha), arabinose (Ara), galactose (Gal), glucose (Glc), mannose (Man), and xylose (Xyl). DOC-normalized yields of TDAA and TDNS were calculated as the percentage of DOC as amino acids and neutral sugars, respectively.

Lignin phenols were analyzed using the CuO oxidation method (Kaiser and Benner 2011). Lignin phenols were measured as trimethylsilyl derivatives using an Agilent 7890A gas chromatograph equipped with a DB-5 capillary column and an Agilent 5975 mass selective detector using selected ion monitoring. Eleven dissolved lignin phenol oxidation products ($TDLP_{11}$) were quantified: *p*-hydroxybenzaldehyde (PAL), *p*-hydroxyacetophenone (PON), *p*-hydroxybenzoic acid (PAD), vanillin (VAL), acetovanillone (VON), vanillic acid (VAD), syringaldehyde (SAL), acetosyringone (SON), syringic acid (SAD), *p*-coumaric acid (CAD), and ferulic acid (FAD). DOC-normalized yields of $TDLP_{11}$ were calculated as the percentage of DOC as lignin phenols. For comparison purposes, the traditional lignin parameters, Λ_6 and Λ_8 (mg lignin phenols × [100 mg organic carbon]$^{-1}$), are presented in the text. Λ_6 was calculated based on the sum of vanillyl (VAL, VON, VAD) and syringyl phenols (SAL, SON, SAD), whereas Λ_8 also included the cinnamyl phenols (CAD and FAD). Molar ratios of lignin phenols are presented in this article.

CDOM absorbance spectra (250–800 nm) were measured using a dual-beam Shimadzu 1601 spectrophotometer and quartz cuvettes (1- or 5-cm pathlength). Absorbances were converted to absorption coefficients, $a_{CDOM}(\lambda)$ (m^{-1}), where λ is the wavelength. $a_{CDOM}(350)$ is reported in this study. Spectral slope coefficients, $S_{275–295}$ (nm^{-1}), were calculated over the range of 275–295 nm assuming an exponential function and using a linear fit of log-linearized $a_{CDOM}(\lambda)$:

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0) \exp[-S(\lambda - \lambda_0)] \quad (1)$$

where $a_{CDOM}(\lambda)$ and $a_{CDOM}(\lambda_0)$ are absorption coefficients at wavelengths λ and λ_0 ($\lambda_0 < \lambda$). The DOC-normalized

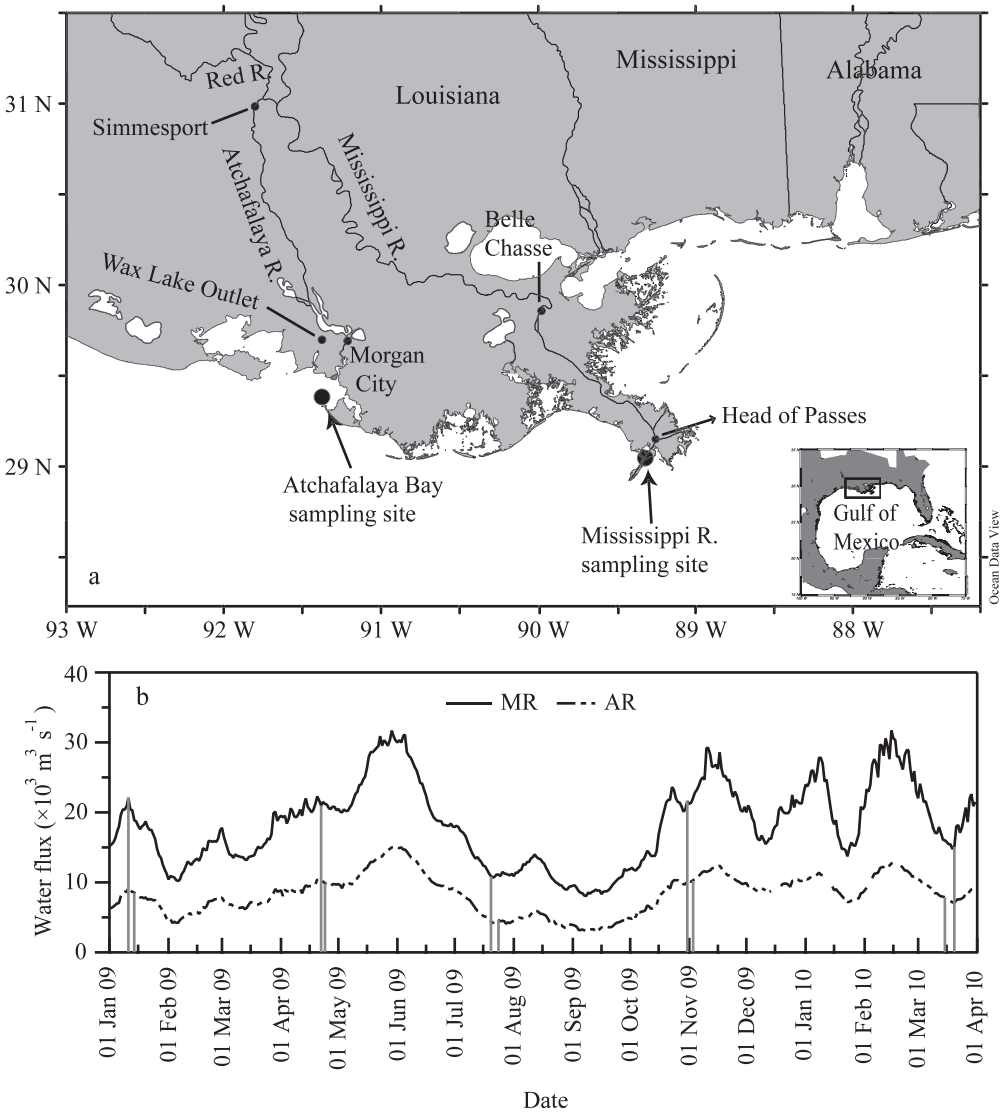

Fig. 1. (a) Map of sampling sites and (b) water fluxes in the Mississippi (MR) and Atchafalaya Rivers (AR). Water samples were collected during five cruises (highlighted by gray bars in (b)) between January 2009 and March 2010 from the Mississippi delta near the Head of Passes (29.0465°N, 89.3169°W) and in Atchafalaya Bay (29.3824°N, 91.3747°W). Five cruises were conducted at various stages of the hydrograph. Daily water discharge at Belle Chasse (MR) and the combined discharges at Morgan City and Wax Lake Outlet (AR) were obtained from the United States Geological Survey (USGS). The map was generated with Ocean Data View.

