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NITROGEN AND CARBON EXPORT TO THE GULF OF MEXICO BY THE ATCHAFALAYA RIVER, A MAJOR DISTRIBUTARY OF THE MISSISSIPPI RIVER

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The School of Renewable Natural Resources

by
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ABSTRACT

Summer hypoxia in the Northern Gulf of Mexico has been attributed to large nutrient inputs, especially nitrate-nitrogen, from the Mississippi-Atchafalaya River system. The 2008 Gulf Hypoxia Action Plan calls for river corridor wetland restoration to reduce nitrate loads, but it is largely unknown how effective riverine wetland systems in the lower Mississippi River (MR) are for nitrate removal. This dissertation research examined nitrate and carbon export from the Atchafalaya River (AR) to: (1) determine nitrate processing by a river swamp basin under varied seasons, (2) investigate nitrate retention and processing in the AR during a major flood event, and (3) assess the relationship of nitrate with organic and inorganic carbon in the AR and MR. I investigated changes in nitrate, $\delta^{15}N_{NO3,}$and $\delta^{18}O_{NO3}$ for water samples collected biweekly to monthly from April 2007 to April 2009 at the ARinput- (Simmesport) and outlets (Morgan City and Wax Lake) and on the MR at Baton Rouge. Water samples were also collected weekly during the 2011 majorMR spring flood (May to July) and analyzed for nitrate isotopes and concentrations. AR outflow had significantly, but only slightly lower mean nitrate concentrations (1.1 mg L^{-1}) and $\delta^{15}N_{NO3}$ ($7.0^{o}/_{oo}$) than the MR (1.5 mg L^{-1}, $7.7^{o}/_{oo}$); with no difference in $\delta^{18}O_{NO3}$ ($4.6^{o}/_{oo}$). Limited differences in both isotope values between the two rivers reflect limited nitrate processing in the Atchafalaya. During the 2011 spring flood a total nitrate-nitrogen mass load of 89,600 megagrams (Mg) entered the basin and 83,200 Mg exited the basin, resulting in a low 7% retention of NO_3N. There was little variation in $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values between the input and two outlets, further indicating little nitrate processing in this system. The AR appears to have an additional and potentially higher quality organic carbon source from the Red River. The findings in this dissertation research show that as currently designed, dissolved nutrients like nitrate and DOC in the Atchafalayaare transported with little processing. This suggests the Atchafalaya and potentially other similarsystems may be

ineffective in reducing riverine nitrate because of limited residence time necessary for the biochemical reactions to occur.

CHAPTER 1. INTRODUCTION

1.1 Background

Nitrogen fixation and denitrification act to balance nitrogen availability for many life forms. Diatomic nitrogen (N_2) in the atmosphere is the largest source of nitrogen, however, very few organisms can perform the energy intensive process of nitrogen fixation (e.g. Alexander et al., 2000; Reddy and Delaune, 2008). Anthropogenic effects have greatly influenced the delicate balance of available nitrate for organismal uptake. The Haber-Bosch process enabled the creation of reactive nitrogen (Smil, 2001) resulting in increased fertilizer use and subsequently increased nitrogen reaching waterbodies. Undesirable consequences of excess N such as eutrophication; i.e. dominance by undesirable vegetation, which in turn degrades fish and wildlife habitat, has become widespread in waterbodies. Denitrification is an important process in removing reactive nitrogen from the environment and returning it to the atmosphere. Although the lack of availability of a necessary nutrient to organisms can limit growth, in areas with high nitrate concentrations, the conversion of reactive N to inactive N_2 through denitrification effectively removes N from the system and reduces the undesirable consequences of excess N (Davidson and Seitzinger, 2006).

Floodplain systems have been reported to be effective sinks for riverine nutrients through removal mechanisms including denitrification, assimilation, and subsurface transport (Lindau et al., 1994; Tockner et al., 1999; Forshay and Stanley, 2005). However, it has also been reported that denitrification in a river is rather low because of unfavorable conditions (e.g. Hill, 1979; Alexander et al., 2000). Conditions that favor denitrification include high concentrations of nitrate and organic carbon with high water temperatures flowing over anoxic soil (Pina-Ochoa and Alvarez-Cobelas, 2006). Of these conditions, nitrate concentration in the overlying water was determined as the dominant control on denitrification potential followed by the thickness of

the oxic surface layer (Christensen et al., 1990). Racchetti et al. (2011) argued that riverine wetlands increase interaction surface for denitrification while supplying nitrate constantly to soil and therefore, encourage higher rates of nitrogen removal.

The Mississippi River, draining 41% of the continental United States, delivers each year approximately 953,000 Mg nitrate-nitrogen (Goolsby and Battaglin, 2001) into the Northern Gulf of Mexico (NGOM). About 174,600 Mg of the nearly 1 million Mg of nitrate input is discharged from the Mississippi River's largest distributary, the Atchafalaya River (Xu, 2006). The excess nitrogen is one of the major causes of the hypoxic dead zone (a condition when dissolved oxygen concentration in the deepwater is below 2 mg L^{-1}) occurring in NGOM during late spring and summer for the past two decades (Rabalais et al., 2007, Turner et al., 2008). The fluctuation of the hypoxic dead zone has been found to be partially dependent on nitrogen load from the Mississippi River (Wang and Justic, 2009), especially during May and June (e.g., Rabalais et al., 1996), which is a function of river discharge and nitrogen concentration. To reduce the large nitrogen input to NGOM, several options were suggested in the action plan released in 2008 by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (MR/GOMWNTF, 2008), including diversion of the nitrogen-rich Mississippi water into floodplain wetland systems such as the Atchafalaya River Basin.

Because water can more easily interact with surrounding landscape in the Atchafalaya Basin, it is considered a potential area in the lower Mississippi River region for nitrate removal through denitrification. The Atchafalaya is thought to be potentially a nitrogen sink as it already has been shown to trap large amounts of suspended sediment annually with rates in some areas the highest in the United States (Hupp et al., 2008). Additionally, 27% of total Kjeldahl nitrogen (TKN: sum of organic nitrogen, ammonia, and ammonium) retention was estimated in the basin

(Xu, 2006a). However, the output had slightly higher nitrate than the input in the Atchafalaya (Xu, 2006b, Turner et al., 2007). Although it is clear that the basin is a sink for organic nitrogen, the fate of nitrate, the problematic species contributing to the "dead zone" in the Northern Gulf of Mexico, is unclear.

Natural isotopic tracers combined with mass balance data can provide insights into the complex transformations and transport of nitrogenous compounds and have been successfully used to investigate nitrogen cycling in stream and riverine systems (e.g., Kohl et al., 1971; Kellman and Hillaire-Marcel, 1998; Panno et al., 2006; Sebilo et al., 2006; Burns et al., 2009). Utilizing isotopic ratios can reveal if the basin is simply transporting the nitrogen from the Mississippi River to the Gulf of Mexico or the wetlands are holding nutrients, potentially allowing for denitrification.

The continuum from terrestrial to headwater streams to rivers to marine environment represents a shift from N-limitation in a C-rich environment to C-limitation in an N-rich environment (Taylor and Townsend, 2010). The Atchafalaya likely fits closer to the terrestrial carbon source in this continuum than the Mississippi River because of its more natural floodplain as compared to the more closely leveed system in the Mississippi River. Therefore, the Atchafalaya may have high quality organic carbon sources. Organic carbon quality (i.e. degradability), higher temperatures, and higher nitrate concentrations correlate with higher denitrification potential (Sirivedhin and Gray, 2006). As this shift also impacts relative nitrogen processing — both rate and type (assimilation, nitrification, denitrification) — it is important to examine carbon in light of nitrate.

1.2 Research Objectives and Hypotheses

With the above background, this dissertation research aimed to investigate a central question of whether a river basin with extensive corridor wetlands, large floodplains, and backwaters has the capacity of removing nitrate nitrogen. Specifically, the research was to (1) determine nitrate processing by a river swamp basin under varied seasons, using the Atchafalaya River as a casestudy; (2) investigate nitrate retention and processing in the Atchafalaya River during an extreme flood event, and (3) assess the relationship of nitrate with dissolved organic and inorganic carbon in the Atchafalaya and Mississippi Rivers. The Atchafalaya River may be an area that can be managed for nitrate removal; therefore, determining what actually occurs to the nitrate in the Atchafalaya during varied flow conditions and seasonally should determine if the Atchafalaya River is different from the Mississippi River in terms of nitrate processing.Two main hypotheses were made: (1) the Atchafalaya River acts a significant sink for nitrate nitrogen, especially during high flows when the river water interacts with its wide floodplain; and (2) there is a significant change in dissolved organic carbon in the Atchafalaya River due to denitrification processing.

