Journal of Hydrology X 2 (2019) 100018

Contents lists available at ScienceDirect

Journal of Hydrology X

journal homepage: www.elsevier.com/locate/hydroa

Research papers

Role of the Atchafalaya River Basin in regulating export fluxes of dissolved organic carbon, nutrients, and trace elements to the Louisiana Shelf

DongJoo Joung [a,*], Laodong Guo [a,b], Alan M. Shiller [a]

[a] Division of Marine Science, The University of Southern Mississippi, 1020 Balch Blvd, Stennis Space Center, MS 39529, USA
[b] School of Freshwater Sciences, University of Wisconsin-Milwaukee, 600 East Greenfield Avenue Milwaukee, WI 53204, USA

ARTICLE INFO

Article history:
Received 9 August 2018
Revised 29 December 2018
Accepted 3 January 2019
Available online 8 January 2019

Keywords:
Atchafalaya River Basin
Wetlands
Trace elements
Nutrients
Dissolved organic carbon

ABSTRACT

The abundance and fluxes of selected dissolved trace elements (TE), nutrients, and dissolved organic carbon (DOC) were quantified in the Atchafalaya River Basin to better understand its influence on the chemical regime of the Louisiana Shelf, a region where bottom water hypoxia occurs annually during late spring to early fall. Water samples were collected from throughout the entire Atchafalaya River Basin including from the Mississippi and Red Rivers as well as basin swamp waters during April and November 2010, and June 2011, which represent "typical" high and low, and "unusual" high river discharges, respectively. Within the total dissolved (<0.45 μm) pool, most of the TEs were mainly partitioned to the <0.02 μm dissolved phase with the exception of Cr, Cs, Fe, Pb and Zn which were dominantly in the colloidal (0.02–0.45 μm) phase. In the Atchafalaya River, seasonal concentration variations in nutrients, DOC and most TEs were similar to those in the Mississippi River, reflecting a major contribution of water from the Mississippi River. Contributions of the Red River to the Atchafalaya River's DOC and nutrients were estimated to be 1–35%, similar to previous estimates for this system. The Red River contribution to the fluxes of Co, Cr, Cs, Fe, Mn, Pb, Rb, and Zn was generally disproportionally high (>20%), exceeding its hydrological contribution (~10%) to the Atchafalaya River, due to greatly enriched concentrations of these elements in the Red River. The Atchafalaya River Basin wetland/floodplain contribution to chemical constituents was noticeable, accounting for more than a 20% decrease of some elements (Cd, Cs, Cr, Cu, Fe, Mo, P, U, and Zn). Mn was the only element with persistent addition during all sampling campaigns. However, the contributions from the Red River were greater than the wetland/floodplain contributions for DOC, nutrients and most of TEs (except Mn), suggesting that the Red River plays a disproportionate role in regulating water quality in the Atchafalaya River. Overall, the Atchafalaya River with its chemical modification of Mississippi River water via contributions from the Red River and interactions with floodplain wetlands, plays a critical role in chemical distributions on the Louisiana Shelf in the Northern Gulf of Mexico. Thus, the Atchafalaya River contribution should be adequately accounted for in biogeochemical studies and models of trace elements and nutrients on the Louisiana Shelf, particularly during periods of bottom water hypoxia.

1. Introduction

Freshwater wetlands, including marshes, floodplains, and swamps, are an interface between the land and river water, and play an important role in regulating water quality in rivers and ultimately the estuaries and coastal zones fed by those rivers (Correll et al., 1992; Cai et al., 2016). In fact, some wetlands are utilized for the treatment of waste waters polluted with nutrients, heavy metals, and organic contaminants (Verhoeven et al., 2006 and references therein; Mays and Edwards, 2001). Wetlands in lower floodplains also could play a significant role in the productivity and water quality of coastal ecosystems by regulating nutrient and organic matter transport to the coastal ocean (Verhoeven et al., 2006). Thus, biogeochemical processes in these wetland systems may additionally impact other coastal environmental processes such as bottom water hypoxia. Despite their potentially great importance, the role of floodplain wetlands in affecting the coastal ocean is not well-understood, particularly along the Louisiana coast in the northern Gulf of Mexico where bottom waters experience seasonal hypoxia (Rabalais et al., 2010).

* Corresponding author at: Earth and Environmental Sciences, University of Rochester, 227 Hutchison Hall, P.O. Box 270221, Rochester, NY 14627, USA.
E-mail addresses: dongjoo.joung@usm.edu (D. Joung), guol@uwm.edu (L. Guo), alan.shiller@usm.edu (A.M. Shiller).

https://doi.org/10.1016/j.hydroa.2019.100018
2589-9155/

Many biogeochemical processes can affect the distributions of chemical constituents from wetlands. In general, nutrients, dissolved organic matter (DOM), and major and trace element (TE) distributions within wetlands systems can be affected by biological uptake (Junk et al., 1989; Bayley, 1995; Fisher and Acreman, 2004; Weis and Weis, 2004), microbial activity (Chow et al., 2013; Mulholland, 1981; Roden and Wetzel, 1996; Hamilton et al., 1997), adsorption onto particles (Olivie-Lauquet et al. 2001), redox processes (Olivie-Lauquet et al. 2001), sedimentation (Grybos et al., 2007), and seasonal hydrological changes such as extent of flooding (Kerr et al., 2008). Thus, depending on the seasonal and temporal variations of environmental conditions, wetlands can act as either sinks (e.g., Emmett et al., 1994; Fisher and Acreman, 2004; Khan and Brush, 1994) or sources (Rücker and Schrautzer, 2010; Kerr et al., 2008; Christopher et al., 2006; Seyler and Boaventura, 2003; Dawson et al., 2008; Mulholland, 1981; Noe and Hupp, 2007; Hansson et al., 2005; Kinsman-Costello et al., 2016).

Indeed, other recent studies have also suggested that wetlands can be both material sources and sinks, depending on the seasonal changes in hydrology as well as chemical speciation of the element. For instance, Cai et al. (2016) and Shim et al. (2017) investigated floodplain wetland influence on carbon speciation and TEs in a southern Mississippi/Louisiana (East Pearl River) system having similar climate and physiographic characteristics to the study area discussed here. Based on a mass balance approach of annual C fluxes, Cai et al. (2016) revealed that the Pearl River wetlands could reduce the dissolved inorganic and particulate organic carbon export fluxes by 24% and 40%, respectively, but enhance the annual riverine DOC export by 25% at the same time. Shim et al. (2017) reported downstream variations of TEs in the East Pearl River, which were linked to river stage. Specifically, they noted a downstream increase (by 20% or more) of TEs (e.g., Fe, Mn, Zn, Cd) that was observed only during moderately high discharge, but not during the highest and low river discharges. They interpreted their observations as indicating inputs from floodplain wetlands during moderately high river discharge, rate-limiting of wetland inputs during the highest river discharges, and saltwater intrusion as well as hyporheic zone interactions during low river discharge.

The Atchafalaya River carries about 30% of the combined flow of the Mississippi and Red Rivers and the basin of the Atchafalaya contains the largest wetlands in North America (Ford and Nyman, 2011). Although the Atchafalaya River is a significant contributor of water and other fluvial materials to the Louisiana Shelf, studies of how the Atchafalaya River Basin wetlands modify the fluxes of nutrients and DOC are still limited (Scott et al., 2014; Shen et al., 2012; Turner et al., 2007; Lane et al., 2002), and the basin's effect on dissolved TE fluxes has yet to be determined. So far, studies of the Atchafalaya River Basin's role on chemical constituents have found significant DOC and nutrient alterations in the basin. Shen et al. (2012) reported that DOC was about 150% higher in the Atchafalaya River compared to the Mississippi River due to the input from wetland waters in the Atchafalaya River Basin. Lambou and Hern (1983) explained that the increased DOC in Atchafalaya River waters was due to primary production within overflow areas during high river discharge relative to low river discharge. Turner and Rabalais (1991) reported relatively lower nitrate and silicate (31% and 6%, respectively) and higher total phosphorous (30%) in the Atchafalaya River than in the Mississippi River and suggested that these differences were probably due to differences in the contribution from the Red River. However, nitrate input from the Red River was found to be negligible, accounting for <3% in comparison to total loading of nitrate from the Mississippi River (Turner et al., 2007). Xu (2006) reported about 27% removal of total Kjeldahl nitrogen by comparing composition of waters entering and exiting the Atchafalaya River Basin. The removal was closely related to the interaction of river water with the swamp, where denitrification was found to be a major process for nitrogen removal (Xu, 2006; Lindau et al., 2008; Scaroni et al., 2011). During the 2011 flooding of the Atchafalaya Basin, Scott et al. (2014) demonstrated floodplain reduction of the Atchafalaya River's nitrate load and a small increase in phosphate and ammonium loads. Reiman et al. (2018) examined the flux of 'total recoverable' metals through the Atchafalaya Basin. However, for most elements their method determines a largely particulate metal fraction of their unfiltered samples. Thus, not surprisingly, they found that the Atchafalaya wetlands were a sink for total recoverable metals just as they are for suspended sediments. However, this provides limited insight into how the wetlands affect transport of metals in the dissolved and colloidal phases, which is likely the more important, bioactive phase for most trace elements.

Despite this prior work, no studies have yet examined the effect of the Atchafalaya River Basin on dissolved TE fluxes to the Louisiana Shelf. Clearly, though, various processes including biological uptake, microbial remineralization of organic matter, and changing redox state as well as input from the Red and Mississippi Rivers could affect trace element distributions in the basin. Therefore, we hypothesize that 1) chemical contributions from the Red River and wetland interactions can be significant, altering the chemical compositions of the Atchafalaya River, and 2) Red River and wetland contributions vary seasonally following the changes in river discharges and floodplain inundation. Herein, we report our investigations of DOC, nutrient, and dissolved trace element distributions in waters from the Atchafalaya River Basin, including the main river channels and surface waters of the surrounding swamps. The objective of this study was to quantify the contributions from the Red River and wetlands within the basin to chemical fluxes through the Atchafalaya River to the Louisiana Shelf during different flow stages.