$a_{CDOM}(350)$ absorption coefficients ($a_{CDOM}(350)$ DOC^{-1}, L mol^{-1} cm^{-1}) were calculated as ratios of $a_{CDOM}(350)$ to DOC concentrations.

Calculations of riverine DOM export—Daily water discharge at Belle Chasse and combined discharge at Morgan City and Wax Lake Outlet from January 2009 to March 2010 were obtained from the United States Geological Survey (USGS) and used as river discharge for the MR and the AR, respectively. Concentrations of DOC, $TDLP_{11}$, TDAA, TDNS, and TDN from the five sampling dates were averaged to calculate their mean concentrations. For each parameter, a prediction interval for the concentration was calculated using the Student's *t*-distribution (80% confidence level). Normality of distribution was assumed. Daily fluxes of each parameter were calculated as a range by multiplying their concentration intervals by daily water discharge. Ranges of the annual export of DOC, $TDLP_{11}$, TDAA, TDNS, and TDN from the two rivers were calculated as the sum of daily flux ranges of individual parameters in 2009.

Historic (1996–2010) water discharge and DOC concentrations from U.S. Army Corps of Engineers (USACE) and USGS National Stream Quality Accounting Network (NASQAN), respectively, were used to provide more accurate estimates of DOC export from the MR and the AR. Daily discharge data for the MR (at Tarbert Landing, Mississippi) and the AR (at Simmesport, Louisiana) are

Table 1. Summary of physical and chemical characteristics of water samples collected from the Mississippi (MR) and Atchafalaya River (AR). Avg = average; SD = standard deviation; nd = not determined.

	Water discharge (m^3 s^{-1})*		DOC (μmol L^{-1})		TDN (μmol L^{-1})		$TDLP_{11}$ (nmol L^{-1})		$a_{CDOM}(350)$ (m^{-1})		$S_{275–295}$ ($\times 10^{-3}$ nm^{-1})		TDAA (μmol L^{-1})		TDNS (μmol L^{-1})	
Sampling date	MR	AR	MR	AR	MR	AR	MR	AR	MR	AR	MR	AR	MR	AR	MR	AR
Jan 2009	21,143	8665	346	486	109	83	166.7	301.8	5.29	10.20	15.2	14.5	1.01	3.98	1.67	3.24
Apr 2009	21,662	10,071	278	402	98	76	142.9	191.6	5.19	9.00	15.9	15.5	1.14	1.78	nd	nd
Jul 2009	11,299	4619	268	343	98	65	76.1	106.5	4.95	6.45	16.6	16.9	0.78	1.02	1.38	1.34
Oct–Nov 2009	20,709	10,156	357	599	55	39	227.2	523.2	8.29	17.52	14.5	13.5	1.23	2.38	1.35	2.07
Mar 2010	15,102	7948	232	359	69	37	118.3	293.4	3.96	8.95	15.9	14.6	0.81	1.61	1.09	2.62
Avg	17,524	8004	296	438	86	60	146.2	283.3	5.54	10.43	15.6	15.0	0.99	2.15	1.37	2.32
SD	5757	2945	54	106	23	21	56.3	156.3	1.63	4.19	0.8	1.3	0.20	1.13	0.24	0.81

* Both the average and standard deviation of discharge were calculated using 365 daily discharge values provided by United States Geological Survey in 2009. The calculations of the average and standard deviation for other parameters (i.e., DOC, TDN, $TDLP_{11}$, etc.) were based on five measurements (four for TDNS).

available from http://www.mvn.usace.army.mil/eng/edhd/wcontrol/discharge.asp. DOC concentrations in the MR (near St. Francisville, Louisiana) and the AR (at Melville, Louisiana) are available from http://water.usgs.gov/nasqan/, with 209 measurements in each river. Linear interpolations were performed between successive measurements to estimate the concentrations of DOC during ungauged periods. The daily DOC fluxes in the two rivers were determined by multiplying their daily DOC concentrations by daily water discharge. Daily DOC fluxes within a year were summed up to calculate the annual DOC export.

Statistical analyses—Statistically significant differences between the two rivers were tested using the paired-samples *t*-test (two-tailed, $\alpha = 0.1$). A least-squares-fit linear regression was used to examine the relationship between variables. Statistical analyses were performed in IBM Statistical Package for the Social Sciences (SPSS) version 19.

Results

Summary of river discharge during sampling seasons—In 2009, water discharge in the MR (at Belle Chasse) and the AR (at Morgan City and Wax Lake Outlet) averaged 17,524 and 8004 m^3 s^{-1} and ranged from 8042–31,715 m^3 s^{-1} and from 2866–15,093 m^3 s^{-1}, respectively (Table 1; Fig. 1). The MR and the AR exhibited similar discharge patterns (Fig. 1), with a nearly constant water discharge ratio of 7:3 as regulated by the Old River Control Structure. In 2009, high discharge occurred between late spring and early summer, followed by low discharge from midsummer to early fall. Discharge in spring 2010 was more variable and generally higher than in spring 2009 (Fig. 1). The five sampling dates occurred during representative stages of the hydrograph (Fig. 1).

Concentrations of DOM in the Mississippi and Atchafalaya Rivers—Significantly higher concentrations of DOC (*t*-test, $t = -5.2$, df = 4, $p < 0.01$), $TDLP_{11}$ (*t*-test, $t = -2.9$, df = 4, $p < 0.05$), TDAA (*t*-test, $t = -2.4$, df = 4, $p < 0.1$), TDNS (*t*-test, $t = -2.5$, df = 3, $p < 0.1$), and $a_{CDOM}(350)$ absorption coefficients (*t*-test, $t = -3.9$, df = 4, $p < 0.02$) were observed in the AR compared to those in the MR (Fig. 2a–e). Concentrations of DOC in the AR ranged from 343–599 μmol L^{-1} and were significantly higher than those (232–357 μmol L^{-1}) in the MR (Table 1). Average concentrations of $TDLP_{11}$, TDAA, TDNS, and $a_{CDOM}(350)$ absorption coefficients in the AR were almost 2-fold higher than those in the MR (Table 1). In contrast, TDN concentrations (37–83 μmol L^{-1}) in the AR were significantly lower than those (55–109 μmol L^{-1}) in the MR (*t*-test, $t = 8.2$, df = 4, $p < 0.002$; Fig. 2f; Table 1). There was greater temporal variability in concentrations of DOC, $TDLP_{11}$, TDAA, TDNS, and $a_{CDOM}(350)$ in the AR than in the MR (Fig. 2a–e). In both the MR and the AR, the highest concentrations of DOC, $TDLP_{11}$, and $a_{CDOM}(350)$ were observed in October–November 2009. The long-term (1996–2010) data set revealed that the concentrations of DOC were weakly correlated with water discharge in the two rivers (data not shown; MR: linear

