

Article

Dissolved Carbon Transport and Processing in North America's Largest Swamp River Entering the Northern Gulf of Mexico

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Received: 21 April 2019; Accepted: 4 July 2019; Published: 7 July 2019



Abstract: Transport and transformation of riverine dissolved carbon is an important component of global carbon cycling. The Atchafalaya River (AR) flows 189 kilometers through the largest bottomland swamp in North America and discharges ~25% of the flow of the Mississippi River into the Gulf of Mexico annually, providing a unique opportunity to study the floodplain/wetland impacts on dissolved carbon. The aim of this study is to determine how dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in the AR change spatially and seasonally, and to elucidate which processes control the carbon cycling in this intricate swamp-river system. From May 2015 to May 2016, we conducted monthly river sampling from the river's inflow to its outflow, analyzing samples for concentrations and $\delta^{13}\text{C}$ stable isotope composition of DOC and DIC. We found that DIC concentrations in the AR were three times higher than the DOC concentrations on average, and showed more pronounced downstream changes than the DOC. During the study period, the river discharged a total of 5.35 Tg DIC and a total of 2.34 Tg DOC into the Gulf of Mexico. Based on the mass inflow–outflow balance, approximately 0.53 Tg (~10%) of the total DIC exported was produced within the floodplain/wetland system, while 0.24 Tg (~10%) of the DOC entering the basin was removed. The AR's water was consistently oversaturated with CO_2 partial pressure ($p\text{CO}_2$) above the atmospheric $p\text{CO}_2$ (with $p\text{CO}_2$ varying from 551 μatm to 6922 μatm), indicating a large source of DIC from river waters to the atmosphere as well as to the coastal margins. Largest changes in carbon constituents occurred during periods of greatest inundation of the swamp-river basin and corresponded with shifts in isotopic composition. This effect was particularly pronounced during the initial flood stages, supporting the hypothesis that subtropical floodplains can act as effective enhancers of the biogeochemical cycling of dissolved carbon.

Keywords: carbon biogeochemistry; dissolved organic carbon; dissolved inorganic carbon; swamp-river wetlands; floodplains; $p\text{CO}_2$; Mississippi–Atchafalaya Rivers

1. Introduction

Large rivers play an important role in the global carbon cycling, acting not only as conduits of terrestrial carbon from land to sea, but also as active systems for carbon transformation and processing [1,2]. Riverine dissolved carbon has two primary forms: Dissolved organic carbon (DOC), which includes decaying organic material ($<0.45\ \mu\text{m}$) varying greatly in molecular weight and bioavailability; and dissolved inorganic carbon (DIC), which is the sum of inorganic carbon (CO_2 , CO_3^{2-} , and HCO_3^-) and is derived largely from aerobic respiration (both in runoff from soil and as an in-stream process) and mineral weathering [3]. Recent studies found that wetlands in tropical

floodplains of the central Amazon [4] and Zambezi River basin [5] contributed large inputs of inorganic carbon into the river waters, while other studies have demonstrated varying effects of floodplain interactions on DOC [6–8]. It is, however, not yet clear to what degree extensive floodplains in temperate and subtropical regions affect riverine dissolved carbon fluxes.

Riverine DOC is often partly mineralized in-stream to produce DIC. DIC can be taken up through photosynthesis to produce new organic matter, or can be lost or gained through atmospheric exchange. River systems have been reported to discharge annually a total of 0.17 to 0.78 Pg DOC [9–13] and 0.38 to 2.6 Pg DIC into the world's oceans [13–16]. At the same time, a global net evasion of CO₂ from all fluvial sources to the atmosphere has been estimated to range from 0.26–1.8 Pg C each year [2,17–21]. These large variations of riverine dissolved carbon fluxes demonstrate that, while it has been widely acknowledged that the quality and quantity of endmember carbon exported from rivers to oceans can have profound effects on the carbon cycling in coastal ecosystems, many measurement gaps and uncertainties exist in current estimates of carbon exports for many coastal rivers in the world.

The Mississippi–Atchafalaya River System is the largest river system in North America, draining over 3 million km² land. Together, these two rivers discharged an annual volume of 673 km³ yr^{−1} (MR: 474 km³, [22]; AR: 199 km³, [23]) over the past two decades, contributing nearly 90% of the total flow from the continental United States to the Northern Gulf of Mexico (NGOM). Many estimates have been made regarding the quantity of dissolved carbon exported from this system, and these estimates vary largely among studies. For instance, estimates for DOC export from the Mississippi River (MR) ranged from 1.51 to 3.48 Tg yr^{−1} [24–26], and for DIC from 13.5 Tg yr^{−1} to 18.8 Tg yr^{−1} [24,27,28], but these estimates do not account for the portion of the MR diverted through the AR. Estimates for DOC from the Atchafalaya River (AR) fluctuated from 0.76 to 1.33 Tg yr^{−1} [26,29]. Direct sampling for DOC in the AR's main channel (rather than in its bay, where organic matter may undergo rapid change) has not been recently conducted, so characterization of these fluxes in light of increased mobilization of carbon to rivers in recent years [30] is critical. Currently, to the best of our knowledge, no report exists concerning DIC export from the AR.

Most organic carbon exported in rivers is allochthonous material that is rapidly consumed in headwater streams [31]. Once DOC is mineralized in a fluvial environment, byproducts (CO₂ and CH₄) are emitted from the surface waters to the atmosphere, so that remaining DOC in larger higher-order rivers is generally expected to be older, less labile, higher molecular weight material [32]. The Lower Mississippi River receives highly degraded remnants of organic matter input from its many tributaries. This leads one to expect that the lower MR's and AR's DOC will remain largely unaltered as it finishes its journey to the NGOM. However, most carbon flux estimates for large rivers, including the Mississippi River, are based on measurements within a confined channel often hundred kilometers upstream of the rivers' mouth, limiting our knowledge of the potential extent of dissolved carbon transformation through natural floodplains in lower river basins and their coastal margins.

The Atchafalaya River carries approximately 25% of the flow of the Mississippi River and the total flow of the Red River to the NGOM. The AR is a unique system of high interest because it is the fifth largest river by volume in North America and is highly connected to a large and unconfined floodplain, passing through the largest intact freshwater swamp in the continent. The AR shows higher rates of sediment trapping [23,33] and organic nitrogen removal than the lower reach of the levee-confined Mississippi River due to its unique hydrology [34–36], suggesting that the AR's high connectivity with its basin can also provide necessary time and space for the carbon cycling to occur. Annual mass load of organic carbon in the AR decreases from origin to outlet [29,37], and the endmember dissolved organic matter in the AR is compositionally different from that of the MR [29], indicating biogeochemical processing of riverine carbon in this system. However, uncertainties remain as to the specific effects of extensive floodplain interactions on instream carbon dynamics in this unique system, and what processes lay behind the observed organic carbon compositional shifts and total mass reduction.

Riverine stable carbon isotope analysis, which describes the ratio of ¹³C/¹²C in a sample of water, is useful in identifying the major sources of dissolved carbon as it interacts with the atmosphere, sediment,

and biosphere; isotopic constraining of carbon sources and in-stream processing provides insight regarding the origin and quality of carbon constituents. Carbon derived from the atmosphere, various plant production pathways, and different mineral origins all possess unique $\delta^{13}\text{C}$ signatures [38–41]. Within aquatic systems, the $\delta^{13}\text{C}$ signatures of terrestrially derived carbon sources are impacted by riverine biogeochemical processes. For example, photosynthesis and atmospheric degassing preferentially remove ^{12}C [42], which leaves the remaining aquatic carbon pool enriched in ^{13}C , resulting in a positive shift in $\delta^{13}\text{C}$ values; meanwhile respiration processes result in ^{13}C uptake by organisms and subsequently more negative isotope values in the water column [25]. Studying the isotopic composition of dissolved carbon in the AR may provide useful insight into potential sources and processes responsible for dissolved carbon constituents entering the Atchafalaya River Basin, reflecting water quality and ecological functioning. Furthermore, downstream changes in $\delta^{13}\text{C}$ values will help to indicate floodplain contributions to riverine dissolved carbon cycling.