2. Methods and materials

2.1. Site description

Ford and Nyman (2011) characterize the Atchafalaya River Basin as having one of the largest and most undeveloped floodplains in North America (Fig. 1). Agriculture is common upstream in the Atchafalaya River Basin, while downstream it retains "pristine" river floodplain forest including bayous, lakes, and swamps, which extend about 120 km in length (north to south) and 25–35 km in width (Ford and Nyman, 2011). The eastern and western boundaries are constrained by artificial levees to prevent flooding, and levees on river itself have isolated large portions of the floodplain from the Atchafalaya River at all but the highest river stages during the spring flood pulse (Fontenot et al., 2001). Construction activities related to navigation, flood control, and oil and gas canals have altered the historic water flow patterns, reduced water circulation, and a large portion of wetland areas in Atchafalaya River Basin are experiencing low dissolved oxygen concentrations (Fontenot et al., 2001; Sabo et al., 1999).

Sampling locations (Fig. 1) were chosen to include the major water sources to the Atchafalaya River Basin (Mississippi and Red Rivers), the main exits for water into Atchafalaya Bay (including the mouth of the Atchafalaya River and the Wax Lake outlet), plus other sites in the main channels and swamps throughout the basin. Swamp sampling sites (ARS1-3) were located in the upper part of the Atchafalaya swamp, and include the swamp inner-channel (ARS3), which frequently connects to the main river channel. However, during June 2011, when parts of the Atchafalaya River Basin were flooded due to the opening of the Morganza Spillway, some

Fig. 1. Sampling locations in the Atchafalaya River basin. The white rectangle in the US map shows the location of the study area. White circles represent sampling locations, and red circles are towns/cities. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adjustment of the sampling locations was necessary. That is, the AR 4–5, and 7–10, ARWL, and ARS3 sites were not accessible due to flooding. Also, at that time, we were not able to access the exact same swamp sites as in the previous sampling campaigns, and so, water samples were collected near the previous sites (Supplementary Table 4).

2.2. Sample collection

Sampling campaigns were conducted during April and November 2010, and June 2011 with different river stages. River discharges in April and November 2010 were at high and low stages that are typical of the annual river flow cycle (Fig. 2 and supple-

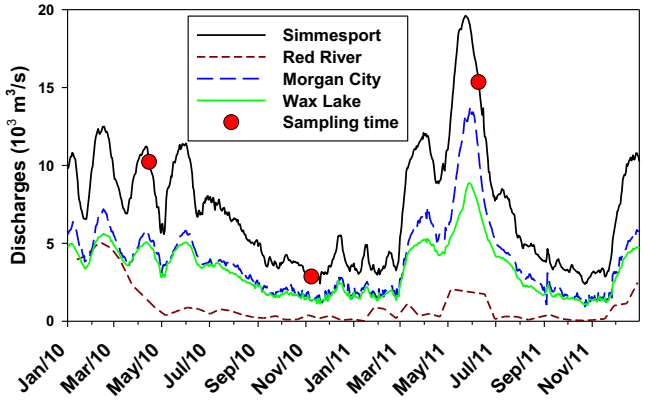

Fig. 2. River discharges (10^3 m^3/s) in the Atchafalaya River Basin and sampling times.

mentary Fig. 1). During June 2011, unusually high Mississippi River discharge resulted in the opening of the Morganza Spillway, inundating large areas of swamp and floodplains in the Atchafalaya River Basin. The spillway is designed to reduce downstream flood pressure in the lowermost Mississippi River basin during major flood events. This was only the second time the spillway was opened since its completion in 1954.

Surface waters were collected for nutrient, dissolved organic carbon (DOC), and trace element analysis. Immediately after collection, nutrient and DOC samples were filtered in the field using 0.45 μm pore size filters (Whatman Puradisc) and kept in an iced cooler for transport back to the lab where they were frozen until analysis. Trace element samples were collected at the same time as nutrients and DOC, using clean sampling techniques (Shiller, 2003). Specifically, an acid-cleaned polyethylene bottle was attached to a non-metallic pole (approximately 5 m length), and the bottle was rinsed 3 times with ambient water. After sample collection, the sample bottle was tightly capped and doubly bagged in new plastic zipper bags and stored in an iced cooler. These samples were then filtered using 0.45 μm (Whatman Puradisc) and 0.02 μm (Whatman Anotop) pore size filters, using acid-cleaned syringes for "total dissolved" (<0.45 μm) and the <0.02 μm dissolved fractions, respectively (Shiller, 2003). The colloidal (0.02–0.45 μm) phase was determined by the difference between the <0.45 μm and <0.02 μm dissolved fractions. This filtration was conducted in a small plastic tent within 2–8 h of sample collection. The trace element samples were subsequently acidified in our clean lab to pH < 2 by addition of ultra-clean 6 M HCl (Seastar Baseline). A small boat was used for the stations that were not accessible by foot. For ancillary data, portable sensors were used for the determination of conductivity, salinity, and temperature (Model 30, YSI Inc.) and pH (Oakton pH 110 series, USA).

2.3. Measurements of nutrients, DOC, and trace elements

The frozen nutrient and DOC samples were thawed overnight at room temperature just before the measurements. Nutrients were analyzed using an Astoria-Pacific A2C2 nutrient auto-analyzer (Astoria-Pacific International, Oregon USA). The detection limits for nutrients were 0.1, 0.05 and 1 μmol/L for nitrate, phosphate and silicate, respectively. Concentrations of DOC were determined using a Shimadzu TOC-V total organic carbon analyzer employing the high temperature combustion method (Guo et al., 1995). For DOC measurements, samples were acidified with concentrated HCl to pH $\leq$ 2 immediately before measurement to remove all the dissolved inorganic carbon. Concentrations were calculated using calibration curves that were generated at the beginning of the sample analysis. Certified DOC standards (University of Miami) and ultrapure water were measured every eight samples during the run as samples to check the performance of the instrument to ensure the data quality. Three to five measurements were made for each sample, and the precision was <2%.

The TE sample analysis was followed well-established procedures, which can be found elsewhere (e.g., Shiller, 2003, Joung and Shiller, 2016; Shim et al., 2017; Boyle et al., 2012). Briefly samples were analyzed using a sector field-inductively coupled plasma-mass spectrometer (SF-ICP-MS; Thermo-Fisher Element 2) as previously described in Shiller (2003). For analysis, samples were diluted 33% by addition of ultra-pure 0.3 M HNO_3 (Seastar Baseline) containing 17 nM In as an internal standard. Arsenic, Ba, Cd, Co, Cr, Cs, Cu, Fe, Mn, Mo, Ni, Pb, Rb, Re, Sr, U, V and Zn were analyzed on the SF-ICP-MS using a Teflon spray chamber and nebulizer. Selected elements were determined at low (Cd, Cs, Pb, Re and U), medium (Co, Cr, Cu, Fe, Mn, Mo, Ni, Rb, Sr, V and Zn), and high resolution for As. To determine concentrations, standard curves were generated at the beginning of each of the analytical runs. The analytical performance was checked by measuring a standard and blank after every 8 sample measurements during each analytical run. The detection limits are shown in Supplementary Table 1, and the recovery of reference materials can be found in Shim et al. (2017).

2.4. River discharge, input and export fluxes estimation

Hydrological data was obtained from the US Army Corps of Engineers (http://www.mvn.usace.army.mil/). For the Red River input to the Atchafalaya River Basin, the daily discharge from the Red River at Alexandria and the Black River at Acme, LA were combined (Fig. 1). For the Mississippi River flow into the Atchafalaya River Basin, the daily discharge was obtained by subtracting the Red River input from the discharge at Simmesport, LA. The Mississippi River flow through the birdfoot delta was taken from the gauge at Tarbert Landing, MS, which is located below the Old River Control Structure where the Mississippi River division is located. During June 2011 flood, the additional Mississippi River discharge to the Atchafalaya River Basin through the Morganza Spillway was obtained from Scott et al. (2014). We note that the hydrological imbalance between inputs (discharge at Simmesport, plus Morganza Spillway for June 2011) and outputs (discharge at Wax Lake outlet + Morgan City) was 1%, 5%, and <1% for April and November 2010, and June 2011, respectively.

To estimate the contributions of various sources to chemical fluxes in the Atchafalaya River Basin, we started by calculating the input concentrations of constituents from the Red and Mississippi Rivers:

$$I_R = f_{RR} \times C_{RR} + f_{MR} \times C_{MR}$$

where I_R is the theoretical fluvial input concentration to the basin derived by assuming conservative mixing of Red and Mississippi River waters, the f's are the percentages of water in the Atchafalaya River derived from the Red and Mississippi River, and the C's are the concentration (<0.45 μm fraction) of the constituent in each river. We use this theoretical conservative estimate of the input concentration rather than the measured concentration at AR1 since that station is located >60 km downstream from the mixing point of the two rivers. To estimate the relative contribution of the Red River to the constituent flux through the basin, we simply took the ratio of $f_{RR} \times C_{RR}/I_R \times 100\%$.

Contributions of wetlands/floodplains to chemical flux modifications were estimated by simple concentration comparisons between the most upstream site (AR1 = Input) and the lower Atchafalaya River Basin (flow-weighted average of sites AR10 and ARWL = Output). The wetland constituent contribution proportions were calculated by ((Output-Input)/Input) × 100%. Thus, neg-

Table 1
Total dissolved (<0.45 μm) chemical constituents in Atchafalaya River Basin. Full data set can be found in Supplementary materials.