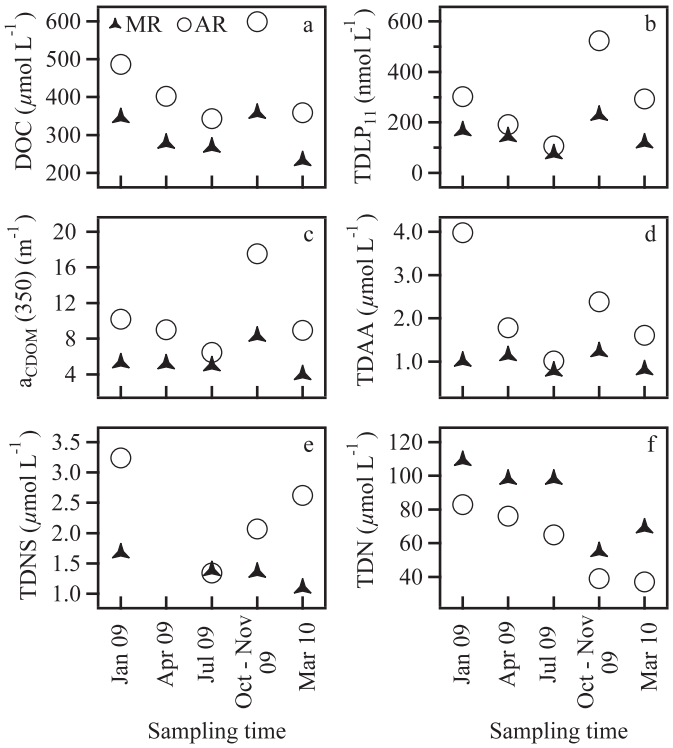

Fig. 2. Seasonal trends in concentrations of (a) dissolved organic carbon (DOC), (b) total dissolved lignin phenols ($TDLP_{11}$), (c) absorption coefficients at 350 nm ($a_{CDOM}(350)$), (d) total dissolved amino acids (TDAA), (e) total dissolved neutral sugars (TDNS), and (f) total dissolved nitrogen (TDN) in the Mississippi and Atchafalaya Rivers.

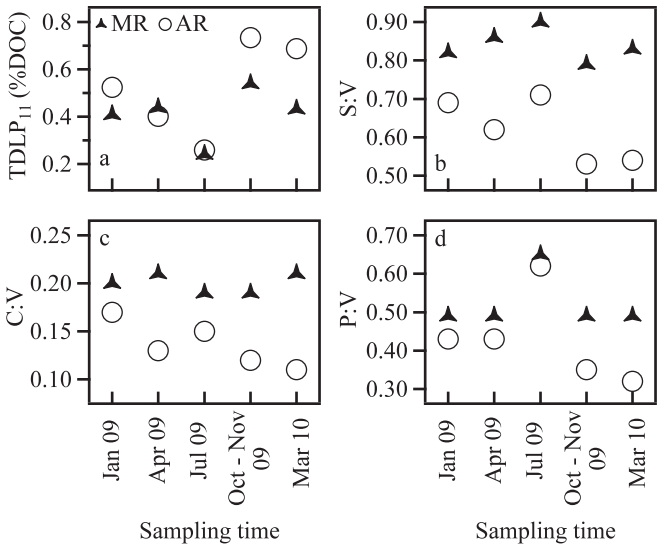

Fig. 3. Seasonal variations in (a) DOC-normalized yields of $TDLP_{11}$ and (b, c, d) compositions of lignin phenols in the Mississippi and Atchafalaya Rivers. S : V = molar ratio of syringyl to vanillyl phenols; C : V = molar ratio of cinnamyl to vanillyl phenols; P : V = molar ratio of *p*-hydroxy to vanillyl phenols.

regression, $R^2 = 0.0218$, $p < 0.05$, $n = 209$; AR: linear regression, $R^2 = 0.0356$, $p < 0.01$, $n = 209$).

DOM compositional differences between the Mississippi and Atchafalaya Rivers—The lignin fraction of DOM in the AR was generally higher than that in the MR. DOC-normalized yields of $TDLP_{11}$ (%DOC) varied from 0.26–0.73 (0.52 ± 0.20) in the AR and 0.24–0.54 (0.41 ± 0.11) in the MR (Fig. 3a; Table 2). The traditional units for lignin phenol yields, Λ_6 and Λ_8 (mg [100 mg organic carbon]$^{-1}$), ranged from 0.31–0.96 (0.67 ± 0.27) and 0.34–1.04 (0.73 ± 0.29) in the AR and from 0.29–0.67 (0.51 ± 0.14) and 0.32–0.74 (0.57 ± 0.15) in the MR, respectively. Yields of $TDLP_{11}$ (%DOC) in the AR were more variable than those in the MR (Fig. 3a). The S : V (0.53–0.71) and C : V values (0.11–0.17) in the AR were significantly lower than those (S : V: 0.79–0.90; C : V: 0.19–0.21) in the MR (S : V: *t*-test, $t = 7.9$, df = 4, $p < 0.002$; C : V: *t*-test, $t = 5.0$, df = 4, $p < 0.01$; Fig. 3b,c). Significantly lower P : V values were also found in the AR (*t*-test, $t = 3.4$, df = 4, $p < 0.05$; Fig. 3d). In both rivers, highest yields of $TDLP_{11}$ (%DOC) and lowest S : V were observed in October–November 2009 (Fig. 3a,b).