1.3 Research Approach and Study Area

This dissertation research was conducted in the Atchafalaya River Basin, a large distributary basin of the Mississippi River. The research utilized a mass balance concept combined with isotope techniques. It treated the Atchafalaya River Basin as a closed system with the only inflow at its upperbasin location, Simmesport, and outflow at its two lower river basin locations, Morgan City and Wax Lake Outlet. From April 2007 to April 2009 water samples along the river were collected biweekly to monthly. In addition, water samples were collected on the Mississippi River at Baton Rouge during the same period. During the 2011 Mississippi River

spring flood, water samples were collected twice to once per week at Simmesport, Wax Lake Outlet, and Morgan City from May 14th to July 20th. To determine ambient conditions at the time of sampling, in-situ measurements including river water temperature, dissolved oxygen, and specific conductance were also made during each sampling event at all sampling locations. All water samples were analyzed for nitrate concentrations and isotope values ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$). Samples from February 2008 to April 2009 were also analyzed for dissolved organic and inorganic carbon.

The Atchafalaya River is formed by the entire Red River flow from western Texas combined with approximately 30% of the Mississippi River's latitudinal flow diverted at the Old River Control Structure (Figure 1). The Old River Control structure was completed in 1963 to restrict the increasing proportion of the Mississippi River shifting to the Atchafalaya River. Because of the shorter path to the Gulf of Mexico, the Atchafalaya would capture the flow of the Mississippi without intervention resulting in drastic economic effects on the large number of ports in the lower Mississippi River (i.e. Roberts, 1998; Ford and Nyman, 2011). The Atchafalaya River flows through south Louisiana from just north of Simmesport, Louisiana (30°59'00" N, 91°48'00" W) into the Gulf of Mexico via two outlets, Morgan City (29°41'35" N, 91°12'43" W) and Wax Lake Outlet (29°41'55" N, 91°22'24" W). The Atchafalaya Basin has wide floodplains reflecting a more natural system than the highly engineered input might suggest. The Atchafalaya Basin has levees on the east and west, but the basin is 25 km to 35 km wide allowing for a more natural floodplain (Ford and Nyman, 2011). In its first 110 kilometers south of the Mississippi River diversion, the Atchafalaya River flows in a well-confined channel. Afterwards, it becomes a series of braided channels that are connected with the

Figure 1.1. Part ofthe Old River Control Structure Complex (Auxiliary) where water from the Mississippi River is diverted into the Atchafalaya River 4.7 km north of Simmesport. Picture taken during the 2011 record spring flood.

surrounding landscape. The sediment rich water from the Mississippi River has resulted in filling in of the basin, converting many of the open water regions in the Atchafalaya River Basin to bottomland hardwood forests especially in the northern part of the basin (Coleman, 1988; Roberts, 1998) reducing connectivity of the river except during high flood events.

The 4,678 km^2 Atchafalaya River Basin is predominantly wooded lowland and cypress-tupelo surface flow swamp with some freshwater marshes in the lower distributary area. The Atchafalaya is channelized to allow for navigation and also managed as a flood control basin. The basin serves as a major floodway for the Mississippi River floodwaters; therefore, more of the Mississippi River water can be directed into the basin from the Morganza Spillway during extremely high flow periods to reduce flooding potential for downriver cities such as Baton Rouge and New Orleans.

Figure 1.2. Sampling location off a houseboat at Wax Lake Outlet.

1.4 Synopsis of Chapters

This dissertation is divided into individual research chapters aimed to address the aforementioned research objectives. In Chapter 2, I compare nitrate isotope values between the Atchafalaya River and the Mississippi River at Baton Rouge during two years to examine what potential nitrate processing might occur over varying seasons and flow regimes. Chapter 3 examines an extreme flood event that reconnected the river channel with its floodplain to determine if nitrate reduction through denitrification occurred. Finally in Chapter 4 I examine dissolved organic and inorganic carbon in the Atchafalaya and Mississippi Rivers, the relationship of nitrate with organic and inorganic carbon.

CHAPTER 2. NITRATE PROCESSING AND EXPORT FROM THE ATCHAFALAYA RIVER BASIN[1]

2.1 Introduction

The Mississippi River, draining 41% of the land area of the continental United States (Eadie*et al*., 1994; Goolsby*et al*., 2001), delivers approximately 953,000 Mg nitrate-nitrogen each year to the Louisiana coast (Goolsby*et al*., 2001). About 174,600 Mg of this input is discharged from Mississippi River's largest distributary, the Atchafalaya River (Xu, 2006a). It is estimated that more than 90% of the nitrate reaching the Mississippi River is transported to the Gulf of Mexico (Alexander *et al*., 2000), implying little nitrate removal within the river system itself. Once the nitrate reaches the leveed channel of the Mississippi River, there is evidently little opportunity for the water to interact with riparian and backwater environments that would favor assimilation and denitrification.

This large nitrogen load is one of the major causes of anextensiveseasonal hypoxic dead zone (dissolved oxygen concentration <2 mg L^{-1}) observed off the coast of Louisiana in the Northern Gulf of Mexico over the past two decades (Rabalais*et al.*, 2007, Turner *et al.*, 2008). This hypoxic area has not only ecological impacts, but also economic consequences from lost fisheries and seafood processing incomes. The average midsummer hypoxic zone has doubled from 8,000 km^2-9,000 km^2 during 1985-1992 to 16,000 km^2-20,700 km^2 during 1993-2001 (Rabalais*et al*., 2001; Rabalais, 2002). The most recent five-year average size of the summer hypoxic zone was 17,500 km^2, more than three times the 5,000 km^2 target set by the Mississippi

[1] This chapter first appeared as "Isotopic signature of nitrate in river waters of the lower Mississippi and its distributary, the Atchafalaya" on June 18, 2012. Reprinted by permissionof "Hydrological Processes", DOI: 10.1002/hyp.9420

River/Gulf of Mexico Watershed Nutrient Task Force (2008; Rabalais and Turner, 2011).Aminimum 45% reduction in riverine total nitrogen input is thought necessary to achieve hypoxic zone reduction to this 5,000 km^2 target (EPA Science Advisory Board, 2007; Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2008). A reduction of this size would require a number of significant changes in land use practices that are difficultto implement, including moving away from row crops of corn and soybeans, modifications of farm practices to improve efficiency of fertilizer use, and use of riparian areas for flood retention rather than the current method of confinement to the flood channel (Mitsch*et al*., 2001). Although these methods are effective (e.g. Panagopoulo*et al.,* 2011), they require a shift from current practices that would likely come at a high economic cost.

Another option proposed by Mitsch and others (2001) to reduce riverinenitrogen as well as organic loadsis to divert river water into wetland areas to promote infiltration, sedimentation and denitrification. In particular, conversion of reactive N species to unreactive nitrogen gas through denitrificationin low O_2 environments effectively removes N from a system therebyamelioratingsubsequenteutrophication (Davidson *et al*., 2006). For example, N processing by headwater streams can decrease N load to downstream systems (Starry *et al*., 2005). Richardson and others (2004) found that backwater areas in the Upper Mississippi River (UMR)do reduce NO_3 reaching the Gulf of Mexico;however, only 30-40% of the total nitrate load that reaches the Gulf of Mexico comes from the UMR, this diversion would only reduce nitrate loads to the Gulf by 5-10%.

About 30% of the Mississippi River's flow is diverted to the Atchafalaya River (Figure 2.1), a 220-km long river with extensive floodplain and backwater swamps that is maintained as a floodway basin for regulating Mississippi River's high flows. Because water canmore easily

interact with surrounding landscape in the Atchafalaya Basin, it is considered a potential area in the lower Mississippi River region for nitrate removal through denitrification. Mass balance calculations examining the difference between input and output concentrations at the upperbasin location (Simmesport)andthe lowerbasin location (Morgan City) produced mixed findings in regard to the basin's potential for nitrogen reduction. There was an estimated 27% organic nitrogen retention by the basin (Xu, 2006a), but a small increase in nitrate (Xu, 2006b, Turner *et al.*, 2007). Although it is clear that the basin is a sink for organic nitrogen, the fate of nitrate, the problematic species contributing to the "dead zone" in the Northern Gulf of Mexico, is unclear. This increase in nitrate may be a result of nitrate production within the basin or a release of older nitrate from backwater areas. Because the mass balance approach is inconclusive regarding whether nitrate is being released or simply transported through the basin, more information on nitrate dynamics is necessary.