To better understand the effects of river floodplains on carbon transport, transformation, and retention, we conducted a series of water sampling and in situ measurements along the Atchafalaya River during a 13-month period, providing much needed data covering a wide range of temperature, flow, and floodplain-river hydraulic connectivity conditions. The study addresses two important unanswered questions: 1) How DIC and DOC concentrations and loads in the AR fluctuate spatially and seasonally, and 2) what factors and processes most likely control this spatiotemporal variability. The primary goal of the study is to test the hypothesis that floodplain interactions in the Atchafalaya River Basin are related with enhanced opportunities for carbon cycling, resulting in net removal of dissolved organic material and production of inorganic carbon. Since the mineralization of organic carbon is closely tied to the production of dissolved inorganic carbon, studying DIC and DOC concentrations and fluxes together with $\delta^{13}\text{C}$ isotopes in the AR may provide new insights into the role of floodplains in riverine carbon processing. If this corridor wetland basin effectively removes riverine organic carbon as well as nutrients and sediment, thorough investigation of how and why this removal occurs may have future management implications for the lower MR and NGOM. Additionally, this study provides much needed estimates of dissolved carbon fluxes from the AR during a 13-month period with abnormally high discharge, which may offer insight into the response of riverine carbon to climate extremes in the light of global climate change.

2. Methods

2.1. Study Area

This study was conducted in the Atchafalaya River Basin (Figure 1), North America's largest freshwater swamp with extensive braided channels and river corridor wetlands. Five hundred river kilometers from its outlet to the Gulf of Mexico, approximately 25% of the Mississippi River's flow is diverted into a large distributary, which joins the Red River (RR) to form the Atchafalaya River. The AR travels southward for ~225 km before entering into the NGOM through two outlets: Morgan City and Wax Lake Outlet. The former is a natural channel which delivers approximately 60% of the AR's water to the Gulf, while the latter was constructed in 1942 to redirect the remaining flow away from Morgan City as a flood control measure. Although the AR is strictly confined by levees in its first 110 km, they later open up to span 35 km across, allowing the river to meander and braid extensively throughout the largest intact wetland forest in North America, spanning 120 km from upstream to downstream. Soils in the basin are a complex amalgamation of soils carried and deposited by the MR and RR from over 30 different states and 2 Canadian provinces, with large amounts of new sediment accretion occurring annually in the basin's abundant low-lying areas with high hydraulic connectivity [34].

The Atchafalaya River Basin (ARB) contains a 2571 km² floodway system which is frequently inundated to varying degrees by constant naturally occurring overbank flow [43]. The majority of the overbank flow occurs to the east of the river in the Buffalo Cove and Fordoche subunits, which mimic seasonal water-patterns of the main channel. In contrast, much of the basin to the

west of the river (Pat Bay subunit) remains relatively isolated from the flow of the main channel, with extent of flooding primarily determined by the local precipitation events [44]. Unpredictable flooding has excluded human development within the basin, allowing for a rich and diverse mosaic of wetland and bottomland hardwood ecosystems. The AR's discharge is seasonally driven, with flows generally increasing in winter, cresting in late spring or early summer, and diminishing sharply in late summer and fall [36,44]. Periods of typical high discharge are associated with the greatest inter-annual variability of discharge [37]. Likewise, floodplain inundation can vary immensely annually and inter-annually, resulting in complex seasonal and spatial variation in water residence times and sediment deposition [23].

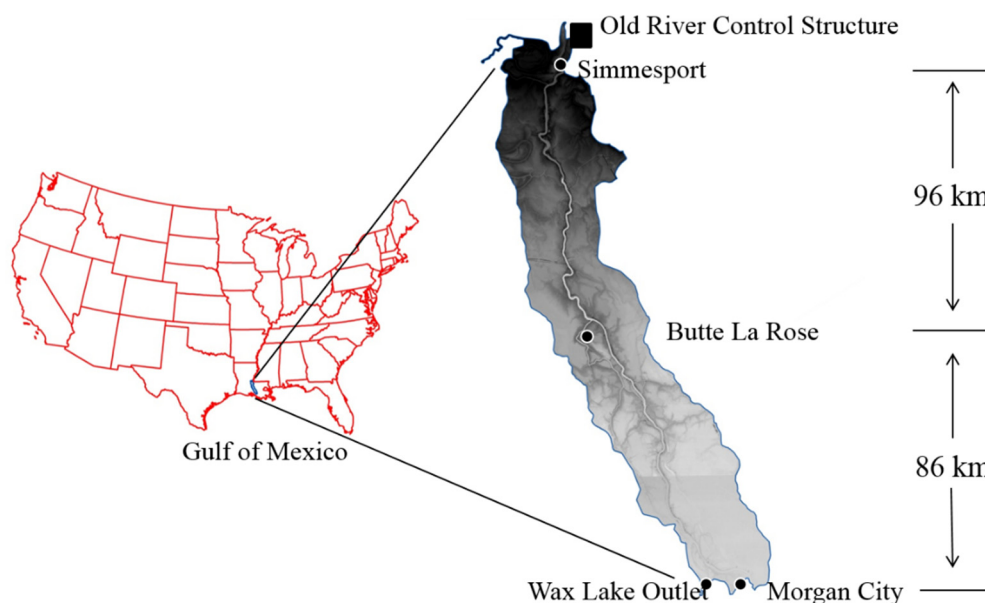


Figure 1. Geographical location of the Atchafalaya River Basin to the Northern Gulf of Mexico in the southern United States. The river carries ~25% of the Mississippi River's water diverted by the Old River Control Structure and the entire flow of the Red River, forming the North America largest river swamp. In this study three sampling sites were chosen for in situ measurements and water sampling: Simmesport (30°58'05.9"N, 91°48'26.2"W) being upstream and two outlets downstream at Wax Lake Outlet and Morgan City (29°42'03.2"N, 91°22'17.6"W; 29°41'50.5"N, 91°12'41.9"W, respectively).

2.2. River Water Measurement and Sampling

From May of 2015 through May of 2016, 13 sampling events were conducted, taking place at monthly intervals covering a range of flow conditions at three sites along the Atchafalaya River: Simmesport, Wax Lake Outlet, and Morgan City, located, respectively, 7.9 km and 189.4 km (both outlet location) southwest of the Old River Control Structure (ORCS). Prior to reaching Butte la Rose, the AR is strictly confined; after that point, in its last 90 km, the AR is heavily braided throughout a wide floodplain (Figure 1).

During each monthly sampling event, ambient parameters including dissolved oxygen (DO), pH, temperature, and specific conductance were measured and recorded using a YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA) at each location. Additionally, surface water samples were collected at each site from the depth of 30–50 cm below water surface using an extendable sampler. Although the chemical constituents in fast-flowing waters of the AR are uniformly mixed [45], three samples were collected for each constituent to be analyzed and mixed to ensure a representative composite sample. DOC samples were collected in acid-washed, stream-rinsed HDPE bottles. Samples to be analyzed for DIC were placed in 20 mL glass vials without headspace and sealed with PTFE/butyl rubber septa to protect against perturbation and gas exchange, and immediately placed on ice along

with samples to be analyzed for DOC. Duplicate samples were collected at one site per trip for quality control purposes. All samples were stored in coolers with wet ice during transportation; DIC samples were refrigerated until chemical analysis, while DOC samples were filtered and frozen immediately upon return from sampling.

2.3. Water Sample Analysis

Upon returning to the lab, samples to be analyzed for DOC were filtered using 0.2 µm nylon syringe filters (Environmental Express, Charleston, SC, USA) and frozen until analysis. DOC and DIC samples were shipped in insulated coolers filled with blue ice packs overnight to the University of California Davis Stable Isotope Facility for analysis.

DIC samples were analyzed for ^{13}C as well as concentration by trace gas using a GasBench II system interfaced to a Delta V Plus IRMS (isotope ratio mass spectrometer) (Thermo Scientific, Bremen, Germany). Samples were injected into septum-capped vials containing 85% phosphoric acid, converting DIC to gaseous CO_2 , which was then transferred to an IRMS via a helium carrier stream to determine concentrations and isotopic composition against a set of known standards. Precision of measurements was better than 0.1%.

Filtered DOC samples were analyzed using an O.I. Analytical Model 1030 TOC Analyzer (OI Analytical, College Station, TX, USA) interfaced to a PDZ Europa 20-20 IRMS (Sercon Ltd., Cheshire, UK). Samples were acidified and purged with helium to remove DIC. Samples were reacted with sodium persulfate to convert DOC into CO_2 , which was transferred to an IRMS in a helium flow for determination of isotopic composition. Samples were run against potassium hydrogen phthalate references, which were used as a calibration curve, with a precision of measurements better than 0.4%. Error for DOC and DIC concentration calculations was better than 5%.

Stable isotope values are expressed as deviations per mil (‰) from Vienna Pee Dee Belemnite (VPDB), a standard reference material based on the ratio of $^{13}\text{C}/^{12}\text{C}$ found in a highly ^{13}C -rich belemnite fossil according to the formula:

$$\delta^{13}\text{C} \text{ ‰} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

where R is the ratio of the numbers (n) of the heavy and light isotope of a carbon ($^{13}\text{C}/^{12}\text{C}$) in the sample and the reference [46].