The CDOM in the AR had significantly higher DOC-normalized absorption coefficients ($a_{CDOM}(350)$ DOC^{-1}: *t*-test, $t = -3.7$, df = 4, $p < 0.05$) and lower spectral slopes ($S_{275–295}$: *t*-test, $t = 2.3$, df = 4, $p < 0.1$) than CDOM in the MR (Fig. 4). The $a_{CDOM}(350)$ DOC^{-1} values ranged from 152–232 L mol^{-1} cm^{-1} in the MR and from 188–292 L mol^{-1} cm^{-1} in the AR. $S_{275–295}$ ranged from 0.0145–0.0166 nm^{-1} in the MR and from 0.0135–0.0169 nm^{-1} in the AR, respectively (Table 1). Seasonally, lower $S_{275–295}$ values and higher $a_{CDOM}(350)$ DOC^{-1} values were observed in October–November 2009, whereas higher $S_{275–295}$ values and lower $a_{CDOM}(350)$ DOC^{-1} values were observed in July 2009 (Fig. 4).

DOC-normalized yields of TDAA (%DOC) and TDNS (%DOC) were not statistically different (*t*-test, $t = -1.7$, df = 4, $p > 0.1$ and *t*-test, $t = -0.8$, df = 3, $p > 0.1$, respectively) between the two rivers, but on average they were higher in the AR than in the MR (Table 2). The yields of TDAA (%DOC) ranged from 0.85–1.40 in the MR and from 0.94–2.95 in the AR (Fig. 5a), and the yields of TDNS (%DOC) ranged from 2.16–2.99 in the MR and from 1.99–4.21 in the AR (Fig. 5b). Variability in TDAA and TDNS yields was greater in the AR than in the MR (Fig. 5). The composition of dissolved amino acids was similar in the two rivers, with Gly, Ala, Asx, and Glx as the dominant amino acids (Table 2). However, the mole percentages of nonprotein amino acids (*β*-Ala and *γ*-Aba) and Gly were significantly lower in the AR than those in the MR (*β*-Ala + *γ*-Aba: *t*-test, $t = 5.6$, df = 4, $p < 0.01$; Gly: *t*-test, $t = 4.6$, df = 4, $p < 0.01$; Table 2). Compared to dissolved amino acids, mole percentages of dissolved neutral sugars were distributed more uniformly (Table 2). An important difference in neutral sugar compositions between the two rivers was the higher mole percentage Glc in the AR than in the MR (*t*-test, $t = -2.3$, df = 3, $p = 0.1$).

DOM export from the Mississippi and Atchafalaya Rivers—In 2009, average export values of $TDLP_{11}$, TDAA, and TDNS in the AR were comparable to those in the MR even though water discharge in the AR was less than half of

Table 2. Mole percentages (mol%) and DOC-normalized yields (%DOC) of amino acids, lignin phenols, and neutral sugars in the Mississippi (MR) and Atchafalaya River (AR). Data are presented as average ± standard deviation. DAA = dissolved amino acids; DLP = dissolved lignin phenols; DNS = dissolved neutral sugars. n = the number of measurements.

	n	MR	AR
Compound*			
Amino acids (DAA, mol%)	5		
Asx		12.7±0.7	13.1±2.0
Glx		8.0±0.8	10.5±3.2
Ser		7.7±1.1	9.9±4.1
Gly		29.3±6.0	24.3±4.0
Thr		7.8±1.7	8.1±1.1
β-Ala		5.3±1.4	4.2±1.6
Arg		2.0±0.5	2.2±0.4
Ala		14.1±1.0	13.0±1.0
γ-Aba		1.4±0.3	1.0±0.3
Tyr		0.8±0.5	1.1±0.2
Val		4.0±1.7	4.9±1.4
Phe		2.4±0.6	2.4±0.4
Ile		2.2±0.6	2.4±0.9
Lys		2.2±0.5	2.9±0.4
Lignin phenols (DLP, mol%)	5		
PAL		5.6±0.1	5.8±0.9
PON		4.5±0.4	4.2±0.7
PAD		10.2±1.7	9.5±1.8
VAL		16.1±1.2	18.4±1.4
VON		8.8±0.3	10.1±0.8
VAD		14.2±0.5	17.5±2.2
SAL		13.4±0.6	12.0±0.7
SON		8.7±0.6	7.1±0.7
SAD		10.7±0.2	9.1±0.2
CAD		3.1±0.2	2.6±0.4
FAD		4.7±0.4	3.7±0.3
Neutral sugars (DNS, mol%)	4		
Fuc		14.5±0.8	11.4±2.1
Rha		14.0±3.5	12.6±1.5
Ara		11.3±1.6	10.6±2.0
Gal		18.9±6.3	14.7±2.4
Glc		17.5±1.6	30.0±10.6
Man		10.9±0.8	8.6±2.9
Xyl		12.8±2.0	12.0±2.2
Yield (%DOC)			
TDAA		1.12±0.20	1.70±0.75
$TDLP_{11}$		0.41±0.11	0.52±0.20
TDNS		2.64±0.35	3.06±1.10

* Abbreviations were provided in the Methods.

that in the MR (Table 3). More than 44% of the total average export of $TDLP_{11}$, TDAA, and TDNS were derived from the AR, whereas only 24% of the total TDN export was derived from the AR (Table 3).

During 1996–2010, the daily export of DOC from the Mississippi–Atchafalaya River system exhibited large annual and interannual variations (Fig. 6a). The daily export of DOC from the river system varied 3–10-fold within a year and 2–4-fold within a month (Fig. 6a). Typically, lower DOC export occurred between late summer and fall (e.g., August–October), and higher export occurred between early spring and midsummer (e.g., February–June), with peak

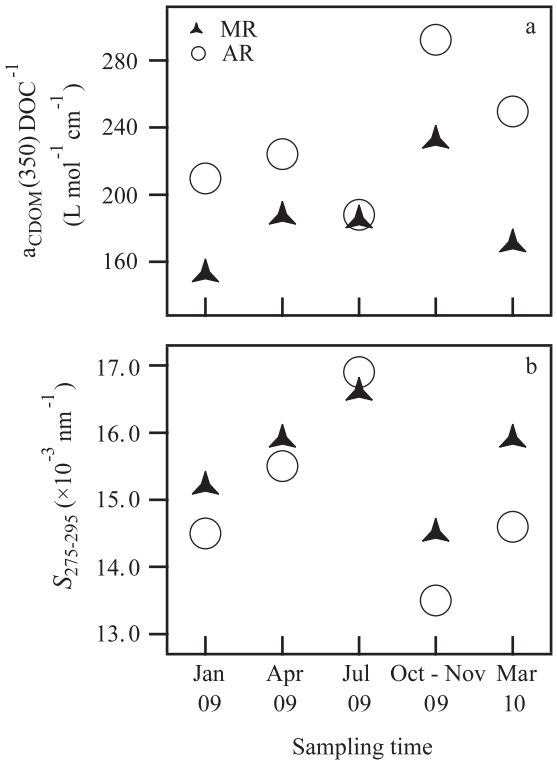

Fig. 4. Seasonal variations in (a) DOC-normalized CDOM absorption coefficients ($a_{CDOM}(350)$ DOC^{-1}) and (b) spectral slopes ($S_{275–295}$) in the Mississippi and Atchafalaya Rivers.