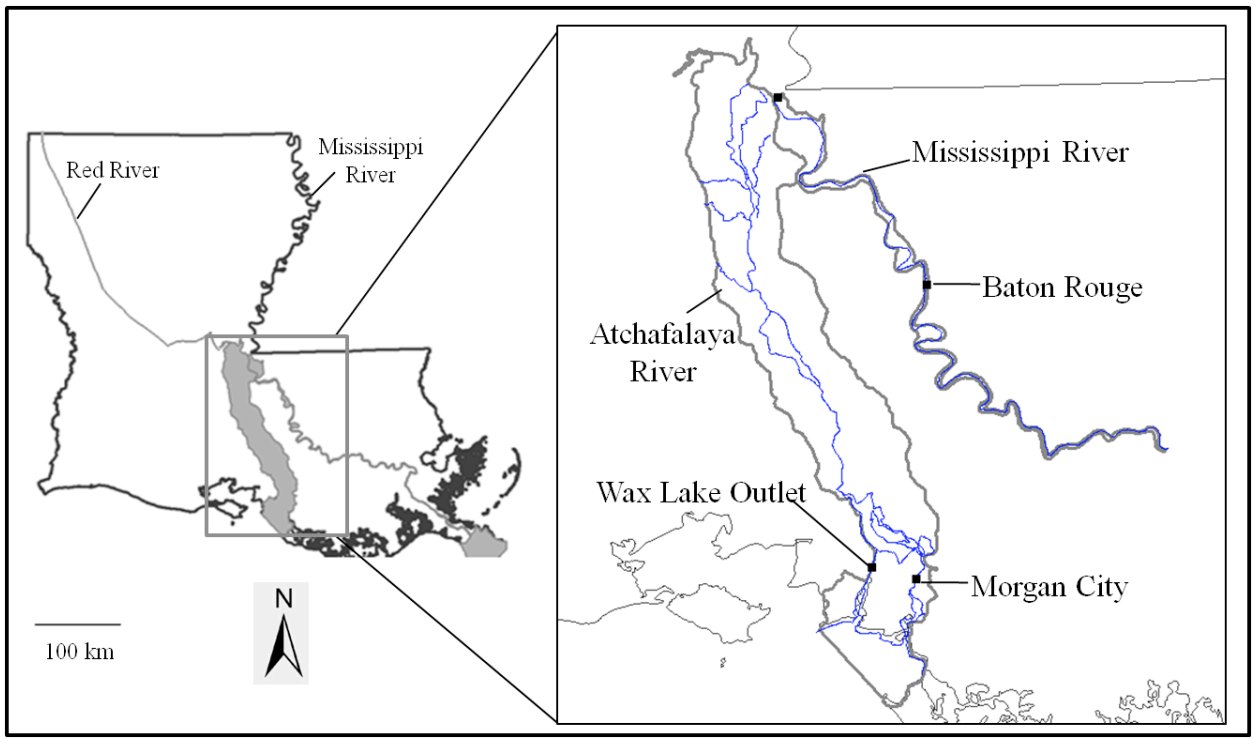


Figure 2.1. Location of sampling sites (Wax Lake Outlet, Morgan City, and Baton Rouge) on the Atchafalaya and Mississippi Rivers in Louisiana.

Natural isotopic tracers can provide insights into the complex transformations and transport of nitrogenous compounds and have been successfully used to investigate nitrogen cycling in stream and riverine systems (e.g., Kohl *et al.,* 1971; Kellman andHillaire-Marcel, 1998; Panno*et al.,* 2006; Sebilo*et al.*, 2006; Burns *et al.,* 2009). Kohl *et al.* (1971) first used ^{15}N to determine the source of riverine nitrate and found that at least 55-60% of nitrate in the Sangamon River, Illinois was a result of fertilizer input from surrounding areas. Measuring both nitrogen and oxygen isotopes of nitrate allows for more specific source identification than is possible with either analysis alone. Crossplots of $\delta^{18}O_{NO3}$and$\delta^{15}N_{NO3}$ can discern between synthetic fertilizer, atmospheric, and nitrification sources (Figure 2.2).

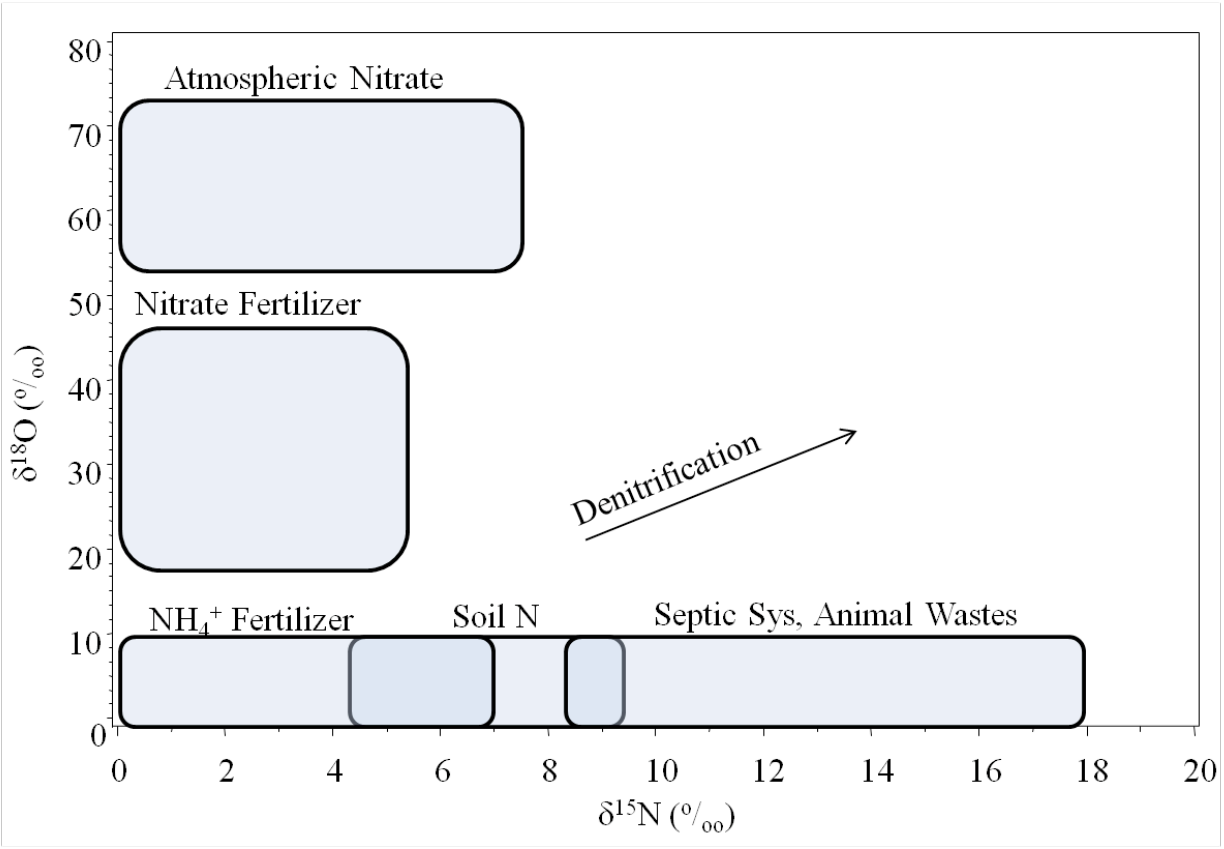


Figure 2.2. Typical range of values for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$. Source identifications are based on the work of previous researchers from Kendall (1998).

In addition to source determination, nitrate isotopes can be used to trace transformations such as nitrification and denitrification(Wassenaar, 1995). Nitrification ($NH_4 \rightarrow NO_3$) may be a particularly important source of nitrate isotopic signatures in our system. If ammonium is being released in the Atchafalaya Basin, it will likely oxidize to nitrate in the well-oxygenated channel. NO_3 derived from synthetic ammonium fertilizer is likely to have a lower $\delta^{15}N$ value than that from other sources such as animal waste and sewage, although it may overlap the range of soil NO_3. Nitrification is a multi-step oxidation process, and there are conflicting results on the magnitude of isotope fractionation that occurs during each step. A wide range in$\delta^{18}O$-NO_3 resulting from nitrification has been observed (Snider *et al.,* 2010 and Casciotti*et al.,* 2010),contrasting with predicted values expected from the 2:1 ratio of oxygen derived from water and molecular oxygen (Andersson and Hooper, 1983). It was previously thought that most of the N-isotope fractionation occurs during the $NH_4 \rightarrow NO_2$ oxidation step because it is the rate determining step (Kendall, 1998).However, there is also inverse kinetic fractionation (i.e. the heavier isotope reacts to form NO_3, leaving the lighter behind in NO_2) that occurs in the $NO_2 \rightarrow NO_3$ oxidation (Buchwald and Casciotti, 2010), which can increase the$\delta^{15}N_{NO3}$ of the resulting NO_3.If all available $NH_4^+$is converted to NO_3^-, no net fractionation would occur. This research has created a picture that is more complicated that the one originally presented by Andersson and Hooper (1983)

Denitrification can be identifiedbecause it causes$\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values to increase linearlyin a ratio close to 2:1 as observed in groundwater (Bottcher*et al.,* 1990). Also, $\delta^{15}N_{NO3}$of the residual nitrate increases exponentially with a fractionation factor of 10-30$^{o}/_{oo}$ (Mariotti*et al.,*

1981; Kellman and Hillaire-Marcel, 1998; Sebilo*et al.,* 2003, 2006). However, the magnitude of these effectscan vary with environmental conditions. Water column denitrificationin the ocean has nearly the same kinetic isotope effect for ^{18}O and ^{15}N (e.g. 1:1; Granger *et al.,* 2004), but sedimentary denitrification has a negligible kinetic isotope effect (e.g. Lehmann *et al.,* 2004). This may be caused by complete denitrification occurring in the sediment leaving no nitrate remaining to diffuse back into the water column. However despite this variation in magnitude, combined information from decreasing nitrate concentration and increasing isotope values can determine if denitrification occurs.