2.4. Mass Flux Calculation, $p\text{CO}_2$ Calculation, and Data Analysis

Mass fluxes of DOC and DIC into and out of the Atchafalaya River basin were estimated using their concentrations and river discharge at Simmesport (i.e., input), Morgan City, and Wax Lake Outlet (i.e., output). Daily river discharge data from 1 May 2015 to 31 May 2016 were collected from the U.S. Geological Survey (USGS) monitoring stations, namely 07,381,490 (Simmesport), 07,381,590 (Wax Lake Outlet), and 07,381,600 (Morgan City). On days without discharge records because of equipment malfunction, the missing data were filled using a linear interpolation. Daily discharge at each site was multiplied by DIC and DOC concentrations measured at corresponding locations in order to determine daily, monthly, and period-total DIC and DOC mass load estimates at each location. For dates between sampling events, DIC and DOC concentrations were assigned as the reported value of the nearest sampling event. This approach is based on the assumption that the DIC and DOC concentration measurements are representative for the corresponding month. While this approach is widely used in mass flux calculation for large rivers, certain error exists in the estimation. In order to provide further accountability for estimates, we also calculated the mass loading for the period using an additional common method wherein the flow-weighted average concentrations for DOC and DIC at each site were multiplied by corresponding total discharge for the period.

The partial pressure of carbon dioxide in water was calculated according to the method shown by Cai and Wang [47], which uses DIC concentration and measured pH data in the equation:

$$p\text{CO}_2 = \frac{[\text{CO}_2]}{K_H} = \frac{C_T \{H\}^2}{(\{H\}^2 + \{H\}K_1 + K_1K_2)K_H} \quad (2)$$

where C_T is the measured DIC value, $\{H\} = 10^{-\text{pH}}$, K_H is the solubility constant [48], and K_1 and K_2 are the dissociation constants of carbonic acid. Since sampled waters possessed salinity measurements of less than 0.2, the K_1 and K_2 of Harned and Davis [49] and Harned and Scholes [50] were used, respectively, for salinities near 0. K_H , K_1 , and K_2 are all adjusted for absolute temperature.

A mass balance of DIC and DOC for the AR basin was established based on their input at Simmesport and combined output at Wax Lake Outlet and Morgan City. The monthly input–output change in mass is considered as the basin’s contribution to dissolved carbon dynamics. Regression analysis was performed to assess various relationships of DIC and DOC concentrations and fluxes with the ambient conditions. Paired t-tests were used to identify downstream changes in chemical constituents from Simmesport to each outlet location using an alpha value of 0.05. Statistical analyses were performed with SAS 9.4 Statistical Software Package (SAS Institute, Cary, NC, USA).

3. Results

3.1. River Ambient Conditions

Mean ($\pm$ SD) daily discharge at Simmesport reported during this 13-month study (1 May 2015 to 31 May 2016) was $8902 \pm 3885 \text{ m}^3 \text{ s}^{-1}$, falling as low as $2166 \text{ m}^3 \text{ s}^{-1}$ in late October and reaching a maximum rate of $17,443 \text{ m}^3 \text{ s}^{-1}$ in mid-January (Figure 2). Mean daily discharge at Wax Lake Outlet was $3983 \pm 1572 \text{ m}^3 \text{ s}^{-1}$, ranging from 529 to $6956 \text{ m}^3 \text{ s}^{-1}$, and mean daily discharge at Morgan City outlet was $4772 \pm 2112 \text{ m}^3 \text{ s}^{-1}$, fluctuating from 571 to $11,114 \text{ m}^3 \text{ s}^{-1}$. Total water volume passing through Simmesport during the study period was approximately 305 km^3 . The flow was slightly higher than the combined outflow from Wax Lake Outlet and Morgan City (300 km^3). On average ($\pm 2.6\%$), Wax Lake Outlet and Morgan City distributed 45.5% and 54.5% of the AR’s flow into the NGOM, respectively.

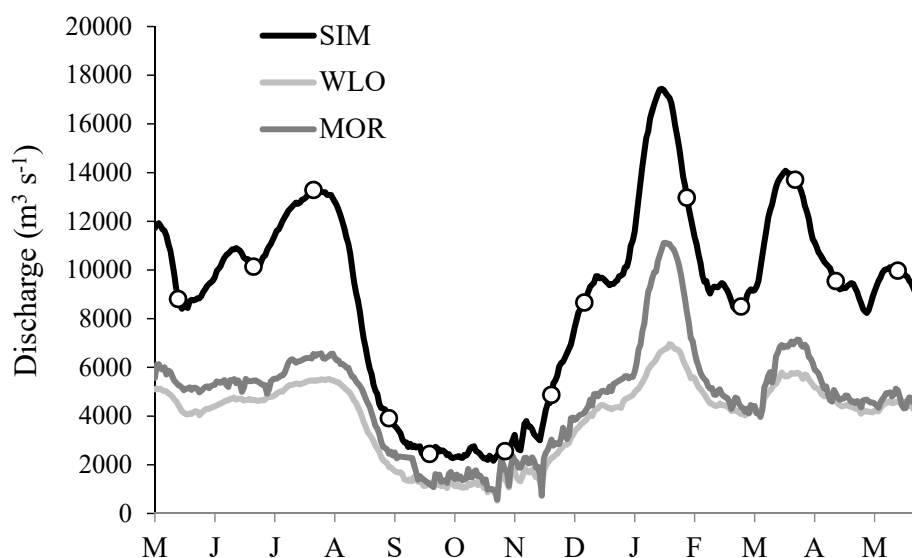


Figure 2. Daily discharge at Simmesport (inflow, SIM), Wax Lake Outlet (outflow, WLO), and Morgan City (outflow, MOR) from 1 May 2015–31 May 2016. Markers indicate discharge at Simmesport during each sampling event. Discharge data were obtained from the USGS National Water Information System Web Interface (<http://waterdata.usgs.gov/nwis>).

For the sake of comparison to average annual flow, average flow for the 12-month period from 1 May 2015 to 30 April 2015 was $8854 \pm 4026 \text{ m}^3 \text{ s}^{-1}$, which was about 35% higher than the long-term (1978–2004) annual average ($6547 \text{ m}^3 \text{ s}^{-1}$) reported by Xu [37], and also exceeded values reported by the USGS for water years 2010–2015 which averaged $6187 \text{ m}^3 \text{ s}^{-1}$ (with yearly averages ranging from 4967 to $7229 \text{ m}^3 \text{ s}^{-1}$).

Mean daily discharge rates varied somewhat dramatically by season. Lowest average daily flows at Simmesport occurred throughout fall ($3126 \text{ m}^3 \text{ s}^{-1}$), followed by summer ($10,401 \text{ m}^3 \text{ s}^{-1}$) and spring ($10,619 \text{ m}^3 \text{ s}^{-1}$), with highest average daily flow occurring in winter ($11,234 \text{ m}^3 \text{ s}^{-1}$). The seasonal fluctuation was similar to the long-term seasonality of discharge from the Mississippi–Atchafalaya River System.

Average temperature recorded during the sampling trips across all three AR sites was $20.5 \text{ }^\circ\text{C}$ (± 7), with individual measurements ranging from 8.1 to $29.9 \text{ }^\circ\text{C}$ throughout the year. Dissolved oxygen (mg L^{-1}) also showed great variation, with a mean value of 7.4 (± 3.1), ranging from 3.3 to 15.6 mg L^{-1} . These two variables showed obvious seasonal trends which mirrored one another (Figure 3), and showed strong negative correlation ($R^2 = 0.79$, $p < 0.001$). pH showed some variation throughout the year (7.7 ± 0.3), with increase occurring from August to October (see Table S1, Supplementary Materials). No significant differences in in-stream conditions were found among the sampling sites.