export occurring between April and early June (Fig. 6b). Annual variations appeared to be more pronounced in periods of higher DOC export and less marked during low export periods (Fig. 6b). The pattern of the 15-yr average daily DOC flux generally followed the hydrograph (Fig. 6b). DOC fluxes were strongly correlated with water discharge in both the MR and the AR (data not shown; MR: linear regression, $R^2 = 0.8650$, $p < 0.0001$, $n = 209$; AR: linear regression, $R^2 = 0.8640$, $p < 0.0001$, $n = 209$). A much weaker relationship was found between DOC fluxes and DOC concentrations in the two rivers (data not shown; MR: linear regression, $R^2 = 0.2246$, $p < 0.0001$, $n = 209$; AR: linear regression, $R^2 = 0.2556$, $p < 0.0001$, $n = 209$).

Annual DOC export during 1996–2010 in the MR and AR varied widely year by year (Table 4). The high DOC export in 1996, 2008, and 2009 was nearly double the low values in 2000 and 2006. Interestingly, the percentage contribution of the AR to the total DOC export from the river system varied within a narrow range (32–38%; Table 4). Over the 15-yr period, the average annual export of DOC from the Mississippi–Atchafalaya River system was 2.70 ± 0.61 Tg yr^{-1} (MR: 1.75 ± 0.40 Tg yr^{-1}; AR: 0.95 ± 0.21 Tg yr^{-1}), with about 35% of the contribution coming from the AR (Table 4).

Discussion

Floodplain contributions to DOM in the Atchafalaya River—The water diverted from the MR at the Old River Control Structure accounts for ~ 75% of the water in the

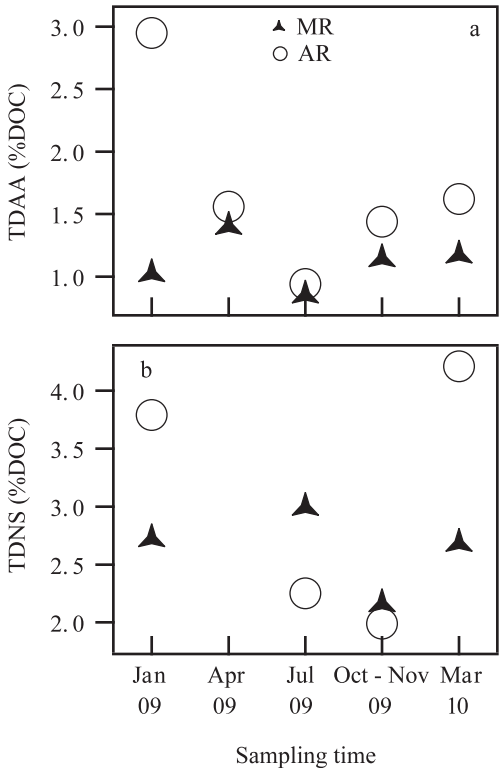

Fig. 5. Seasonal variations in DOC-normalized yields of (a) TDAA and (b) TDNS in the Mississippi and Atchafalaya Rivers.

AR. The Red River joins the Atchafalaya just below the Old River Control Structure and contributes the remaining water forming the AR. Substantially higher concentrations of DOC, dissolved lignin, amino acids, neutral sugars, and CDOM absorption coefficients were measured in the AR compared to the MR in this study, and the long-term (1996–2010) average DOC concentration in the AR is significantly higher than in the MR (*t*-test, $t = -11.2$, df = 207, $p < 0.0001$). The higher DOC concentrations in the AR could be due to the input of high concentrations from the Red River, input from the extensive floodplains and swamp–bayou systems in the Atchafalaya basin, or both. Total organic carbon in the Red River (at Alexandria, Louisiana) during this study averaged 754 μmol L^{-1} (USGS 2009, 2010), and assuming DOC is 60% of total organic carbon (Meybeck 1982), the average DOC concentration in the Red River was $\sim$ 452 μmol L^{-1}. This DOC concentration is higher than the average concentration (296 μmol L^{-1}) in the MR and could account for $\sim$ 13% of the elevated DOC concentrations observed in the AR. This indicates another source of DOM besides the Red River is primarily responsible for elevated DOC concentrations in the AR.

The drainage basins of the MR and the AR have similar climatic conditions but different vegetation, land use, and geomorphological features. About 57% of the Mississippi basin is used for row-crop agriculture (Brown et al. 2005), whereas the Atchafalaya basin is predominantly bottomland hardwood forest, cypress–tupelo swamp, and freshwater marsh (Atchafalaya Basin Program 2009). The Atchafalaya basin is considered to be among the most productive swamps in the world (Atchafalaya Basin Program 2009). The MR is constrained by levees and has limited interaction with floodplain vegetation and soils, whereas the AR flows through vast bayous, swamps, and backwater lakes that flood annually for extended periods (Lambou and Hern 1983). During wet seasons, higher water levels in the AR cause inundation of the surrounding cypress–tupelo swamps, bayous, and organic-rich soils. Watershed vegetation, hydrology, floodplain interactions, and land use have major influences on dissolved constituents in rivers (Hern et al. 1980; Lambou and Hern 1983; Peduzzi et al. 2008), and their influences on the concentration and composition of DOM in the MR and the AR are apparent.

The composition of lignin phenols is particularly useful for distinguishing between angiosperm and gymnosperm vegetation based on the relative abundances of syringyl (S) and vanillyl (V) phenols (Hedges and Mann 1979; Hedges et al. 2000). The relatively high S : V ratios in MR DOM are indicative of a dominant angiosperm source. The S : V values in the AR were significantly lower, indicating important contributions from gymnosperms within the basin or the Red River. Grasses account for nearly half of the vegetation in the Red River watershed, and cottonwood (e.g., *Populus deltoides*), willow (e.g., *Salix nigra*), and oak (e.g., *Quercus alba*) are also common (Matthews et al. 2005). Because these plants are angiosperms, the Red River is an unlikely source of the low S : V values in AR DOM. In contrast, the AR basin encompasses large cypress–tupelo swamps, and cypresses are deciduous gymnosperms that have no syringyl phenols (Opsahl and Benner 1995). The low S : V values in AR DOM are consistent with the input of lignin phenols derived from cypress needles and wood within the numerous swamps and bayous in the floodplains. It is also possible that sorption (Hernes et al. 2007)

Table 3. Annual export of freshwater, DOC, $TDLP_{11}$, TDAA, TDNS, and TDN from the Mississippi (MR) and Atchafalaya River (AR) in 2009.