Prior work found $\delta^{15}N_{NO3}$in the Mississippi River at Baton Rouge ranged from $6.5^{o}/_{oo}$ to $10.5^{o}/_{oo}$ with a flux weighted average of $7.6^{o}/_{oo}$ (Fry and Allen, 2003). A slightly lower range ($4.0^{o}/_{oo}$ to $9.4^{o}/_{oo}$) was found in the Mississippi River for 1997-1998 at St. Francisville, about 30 river miles north of Baton Rouge (Battaglin*et al.,* 2001). These values fall in the range of soil N; however, there is an overlap of signal sources. If there is no processing in the Atchafalaya River, the isotope values at Morgan City and Wax Lake should be in a similar range to that found in the Mississippi River.

The objective of the present study was to compare nitrate isotope values between the Atchafalaya River outlets (Morgan City and Wax Lake outlet) and the Mississippi River at Baton Rouge, Louisiana (river mile: 233.9). Because ammonium concentrations were nearly undetectable in the river waters, we chose to focus solely on nitrate, the dominant inorganic nitrogen species in these rivers. The Mississippi River south of the diversion was used as a reference pointas this reach of the river has a well-confined channel with levees restricting interaction with riparian areas. It is also geographically near the Atchafalaya River, so the two areas have similar climatic conditions, such as rainfall, air temperature, wind condition, and solar

radiation. Water that flows past Baton Rouge has the same nutrient composition as water that is released to the Gulf of Mexico (Rabalais and Turner, 1991). The ultimate goal of the study was to understand the potential differences in nitrate processing a river swamp basin might offer. The Atchafalaya River may be an area that can be managed for nitrate removal; therefore comparing the nitrate concentration and nitrate isotope values shoulduncover possible nitrate removal or addition processes occurring in the river.

2.2 Methods

2.2.1 Study Area

The Atchafalaya River is formed by the entire Red River flow from western Texas combined with approximately 30% of the Mississippi River's latitudinal flow. The river flows through south Louisiana from just north of Simmesport, Louisiana (30°59'00" N, 91°48'00" W) into the Gulf of Mexico via two outlets, Morgan City (29°41'35" N, 91°12'43" W) and Wax Lake Outlet (29°41'55" N, 91°22'24" W) (Figure 2.1). The river and its wide floodplainsareleveed on both east and west. In its first 110 kilometers south of the Mississippi River diversion, the Atchafalaya River flows in a well-confined channel. Afterwards, it becomes a series of braided channels that are highly connected with the surrounding landscape.The 4,678 km^2 Atchafalaya River Basinis predominantly wooded lowland and cypress-tupelo surface flow swamp with some freshwater marshes in the lower distributary area. The basin serves as a major floodway for the Mississippi River floodwaters; therefore, more of the Mississippi River water can be directed into the basin during extremely high flow periods to reduce flooding potential for downriver cities such as Baton Rouge and New Orleans.

2.2.2 Water Sample Collection and In-Situ Measurements

Water samples were collected biweekly to monthly at the two Atchafalaya River outlets, Wax Lake Outlet (minor outlet) and Morgan City (main outlet), and on the Mississippi River at Baton Rouge from April 2007 to April 2009. In addition, rain water samples were collected at Louisiana State University Agricultural Center- Iberia Research Station in Jeanerette, Louisiana (29°54'40" N, 91°39'50" W) on three dates to determine the nitrate isotope signature in rainwater and test for atmospheric sources to the Mississippi-Atchafalaya River Basin (MARB). All water samples were collected in acid washed, 250-mL HDPE bottles. Samples were filtered through a GF/F glass fiber filter (Whatman International Ltd, Maidstone, England) and checked for nitrite using a test kit with NitriVer3 nitrite reagent (NI-15, HACH, Loveland, Colorado, USA) in the lab. Samples were preserved by lowering the pH to 2 with 25% hydrochloric acid and stored at 4^{o}C until isotope analysis.

In addition to water sample collection, in-situ water quality measurements were recorded during each sampling date, at each sampling location. Ambient parameters including dissolved oxygen (DO), temperature, conductivity, and pH were recorded with an YSI 556 multi-probe meter (Yellow Springs Instruments, Yellow Springs, Ohio, USA).

2.2.3Isotopic Analysis

Ratios are used to represent the abundance of heavy to light isotope, as in the case of nitrogen isotope ratio (R_N):

$$R_N = {}^{15}N/{}^{14}N \qquad (1)$$

Isotopic composition is presented in delta (δ) notation:

$$\delta A = [(R_A - R_{St})/ R_{St}] * 1000(‰) \qquad (2)$$

where R_A is the isotope ($^{15}N/^{14}N$ or $^{18}O/^{16}O$) ratio measurement of sample A and R_{St} is the isotope ratio measurement of the standard.

Nitrate concentration was measured using the cadmium reduction method. Samples were prepared for isotopic analysis using the azide method of McIlvin and Altabet(2005). Nitrate was reduced to nitrous oxide in a sealed 20 mL vial with azide/acetic acid buffer. Analysis of the resulting nitrous gas was performed with an Isoprime mass spectrometer (GV Instruments). Delta values are expressed relative to atmospheric nitrogen for $\delta^{15}N\text{-}NO_3^-$ and to VSMOW for $\delta^{18}O\text{-}NO_3$-. Analytical reproducibility ranged from $0.2^o/_{oo}$ $-0.4^o/_{oo}$.The international standards USGS 34, 35, and IAEA N3 were analyzed with every run and used to correct the samples.

2.2.4Data Analysis

Daily average river discharge from April 2007 to April 2009 wasobtained from three USGS stations: Wax Lake (07381590), Morgan City (07381600), and Baton Rouge (07374000). Total flow of the Atchafalaya Riverwas computed as a sum of the discharge from Morgan City and Wax Lake. The resulting ratio was approximately 60% to 40%, respectively, of the combined flow.A paired t-test performed on isotope data from these two sites found no significant difference ($p>0.05$) in isotope values between sites; therefore, isotope measurementsfrom these sites were averaged and reported as values for the Atchafalaya River. Daily nitrate fluxes were calculated by multiplying the combined discharge with the average concentration of riverine nitrate. Flux-weighted isotope values were calculated by:

$$\Sigma(\delta * \text{Flux}) / \Sigma\text{Flux} \qquad (3)$$

Since sampling occurred on the same day on both Atchafalaya and Mississippi Rivers, paired t-test was performed on the data to determine differences in isotopic N between the two rivers.

2.3 Results

2.3.1 River Flow Conditions

For the 2-year study period, Atchafalaya River flow averaged 43% of the Mississippi's flow at Baton Rouge, ranging from 13% to 62% (Figure 2.3). The combined discharge from Morgan City and Wax Lake Outlet on the Atchafalaya River averaged 6,716 m^3s^{-1}, varying from 975 m^3 s^{-1} in the summer of 2007 to a peak of 16,880 m^3 s^{-1} during the 2008 Spring Flood. Discharge on the Mississippi River at Baton Rouge averaged 15,503 m^3s^{-1}, fluctuating from 5,142 m^3s^{-1} to 37,317 m^3 s^{-1}.Seasonally, discharge in both rivers was highest from March to May and lowest from October to November (Figure 2.3).