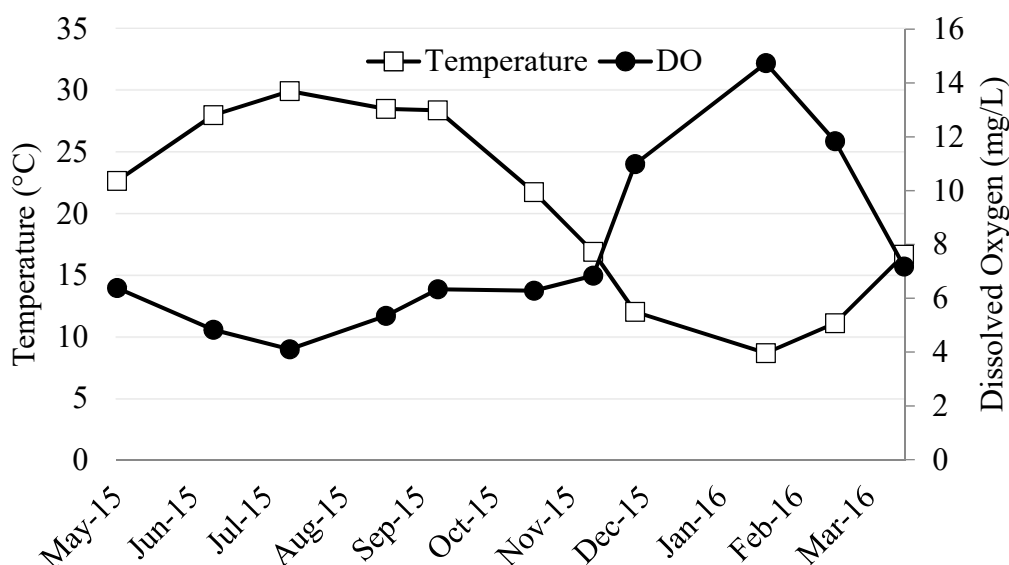


Figure 3. Average temperature and dissolved oxygen concentration fluctuations in the Atchafalaya River (AR) from May 2015 to May 2016.

3.2. Dissolved Inorganic Carbon Concentrations, $p\text{CO}_2$, and $\delta^{13}\text{C}_{\text{DIC}}$

Measured DIC concentrations in the Atchafalaya River's main stem (with all sites included) averaged 1579 (± 521) $\mu\text{mol L}^{-1}$ during the sampling period. All sites showed the same seasonal trend of peak concentrations in late summer and fall, and steady decrease before rising again in late spring (Table 1). This pattern demonstrates the negative correlation between DIC concentrations and riverine discharge, with dilution occurring during spring and winter floods, and higher concentrations occurring during low flow.

DIC concentrations in the Atchafalaya River's main stem tended to increase from origin to outlets (Table 1). However, changes in the concentration were not found to be statistically significant ($\alpha = 0.05$) between Simmesport and Wax Lake ($p = 0.17$, $t = -1.46$) or between Simmesport and Morgan City ($p = 0.13$, $t = 1.61$). Flow-weighted average DIC concentrations (reported in $\mu\text{mol L}^{-1}$ with) at Simmesport, Wax Lake Outlet, and Morgan City were 1175, 1291, and 1284, respectively. Downstream

increases were especially apparent in October and December. Only samples collected in August, September, and February showed slight decreases in DIC concentrations downstream.

Table 1. Dissolved inorganic carbon (DIC) concentrations ($\mu\text{mol L}^{-1}$) and $\delta^{13}\text{C}_{\text{DIC}}$ (‰ Vienna Pee Dee Belemnite (VPDB)) at Simmesport, Wax Lake Outlet, and Morgan City during the 13 sampling events.

Sampling Event	Simmesport		Wax Lake Outlet		Morgan City Outlet	
	DIC	$\delta^{13}\text{C}_{\text{DIC}}$	DIC	$\delta^{13}\text{C}_{\text{DIC}}$	DIC	$\delta^{13}\text{C}_{\text{DIC}}$
5/13/2015	1289	−13.12	1480	−13.20	1485	−13.37
6/21/2015	1510	−14.58	1719	−13.85	1763	−14.26
7/22/2015	1730	−14.11	1884	−13.89	1898	−14.55
8/30/2015	2706	−11.56	2232	−11.12	2294	−12.51
9/20/2015	2508	−10.06	2416	−10.26	2372	−10.13
10/29/2015	1580	−12.19	2258	−12.05	2286	−12.10
11/22/2015	1107	−14.16	1283	−14.06	1297	−13.74
12/9/2015	972	−14.78	1326	−12.95	1497	−13.47
1/31/2016	n/a	n/a	n/a	n/a	n/a	n/a
2/28/2016	1428	−13.18	1366	−13.61	1307	−13.26
3/27/2016	672	−14.86	811	−14.37	835	−14.96
4/17/2016	1118	−16.19	1203	−15.54	1147	−15.60
5/19/2016	1239	−14.65	1264	−13.99	1317	−14.55

Throughout the sampling period, all sites exhibited CO_2 supersaturation with respect to the atmospheric CO_2 pressure (Figure 4). Calculated $p\text{CO}_2$ ranged from 551 μatm to 6922 μatm , with highest values in spring and summer months (particularly June 2015 and April 2016), and lower values throughout fall and winter. Spatially, although $p\text{CO}_2$ showed no statistically significant change from Simmesport to downstream locations at Wax Lake Outlet ($p = 0.16$, $t = 1.52$) or Morgan City ($p = 0.27$, $t = 1.19$), the highest $p\text{CO}_2$ values were recorded at the upstream location. While $p\text{CO}_2$ had no statistically significant relationship with DIC concentrations ($R^2 = 0.08$, $p = 0.12$), it showed a strong negative correlation with $\delta^{13}\text{C}_{\text{DIC}}$ ($R^2 = 0.34$, $p < 0.001$).

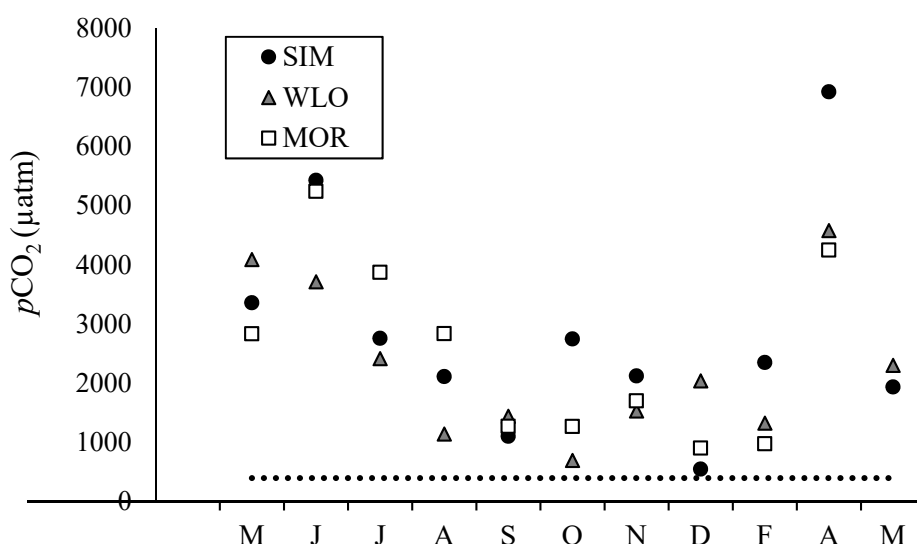


Figure 4. $p\text{CO}_2$ at the upstream (Simmesport) and downstream locations (Wax Lake Outlet and Morgan City, WLO and MOR) of the Atchafalaya River from May 2015 to May 2016 (no measurements from the 31 January 2016 and 27 March 2016 sampling events because of equipment malfunction). The dotted line represents atmospheric equilibrium.

$\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB) values followed a seasonal trend similar to that of DIC concentrations at all sites, with more positive values occurring in late summer and fall, and increasingly negative

values throughout winter (Table 1). Values ranged from -16.19‰ in April 2016 to -10.06‰ in October 2015. $\delta^{13}\text{C}_{\text{DIC}}$ values showed a significant positive shift from Simmesport to Wax Lake Outlet ($p = 0.04$, $t = 2.26$), but did not change significantly from Simmesport to the AR's outlet at Morgan City ($p = 0.63$, $t = 0.49$). Downstream changes were observed in winter through late summer (particularly in December), but little change was observed at downstream locations in fall months. $\delta^{13}\text{C}_{\text{DIC}}$ values showed a strong positive correlation with DIC concentrations ($R^2 = 0.64$, $p < 0.0001$), as well as a strong negative correlation with discharge at Simmesport ($R^2 = 0.57$, $p < 0.0001$).

3.3. Dissolved Organic Carbon Concentrations and $\delta^{13}\text{C}_{\text{DOC}}$

DOC concentrations in the AR were consistently lower than DIC concentrations. Concentrations of DIC were frequently double those of DOC, and were five times higher than DOC in September and October. DIC:DOC ratios (Figure 5) showed trends of increase with temperature and decrease with discharge ($R^2 = 0.28$, $p = 0.002$; $R^2 = 0.40$, $p < 0.001$). Throughout all sampling events and sites, DOC concentrations averaged $674 (\pm 218) \mu\text{mol L}^{-1}$. Mean DOC was lowest in warm summer months, peaked in the fall, and remained relatively high throughout cool months. Lowest concentrations were reported in October 2015 with a mean value of $281 \mu\text{mol L}^{-1}$, and highest concentrations were reported in November 2015 with a mean value of $1069 \mu\text{mol L}^{-1}$. Individual measurements ranged widely from 263 to $1172 \mu\text{mol L}^{-1}$ (site-specific DIC and DOC concentrations for each sampling event are located in Tables 1 and 2).