	Water ($\times 10^{11}$ m^3 yr^{-1})	DOC ($\times 10^{11}$ mol yr^{-1})	$TDLP_{11}$ ($\times 10^{7}$ mol yr^{-1})	TDAA ($\times 10^{8}$ mol yr^{-1})	TDNS ($\times 10^{8}$ mol yr^{-1})	TDN ($\times 10^{10}$ mol yr^{-1})
MR	5.5	1.6($\pm$0.5)	8.1($\pm$5.2)	5.5($\pm$1.8)	7.6($\pm$2.4)	4.7($\pm$2.1)
AR	2.5	1.1($\pm$0.4)	7.2($\pm$6.6)	5.4($\pm$4.8)	5.9($\pm$3.7)	1.5($\pm$0.9)
River system	8.1	2.7($\pm$0.9)	15($\pm$12)	11($\pm$6.6)	13($\pm$6.2)	6.3($\pm$3.0)
AR contribution (%)*	31	40	47	50	44	24

Export is reported as average values with prediction intervals in the parentheses (80% confidence level).
* The relative contribution (%) of the Atchafalaya River to the total DOC export from the river system.

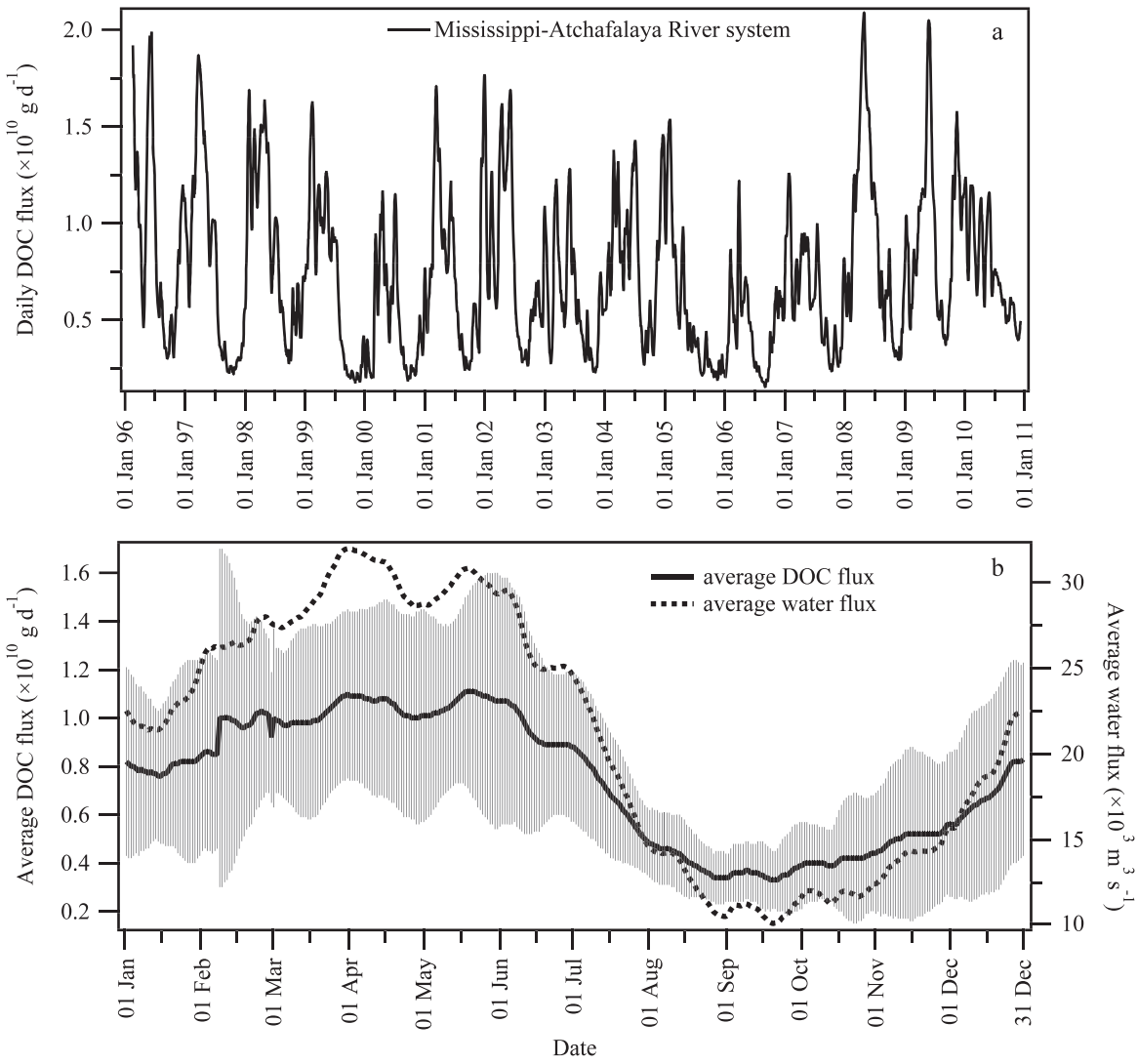

Fig. 6. (a) Long-term (1996–2010) daily DOC fluxes in the Mississippi–Atchafalaya River system, and (b) daily average DOC fluxes (solid line) and water fluxes (dashed line) during the 15-yr period from 1996 to 2010. The gray lines represent the standard deviations of daily average DOC fluxes.

as well as biological and photochemical processes (Benner and Kaiser 2011) play a role in shaping the composition of lignin phenols in the two rivers.