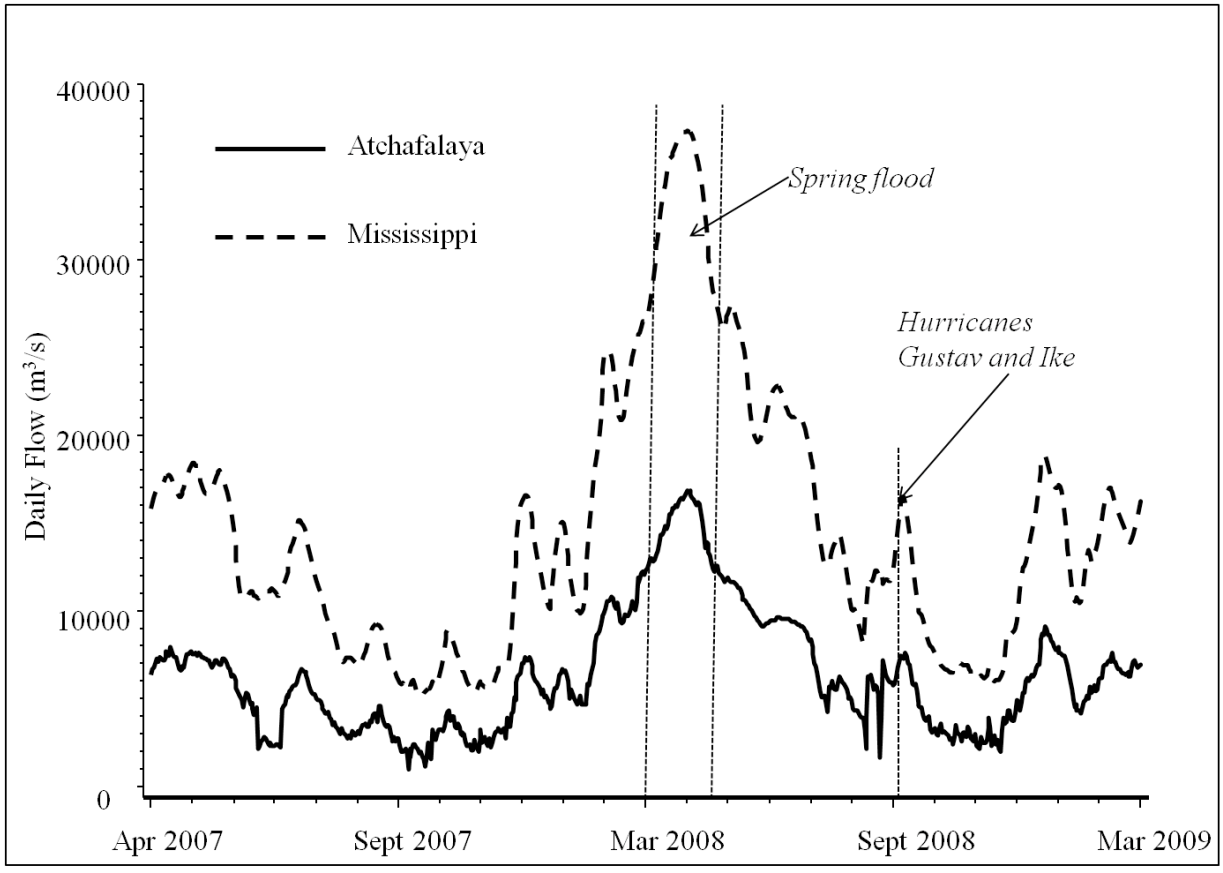


Figure 2.3. Average daily flow at the Atchafalaya Outlets (Wax Lake Outlet and Morgan City) and at Baton Rouge on the Mississippi River from April 2007-April 2009.

In April 2008, the Mississippi River experienced the fifth highest flood stage on record. River stage at Baton Rouge crested at 13.3 m on April 25, 2008, 1.1 m above the major flood stage (12.2 m; NOAA). To deal with this large influx of water, the floodgates of the Bonnet Carre Spillway, south of Baton Rouge, were opened on April 11, 2008 diverting water into Lake Pontchartrain. Although no additional floodgates (i.e. the Morganza Spillway) were open to direct water to the Atchafalaya River, the outlets also experienced high flood stages. Morgan City peaked at 2.4 m, which was 1.2 m above flood stage, while Wax Lake Outlet peaked at 2.6 m.

2.3.2 Ambient Water Quality Conditions

Throughout the study period, both the Atchafalaya and Mississippi Rivers were well oxygenated (DO: 4.1 mg L^{-1} to 13.8 mg L^{-1}), with only one exception. A very low concentration of 1.6 mg L^{-1} was recorded at Morgan City on September 25, 2008, a few weeks after Hurricanes Gustav and Ike that pushed storm surge inland. The Atchafalaya River showed significantly higher ($p<0.01$) average water temperatures (19.1^{o}C) and lower DO (7.5 mg L^{-1}) than the Mississippi (18.1^{o}C, 8.6 mg L^{-1}) (Table 2.1). There was little variation in pH of the river waters, averaging 7.8 in the Mississippi River.

The Mississippi River had a significantly higher average NO_3-N concentration (1.5 mg L^{-1}) than the Atchafalaya River (1.1 mg L^{-1}) (Figure 2.4a). Although the difference between the two locations averaged 0.4 mg L^{-1}, nitrate concentration differed as much as 1 mg L^{-1} for individual sampling efforts (July 2007; Figure 2.4b). In the months following the 2008 Spring Flood, the separation between the rivers' NO_3-N concentration was higher than during other times. The only time in the study period in which the Atchafalaya River (1.7 mg L^{-1}) had higher NO_3-N than the Mississippi River (1.3 mg L^{-1}) was December 2007.

Table 2.1. Monthly average water temperature (°C), dissolved oxygen (DO),nitrate concentrations (mg L^{-1}), and average daily discharge (m3 s^{-1}) for the Atchafalaya River (AR) and Mississippi River (MR).

	Temperature		DO		NO_3-N		Discharge	
Date	AR	MR	AR	MR	AR	MR	AR	MR
Apr-07	15.2		8.1		1.8		7208	17158
May-07					1.9		7115	17184
Jun-07	28.0	27.6	5.9	6.1	1.8	2.5	3870	11235
Jul-07	28.8	28.7	4.7	5.3	1.1	2.0	5201	13043
Aug-07	31.8	32.1	5.2	5.9	0.3	0.6	3508	8314
Sep-07	28.9	26.3	5.2	6.6	0.8	1.5	3415	7808
Oct-07	26.8	26.5	6.6	7.5	1.0	1.2	2256	5865
Nov-07	17.1	16.5	8.1	9.6	1.9	2.4	3015	6802
Dec-07	12.5	11.8	11.0	11.8	1.7	1.7	4306	9772
Jan-08	7.5	6.3	12.8	13.0	1.6	1.8	5821	13074
Feb-08	10.2	8.9	11.2	12.4	1.1	1.3	7075	16346
Mar-08	13.0	12.6	9.9	10.3	1.0	1.4	10923	24401
Apr-08	17.5	16.2	7.0	7.9	0.8	1.1	15426	35254
May-08	22.8	20.3	5.3	7.4	0.9	1.5	13054	29505
Jun-08	27.1	26.3	5.4	6.1	1.4	1.9	9879	22228
Jul-08	29.5	28.6	4.5	5.7	1.4	1.9	8655	19987
Aug-08	28.4	27.7	5.8	6.8	0.8	1.0	5127	11972
Sep-08	25.7	26.5	3.6	7.4	0.3	0.5	5829	12650
Oct-08	21.6	20.8	6.5	8.1	0.7	1.0	4433	9703
Nov-08	13.7	12.8	8.9	10.4	0.9	1.3	2782	6628
Dec-08	11.4	8.8	8.8	11.1	0.7	1.2	4054	9083
Jan-09	8.2		10.1		0.9		7449	16243
Feb-09	7.2	6.4	11.9	12.5	1.3	1.3	5632	13547
Mar-09	14.4		8.8		1.0	1.4	7121	16388
Apr-09	17.0	14.5	8.1	9.3	1.0	1.3	9323	20556

Peak nitrate load occurred about two months following the record high flowin Spring 2008. Mississippi River nitrate loading reached over 4 million kg NO_3-N/day and the Atchafalaya River was about 35% of the Mississippi River at 1.4 million kg NO_3-N per day in July 2008 (Figure 2.5). Although NO_3-N concentrations were elevated on this date— 2.1 mg L^{-1}

in Mississippi River and 1.6 mg L^{-1} in Atchafalaya River— high NO_3-N concentrations also occurred in summer 2007.