DOC concentrations did not show a consistent longitudinal trend ($f = 0.42$, $p = 0.74$), but did tend to decrease from the river's inflow to its outflow. Flow-weighted average DOC concentrations ($\mu\text{mol L}^{-1}$) at Simmesport, Wax Lake Outlet, and Morgan City were 745, 724, and 669, respectively. Overall, downstream changes in DOC concentration were slight compared to observed changes in DIC concentration.

$\delta^{13}\text{C}_{\text{DOC}}$ (‰ VPBD) values showed little variation, ranging from -28.98‰ to -26.76‰ and showed no identifiable spatial or seasonal trend, nor any relationship to DOC concentrations ($R^2 = 0.09$, $p = 0.06$). There were no significant changes observed in $\delta^{13}\text{C}_{\text{DOC}}$ values from Simmesport to downstream locations at Wax Lake Outlet ($p = 0.76$, $t = 0.30$) or the AR's outlet at Morgan City ($p = 0.80$, $t = 0.25$). $\delta^{13}\text{C}_{\text{DOC}}$ values were unrelated to any measured parameter.

Table 2. Dissolved organic carbon (DOC) concentrations ($\mu\text{mol L}^{-1}$) and $\delta^{13}\text{C}_{\text{DIC}}$ (‰ VPDB) at Simmesport, Wax Lake Outlet, and Morgan City during the 13 sampling events.

Sampling Event	Simmesport		Wax Lake Outlet		Morgan City Outlet	
	DOC	$\delta^{13}\text{C}_{\text{DOC}}$	DOC	$\delta^{13}\text{C}_{\text{DOC}}$	DOC	$\delta^{13}\text{C}_{\text{DOC}}$
5/13/2015	508	-27.67	786	-28.98	384	-26.76
6/21/2015	738	-28.43	601	-27.81	720	-28.10
7/22/2015	519	-27.68	548	-27.81	548	-27.93
8/30/2015	358	-28.15	511	-28.33	496	-28.02
9/20/2015	515	-28.79	522	-28.25	442	-29.41
10/29/2015	309	-27.67	270	-27.12	263	-26.99
11/22/2015	1111	-27.43	1172	-27.62	925	-27.67
12/9/2015	847	-27.78	828	-28.54	788	-28.59
1/31/2016	1087	-28.91	807	-28.34	810	-28.15
2/28/2016	635	-27.85	766	-27.90	743	-28.48
3/27/2016	949	-28.77	814	-28.85	724	-28.47
4/17/2016	731	-28.15	759	-28.08	712	-27.90
5/19/2016	692	-27.90	679	-28.16	687	-28.21
Mean	692	-28.09	697	-28.14	634	-28.05

3.4. Relations of DIC and DOC Concentrations with Water Temperature and Discharge

DIC concentrations appeared to be positively correlated with water temperature (Figure 5a), while DOC showed an inverse relationship. DOC showed a positive correlation with total discharge (discharge at Simmesport), while DIC's relationship was negative (Figure 5b). DIC:DOC ratios showed some increase from upstream to the downstream outlets (in 9 out of 12 cases), most notably in October.

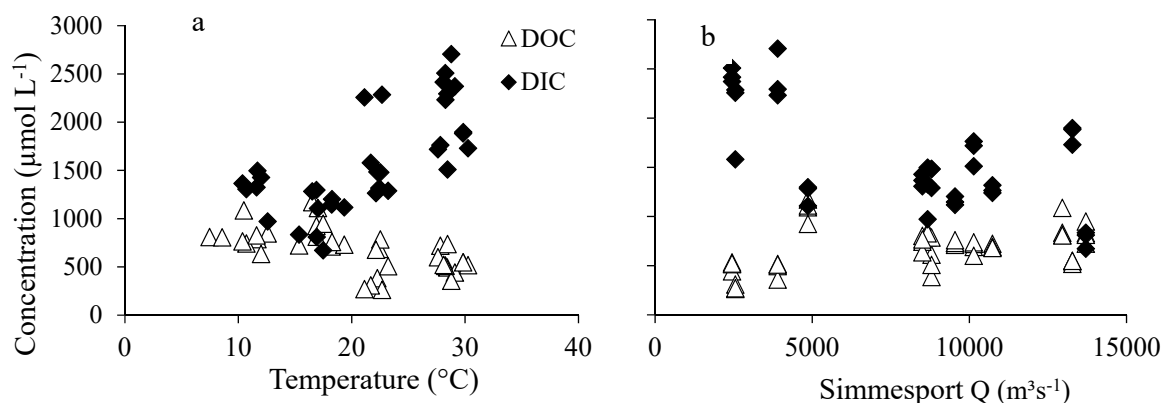


Figure 5. (a) Relationships between DOC concentration and water temperature ($y = -18.9x + 1061.9$, $p < 0.0001$, $R^2 = 0.34$) and DIC concentration and recorded water temperature ($y = 56.0x + 377.7$, $p < 0.0001$, $R^2 = 0.45$); (b) Relationships between DOC concentration and discharge at Simmesport ($y = 0.02x + 478.7$, $p = 0.01$, $R^2 = 0.17$) and DIC concentration and discharge at Simmesport ($y = -0.09x + 2293.7$, $p < 0.0001$, $R^2 = 0.41$).

Ratios of DIC:DOC in this system were highest in summer and early fall, lowest in cooler months and exhibited an inverse relationship to discharge trends ($R^2 = 0.40$, $p < 0.0001$). These ratios did not show a consistent spatial trend (Figure 6).

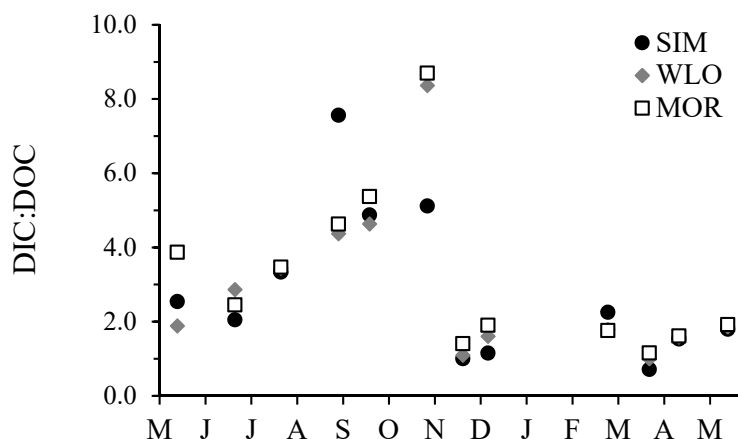


Figure 6. DIC:DOC ratios in the Atchafalaya River at its upstream location (Simmesport) and two outlets (Wax Lake Outlet and Morgan City) from May 2015 to May 2016 (no ratio is available for the sampling event on 31 January 2016).

3.5. DIC and DOC Mass Flux and Mass Balance

Over the 13-month sampling period, the Atchafalaya River delivered an estimated total of 5.346 Tg DIC and 2.473 Tg DOC into the Northern Gulf of Mexico. Both dissolved carbon species showed seasonal mass loading trends that closely followed the AR's hydrograph, with lowest export throughout the fall during low discharge, and peak export during high discharge in January. DOC and DIC mass

export both showed peaks during winter flooding, but in summer months, DIC mass load increases were more pronounced than DOC (Figure 7).