Lignin phenols and CDOM are readily leached from plant litter and surface soils (Benner et al. 1990; Hernes et al. 2007). The elevated DOC-normalized yields of lignin phenols (%DOC) and CDOM ($a_{CDOM}(350)$ DOC^{-1}) in the AR compared to the MR are indicative of floodplain contributions to AR DOM. The lower $S_{275–295}$ values in the AR are indicative of high-molecular-weight CDOM that has experienced minimal photochemical degradation (Helms et al. 2008; Fichot and Benner in press). The average yields (%DOC) of neutral sugars and amino acids are both higher in the AR than in the MR, indicating the occurrence of fresh and bioavailable DOM in the AR (Benner 2003). The relative enrichment of glycine in dissolved amino acids is indicative of an increasing extent of biodegradation (Hedges et al. 1994), and the significantly higher glycine content in MR DOM indicates more extensive biodegradation than was observed in AR DOM. Nonprotein amino acids (β-Ala and γ-Aba) are also indicative of more highly altered DOM (Hedges et al. 2000), and they comprised a significantly larger percentage of the amino acids in MR than AR DOM. Neutral sugar compositions in MR DOM are relatively enriched in deoxy sugars (Rha and Fuc) and depleted in Glc compared with the AR DOM, further indicating the input of fresher DOM in the AR and more altered DOM in the MR (Hedges et al. 2000). These comparisons of DOM composition in the two rivers consistently indicate a strong floodplain source of relatively fresh, less altered, and more bioavailable DOM in the AR.

Significantly lower concentrations of TDN were observed in the AR. This could be due to dilution by the Red River, nitrogen removal in the AR floodplain, or both. Dissolved inorganic nitrogen in the Red River (at Alexandria, Louisiana) during this study averaged 14 μmol L^{-1} (USGS 2009, 2010). This value is about 4–8 times lower than the dissolved nitrogen concentrations in

Table 4. Long-term (1996–2010) annual DOC export from the Mississippi (MR) and Atchafalaya River (AR). Avg = average; SD = standard deviation.

Year	MR (Tg yr^{-1})	AR (Tg yr^{-1})	River system (Tg yr^{-1})	AR contribution (%)*
1996	2.34	1.21	3.54	34
1997	1.83	1.02	2.85	36
1998	2.21	1.03	3.24	32
1999	1.66	0.89	2.55	35
2000	1.13	0.70	1.83	38
2001	1.77	1.04	2.81	37
2002	1.87	1.07	2.94	36
2003	1.44	0.78	2.22	35
2004	1.95	1.11	3.06	36
2005	1.26	0.64	1.90	34
2006	1.09	0.59	1.69	35
2007	1.48	0.82	2.31	36
2008	2.21	1.14	3.35	34
2009	2.22	1.31	3.53	37
2010	1.87	0.90	2.77	32
Avg	1.75	0.95	2.70	35
SD	0.40	0.21	0.61	2

Both the average and standard deviation were calculated using data collected over 15 yr from 1996–2010.

* The relative contribution (%) of the Atchafalaya River to the total DOC export from the river system.

the MR and is largely responsible for the lower TDN concentrations in the AR. A variety of processes, such as biological assimilation, denitrification, and sedimentation in the AR floodplain can also remove dissolved nitrogen from river water. Nitrogen assimilation by floodplain vegetation in the AR is likely to be substantial given its high productivity (Atchafalaya Basin Program 2009). Denitrification has been observed in a variety of habitats in the Atchafalaya floodplain (Lindau et al. 2008). The deposition and resuspension of sediments in Atchafalaya floodplain soils enhances the biogeochemical processing of nitrogen, and high sedimentation rates lead to storage of nitrogen in floodplain sediments (Xu 2006). The Atchafalaya floodplain has been reported to be a sink for total nitrogen (Xu 2006). It appears nitrogen removal processes in the lower MR are less efficient because flood-control levees limit interactions with floodplains.

Concentrations of DOC, lignin phenols, amino acids, neutral sugars, and CDOM varied seasonally. Temporal variability in the concentrations and compositions of DOM was more pronounced in the AR than in the MR. Differences in DOM concentrations and compositions between the two rivers were enhanced during higher water discharge. Particularly high concentrations of DOC, $TDLP_{11}$, and CDOM absorption coefficients and their DOC-normalized yields were observed in the AR during October–November 2009. Litterfall in bottomland hardwood and cypress–tupelo swamps is maximal during September through November in southern Louisiana (Conner and Day 1976), and the observed increases in DOC, $TDLP_{11}$, and CDOM during October–November 2009 coincided with peak litterfall in the Atchafalaya floodplain. The highest yields of $TDLP_{11}$ and the lowest S : V values in the AR were observed at this time and are consistent with greater input from cypress. These observations taken together suggest that the coupling between the floodplain and hydrology greatly regulates seasonal trends in the concentrations and compositions of riverine DOM (Peduzzi et al. 2008).

Export of DOC from the Mississippi–Atchafalaya River system—The 15-yr (1996–2010) average DOC export from the MR was estimated to be 1.75 Tg yr^{-1}. Previous estimates of DOC export from the MR are quite variable,

Table 5. Comparison of DOC export estimates in the Mississippi and Atchafalaya Rivers. n = the number of DOC measurements; nd = not determined.

Year	Discharge ($\times 10^{11}$ m^3 yr^{-1})	DOC* (μmol L^{-1})	n	DOC export (Tg yr^{-1})†		Reference
				Calculated	Reported	
MR						
1969	4.5	293±62	6	1.59	1.72	Malcolm and Durum 1976
nd	4.4	500	nd	2.63	3.48	Leenheer 1982
1998–1999	4.9	489±163	6	2.88	3.11	Bianchi et al. 2004
May 2000–May 2001	3.8	375±42	13	1.72	1.51	Dubois et al. 2010
2009	5.5	312±46	4	2.07	1.96	This study
2009	5.8	321±27	12	2.22	nd	USACE and NASQAN
1996–2010	4.6	309±63	209	1.75	nd	USACE and NASQAN
AR						
1974–1977	2.1	517±167	770	1.30	nd	Hern et al. 1980
nd	1.2	533	nd	0.74	0.76	Leenheer 1982
1976–1977	1.2	333	36	0.46	0.46	Lambou and Hern 1983
2009	2.5	458±111	4	1.39	1.33	This study
2009	2.5	431±64	12	1.31	nd	USACE and NASQAN
1996–2010	2.0	386±111	209	0.95	nd	USACE and NASQAN

* DOC concentrations are reported as average values ± standard deviations.