Table 2.2. Monthly average specific conductance (SpCond), pH, and dissolved oxygen saturation (DO%)

	SpCond		pH		DO%	
Date	MR	AR	MR	AR	MR	AR
Apr-07		0.342		7.6		80.9
May-07						
Jun-07	0.521	0.513	7.7	7.3	78.1	75.4
Jul-07	0.506	0.536	7.7	7.6	69.0	61.2
Aug-07	0.457	0.482	8.1	7.7	80.8	70.9
Sep-07	0.440	0.485	8.0	7.9	82.1	67.1
Oct-07	0.540	0.513	8.0	8.0	93.1	82.6
Nov-07	0.503	0.480	8.0	7.9	98.4	84.5
Dec-07	0.469	0.492	7.9	8.0	108.7	103.0
Jan-08	0.368	0.358	7.2	7.5	105.6	107.0
Feb-08	0.344	0.324	7.6	7.5	107.0	99.6
Mar-08	0.322	0.297	7.0	7.3	96.8	94.2
Apr-08	0.295	0.271	7.3	7.2	80.5	72.7
May-08	0.360	0.320	7.5	7.1	81.4	61.7
Jun-08	0.407	0.382	7.7	7.5	77.1	66.5
Jul-08	0.398	0.395	7.7	7.7	73.2	62.5
Aug-08	0.422	0.380	7.9	7.6	86.2	75.2
Sep-08	0.353	0.564	7.4	7.3	92.3	44.1
Oct-08	0.468	0.363	7.6	7.4	90.5	73.5
Nov-08	0.561	0.463	7.9	7.7	98.2	86.1
Dec-08	0.467	0.306	7.7	7.6	96.0	80.9
Jan-09		0.305		7.4		85.7
Feb-09	0.403	0.395	7.7	7.8	101.8	98.4
Mar-09		0.364		7.9		94.8
Apr-09	0.391	0.306	7.4	7.5	91.9	81.2

2.3.3Nitrate Isotopic Analysis

On average, the Mississippi River had higher $\delta^{15}N_{NO3}$ values (7.7$\pm$ standard error: 0.3$^{o}/_{oo}$) than the Atchafalaya River (7.0$\pm$0.3$^{o}/_{oo}$) (Figure 2.6), though the difference was small, it was statistically significant (p=0.01). Flux-weighted averages were lower than overall average values,

but the Mississippi River still showed a significantly higher $\delta^{15}N_{NO3}$ value (7.4‰) than the Atchafalaya River (6.5‰). Although the Mississippi River had on average 0.7‰higher $\delta^{15}N_{NO3}$ values, individual sample dates reflect a difference up to 4‰ higher and lower (Figure 2.6). For example, the Atchafalaya River (13.4‰) was 4.1‰ higher than the Mississippi River (9.2‰) in July 2008. In April 2009 there was a smaller difference, but the Atchafalaya River (6.1‰) was 2.4‰ higher than the Mississippi River (3.7‰). However, in October and December 2008, the Mississippi River (10.6‰ and 11.2‰, respectively) was about 4‰ higher than the Atchafalaya River outlets (6.8‰ and 7.2‰, respectively).

In the first year of the study (April 2007-April 2008), the Mississippi River showed a wider range of $\delta^{15}N_{NO3}$ values with a low of 5.1‰ in February 2008 and a high of 10.6‰ in October 2007, than those found in the Atchafalaya River with a low of 5.6 ‰ in February 2008 and a high of 8.9 ‰ in September 2007 (Figure 2.6). During the second year of the study (April 2008 - April 2009), both rivers had a wider range of $\delta^{15}N_{NO3}$ values than the first year. In the Mississippi River both the minimum and maximum values occurred in back to back sampling events from September to November 2008 (3.4‰ to 11.8‰).

Average $\delta^{18}O_{NO3}$ values were not different between the Atchafalaya (4.6 ± 0.3‰) and the Mississippi (4.6 ± 0.3‰) Rivers. Flux-weighted $\delta^{18}O_{NO3}$ for both rivers was slightly lower (4.4‰). Except for three sampling dates in September and early October 2007, $\delta^{18}O_{NO3}$in the Atchafalaya River during the study's first year fluctuated within a narrow range, 4.0‰ - 5.8 ‰ (Figure 2.7). The Mississippi River had higher variation in $\delta^{18}O_{NO3}$values during the entire study period, especially in the second year of the study (1.3‰ - 8.4‰).

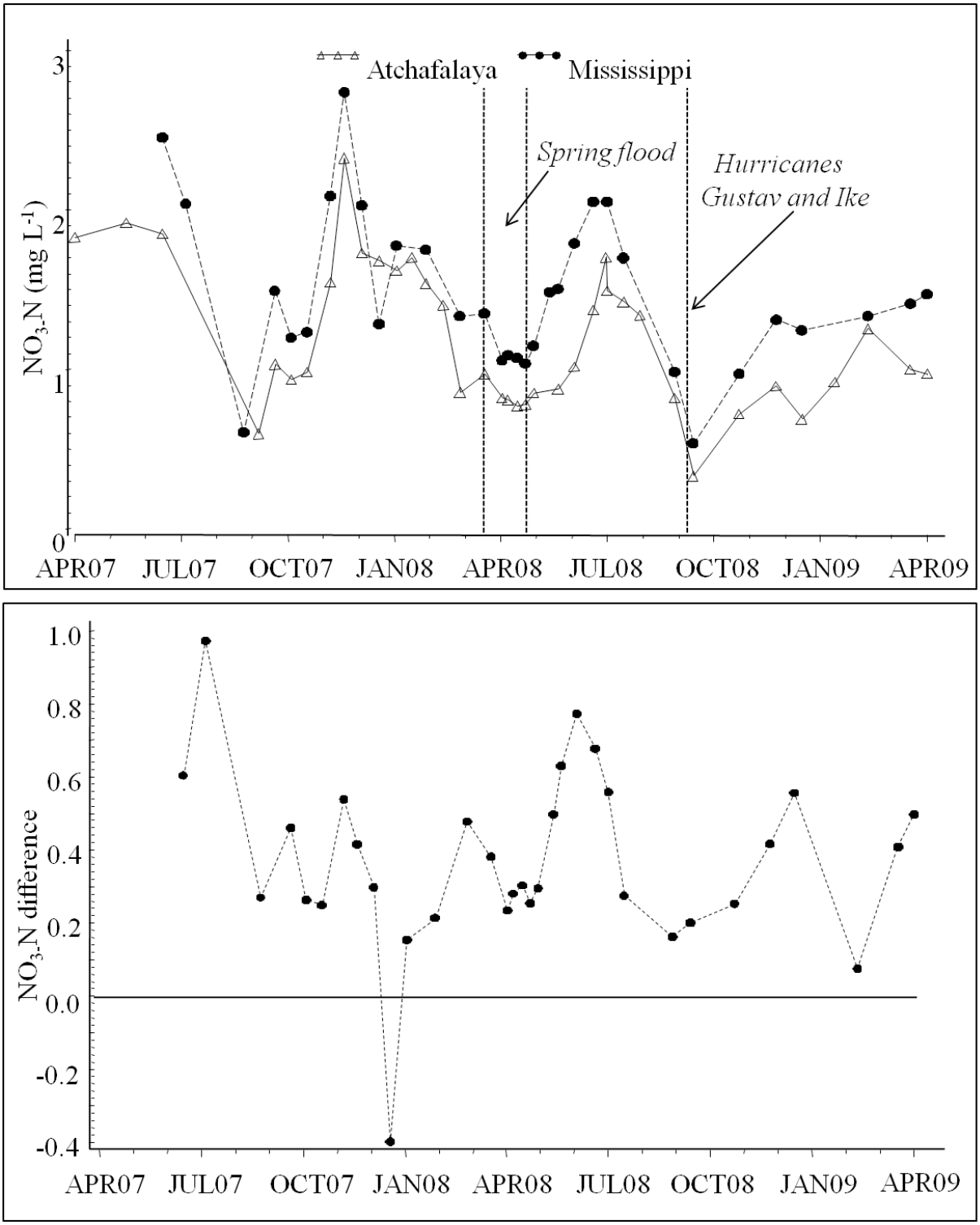


Figure 2.4. A. Nitrate concentration at Mississippi River at Baton Rouge and Atchafalaya River Outlets from April 2007 to April 2009. B. Difference in nitrate concentration between Mississippi River and Atchafalaya River Outlets from April 2007 to April 2009.