	Cont.[€] (%)	DOC (μmol/kg)	NO_3^-	PO_4^-	$Si(OH)_4$	As (nmol/kg)	Ba	Cd	Co	Cr	Cs	Cu	Fe	Mn	Mo	Ni	Pb	Rb	Re	Sr	U	V	Zn
April 2010																							
MR	87	298	117.3	1.60	117	14.8	447	0.12	1.01	1.6	0.023	19.6	518	31	8.04	23.9	0.183	14.4	0.086	1887	4.3	24.7	6.1
RR	13	510	2.1	0.95	62	11.6	481	0.09	2.89	3.7	0.081	16.2	5340	1375	5.41	23.8	0.982	28.9	0.012	2635	2.7	31.1	12.1
AR1		325	113.6	1.34	109	14.5	448	0.11	1.09	1.9	0.037	17.8	1358	35	6.87	23.5	0.412	16.0	0.074	1947	3.8	24.2	6.1
Lower ARB[*]		314	102.4	1.02	103	13.5	446	0.11	1.24	1.7	0.030	17.8	1287	144	7.11	24.0	0.416	17.5	0.060	2091	3.5	25.0	6.6
Swamp[**]		900	1.5	1.68	131	28.6	1392	0.04	3.81	0.4	0.014	2.67	958	13,003	3.22	15.9	0.016	22.7	0.016	10,922	4.3	6.2	2.2
Theo. RR + MR[#]		326	102.3	1.51	110	14.4	451	0.12	1.26	1.9	0.031	19.2	1145	205	7.70	23.9	0.287	16.3	0.076	1984	4.1	25.5	6.8
RR's Cont. (%)[§]		***20***	***0***	***8***	***7***	***11***	***14***	***10***	***30***	***26***	***35***	***11***	***61***	***87***	***9***	***13***	***44***	***23***	***2***	***17***	***9***	***16***	***23***
ARB's Cont. (%)[¥]		***−3***	***−10***	***−24***	***−5***	***−7***	***−1***	***1***	***13***	***−12***	***−20***	***0***	***−5***	***311***	***3***	***2***	***1***	***9***	***−19***	***7***	***−8***	***3***	***9***
November 2010																							
MR	91	296	101.8	1.13	222	25.5	546	0.12	1.26	1.1	0.014	19.1	258	48	19.01	26.2	0.081	15.5	0.135	2540	7.8	40.3	4.3
RR	9	332	4.3	0.68	153	26.2	583	0.06	0.79	0.4	0.020	11.3	229	442	12.66	11.6	0.047	34.7	0.020	2866	1.4	31.0	1.3
AR1		331	108.2	1.88	227	27.4	647	0.17	1.24	1.1	0.014	20.1	233	30	23.58	28.4	0.071	18.3	0.141	3313	9.6	45.6	7.1
Lower ARB		346	102.8	1.94	232	26.6	619	0.09	1.41	1.1	0.014	20.7	252	73	15.31	26.0	0.083	17.5	0.130	2808	6.8	46.2	5.3
Swamp		713	1.5	1.47	275	22.3	1582	0.03	2.00	0.3	0.013	1.44	1306	5062	3.11	9.9	0.013	32.1	0.014	12,134	4.0	3.8	2.5
Theo. RR + MR		299	93.0	1.09	216	25.6	549	0.11	1.22	1.1	0.015	18.4	255.3	83	18.44	24.9	0.078	17.2	0.125	2569	7.2	39.4	4.0
RR's Cont. (%)		***10***	***0***	***6***	***6***	***9***	***10***	***5***	***6***	***4***	***12***	***5***	***8***	***48***	***6***	***4***	***5***	***18***	***1***	***10***	***2***	***7***	***3***
ARB's Cont. (%)		***5***	***−5***	***3***	***2***	***−3***	***−4***	***−45***	***13***	***−2***	***−3***	***3***	***8***	***141***	***−35***	***−8***	***17***	***−4***	***−8***	***−15***	***−29***	***1***	***−26***
June 2011																							
MR	90	282	94.3	2.00	145	20.7	456	0.11	1.24	1.8	0.038	20.2	1547	68	10.41	25.9	0.477	15.5	0.078	1757	2.9	28.9	8.1
RR	10	701	7.0	2.09	112	19.5	271	0.07	1.68	4.5	0.125	18.7	8098	289	3.67	30.8	0.855	45.1	0.009	828	0.3	36.8	26.9
AR1		370	74.9	2.30	137	20.9	425	0.09	1.48	2.2	0.048	21.2	2514	168	8.12	26.7	0.638	21.2	0.062	1589	2.6	31.1	9.4
Lower ARB		357	51.9	2.31	146	23.6	454	0.06	1.56	1.5	0.029	16.1	1824	485	7.67	24.4	0.560	20.0	0.065	1570	1.7	26.9	7.8
Swamp		581	1.2	9.67	178	30.2	531	0.06	2.77	0.9	0.017	7.2	2406	2087	4.62	18.2	0.187	30.4	0.055	1523	0.3	11.5	7.6
Theo. RR + MR		324	85.6	2.01	141	20.6	438	0.10	1.29	2.1	0.047	20.1	2202	91	9.73	26.4	0.515	18.5	0.071	1664	2.7	29.7	10.0
RR's Cont. (%)		***22***	***1***	***10***	***8***	***9***	***6***	***6***	***13***	***22***	***27***	***9***	***37***	***32***	***4***	***12***	***17***	***24***	***1***	***5***	***1***	***12***	***27***
ARB's Cont. (%)		***−3***	***−31***	***0***	***7***	***13***	***7***	***−30***	***5***	***−33***	***−39***	***−24***	***−27***	***188***	***−6***	***−8***	***−12***	***−6***	***4***	***−1***	***−35***	***−14***	***−18***

[*]: Lower ARB: averaged (discharge-weighted) concentrations between AR10 and ARWL. For June 2011, we used concentrations in AR6.
[**]: Concentrations of chemical constituents in swamp waters were averaged value from 2 (June 2011) and 3 (April and November 2010) different locations.
[§] and [¥]: contributions of Red River and wetlands/floodplains, respectively. Red River contributions = Red River concentration/total theoretical chemical concentrations (Red + Mississippi Rivers) × 100. ARB (wetlands/floodplains) contributions = (output concentrations at lower ARB – Input at AR1)/Input) × 100, and thus, the negative values indicate removal of the constituents while flowing through the lower ARB.
[#]: Theoretical chemical concentrations based on conservative mixing between the Red River and Mississippi River (i.e., faction of Red River discharge × concentrations + fraction of Mississippi River discharge × concentrations).
[€]: Hydrological contributions.

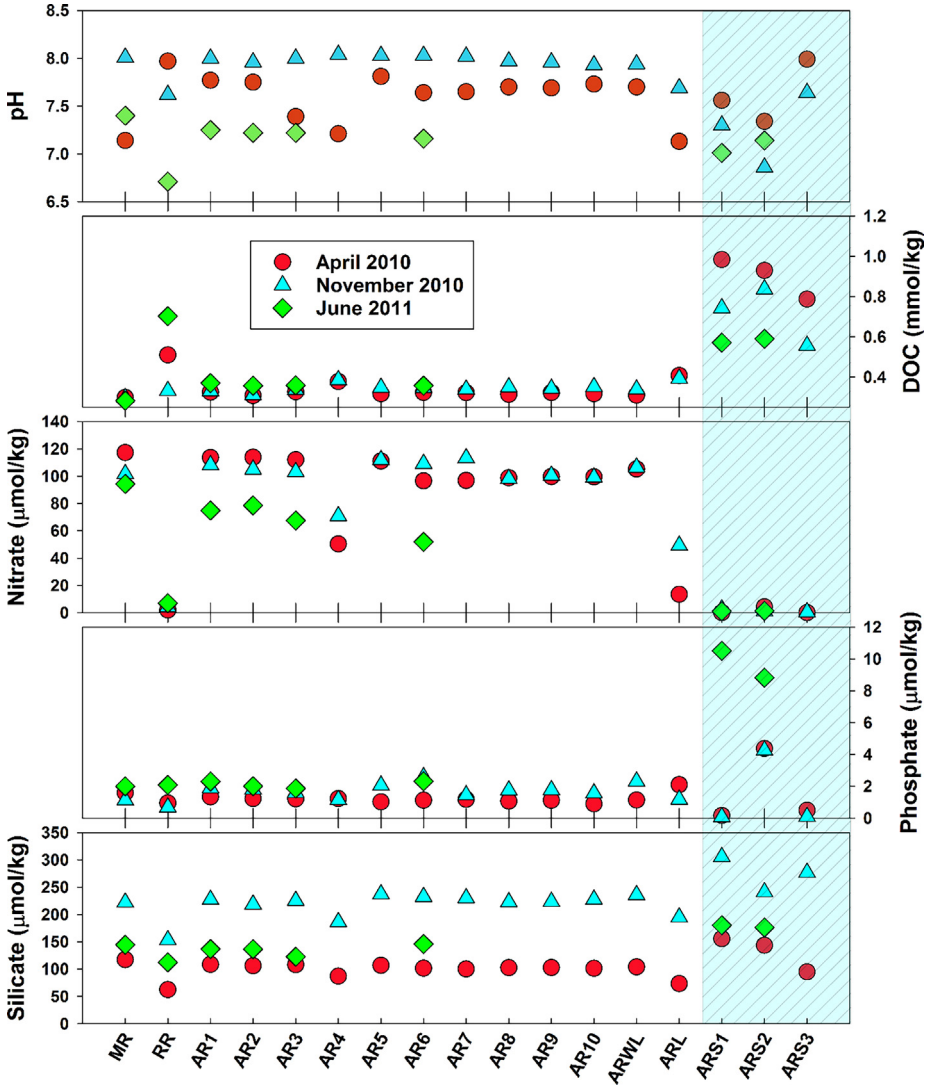

Fig. 3. Distributions of pH, DOC, nitrate, phosphate and silicate during April (circles) and November (triangles) 2010, and June 2011 (diamonds). Mainstem sampling sites are shown on the x-axis from upsteam locations to downstream (see Fig. 1); swamp water sampling sites are shown in the shaded area. Sites in eastern and western sides of basin are not presented here, but are included in Supplementary Tables 2–4 and Supplementary Figs. 1-3. Error bars were not expressed but were typically less than 2% of the values.

ative values indicate a removal during interactions between wetlands/floodplains and river water (Table 1). In June 2011, due to our inability to collect samples from AR10 and ARWL, we used concentrations of constituents at site AR6 to represent the lower Atchafalaya River Basin concentrations (i.e., Output). For estimating the effects of Red River and wetlands contributions to the Atchafalaya fluxes, we considered only concentration differences >20% to be significant (Shim et al., 2017). This accounts for both analytical error and possible short-term temporal variability in river concentrations as well as uncertainty in river mixing ratios, and is based on the highest standard deviation (i.e., 7% for U) of the reference materials and the estimated input/output discharge imbalance for the Atchafalaya River Basin. Thus, 20% or greater differences represent at least twice the flux uncertainties (e.g., Shim et al., 2017). For DOC and nutrients, we accepted differences of 10% or greater as significant variations because the standard variation of DOC reference materials was typically <2%.