† Except for USACE and NASQAN, calculated DOC export for other studies was determined by multiplying the average DOC concentrations by water discharge.

ranging from 1.51–3.48 Tg yr^{-1} (Table 5). Differences among export estimates could be due to the use of different calculation methods, variability in DOC concentrations, and the interannual variability in water discharge. Leenheer (1982) reported the highest DOC export from the MR, and based on our simple calculation it appears that the methods used by Leenheer (1982) to calculate DOC export were, in part, responsible for the high export estimate (Table 5). Bianchi et al. (2004) reported a relatively high DOC export (3.11 Tg yr^{-1}) for 1998–1999, but their water discharge (5.3×10^{11} m^3 yr^{-1}) value obtained from Meade (1996) included discharge from both the MR and the AR. In the calculated DOC export presented in Table 5 (2.88 Tg yr^{-1}), discharge (4.9×10^{11} m^3 yr^{-1}) from the MR during sampling years (1998–1999) was used. The similarity between reported DOC export and calculated values for other studies suggests relatively little effect of calculation approaches on reported export from the MR and AR (Table 5). Estimates of the MR DOC export in 2009 using data from this study and data from USACE and NASQAN were similar, but they were relatively high compared with the 15-yr average value (Table 5). The relatively high DOC export in 2009 was associated with El Niño and hurricane events that caused higher than normal precipitation and water discharge.

The 15-yr (1996–2010) average DOC export from the AR was estimated to be 0.95 Tg yr^{-1}. As observed in the MR, differences among previous DOC export estimates (0.46–1.40 Tg yr^{-1}) from the AR were largely due to varying discharge and DOC concentrations (Table 5). Low DOC export estimates (0.46 and 0.74 Tg yr^{-1}) were associated with low water discharge (Leenheer 1982; Lambou and Hern 1983). The AR discharge reported by Leenheer (1982) was recorded at Morgan City, which did not include discharge through the Wax Lake Outlet (30–40% of total AR discharge). Comparable DOC export estimates (1.06–1.23 Tg yr^{-1}) were obtained by including the discharge through the Wax Lake Outlet. Discharge values reported by Lambou and Hern (1983) were measured in the AR floodway during 1976–1977 when the discharge was much lower than historic values and therefore the DOC export estimate was relatively low. The low DOC concentration reported by Lambou and Hern (1983) also contributed to the low DOC export estimate for 1976–1977 (Table 5). Estimates of the AR DOC export in 2009 using data from this study and data from USACE and NASQAN were similar.

The AR accounts for $\sim$ 30% of the total water discharge in the Mississippi–Atchafalaya River system. However, DOC budgets for the northern Gulf of Mexico typically do not include the AR contribution. The long-term (1996–2010) average DOC export from the AR accounted for 35% of the total export from the river system. In 2009, the export of total dissolved lignin, amino acids, and neutral sugars from the AR was comparable to those from the MR. Therefore, the export of DOM from the AR should be considered in future studies of the effects of riverine materials on coastal processes, such as coastal productivity and hypoxia in the northern Gulf of Mexico. Here, we suggest using the 15-yr average DOC export value. The average export of DOC from the Mississippi–Atchafalaya River system between 1996 and 2010 was 2.70 Tg yr^{-1}. Global riverine DOC export is estimated to be 250–360 Tg yr^{-1} (Meybeck 1982; Aitkenhead and Mcdowell 2000); thus, the Mississippi–Atchafalaya River system supplies 0.8–1.1% of riverine DOC to the global ocean.

Large temporal (annual and interannual) variations in DOC export from the river system were apparent between 1996 and 2010. Regression analyses indicated DOC export from the two rivers was influenced by DOC concentrations, but export was predominantly controlled by water discharge, which explained $>$ 86% of the variation in DOC export from both rivers. Riverine DOC export increases in December and crests between April and early June, when high discharge normally occurs. Seasonal lows in water discharge normally occur during late summer and early fall, sharply reducing the export of DOC from the rivers. High annual DOC export occurred during years (1996, 2008, and 2009) with high water discharge, whereas low DOC export occurred in years (2000 and 2006) with historically low water discharge.

Comparisons with other large river systems—The three largest river systems in terms of water discharge are the Amazon, Congo, and Orinoco Rivers (Milliman and Meade 1983). The DOC export from the Mississippi–Atchafalaya River system (2.70 Tg yr^{-1}) is much lower than that from the Amazon (22.1 Tg yr^{-1}; Richey et al. 1990), Congo (12.4 Tg yr^{-1}; Coynel et al. 2005), and Orinoco Rivers (5.0 Tg yr^{-1}; Lewis and Saunders 1989), largely due to the substantially higher water discharge from the three largest rivers and, in the case of the Congo River, due also to higher DOC concentrations. The two largest Arctic rivers, the Yenisei and Lena, have comparable water discharge to the Mississippi–Atchafalaya River system but $\sim$ 2-fold higher DOC export (4.69 and 5.83 Tg yr^{-1}, respectively) due to their higher DOC concentrations (Raymond et al. 2007). Dissolved lignin ($TDLP_{11}$) export from the Yenisei and Lena Rivers were recently estimated (75 and 122 Gg yr^{-1}, respectively; R. M. W. Amon unpubl.) and are 3–5-fold higher than that from the Mississippi–Atchafalaya River system (25 Gg yr^{-1}). The greater relative export of DOC and lignin from the Yenisei and Lena Rivers compared with the Mississippi–Atchafalaya River system could be related to floodplain interactions during peak discharge of Arctic rivers in the spring, but additional studies are needed to explore this possibility.

Floodplains are typically very productive environments with diverse metabolic and physicochemical gradients that influence the fluxes, transformations, and fates of dissolved and particulate materials in rivers. Comparisons of DOM in the Mississippi and Atchafalaya Rivers revealed that floodplain interactions increase DOC concentrations, alter DOM compositions, and reduce nitrogen loading in the Atchafalaya River. Similar observations can be gleaned from comparisons of CDOM from other free-flowing and regulated rivers. Higher CDOM absorption coefficients and DOC-normalized yields were observed in the Congo (Spencer et al. 2009), Orinoco (Battin 1998), Mackenzie (Osburn et al. 2009), Yukon (Spencer et al. 2008), and

Atchafalaya Rivers (this study), compared to regulated rivers like the Yangtze (Guo et al. 2007), Mississippi (this study), and Rhône Rivers (Para et al. 2010). Additional studies are needed to gain further insights about the roles of floodplains in shaping the concentrations and compositions of DOM in rivers. The processes occurring in river floodplains affect the photochemical and microbial reactivity of riverine DOM exported to the coastal ocean and thereby influence the metabolic balance and air–sea carbon dioxide exchange in ocean margins.

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