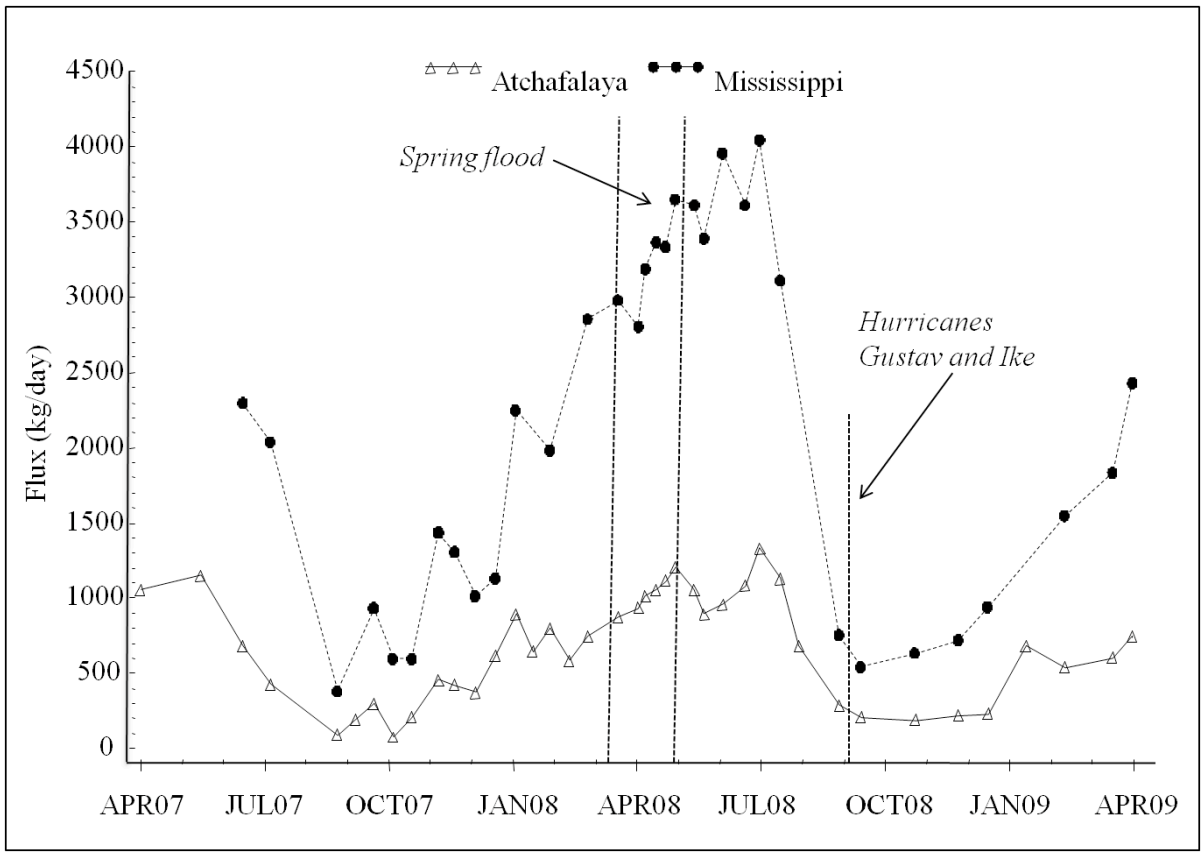


Figure 2.5.Daily flux (Mg) of nitrate at the Atchafalaya Outlets (Wax Lake Outlet and Morgan City) and at Baton Rouge on the Mississippi River from April 2007 to April 2009.

The largest separation of isotope values between the two rivers occurred during the post 2008 Spring Flood period. $\delta^{15}N_{NO3}$and $\delta^{18}O_{NO3}$ were 4‰ and 5‰, respectively, higher in the Atchafalaya River in June and July, 2008. Although NO_3-N concentrations were higher in both rivers in July 2008 as compared to other months, the Atchafalaya River had 0.6 mg L^{-1} lower NO_3-N than the Mississippi River. With the increased isotope values of both $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ combined with a lower NO_3- concentration in the Atchafalaya River, the small amount of nitrate removal may be attributed to denitrification in the backwaters.

2.4 Discussion

2.4.1 Nitrate Source and Transformation in the Atchafalaya and Mississippi Rivers

Mississippi riverine $\delta^{15}N_{NO3}$ values ($7.4^{o}/_{oo}$) and to some extent the $\delta^{15}N_{NO3}$ seasonal trend found in this study are similar to previous studies. The Mississippi River at Baton Rouge had a flux-weighted average of $7.6^{o}/_{oo}$ in 2000 (Fry and Allen, 2003), which is very close to the flux weighted average ($7.4^{o}/_{oo}$) found in this study. Battlin*et al.* (2001) analyzed samples collected from eight sites on the Mississippi River with one site at St. Francisville, Louisiana (river mile: 266), located about 30 river miles north of Baton Rouge (river mile: 233.9). It is the only published data we are aware of for both $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ signatures in the lower reach of the Mississippi River. From spring to fall, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ increased ($\delta^{15}N_{NO3}$: $4.0^{o}/_{oo}$ - $9.4^{o}/_{oo}$) in the Mississippi River (Battlin*et al.,* 2001). The first year of our study showed a similar trend from April to September (Figure 2.6) for $\delta^{15}N_{NO3}$; however, $\delta^{18}O_{NO3}$ tended to decrease early fall (Figure 2.7). The modest differences between this prior study and ours can be readily attributed to differences in analytical methods and sampling resolution as well as interannual variation. Determination of $\delta^{18}O_{NO3}$ can be methods dependent, so direct comparison of our findings with those of Battlin*et al.* (2001) may be inappropriate in this respect. Also,sampling was limited to once a month for five months of the year (April-July, September) in the study by Battlin*et al*. (2001), which is likely to reflect seasonal variations and skew average results. Although average $\delta^{15}N_{NO3}$found in our study was higher than that reported by Battlin*et al.* (2001), even when excluding months October to March when Battlin*et al.* (2001) did not sample, the small increase likely reflects year-to-year variation in nitrate isotopic composition.

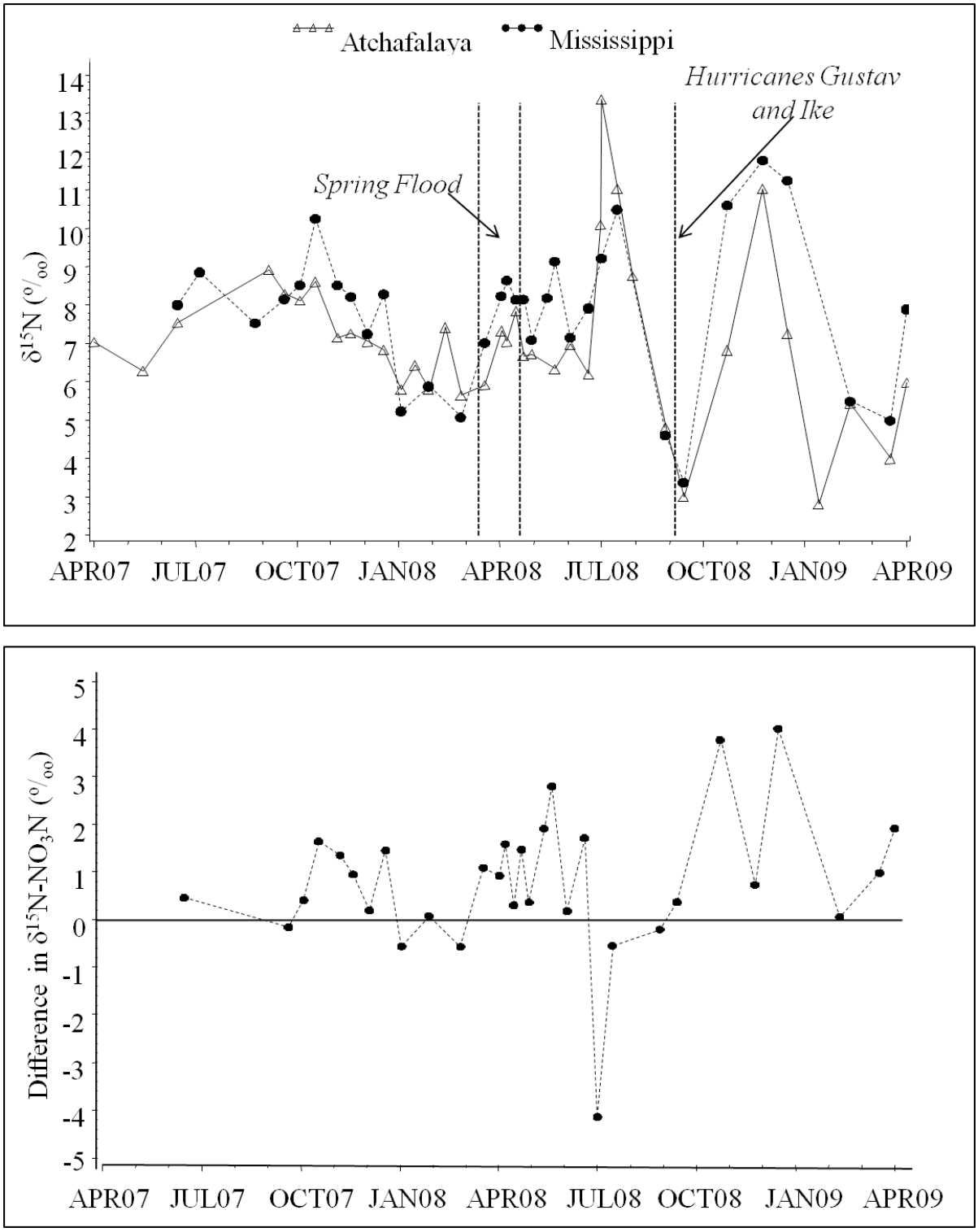


Figure 2.6. A. $\delta^{15}N_{NO3}$ at Mississippi River at Baton Rouge and Atchafalaya River Outlets from April 2007 to April 2009. B. Difference in $\delta^{15}N_{NO3}$ between Mississippi River and Atchafalaya River Outlets from April 2007 to April 2009.