3. Results

River discharges varied significantly seasonally (Fig. 2 and supplementary Fig. 1). Discharge for the Atchafalaya River at Simmesport, LA was 10.2×10^3 and 2.8×10^3 m^3/s during April and November 2010, respectively, whereas it was 15.9×10^3 m^3/s during June 2011. In June 2011, the additional Mississippi River discharge to the Atchafalaya River Basin through the Morganza Spillway was $>2.8 \times 10^3$ m^3/s for the two weeks of the spillway opening (Scott et al., 2014). Results for DOC, nutrients, TEs, and ancillary parameters such as pH, conductivity, and temperature are shown in Figs. 3 and 4, and Supplementary Figs. 2–4 and Supplementary Tables 2–4. Though seasonal variations of TEs and nutrients were observed in the most eastern (ARE1) and western (ARW1) sides of the basin, their contributions to the fluxes in the Atchafalaya River main stem are likely unimportant due to low water flows and concentrations similar to the main stem; thus, the data for these stations are listed in the supplementary figures and tables and not further displayed herein.

DOC concentrations were always higher in the Red River than the Mississippi River during our studies (Fig. 3 and Supplementary Tables 2–4). The DOC concentrations showed low variability along the river from AR1 to the Atchafalaya River outlets (AR10 and ARWL) except for a DOC maximum in the middle of basin (AR4) during April and November 2010. In swamp waters (ARS1-3), DOC concentrations were in general about 2 to 3-fold higher than

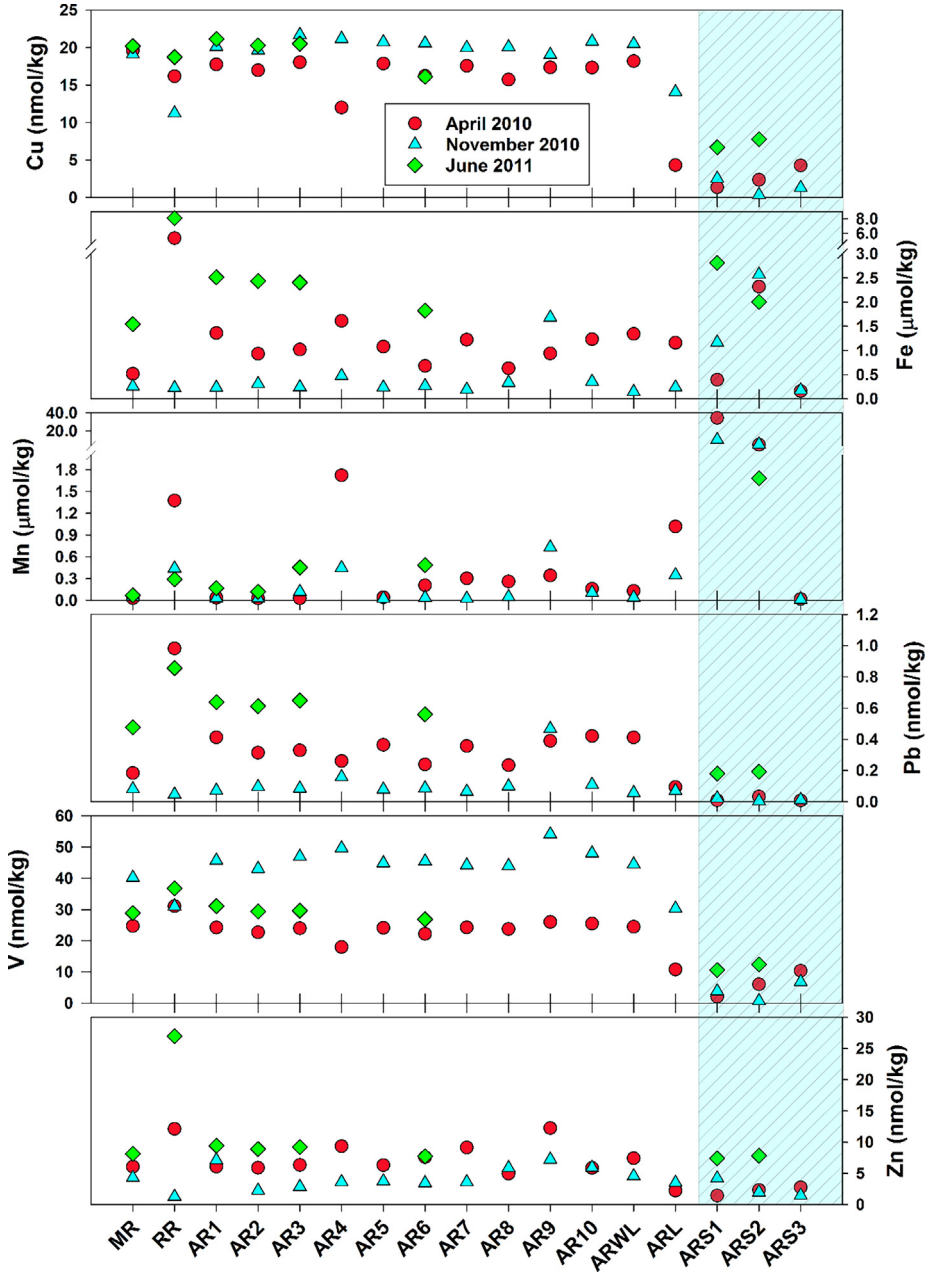

Fig. 4. Example distributions of total dissolved (<0.45 μm) Cu, Fe, Mn, Pb, V, and Zn during April (circle) and November (triangle) 2010, and June 2011 (diamond). Distributions of other trace elements as well as dissolved (<0.02 μm) and colloidal (0.02–0.45 μm) phases are shown in Supplementary Figs. 1-3. Mainstem sampling sites are shown on the x-axis from upsteam locations to downstream (see Fig. 1); swamp water sampling sites are shown in the shaded area. Sites in eastern and western sides of basin are not presented here, but are included in Supplementary Tables 2–4 and Supplementary Figs. 1-3. Error bars were not experessed but were typically less than 2% of their concentrations.

the concentrations in the Atchafalaya River main channel waters throughout the study. Nitrate and silicate concentrations were higher in the Mississippi River than the Red River in all sampling periods. Phosphate was also slightly higher in the Mississippi River than the Atchafalaya River during April and November 2010, though concentrations were comparable in both rivers during June 2011. At the mid-basin station where the DOC maximum was observed (AR4), nitrate and silica showed a minimum during April and November 2010; however, phosphate showed a minimum only in November and not in April 2010. In the lower basin (AR6-10) and the Wax Lake outlet (ARWL), concentrations of all studied nutrients generally showed little variability along the flow path. Swamp waters showed very low nitrate concentrations relative to the Atchafalaya River mainstem regardless of season. Phosphate concentrations in waters from swamps were lower than the concentrations in the mainstem of the Atchafalaya River except during June 2011 as well as waters from ARS2. Silicate concentrations in swamp waters were higher in comparison to main channel waters. Ammonia and nitrite were generally very low throughout the basin, <1% of the nitrate concentrations, except in swamp waters where ammonia was as high as 20 μmol/kg during November 2010 (Supplementary Tables 2–4).

Dissolved trace element distributions are shown in Fig. 4 (see also Supplementary Tables 2–4 and Supplementary Figs. 1–3). Most of the studied trace elements were mainly in the <0.02 μm dissolved fraction except for Cr, Cs, Fe, Pb and Zn. Among those five

elements, Fe and Pb were the most extreme in that the 0.02–0.45 μm colloidal phase accounted for >80% of the total dissolved (<0.45 μm) pool. For Cr, Cs and Zn, the colloidal phase was considerable, accounting for over 50% for many samples.

Total dissolved (<0.45 μm) Cd, Cu, Re, U and Mo concentrations were higher in the Mississippi River than Red River during our sampling campaigns, whereas total dissolved Cs, Fe, Mn and Rb were higher in the Red River than Mississippi River. Other elements showed seasonal changes in which source had the higher concentration. For example, total dissolved Ba was higher in the Mississippi than Red River during June 2011, but it was lower in the Mississippi than Red River during the other sampling campaigns. In general, total dissolved Cd, Cr, Cs, Fe, Mn, Pb and Zn in the mainstem of the Atchafalaya River were higher during April 2010 and June 2011 than during November 2010. In contrast, concentrations of total dissolved As, Ba, Cu, Mo, Ni, Re, Sr, U and V were higher in the Atchafalaya River mainstem during November 2010 than the other two periods. Other elements, including total dissolved Co and Rb also varied seasonally, but with slightly higher (~5%) concentrations in June relative to April and November. In the mid-basin (AR4) where the DOC maximum and low nitrate concentrations were observed, total dissolved Cd, Re, U, and Ni concentrations showed a minimum, whereas a maximum was observed at that site for Fe, Mn and Co. In swamp waters, total dissolved Fe, Mn and Co were enriched in comparison to the main channel waters, whereas total dissolved Cd, Ni, Cs, Re, V, Cr, Pb, Cu and Mo were relatively low in swamp waters. Other elements such as As, Ba, Rb, Sr and Zn showed similar concentrations in the mainstem and swamp waters.

4. Discussion

4.1. Distributions of DOC, nutrients, and trace elements

Seasonal variations of DOC, nutrients, and trace elements were observed in the Atchafalaya River Basin as well as the Mississippi and Red Rivers (Figs. 3, 4 and Supplementary Tables 2–4 and Supplementary Figs. 2–4). Where applicable, these observations are similar to previous reports for the main channel (Shen et al., 2012; Duan et al., 2007, 2010; Bianchi et al., 2004; Dubois et al., 2010; Shiller, 1997, 2002; Stolpe et al., 2010). The seasonal variations of DOC, nutrients and some trace elements in the Mississippi River have been suggested to result from temporal changes in relative tributary contributions (e.g., Ohio, Missouri, and Upper Mississippi Rivers) to the Mississippi River main stem (Shen et al., 2012; Duan and Bianchi, 2006; Bianchi et al., 2004, 2007; Duan et al., 2007, 2010; Shiller, 1997, 2002) and from redox effects (Shiller, 1997, 2002; Shiller and Stephens, 2005). This may also lead to seasonal variability of the chemical constituents in the Atchafalaya River, since the Mississippi River is the major hydrological contributor to the Atchafalaya River, accounting for typically >85% of the Atchafalaya River discharge.