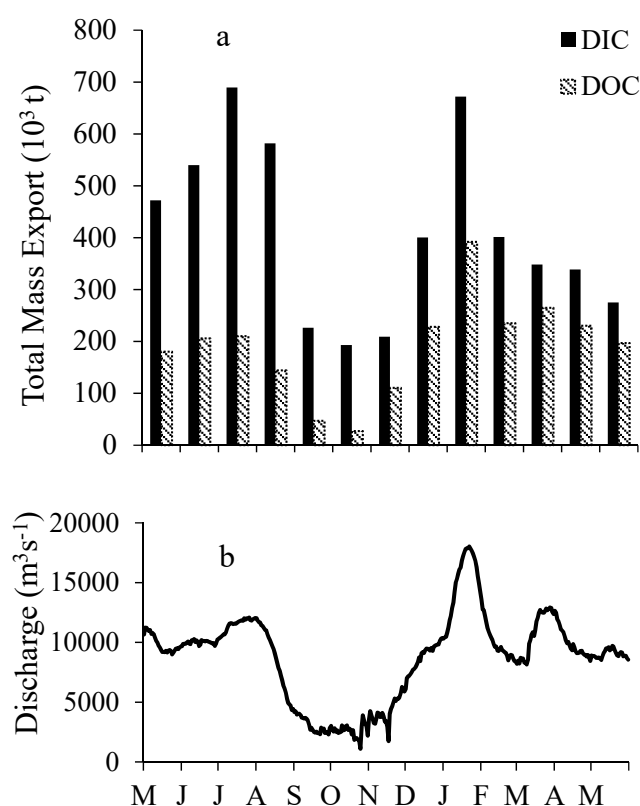


Figure 7. (a) Monthly mass export of DOC and DIC from the Atchafalaya River's two outlets, Wax Lake outlet and Morgan City, into the Northern Gulf of Mexico during the period from May 2015 to May 2016; (b) corresponding with daily combined average discharge from the two outlets.

Over the entire sampling period, an estimated 0.524 Tg of the total DIC discharged into the NGOM was produced within the Atchafalaya basin, and 0.243 Tg of the total DOC entering the basin was retained (Table 3). DIC mass load showed a net increase from origin to outlets in all but two months (February–March). DIC instream load increase was notably smallest from mid-summer to early fall, with largest mass load increases at the outflow occurring in December and January. Conversely, DOC mass load decreased from origin to outlets most months, with slight increases observed in May, and August–October (Figure 8).

Table 3. Summary of discharge (Q), DIC, and DOC mass flux and balance for the entire sampling period from 1 May 2015 to 31 May 2016. Negative values indicate loss from origin to outlet.

Location		Q (km^3)	DIC Load (Tg)	DOC Load (Tg)
Input	Simmesport	305.342	4.822	2.717
Output	Wax Lake	136.619	2.440	1.167
	Morgan City	163.694	2.905	1.307
	Combined	300.313	5.346	2.473
Balance	(Output–Input)	−5.030	0.524	−0.243

In order to provide further accountability for these estimates, we also calculated the mass loading of DIC and DOC for this study period using the flow-weighted average concentrations at each site

and their respective average discharges. This secondary method estimated that 4.644 Tg DIC and 2.504 Tg DOC were discharged into the NGOM by the AR's combined outlets. This method estimated that 0.076 Tg of the DOC entering the AR at Simmesport was retained by the basin, while 0.572 Tg of DIC were produced within the basin. Both methods agree that the AR acted as a sink for DOC, and a source for DIC. This method may be less accurate since it cannot account for relationships between concentrations and discharge.

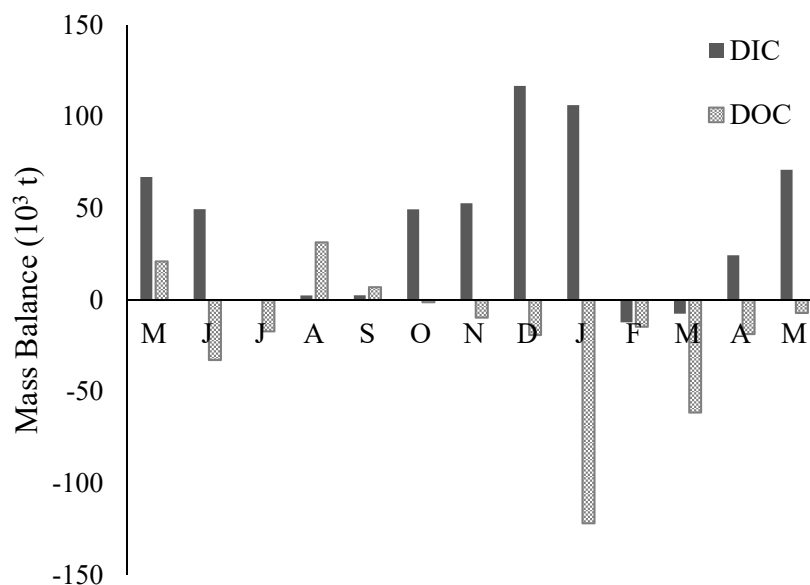


Figure 8. DIC and DOC monthly mass balance in the Atchafalaya River Basin (Mass Balance = monthly export from outlets – monthly input at Simmesport). Positive values indicate mass load increase from inflow to outflow.

4. Discussion

The results of this study indicate that the Atchafalaya River and its floodplain wetlands act as a significant source for dissolved inorganic carbon, both to coastal margins and to the atmosphere, as well as a potential sink for dissolved organic carbon. Throughout the study period, calculated mass loads of DIC increased significantly ($p < 0.01$) from the AR's origin to its combined outlets (Figure 8). Though not statistically significant at the $\alpha = 0.05$ level, our findings also clearly showed consistent increases in DIC concentrations from inlet to outlets, as well as increases in $p\text{CO}_2$, and significant changes in $\delta^{13}\text{C}_{\text{DIC}}$ values. Many factors may have contributed to this increase, but without additional research it is not possible to separate them. However, based on the strong seasonal signal of the observed trends, we draw several very likely inferences. First, we suggest that strong net heterotrophy in the river and its adjacent floodplains was responsible for some of the observed downstream increase in DIC during summer months. Second, we suggest that during periods of extensive floodplain inundation, the Atchafalaya's waters come into contact with large amounts of DIC stored in the river's floodplains as byproducts of soil and root respiration, the mineralization of labile organic matter within the basin, and direct inputs of CO_2 into the water column by wetland vascular plants, greatly increasing DIC mass loads at outlet locations.

4.1. Dissolved Inorganic Carbon Dynamics

The mineralization of organic matter to DIC through aerobic respiration may play a major role in in-stream DIC increase in this system [3]. Abundant primary production in summer months can lead to a strong heterotrophic response in riverine systems, where respiration rates outpace the rate of photosynthesis [51–54]. Respiration rates have been observed to be highest in the AR delta in

summer months, corresponding with highest rates of nutrient uptake for primary production [55]. This study suggests that this is likely also the case for the AR's upstream floodplain ecosystems and main stem. The consistent and significant mass load increases in DIC from origin to outlet found in this study (Figure 8) might reflect that high productivity in this nutrient rich, subtropical basin leads to a strong heterotrophic response, rapidly mineralizing organic material and subsequently causing DIC to accumulate as waters continue downstream.

Concentrations and total mass export of DIC from this system into the NGOM were both found to be high in summer and early fall (June–August: Table 1; Figure 7), but downstream increases of DIC within the basin were small during the same period (July–September) (Figure 8). Concentrations even showed an uncharacteristic decrease from origin to both outlets in August and September. This lack of in-stream increase may seem counterintuitive if respiration rates are highest in warm productive months. However, outgassing of aqueous carbon dioxide to the atmosphere, which is known to occur in most rivers, particularly during highly saturated summer months when the water–air $p\text{CO}_2$ gradient is large [1,51,56] may provide explanation. This study shows that the AR was supersaturated with CO_2 in spring and summer months (Figure 4), to a greater extent than found in the lower Mississippi River by Reiman and Xu [57]. This degree of supersaturation will lead to rapid degassing of CO_2 to the atmosphere co-occurring with DIC production [1,52], resulting in little net change in DIC concentrations and mass loads downstream. The positive shift in $\delta^{13}\text{C}_{\text{DIC}}$ values from August through October (Table 1) can also provide evidence of high rates of degassing simultaneous with DIC production. As reported by Geldern et al. [58], during CO_2 evasion the lighter ^{12}C isotope is preferentially outgassed, leaving the resulting aqueous carbon pool enriched in ^{13}C (thus, less negative values for $\delta^{13}\text{C}_{\text{DIC}}$).

Although net heterotrophy is indicated in the AR, heterotrophy in main channels normally can only account for less than 20% of CO_2 outgassing flux [59,60]. Other carbon sources from within the AR's floodplains must then contribute dissolved carbon to the AR's main channel. For example, October showed the greatest change in DIC concentrations, which increased by >42% at both outlet locations while DOC concentrations were reduced at both outlet locations by only >12%. Direct mineralization of riverine DOC to DIC cannot then be the only cause of DIC increase. Despite increasing DIC concentrations downstream, there was a large reduction in riverine $p\text{CO}_2$ from 2748 μatm at Simmesport to 697 μatm and 1268 μatm at Wax Lake and Morgan City outlets, respectively. Thus, CO_2 may have been lost to the atmosphere without rapid replacement by respiration as was indicated in summer months. Although some mineralization of DOC to DIC likely took place, a more appropriate explanation for these increases in DIC concentrations downstream is may be the increased influence of carbon weathering in local soils on DIC concentrations during low-flow periods, wherein floodplain contributions to riverine DIC concentration are less diluted. Low flows can also allow for increased DIC concentrations despite lowered $p\text{CO}_2$ due to mineral impacts on alkalinity, which may shift the direction of the DIC equilibrium equation.