Similar to previous observations within the Atchafalaya River Basin, DOC was enriched in swamp waters (e.g., stations ARS1-ARS3) relative to main channel river waters, likely due to decomposition of plant detritus and DOC production in the swamp (Cai et al., 2016; Shen et al., 2012; Lambou and Hern, 1983; Battle and Mihuc, 2000). Nitrate and phosphate were, however, depleted in Atchafalaya River Basin swamp waters. This is typical in swamp waters and is generally the result of biological activity such as

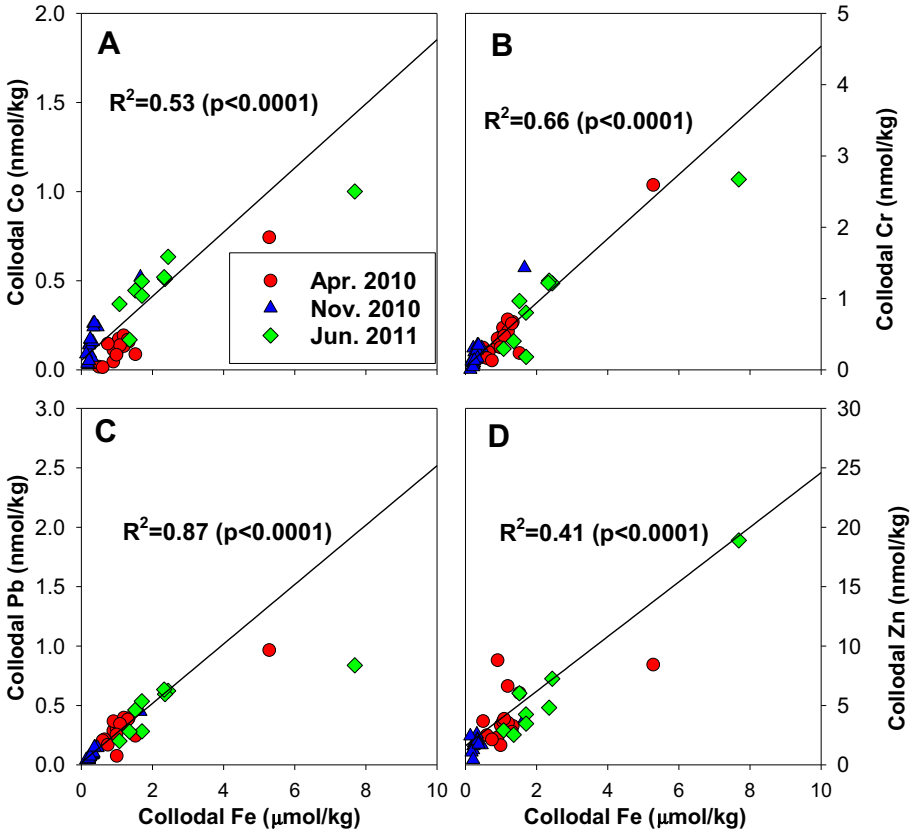

Fig. 5. Example distributions of colloidal Fe versus colloidal (A) Co, (B) Cr, (C) Pb, and (D) Zn in mainstem of AR (n = 41). For better regression, two data points from RR in April 2010 and June 2011 were excluded due to much greater colloidal Fe concentrations. Regression slopes and intercepts are listed in Supplemtary Table 5. Other colloidal trace element (Cs and Cu) are shown in Supplementary Figs. 7.

uptake and/or denitrification as well as ammonification (Lindau et al., 2008; Scaroni et al 2010, 2011; Strohm et al., 2007), and formation of ferrous phosphate minerals (e.g., vivianite) under organic-enriched, anoxic conditions (Withers and Jarvie, 2008; House, 2003). The high ammonium concentrations in swamp waters may have been derived from decomposition of wetland vegetation, as observed in other natural wetlands (García-García et al., 2009).

Swamp waters were enriched with total dissolved (<0.45 μm) Fe, Mn and Co, while Cd, Cu, Mo, Re, Sr, and V were depleted, relative to the concentrations in the main channel waters. This is likely due to reductive dissolution (Fe, Mn and Co), adsorptive loss into the sediment (Mo, Re, U and V), and/or formation of mineral phases (Cd, Cu) under reducing conditions in swamp sediments/pore waters (Tribovillard et al., 2006; Elbaz-Poulichet et al., 1997; Jacobs et al., 1985; Shea and Helz, 1988; Jiann et al., 2005).

In the mainstem of the Atchafalaya River, some metals co-varied with other metals. For example, there were positive correlations between colloidal Fe and colloidal Co, Cr, Cs, Pb, and Zn, and between colloidal Mn and only colloidal Co (not with others for Mn) regardless of season in the mainstem of the Atchafalaya River (Fig. 5 and Supplementary Figs. 5 and 6). In contrast, in the <0.02 μm dissolved phase, Fe was not correlated with Co, Cr, Cs, Pb and Zn. The similar distributions of Cr, Cs, Pb and Zn in the colloidal phase suggest either their adsorption onto Fe/Mn-(oxy) hydroxides and concurrent removal (Zachara et al., 2001; Means et al., 1978; Johnson et al., 1992; Brick and Moore, 1996; Shiller, 1997; Pokrovsky and Schott, 2002; Gossuin et al., 2002), and/or the same sources (i.e., Mississippi or Red Rivers) for the colloidal TEs. However, these Fe-metal relationships were not observed in swamp waters. This is probably related with great concentration differences between Fe and other elements, in that Fe concentrations (both phases) were at least 2–3 orders of magnitude higher than other elements in swamp waters, which hinders observation of small changes of these elements relative to Fe. Or, it may simply reflect more metal-organic matter complexation relative to metal-Fe-hydroxides in organic rich swamp water than river main channel waters (Grybos et al., 2007). For As, Ni and Rb (regardless of size), we do not observe any correlation with pH, DOC, or colloidal Fe/Mn, and this is probably due to other parameters having the dominant influence on their behaviors (e.g., sulfur or clay minerals; Cempel and Nikel, 2006; Ferguson and Gavis, 1972; Butterman and Reese, 2003).

With other biogeochemical parameters such as DOC and pH, however, we have not observed correlations (Supplementary Figs. 7–9) that have commonly been observed in other systems. In particular, Fe and Mn often co-vary with DOC and pH (as for acid leachable metals under low oxygen). Thus, significant correlations between Fe/Mn and DOC (or pH) have been commonly reported in wetland systems (Shim et al., 2017; Mora et al., 2010; Olivie-Lauquet et al., 2001; Pokrovsky and Schott, 2002; Küchler et al., 1994; Viers et al., 1997, 2000; Brick and Moore, 1996). This good correlation implies that there can be a single dominant process affecting TE distribution in some wetlands systems, such as activity of microorganisms (Olivie-Lauquet et al., 2001) or biological (macrophytes, perennial tree) uptake (Viers et al., 2005). Though these activities would likely occur in the Atchafalaya River Basin as well, nonetheless, our observations suggest that the TE distributions in the Atchafalaya River Basin were governed not by the single dominant factor, but by the combination of multiple parameters such as hydrological regime, redox conditions, pH, DOC, and biological (plant and microbial) activity as well as changing proportions in and of the different element sources (Red River, Mississippi River, and swamp).

4.2. Contributions of DOC, nutrients and trace elements from the Red River and wetlands

4.2.1. Input from the Red River

As mentioned earlier, the Atchafalaya River is comprised of the combined flow of the entire Red River discharge and a fraction of the Mississippi River. Typically, 85% of the discharge of the Atchafalaya is Mississippi River water (Fig. 2). Note that because our first sampling site (AR1) was located ~60 km downstream from where the Red River enters the Atchafalaya River, there may be floodplain input or removal in that 60 km reach (see below and Table 1). Thus, in the estimates in this section, instead of using actual concentrations at AR 1, we used theoretical concentrations of chemical constituents estimated assuming conservative mixing between Red and Mississippi Rivers waters.

During our sampling periods, the Red River contributed 9–13% of the Atchafalaya River water (Table 1). However, despite its relatively low hydrological contribution, the Red River contribution to the Atchafalaya River flux of some constituents exceeded its hydrological contribution. For example, due to the substantially higher DOC concentration in the Red River than in the Mississippi River (Supplementary Tables 2–4), DOC from the Red River accounted for over 20% of the DOC entering the Atchafalaya River Basin (i.e., Red + Mississippi Rivers) during April 2010 and June 2011, and 10% for November 2010. Shen et al. (2012) roughly estimated the Red River as contributing about 13% of the DOC flux in the Atchafalaya River Basin (Red + Mississippi Rivers + Swamp), which is comparable with our estimate. In contrast, due to the low nitrate in the Red River (<10 μmol/kg) compared with the Mississippi River (~100 μmol/kg), the Red River diluted the Mississippi River's nitrate by about ~10%. Phosphate and silicate were also usually lower in the Red River than in the Mississippi River.

The Red River was a significant source to the Atchafalaya River for some TEs (Table 1). During April 2010 and June 2011, the Red River contributed >20% of the total dissolved (<0.45 μm) Co, Cr, Cs, Mn, Fe, Pb, Rb, and Zn inputs from the Mississippi and Red Rivers, i.e., an amount in excess of the Red River's contribution to the Atchafalaya discharge. This was due to the 5–10-fold higher Red River concentrations of these elements as compared with the Mississippi River. During November 2010, the Red River contributions of these elements were relatively low in comparison to the other two periods because of both seasonally low Red River concentrations and also the low Red River discharge contribution to the Atchafalaya River. Manganese was the most extreme case, in that its concentration was 45-fold higher in the Red River than the Mississippi River during April 2010, and 5–10-fold greater during November 2010 and June 2011. This indicates that about 87% of Mn loading into the Atchafalaya River Basin was derived from the Red River during April 2010 and ~40% for other two periods. Thus, the Red River can play a disproportionate role (relative to its water discharge) in the supply of some constituents (DOC and certain trace elements) into the Atchafalaya River Basin, though it is still usually not the main source of these constituents to the basin or the Louisiana Shelf.

In Table 1, we compare estimates of the initial composition of the Atchafalaya River Basin based on conservative, discharge-weighted mixing of Red and Mississippi Rivers concentrations with observed concentrations at AR1. Differences between the two numbers reflect both non-conservative mixing (e.g., adsorption/desorption due to differences in pH, DOC, and SPM) as well as additional inputs to the Atchafalaya River as it flows through the northern part of the floodplain. Among DOC and nutrients, only phosphate during one sampling (November 2010) was observed to mix non-conservatively. Among the trace elements (<0.45 μm),

As, Ba, Co, Cs, Cr, Cu, Fe, Ni, Re, Rb, and V always mixed roughly conservatively. Only Mn was observed to behave non-conservatively during all three sampling campaigns, showing removal in April and November 2010 but addition during June 2011. During April 2010, Pb showed addition with only Mn showing removal. During November 2010, Cd, Mo, PO_4, Sr, U, and Zn showed addition with Mn again being the only element to show removal. During June 2011, Mn and Pb showed addition with no elements showing removal. Note that although overland flow of Mississippi River water due to the opening of the Morganza Spillway in May/June 2011 provided an extra input to the Atchafalaya River, the extra >2800 m^3/s flow through the spillway (Scott et al., 2014) only changed the water mixing ratio slightly, even assuming that all of this flow reached AR1, which it did not.

Because mixing experiments were not performed, it is difficult to ascribe causes to the apparent non-conservative behaviors. However, because the upper Atchafalaya River is highly leveed, it seems more likely that observed increases in constituent concentrations are due to desorption processes or hyporheic input rather than to an overland input from the surrounding floodplain. We also note that the least amount of non-conservative behavior was observed during "typical" high discharge (April 2010) and the greatest amount during the lowest discharge (November 2010). This either indicates that at low discharge additional sources (hyporheic or anthropogenic) are relatively more important or that with increased velocity at high discharge, river flow would be too fast to fully interact with floodplains. The observation that Mn is the only constituent to show removal may indicate that the Mississippi River is "seeding" the more Mn-rich Red River waters with Mn-removing microbial activity (e.g., Shiller and Stephens, 2005).

4.2.2. Interaction with wetlands in the Atchafalaya River Basin

Another important factor potentially altering the chemical constituents in the Atchafalaya River Basin is the interactions with the wetlands/floodplain in the mid- to lower basin. Though conservative behavior appears to characterize the mixing of most of the TEs up to the initial Atchafalaya River sampling location (AR1), concentration changes going downstream are not always smooth or monotonic. For instance, during April and November 2010, the mid-basin (AR4) showed increased concentrations of DOC, Co, Fe, Mn and Zn, and decreased concentrations of nitrate, silicate, Cd, Cr and Ni relative to surrounding stations (Figs. 3 and 4, Supplementary Figs. 2–4). A similar phenomenon was observed at ARW2 (see Supplementary Figs. 2–4). Compositionally, the observed concentration changes at AR4 and ARW2 are consistent with what would be expected from input of water from the wetlands. However, the fact that those changes do not persist downstream suggests that these sampling sites were at locations of incomplete mixing of wetland and river water. Nonetheless, these more swamp-like element distributions in mid-basin clearly indicate that there was an input (or interaction) from the surrounding wetlands either by overland flow or groundwater.

In Table 1, we also compare the concentrations of chemical constituents between the input to the basin at AR1 and the output from the lower Atchafalaya River Basin to understand the modification created by interaction between river water and the floodplain. For the lower Atchafalaya River Basin output, we used a flow-weighted average of our samples at the mouth of the river (AR10) and at the Wax Lake delta (ARWL), except in June 2011 when we used the concentration at AR6. As noted above, the AR1 composition already accounts for the Red River input and in-stream process (e.g., biological uptake, desorption, hyporheic interaction) up to that point as well as some of the extra Mississippi River input through the Morganza Floodway in June 2011.

The DOC output concentrations differed little from the input during all our sampling periods with concentration variations <15 μmol/kg (or <5%) between in-/output, suggesting insignificant DOC input or sources and sinks were balanced. For nutrients, during April and November 2010 the differences of export relative to input for nitrate and silicate were insignificant. However, during June 2011 nitrate was removed by 23 μmol/kg (or 31%) relative to the concentration at AR1 while river flows the Atchafalaya River Basin. Our result is similar to that of Scott et al. (2014) who likewise found about 30% removal of nitrate in the basin during June 2011 which they attributed to denitrification. Phosphate was removed by 0.3 μmol/kg in the Atchafalaya River Basin during April 2010, whereas during the other two sampling campaigns, the input/output differences were insignificant.

For trace elements (<0.45 μm), some showed different seasonal behaviors (removal or addition) and changes in the magnitudes of their input–output differences. For example, during April 2010, only Mn varied significantly with addition of over 100 nmol/kg, while other elements varied within our limitation (20%). During November 2010, Mn was again the only element showing an increase, while Cd, Mo, U and Zn decreased slightly, but by and large most elements were unchanged during passage through the basin. However, during June 2011, more elements were affected than at the other two times including apparent removal of Cd, Cr, Cs, Cu, Fe, and U as well as input of Mn.

Our swamp water results generally support the idea that the input/output concentration differences are due to input/removal by the wetlands. That is, although there were significant spatial variations in concentrations in our swamp samples, nonetheless, the swamp water samples were greatly enriched in Mn and Fe (November only) and depleted in Cd, Cs, Cr, Cu, Fe, and U relative to the concentrations in main river channel waters (Table 1; Fig. 4). Manganese was the most extreme in that its average concentrations were >10-fold greater (>10× in June 2011 and >100× greater in April and November 2010) in swamp waters than in main river channel water. This suggests that even small amounts of swamp water introduction into the river could significantly modify for Mn in main river channel water particularly during flooding or high river discharge periods with better hydrological connectivity.

Seasonally or with respect to river stage, we observed that more elements were affected by the passage through the basin during the highest river discharge in June 2011 than at the other times. This is likely a consequence of the Morganza Spillway opening, which resulted in up to 27% of the water passing through the basin via overland flow. Stated another way, this was enough volume to fill the lower Atchafalaya River Basin to about 1.7 m during peak flooding, and resulted in the inundation of large areas that are rarely exposed to flood waters (Falcini et al., 2012; Scott et al., 2014). In a sense, as suggested by Scott et al. (2014), the opening of the Morganza Spillway and resultant induced interaction between substantial quantities of Mississippi River water and the floodplain was a large-scale diversion "experiment". This "experiment" shows the potential of and possible limits on the floodplain's ability to alter fluvial TE fluxes. In contrast, during low river discharge, the hydrological connectivity between river and swamp can be very poor. Additionally, immediately before and during our low discharge sampling (November 2010) there was no precipitation in the Atchafalaya River Basin. Thus, the chemical flux alterations we observed then were not likely derived from overland or rain-associated groundwater inputs. We suggest interactions with the hyporheic zone as the probable mechanism for our low flow changes (Boano et al., 2010, Shim et al., 2017). Finally, we note that during our April 2010 ("typical" high river flow) sampling, we observed the fewest alterations of trace elements in the Atchafalaya River Basin, suggesting that the additional interactions (via swamp or hyporheic zone) were at a minimum relative to the river discharge.

Interestingly, our result showing the fewest number of TE alterations during typical high flow in April 2010 is similar to observations in the nearby Pearl River Basin, which has a similar climate and ecosystem to our study site. In that study, Shim et al. (2017) also reported minimal wetland contribution to Pearl River TE fluxes during high river discharge. Shim et al. (2017) suggested that the wetland inputs to the river may have been limited at high discharge due to the faster flushing of water than input/removal rates of biogeochemical processes. They suggested that moderate discharge periods are "just right" for the river-wetlands interactions, allowing both river-wetland connectivity and residence time for sustaining biogeochemical processes particularly for the Pearl River basin. For the Atchafalaya Basin, this sort of rate limitation (Rennert and Rinklebe, 2010) may also be exacerbated by the leveeing of the system, which further limits hydrological connectivity between river channel and floodplain. Nonetheless, it is important to recognize that, though both studies reported similar chemical alterations in river water interacting with floodplains/wetlands, the seasons of the maximum chemical alterations upon hydrological regimes can be completely different due to a basin's physiographic configuration, which may be related with river flood pulse as well as riverscape heterogeneity (Tockner et al., 2000). Our estimates of the impact of Red River and floodplain/wetland contributions to the flux of material through the Atchafalaya River suggest that in most instances the Red River has the greater impact (Table 1). Only for Mn was the impact of the wetlands, including hyporheic effects, a dominant factor during all sampling periods. Even DOC showed negligible (within our uncertainty) addition from the wetlands. This contrasts with the conclusion of Shen et al. (2012) who found a substantial DOC increase (~150%) in the Atchafalaya relative to the Mississippi River, which they attributed to wetland inputs. This difference in our conclusions might have resulted from Shen et al. having made too low an estimate of Red River DOC from the USGS total organic carbon data they used for the Red River contribution. Alternatively, the difference may also be due to inter-annual variations in that several of their lower Atchafalaya River DOC concentrations were much higher than all of our determinations.