Carbon dioxide stored in soils is often a result of root respiration and microbial oxidation of soil organic matter [61,62]. Evidence suggests that in a floodplain swamp, up to half of the CO_2 flux can be attributed to live root respiration rather than biological mineralization [63]. Both of these processes can be expected to be abundant in a productive and extensive swamp river system such as the AR. Soil $p\text{CO}_2$ shows strong seasonal and geographical variation. For example, one study described fluctuations in temperate hardwood-forested catchment soils ranging from 907 ppmv in winter to 35,313 ppmv in summer [64], while another study reported a near-constant $p\text{CO}_2$ of ~52,000 in undisturbed forested areas in the Amazon basin [65]. The anoxic soil conditions found in wetlands provide optimal environment for the sequestration of large amounts of carbon; in fact, wetlands are estimated to store up to 30% of global soil carbon pool [66]. Subsequently, overbank flooding of the AR may lead to further interactions with CO_2 that is sequestered in the soils of its floodplains.

4.2. Impacts of River Corridor and Floodplain Wetlands

The period during which this study took place included a very wet summer, and included abnormally high winter flows. Gauge height at Butte la Rose (Figure 1) is significantly related to the percentage of floodplain inundation in the 2571 km Atchafalaya Basin Floodway System (ABFS) ($R^2 = 0.88$, $p < 0.01$; [43]) due to the gauging station's post-channelization location. Using a prediction interval based on the findings of Allen et al. [43], we calculated the approximate percentage of the ABFS flooded at different points during this study with river gauge records at Butte la Rose. Approximately 61% ($\pm 18\%$) of the total area of the ABFS was inundated on an average during this study period, ranging from 28% in October to 89% in late January. The extent of flooding consistently exceeded the long-term mean daily statistic calculated using gauge height data at Butte la Rose from 1997–2015 (Figure 9).

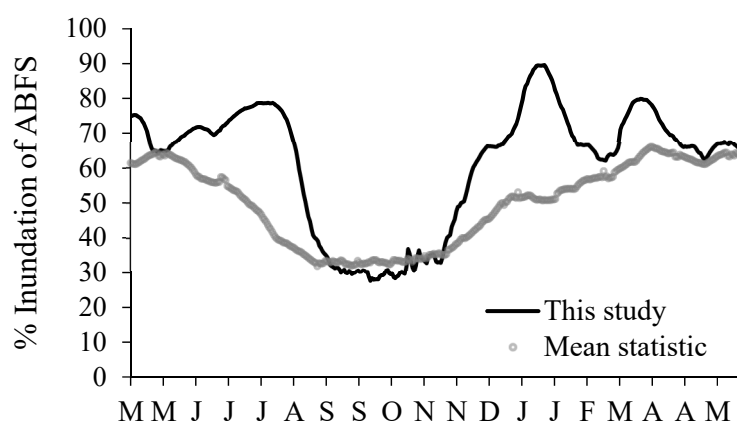


Figure 9. Estimated percent inundation of the Atchafalaya Basin Floodway System (ABFS) for this period of study compared to daily means calculated from data for water years 1996–2015. Data was obtained from the U.S. Geological Survey (USGS) National Water Information System Web Interface (<http://waterdata.usgs.gov/nwis>).

The greatest increases in DIC mass load from upstream to the downstream outlets occurred during the greatest floodplain inundation (Figures 8 and 9), strongly suggesting that the floodplains of the AR are a major inorganic carbon source to its main channel. Wetlands are known to contribute large amounts of CO_2 to river channels [67], particularly in productive subtropical and tropical regions. In addition to interactions with soil $p\text{CO}_2$, other sources of DIC in the AR's floodplains should also be considered. For example, one study found that the isotopic signature of riverine CO_2 in the Amazon River was composed disproportionately of processed river-corridor and floodplain C4 grasses, which were more bioavailable than other DOC sources present [68]. Another study in the floodplains of the Amazon River demonstrated that water $p\text{CO}_2$ was highest when floodplains were most flooded and attributed these heightened levels of dissolved inorganic carbon to the direct transfer of atmospheric CO_2 to the water column through wetland vascular plants, which exported half of their gross primary production to Amazonian waters [4]. Increases in riverine DIC concentrations have also been reported for waters passing through rice paddies, which act as wetland systems [69]. When the AR's floodplains are highly inundated, this extensive wetland system may contribute large loads of DIC to the main channel via inputs from the wetland soil and root respiration, bio-mineralization of floodplain organic material, and through washout of stored DIC in soils and backwaters.

This is especially evident in December 2015, when a winter flood-peak led to rapid inundation of the floodplain, with water reaching areas which had been severed from the main channel for several months beforehand (Figure 9). During December, DIC concentrations increased from Simmesport to outlet locations at Wax Lake and Morgan City by 36% and 54%, respectively, leading to the study period's largest monthly DIC mass load increase from origin to combined outlets (totaling 116.9×10^3

tonnes) (Figure 8). In December, $p\text{CO}_2$ of the river waters was relatively close to the atmospheric $p\text{CO}_2$ at Simmesport (551 μatm) but increased to 2041 μatm and 905 μatm at Wax Lake and Morgan City outlets, respectively (Figure 4). This large increase in $p\text{CO}_2$ may be attributed to interactions with high concentrations of soil $p\text{CO}_2$ stored within the typically low-flow and no-flow regions of the floodplain. Tockner et al. [8] demonstrated that different phases of river-floodplain connectivity are associated with different biological and chemical properties. Under low flow conditions (termed “phase I”), phytoplankton competed for nutrients and grazing rates were high, but during early flood stages, influx of riverine nutrients and longer water residence time favored increased biological response (“phase II”). Finally, during large overbank flood pulses (“phase III”), large washout of chemical constituents which had accumulated in floodplains was observed.

Additional evidence of this proposed “washout” of stored DIC during flood pulses in the AR comes from the largest positive shift in $\delta^{13}\text{C}_{\text{DIC}}$ values which occurred in December (from -14.78‰ at Simmesport, to -12.95‰ and -13.47‰ at Wax Lake and Morgan City outlets, respectively). A weak water–air $p\text{CO}_2$ gradient at Simmesport and a large downstream increase in $p\text{CO}_2$ at both outlet locations suggests relatively lower rates of atmospheric degassing. This positive shift in isotope values should then be most reflective of extensive interaction with soil-stored CO_2 and carbonate weathering, thereby describing the major source of this large change in DIC concentrations and mass loads.

Floodplain inundation was also high during annual spring flooding from May through August in 2015 (Figure 9), but less drastic changes in DIC concentrations, mass loads, and isotope values took place. This is probably because the ABFS had already reached a high level of inundation prior to the beginning of the sampling period. Observed changes in December were most likely an initial “flushing out” of soil CO_2 which had accumulated during the drier period from August through November, when the river was not extensively interacting with its floodplains. Although sources of DIC in the AR cannot be unambiguously assigned by the data gathered for this study, floodplain soil interactions seem to be strongly implicated. It is clear that biogeochemical cycling of carbon is occurring in this dynamic swamp river system, and is impacting end-member dissolved inorganic carbon loads.

4.3. Dissolved Organic Carbon Dynamics

DOC concentrations, mass loads, and $\delta^{13}\text{C}_{\text{DOC}}$ showed no identifiable trend from upstream to the downstream locations. While calculated monthly mass loads did decrease from the AR’s origin to its combined outlets during 10 of the 13 sampling months (Figure 8), the differences in monthly mass load from inflow to outflow were not found to be statistically significant at ($p = 0.09$). With net heterotrophy indicated as one potential source of DIC increase, some loss of DOC can likewise be explained by decomposition and mineralization of organic matter, which has been found to intensify in anthropogenically altered rivers [24,70] such as the MARS. However, since loss of DOC was far less than gain in DIC throughout the majority of this study period, it is difficult to determine how large of a role riverine DOC entering the main channel at Simmesport may play. DOC in large, low-lying rivers is typically very degraded in quality [32], so DOC delivered to the AR via the MR may not be fresh enough to be a desirable food source, and uptake by the AR may subsequently be relatively small.