We also note that our estimates of fluxes are based on the <0.45 μm dissolved load, and do not include the particulate forms, which would likely have a large increase in total export during floods such as June 2011 (Falcini et al., 2012) but have been retained during other flow conditions (Reiman et al., 2018). Also, our snapshot sampling, though designed to highlight distinct flow regimes, may bias our understanding of the annual impact of wetland interactions. Thus, to fully understand the relative contributions of wetlands and the Red River to Atchafalaya River fluxes, future studies should utilize more frequent time series sampling. Regardless of the source(s) of chemical alterations of the Atchafalaya River water, fluxes of most of the chemical constituents we studied were significantly modified during their transit through the river basin. This suggests that the chemical modification in the Atchafalaya River basin significantly alters the flux of material reaching the Louisiana Shelf. Recently, based on surface water $\delta^{18}O$ and $\delta^{2}H$, Strauss et al. (2012) suggested that Louisiana Shelf water was mainly influenced by the Atchafalaya River during July 2008. Similarly, based on the $\delta^{18}O$-salinity relationship of the shelf surface, middle and bottom waters, Joung and Shiller (2014) suggested a considerable freshwater influence of the Atchafalaya River on the Louisiana Shelf during June/July 2009. These findings indicate that during times of shelf bottom water hypoxia, the Atchafalaya River freshwater influence could be more (or equally) important for dissolved phases of chemical constituents in the shelf surface than the Mississippi River delta outflow, despite the lower overall outflow of the Atchafalaya. Given our estimates of the chemical modification of Atchafalaya River water, this could well impact the establishment, maintenance, and ecosystem effects of Louisiana Shelf hypoxia.

5. Conclusions

Investigation of temporal and spatial variations of trace elements, DOC, nutrients, and other biogeochemical properties in the Atchafalaya River as well as the Mississippi and Red Rivers provides important information regarding the chemical transport to the Louisiana Shelf. Our results indicate that TE distributions in floodplain/swamp and associated river waters in Atchafalaya River Basin were not governed by a single dominant factor but by combinations of multiple biogeochemical processes as well as by relative mixing ratios of source waters. Seasonal trends of Atchafalaya River chemical constituents generally followed those in the Mississippi River, due to the major hydrological contribution of the Mississippi River to the Atchafalaya River (i.e., >85%). Despite its low hydrological contribution relative to the Mississippi River, Red River contributions for some chemicals (DOC, Co, Cr, Cs, Fe, Mn, Pb, Rb, and Zn) were significant and exceeded its hydrological contribution (~10% of Atchafalaya River discharge), e.g., accounting for >40% of Mn loading to the lower Atchafalaya River. Interestingly, during all our study periods the Red River effects on constituent concentrations were generally greater than the effects of the floodplain wetlands, though some TEs did show observable wetlands impact. During all our sampling campaigns, Mn was only the element that showed consistent addition from wetlands to river, while some others were at times removed (Cd, Cs, U, Cr, Fe, and Cu removed in June 2011; Cd, U, Zn, and Mo removed in November 2010; no downstream decrease in April 2010). Our results show that chemical alterations in the Atchafalaya River Basin were greatest during June 2011 due to the abnormally high river flow and resulting extra inputs through wetlands that were rarely exposed to flooding. Overall, the Atchafalaya River with its chemical modification of Mississippi River water via contributions from the Red River and interactions with floodplain wetlands, plays a critical role in chemical distributions on the Louisiana Shelf. Thus, the Atchafalaya River contribution should be adequately accounted for in biogeochemical studies and models of trace elements and nutrients on the Louisiana Shelf, particularly during periods of bottom water hypoxia.

Declaration of interest statement

All authors declared that there is no conflict of interest.

Acknowledgements

We thank Gopal Bera, Yihua Cai, Zhengzhen Zhou, and Kevin Martin for their assistance in sample collection and analysis, and two anonymous reviewers for their comments which improved the manuscript. This work was funded by the National Science Foundation Chemical Oceanography Program (OCE-0728775).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydroa.2019.100018.

References

Battle, J., Mihuc, T., 2000. Decomposition dynamics of aquatic macrophytes in the lower Atchafalaya, a large floodplain river. Hydrobiologia 418, 123–136.
Bayley, P.B., 1995. Understanding large river: floodplain ecosystems. Bioscience, 153–158.

Bianchi, T.S., Filley, T., Dria, K., Hatcher, P.G., 2004. Temporal variability in sources of dissolved organic carbon in the lower Mississippi River. Geochim. Cosmochim. Acta 68, 959–967.
Bianchi, T.S., Wysocki, L.A., Stewart, M., Filley, T.R., McKee, B.A., 2007. Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries. Geochim. Cosmochim. Acta 71, 4425–4437.
Boano, F., Demaria, A., Revelli, R., Ridolfi, L., 2010. Biogeochemical zonation due to intrameander hyporheic flow. Water Resour. Res. 46, W02511. https://doi.org/10.1029/2008WR007583.
Boyle, E.A., John, S., Abouchami, W., Adkins, J.F., Echegoyen-Sanz, Y., Ellwood, M., Flegal, A.R., Fornace, K., Gallon, C., Galer, S., Gault-Ringold, M., 2012. GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration. Limnol. Oceanogr.-Meth. 10 (9), 653–665.
Brick, C.M., Moore, J.N., 1996. Diel variation of trace metals in the upper Clark Fork River, Montana. Environ. Sci. Technol. 30, 1953–1960.
Butterman, W.C., R.G. Reese Jr. (2003) Mineral Commodity Profiles–Rubidium. No. 2003-45.
Cai, Y., Shim, M.J., Guo, L., Shiller, A.M., 2016. Floodplain influence on carbon speciation and fluxes from the lower Pearl River. Mississippi. Geochim. Cosmochim. Acta 186, 189–206.
Chow, A.T., Dai, J., Conner, W.H., Hitchcock, D.R., Wang, J.-J., 2013. Dissolved organic matter and nutrient dynamics of a coastal freshwater forested wetland in Winyah Bay, South Carolina. Biogeochemistry 112, 571–587.
Christopher, S.F., Page, B.D., Campbell, J.L., Mitchell, M.J., 2006. Contrasting stream water NO_3^- and Ca^{2+} in two nearly adjacent catchments: the role of soil Ca and forest vegetation. Global Change Biol. 12, 364–381.
Cempel, M., Nikel, G., 2006. Nickel: a review of its sources and environmental toxicology. Polish J. Environ. Stud. 15 (3), 375–382.
Correll, D.L., Jordan, T.E., Weller, D.E., 1992. Nutrient flux in a landscape: effects of coastal land use and terrestrial community mosaic on nutrient transport to coastal waters. Estuaries 15 (4), 431–442.
Dawson, J., Soulsby, C., Tetzlaff, D., Hrachowitz, M., Dunn, S., Malcolm, I., 2008. Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. Biogeochemistry 90, 93–113.
Duan, S., Bianchi, T.S., 2006. Seasonal changes in the abundance and composition of plant pigments in particulate organic carbon in the lower Mississippi and Pearl Rivers. Estuaries and Coasts 29, 427–442.
Duan, S., Bianchi, T.S., Sampere, T.P., 2007. Temporal variability in the composition and abundance of terrestrially-derived dissolved organic matter in the lower Mississippi and Pearl Rivers. Mar. Chem. 103, 172–184.
Duan, S., Bianchi, T.S., Santschi, P.H., Amon, R.M., 2010. Effects of tributary inputs on nutrient export from the Mississippi and Atchafalaya Rivers to the Gulf of Mexico. Mar. Freshwater Res. 61, 1029–1038.
Dubois, K.D., Lee, D., Veizer, J., 2010. Isotopic constraints on alkalinity, dissolved organic carbon, and atmospheric carbon dioxide fluxes in the Mississippi River. J. Geophys. Res.: Biogeosciences 2005–2012, 115.
Elbaz-Poulichet, F., Nagy, A., Cserny, T., 1997. The distribution of redox sensitive elements (U, As, Sb, V and Mo) along a river-wetland-lake system (Balaton Region, Hungary). Aquat. Geochem. 3, 267–282.
Emmett, B., Hudson, J., Coward, P., Reynolds, B., 1994. The impact of a riparian wetland on streamwater quality in a recently afforested upland catchment. J. Hydrol. 162, 337–353.
Falcini, F., Khan, N.S., Macelloni, L., Horton, B.P., Lutken, C.B., McKee, K.L., Santoleri, R., Colella, S., Li, C., Volpe, G., D'Emidio, M., 2012. Linking the historic 2011 Mississippi River flood to coastal wetland sedimentation. Nat. Geosci. 5 (11), 803–807.
Ferguson, J.F., Gavis, J., 1972. A review of the arsenic cycle in natural waters. Water Res. 6 (11), 1259–1274.
Fisher, J., Acreman, M., 2004. Wetland nutrient removal: a review of the evidence. Hydrol. Earth Syst. Sci. 8, 673–685.
Fontenot, Q., Rutherford, D., Kelso, W., 2001. Effects of environmental hypoxia associated with the annual flood pulse on the distribution of larval sunfish and shad in the Atchafalaya River Basin, Louisiana. Trans. Am. Fish. Soc. 130, 107–116.
Ford, M., Nyman, J., 2011. Preface: an overview of the Atchafalaya River. Hydrobiologia 658, 1–5.
García-García, V., Gómez, R., Vidal-Abarca, M., Suárez, M., 2009. Nitrogen retention in natural Mediterranean wetland-streams affected by agricultural runoff. Hydrol. Earth Syst. Sci. 13, 2359–2371.
Gossuin, Y., Colet, J.-M., Roch, A., Muller, R.N., Gillis, P., 2002. Cesium adsorption in hydrated iron oxide particles suspensions: an NMR study. J. Magn. Reson. 157, 132–136.
Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? J. Colloid Interface Sci. 314 (2), 490–501.
Guo, L., Santschi, P.H., Warnken, K.W., 1995. Dynamics of dissolved organic carbon (DOC) in oceanic environments. Limnol. Oceanogr. 40, 1392–1403.
Hamilton, S.K., Sippel, S.J., Calheiros, D.F., Melack, J.M., 1997. An anoxic event and other biogeochemical effects of the Pantanal wetland on the Paraguay River. Limnol. Oceanogr. 42 (2), 257–272.
Hansson, L.A., Brönmark, C., Anders Nilsson, P., Åbjörnsson, K., 2005. Conflicting demands on wetland ecosystem services: nutrient retention, biodiversity or both? Freshwater Biology 50 (4), 705–714.
House, W.A., 2003. Geochemical cycling of phosphorus in rivers. Appl. Geochem. 18, 739–748.
Jacobs, L., Emerson, S., Skei, J., 1985. Partitioning and transport of metals across the O2H2S interface in a permanently anoxic basin: Framvaren Fjord, Norway. Geochim. Cosmochim. Acta 49, 1433–1444.
Jiann, K.T., Wen, L.S., Santschi, P.H., 2005. Trace metal (Cd, Cu, Ni and Pb) partitioning, affinities and removal in the Danshuei River estuary, a macro-tidal, temporally anoxic estuary in Taiwan. Mar. Chem. 96 (3–4), 293–313.
Joung, D.-J., Shiller, A.M., 2014. Dissolved barium behavior in Louisiana Shelf waters affected by the Mississippi/Atchafalaya River mixing zone. Geochim. Cosmochim. Acta 141, 303–313.
Joung, D.-J., Shiller, A.M., 2016. Temporal and spatial variations of dissolved and colloidal trace elements in Louisiana Shelf waters. Mar. Chem. 181, 25–43.
Johnson, C.A., Sigg, L., Lindauer, U., 1992. The chromium cycle in a seasonally anoxic lake. Limnol. Oceanogr. 37, 315–321.
Junk, W.J., Bayley, P.B., Sparks, R.E., 1989. The flood pulse concept in river-floodplain systems. Can. Spec. Publ. Fish. Aquat. Sci. 106, 110–127.
Kerr, S.C., Shafer, M.M., Overdier, J., Armstrong, D.E., 2008. Hydrologic and biogeochemical controls on trace element export from northern Wisconsin wetlands. Biogeochemistry 89, 273–294.
Khan, H., Brush, G.S., 1994. Nutrient and metal accumulation in a freshwater tidal marsh. Estuaries 17, 345–360.
Kinsman-Costello, L.E., Hamilton, S.K., O'Brien, J.M., Lennon, J.T., 2016. Phosphorus release from the drying and reflooding of diverse shallow sediments. Biogeochemistry 130 (1–2), 159–176.
Küchler, I.L., Miekeley, N., Forsberg, B.R., 1994. Molecular mass distributions of dissolved organic carbon and associated metals in waters from Rio Negro and Rio Solimões. Sci. Total Environ. 156, 207–216.
Lambou, V.W., Hern, S.C., 1983. Transport of organic carbon in the Atchafalaya Basin, Louisiana. Hydrobiologia 98, 25–34.
Lane, R.R., Day, J.W., Marx, B., Reves, E., Kemp, G.P., 2002. Seasonal and spatial water quality changes in the outflow plume of the Atchafalaya River, Louisiana, USA. Estuaries 25, 30–42.
Lindau, C., Delaune, R., Scaroni, A., Nyman, J., 2008. Denitrification in cypress swamp within the Atchafalaya River Basin, Louisiana. Chemosphere 70, 886–894.
Mays, P., Edwards, G., 2001. Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. Ecol. Eng. 16, 487–500.
Means, J.L., Crerar, D.A., Borcsik, M.P., Duguid, J.O., 1978. Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments. Geochim. Cosmochim. Acta 42, 1763–1773.
Mora, A., Baquero, J.C., Alfonso, J.A., Pisapia, D., Balza, L., 2010. The Apure River: Geochemistry of major and selected trace elements in an Orinoco River tributary coming from the Andes, Venezuela. Hydrol. processes 24, 3798–3810.
Mulholland, P.J., 1981. Organic carbon flow in a swamp-stream ecosystem. Ecol. Monogr., 307–322
Noe, G.B., Hupp, C.R., 2007. Seasonal variation in nutrient retention during inundation of a short-hydroperiod floodplain. River Res. Appl. 23, 1088–1101.
Olivie-Lauquet, G., Gruau, G., Dia, A., Riou, C., Jaffrezic, A., Henin, O., 2001. Release of trace elements in wetlands: role of seasonal variability. Water Res. 35, 943–952.
Pokrovsky, O., Schott, J., 2002. Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). Chem. Geol. 190, 141–179.
Rabalais, N., Diaz, R., Levin, L., Turner, R., Gilbert, D., Zhang, J., 2010. Dynamics and distribution of natural and human-caused hypoxia. Biogeosciences 7, 585–619.
Reiman, J.H., Xu, Y.J., He, S., DelDuco, E.M., 2018. Metals geochemistry and mass export from the Mississippi-Atchafalaya River system to the Northern Gulf of Mexico. Chemosphere 205, 559–569.
Rennert, T., Rinklebe, J., 2010. Release of Ni and Zn from contaminated floodplain soils under saturated flow conditions. Water, Air, Soil, and Pollution 205, 93–105.
Roden, E.E., Wetzel, R.G., 1996. Organic carbon oxidation and suppression of methane production by microbial Fe (III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. Limnol. Oceanogr. 41 (8), 1733–1748.
Rücker, K., Schrautzer, J., 2010. Nutrient retention function of a stream wetland complex—A high-frequency monitoring approach. Ecol. Eng. 36, 612–622.
Sabo, M.J., Bryan, C.F., Kelso, W.E., Rutherford, D.A., 1999. Hydrology and aquatic habitat characteristics of a riverine swamp: II. Hydrology and the occurrence of chronic hypoxia. Regul. Rivers: Res. Manage. 15, 525–544.
Scaroni, A.E., Lindau, C.W., Nyman, J.A., 2010. Spatial variability of sediment denitrification across the Atchafalaya River Basin, Louisiana, USA. Wetlands 30, 949–955.
Scaroni, A.E., Nyman, J.A., Lindau, C.W., 2011. Comparison of denitrification characteristics among three habitat types of a large river floodplain: Atchafalaya River Basin, Louisiana. Hydrobiologia 658, 17–25.
Scott, D.T., Keim, R.F., Edwards, B.L., Jones, C.N., Kroes, D.E., 2014. Floodplain biogeochemical processing of floodwaters in the Atchafalaya River Basin during the Mississippi River flood of 2011. J Geophys Res-Biogeo 119 (4), 537–546.
Seyler, P.T., Boaventura, G.R., 2003. Distribution and partition of trace metals in the Amazon basin. Hydrol. processes 17, 1345–1361.
Shea, D., Helz, G.R., 1988. The solubility of copper in sulfidic waters: Sulfide and polysulfide complexes in equilibrium with covellite. Geochim. Cosmochim. Acta 52, 1815–1825.
Shen, Y., Fichot, C.G., Benner, R., 2012. Floodplain influence on dissolved organic matter composition and export from the Mississippi-Atchafalaya River system to the Gulf of Mexico. Limnol. Oceanogr. 57, 1149–1160.

Shiller, A.M., 1997. Dissolved trace elements in the Mississippi River: seasonal, interannual, and decadal variability. Geochim. Cosmochim. Acta 61, 4321–4330.
Shiller, A.M., 2002. Seasonality of dissolved rare earth elements in the lower Mississippi River. Geochem. Geophys. Geosyst. 3, 1–14.
Shiller, A.M., 2003. Syringe filtration methods for examining dissolved and colloidal trace element distributions in remote field locations. Environ. Sci. Technol. 37, 3953–3957.
Shiller, A.M., Stephens, T.H., 2005. Microbial manganese oxidation in the lower Mississippi River: methods and evidence. Geomicrobiol. J. 22, 117–125.
Shim, M.J., Cai, Y., Guo, L., Shiller, A., 2017. Floodplain Effects on the Transport of Dissolved and Colloidal Trace Elements in the East Pearl River, Mississippi. Hydrolog. Proce. 31, 1086–1099. https://doi.org/10.1002/hyp.11093.
Stolpe, B., Guo, L., Shiller, A.M., Hassellöv, M., 2010. Size and composition of colloidal organic matter and trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as characterized by flow field-flow fractionation. Mar. Chem. 118, 119–128.
Strauss, J., Grossman, E.L., DiMarco, S.F., 2012. Stable isotope characterization of hypoxia-susceptible waters on the Louisiana shelf: Tracing freshwater discharge and benthic respiration. Cont. Shelf Res. 47, 7–15.
Strohm, T.O., Griffin, B., Zumft, W.G., Schink, B., 2007. Growth yields in bacterial denitrification and nitrate ammonification. Appl. Environ. Microbiol. 73, 1420–1424.
Tockner, K., Malard, F., Ward, J.V., 2000. An extension of the flood pulse concept. Hydrolog. Proce. 14 (16–17), 2861–2883.
Tribovillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and paleoproductivity proxies: an update. Chem. Geol. 232, 12–32.
Turner, R.E., Rabalais, N.N., 1991. Changes in mississippi river water quality this century. Bioscience 41, 140–147.
Turner, R.E., Rabalais, N.N., Alexander, R.B., McIsaac, G., Howarth, R.W., 2007. Characterization of nutrient, organic carbon, and sediment loads and concentrations from the Mississippi River into the northern Gulf of Mexico. Estuaries and Coasts 30, 773–790.
Verhoeven, J.T.A., Arheimer, B., Yin, C., Hefting, M.M., 2006. Regional and global concerns over wetlands and water quality. Trends Ecol. Evol. 21, 96–103.
Viers, J., Barroux, G., Pinelli, M., Seyler, P., Oliva, P., Dupré, B., Boaventura, G.R., 2005. The influence of the Amazonian floodplain ecosystems on the trace element dynamics of the Amazon River mainstem (Brazil). Sci. Total Environ. 339, 219–232.
Viers, J., Dupré, B., Braun, J.-J., Deberdt, S., Angeletti, B., Ngoupayou, J.N., Michard, A., 2000. Major and trace element abundances, and strontium isotopes in the Nyong basin rivers (Cameroon): constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments. Chem. Geol. 169, 211–241.
Viers, J., Dupré, B., Polvé, M., Schott, J., Dandurand, J.-L., Braun, J.-J., 1997. Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon): comparison between organic-poor and organic-rich waters. Chem. Geol. 140, 181–206.
Weis, J.S., Weis, P., 2004. Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. Environ. Int. 30, 685–700.
Withers, P.J.A., Jarvie, H.P., 2008. Delivery and cycling of phosphorus in rivers: a review. Sci. Total Environ. 400, 379–395.
Xu, Y.J., 2006. Organic nitrogen retention in the atchafalaya river swamp. Hydrobiologia 560, 133–143.
Zachara, J.M., Fredrickson, J.K., Smith, S.C., Gassman, P.L., 2001. Solubilization of Fe (III) oxide-bound trace metals by a dissimilatory Fe(III) reducing bacterium. Geochim. Cosmochim. Acta 65, 75–93.