DIC production is more likely occurring largely in soils and floodplain ecosystems using fresher and more reactive sources of organic material produced within the AR Basin. A recent study indicated the Red River may contribute bioavailable DOC to the AR [71], which may explain some of the labile organic material present. Leaf litter from within the basin may provide further source of less degraded organic carbon for respiration; leaf leachates as well as the breakdown of large organic materials to DOC by bacteria and fungi are major sources of DOC to waters [72–74]. Organic material in the AR are compositionally different from that of the MR, indicating significant leaf litter inputs from its landscape as well as the Red River [29,71]. The timing of leaf litter input within this basin corresponds with the only months where DOC mass loads increased from origin to outlet (August–October).

Though $\delta^{13}\text{C}_{\text{DOC}}$ did not show any strong or consistent seasonal or longitudinal trends, there was a noteworthy increase in values in October and November. This supports an indication of a different

source of DOC in fall, which may be fresher based on these less negative values (i.e., leaf litter). These potential in-stream and in-basin sources of fresh dissolved organic material (e.g., algal production and detrital input) may explain some portion of the disparity between calculated total mass balances, which describe significant DIC production within the basin (~ 0.524 Tg) and relatively lower total DOC retention (~ 0.243 Tg) during this study period (Table 3; Figure 8).

During the period of most extensive floodplain inundation, in winter, DOC also experienced its greatest reduction in both concentration and mass load from origin to outlet. Concentrations at both outlet locations were more than 25% lower than at Simmesport. The largest loss of DOC occurred in January ($\sim 122,000$ tonnes, over 45% of the DOC retention observed throughout the entire period), when inundation rose to an estimated 90% of the floodway system. This loss might be attributed to extensive interaction with typically disconnected areas of the floodplain normally containing slower-moving water, which are suspected to contain stronger microbial communities and biofilms capable of rapid biological oxidation [75,76] and inorganic carbon production. In addition to microbial degradation, flocculation has been described as a cause of DOC removal in low salinity waters [77]. This loss of DOC during high floodplain inundation agrees with a previous study on AR total organic carbon (TOC) which showed that 83% of the variation in average monthly TOC retention in the AR was explained by average monthly inflow [37], where no sure mechanism for variation in retention could be constrained. A study in Australian wetlands showed that while shallow flooding led to high levels of DOC, deeper and more extensive flooding led to DOC reduction [6]; though no process is indicated, this agrees with the findings of this current study, which showed greatest reduction in DOC mass loads during prolonged floodplain inundation. A study in the nearby forested Pearl River Basin also demonstrated that floodplain interactions can significantly alter riverine carbon fluxes by varying amounts according to season and discharge [7]. The importance of floodplain interactions and associated biogeochemical processes in influencing dissolved organic carbon flux is likewise indicated in this system.

4.4. Annual DOC and DIC Mass Load Estimates

The estimated DOC mass export of 2.473 Tg from the Atchafalaya River into the Northern Gulf of Mexico for this 13-month sampling period was higher than the existing estimates would predict but is plausible when considering the AR's conditions throughout the study. Shen et al. [29] compared existing estimates of annual DOC flux from the MR and AR and found that variations in estimates were largely not due to methodology, but to inter-annual variations in discharge and concentrations, with high-flow years producing nearly double the amount of DOC observed in low-flow years. Discharge at Simmesport during this sampling period was 37% higher than the long-term annual average ($6547 \text{ m}^3 \text{ s}^{-1}$) reported by Xu [36]. The reported average concentration of $673 \pm 218 \mu\text{mol DOC L}^{-1}$ at the AR's outlets was 74% higher than the long-term (1996–2010) annual average, and the calculated mass flux of DOC reported during this 13-month study was more than double the long-term estimate for the AR ($386 \pm 111 \mu\text{mol L}^{-1}$; 0.95 Tg yr^{-1}) found by Shen et al. [29]. Organic matter is transported disproportionately during high flows and storm events [28,78,79]. The effects of high precipitation and discharge on dissolved carbon fluxes is evident in this study due to an unusually warm and wet winter across the MR watershed associated with a strong El Niño year and a series of winter storms. In the AR, seasonal peak discharge normally occurs in the spring as a result of snowmelt in the northern tributaries [44]. Similarly, according to long-term averages, DOC export from the MR and AR, which generally follows the hydrograph, should increase in December and crest between April and June [29,37]. During our study, however, both discharge and DOC flux peaked in winter. All peaks also exceeded USGS reported median daily statistics. Our dissolved organic carbon mass load estimates are proportionally affected.

Total estimated DIC loading into the NGOM calculated for this 13-month sampling period was 5.346 Tg DIC. This represents the first estimate of DIC flux from the AR. This new estimate agrees proportionally with existing literature describing MR DIC flux; it is an approximate one-third of a 2008 estimate of the MR's average annual DIC load, $\sim 15 \text{ Tg DIC yr}^{-1}$, made using daily alkalinity

measurements recorded in New Orleans, LA [80]. There are currently no other available estimates of AR DIC flux to compare the magnitude with. The year of 2008 and our study year were both high flow years of the Mississippi–Atchafalaya Rivers. Future studies are needed to determine mass proportion of DIC and DOC between the two rivers under low flow conditions.

Due to the higher-than-average discharge and floodplain inundation seen during this 13-month study period, these estimates can serve to illustrate the potential effects of climate extremes on riverine dissolved carbon dynamics. Other studies have demonstrated that climate extremes result in increased loads of organic carbon [28,81]. Temperature and precipitation account for the greatest portion of seasonal and annual variability in estimates of organic and inorganic carbon export [28], making DIC and DOC estimates during unusually warm and wet years, such as the year spanned by this study, of high interest in light of increases in both river discharge and temperatures projected by climate change models [82,83]. The results of this study provide evidence that during high discharge events, the extensive floodway system in the Atchafalaya River Basin may provide a suitable environment for the removal of excess dissolved organic carbon within its floodplains, with corresponding increases in DIC export and atmospheric degassing. Such information can be useful for future management of nutrient and carbon fluxes into the NGOM, as the discharge of the Mississippi is projected to increase largely by the end of this century (i.e., ~11–60%, [84]).

5. Conclusions

This study demonstrates that a large river with extensive river corridor and floodplain wetlands in its coastal margin can act as a significant source of dissolved inorganic carbon both to coastal systems and to the atmosphere, and may also be important sinks for dissolved organic carbon. This effect is particularly pronounced during higher-than-average flow periods where extensive interactions between river and floodplain soils and backwaters are able to take place, especially during initial flood stages. The influence of floodplain interactions on biogeochemical cycling of carbon in this system may be due to a net heterotrophic response to high productivity within this large subtropical river swamp system, with high CO₂ production occurring in floodplain soils, vascular plant root zones, and in the water column. This is indicated by trends in dissolved carbon concentrations, mass loads, and isotopic composition from inlet to outlet locations, as well as seasonal trends in *p*CO₂ and DIC:DOC throughout the study period. This study was conducted during an abnormally wet summer and winter, which resulted in very high flow and high mass exports of dissolved organic and inorganic carbon into the Northern Gulf of Mexico. These results are of particular interest as we continue to evaluate changes in riverine carbon transport and processing in the light of our rapidly changing climate. As discharge of many of the world's rivers are projected to increase in coming years due to global warming and intensified hydrological cycling, increased carbon fluxes to coastal zones should be anticipated. Low-lying floodplain systems such as the studied Atchafalaya River swamp basin must be taken into account when examining modern carbon budgets, and may need to be looked into in future years for the filtration and removal of organic materials, which impact coastal margins and ocean ecosystems as a whole.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/11/7/1395/s1>: Table S1: Temperature, pH, and dissolved oxygen at Simmesport (SIM), Wax Lake Outlet (WLO), and Morgan City (MOR) for the 13 sampling events.

Author Contributions: Y.J.X. conceived and designed the study; E.M.D. performed the field sampling, measurements, and data analysis; E.M.D. and Y.J.X. wrote and revised the manuscript.

Funding: This study was mainly supported through a grant from the National Fish and Wildlife Foundation [Grant #: 8004.12.036402]. Also, a grant from the United States Department of Agriculture Hatch Funds [Grant #: LAB94230] covered some field trip costs.

Acknowledgments: We thank the United States Geological Survey for making the river discharge data available for carbon flux estimation. The statements, findings, and conclusions are those of the authors and do not necessarily reflect the views of the funding agencies. Thanks also go to Songjie He, Olivia Bramlett, and Cassandra Skaggs for

their great help in field and laboratory assistance. Finally, we appreciate three anonymous reviewers for their helpful comments and suggestions to improve this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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