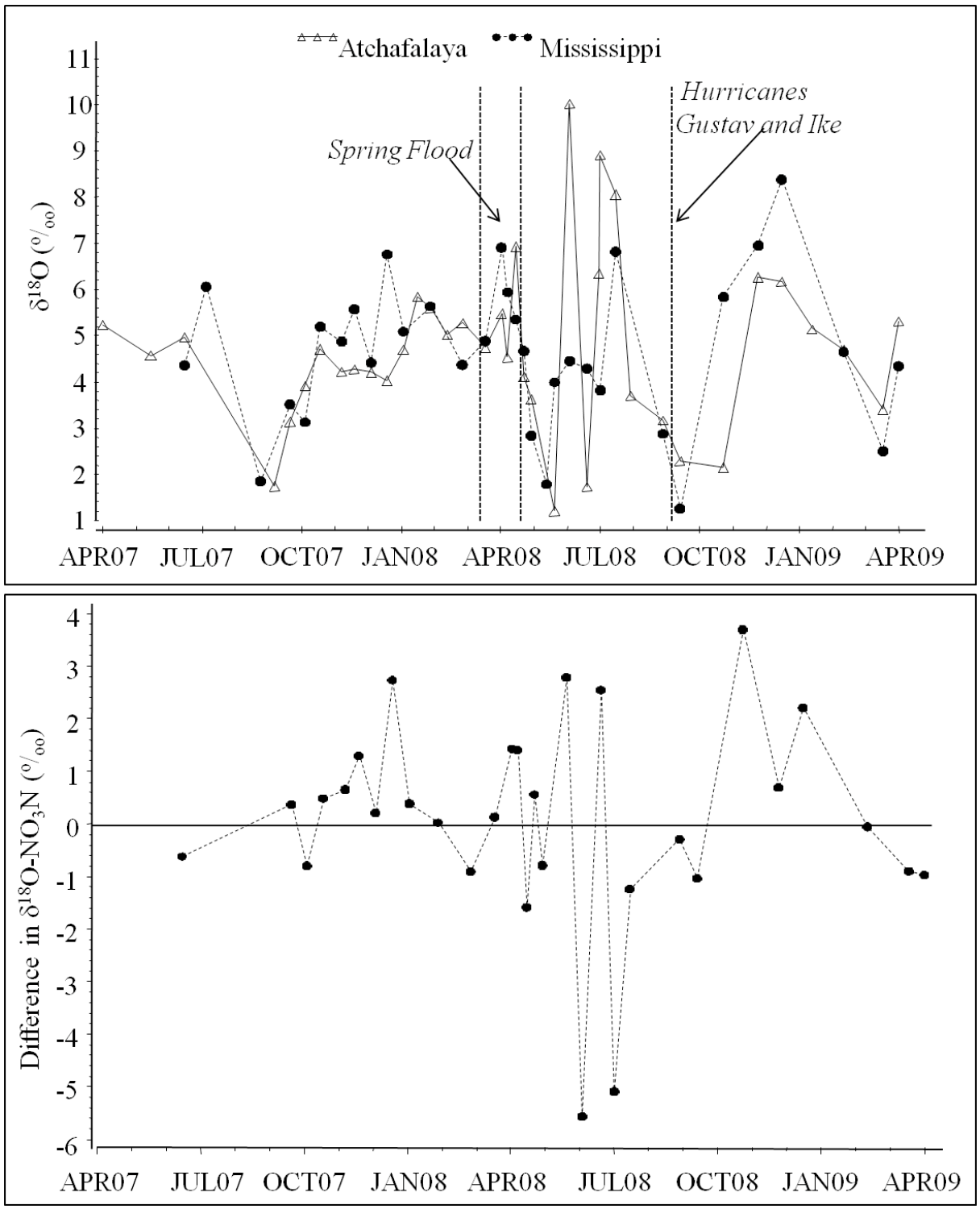


Figure 2.7. A. $\delta^{18}O_{NO3}$at Mississippi River at Baton Rouge and Atchafalaya River Outlets from April 2007 to April 2009. B. Difference in $\delta^{18}O_{NO3}$ between Mississippi River and Atchafalaya River Outlets from April 2007 to April 2009.

We observed a similar trend of increasing $\delta^{15}N_{NO3}$ values from spring to fall to those found by Johannsen*et al.* (2008) in their study on nitrate transport in five rivers in Germany. Kendall (1998) suggestedwarmer months could produce heavier $\delta^{15}N_{NO3}$while cooler months would produce lighter $\delta^{15}N_{NO3}$ signal as a result of biological processing. Another possible cause for lower$\delta^{15}N_{NO3}$values found in our study during the spring is seasonal variation in nitrate source. Fertilization activities in the Midwestern United States occur in late autumn when soil is more likely to be dry and fertilizer price is often lower (Wortman*et al.,* 2006, Millar *et al.,* 2010); however, snow melt and spring rains after this period easily mobilizes the nitrate resulting in a low $\delta^{15}N_{NO3}$ isotope value reflecting the nitrate fertilizer source (Panno*et al*., 2006).

Land use is one of the major factors affecting riverine isotope values. Voss and others (2006) reported that river isotope values in the Baltic Sea catchments have a seasonal relationship reflecting the land use. In the Mississippi-Atchafalaya River Basin, Alexander and others (2008) found that more than 70% of riverine nitrogen originated from agricultural sources. In their study on land use effect using nitrate isotopein a German agricultural river system, Deutsch *et al.* (2006) determined that 86% of the river nitrate was from agricultural drainage waters. Rain samples in our study exhibited typically high values of $\delta^{18}O_{NO3}$ ($66^{o}/_{oo}$), but the river samples had a much lower $\delta^{18}O_{NO3}$, indicating that rainfall and atmospheric nitrateare not major contributing sources of nitrate. Mayer *et al.* (2002) concluded that $\delta^{18}O_{NO3}$ values less than $15^{o}/_{oo}$ indicate no direct impact from atmospheric nitrate. In our study, nitrate isotope values largely fall in the overlapping ranges for soil and animal waste/sewage (Figure 2.2), indicating a dominant influence of agriculture activities on riverine nitrate from the upper Mississippi River Basin.

Decreasing$\delta^{15}N_{NO3}$ with increasing nitrate concentration signifies a new nitrate source, i.e. nitrification. Increasing $\delta^{15}N_{NO3}$ with decreasing nitrate concentrations suggestsdenitrification. However, in our study, we did not find a relationship between nitrate concentrations and$\delta^{15}N_{NO3}$. There have been controversial reports with regard to this relationship. For instance, Mayer and others (2002) found a correlation between $\delta^{15}N_{NO3}$ and NO_3 concentrations in watershed outlets in the mid-Atlantic and New England states.But in a study on nitrogen isotopic signature in the Upper Mississippi River, Chang and others (2002) did not find such a correlation; instead, they reported that for at least one location, the $\delta^{15}N_{NO3}$ values were "chaotic" when compared to nitrate concentrations. The researchers attributed the lack of relationship between $\delta^{15}N_{NO3}$ and nitrate concentrations in large rivers to dilution and mixing of nitrate sources. This may be especially true for the lower Mississippi and Atchafalaya Rivers, where flow and nitrogen source come from the various large tributaries.

$\delta^{18}O_{NO3}$ is typically a marker for turnover because nitrate oxygen is exchanged during high microbial activity incorporating a large fraction of the signal from the $\delta^{18}O$ of water (Mengis*et al*., 2001). Water-^{18}O varies based on season, resulting in heavier ^{18}O-H_2O in summer when evaporation is highest (e.g. Kendall and Coplen, 2001; Reddy *et al*., 2006). Typical ^{18}O values of water in the Mississippi-Atchafalaya region range from -6$^{o}/_{oo}$ to -2$^{o}/_{oo}$ (Kendall and Coplen, 2001).Therefore, new nitrate formed from nitrification in the river should reflect a lighter ^{18}O of nitrate. Newly formed nitrate generally has higher $\delta^{18}O_{NO3}$ than the source water because of DO incorporation (Snider *et al*., 2010). This may account for the $\delta^{18}O_{NO3}$values we found during late summer 2007 and 2008; however, nitrification should also correspond to an increase in nitrate if there are no removal terms. We observed lower nitrate in the Atchafalaya River than the Mississippi River in July of both 2007 and 2008, which is opposite than what we

would expect if nitrification is a dominant process in the Atchafalaya River. Groundwater also has lower $\delta^{18}O_{NO3}$ values than surface water (Kendall and McDonnell, 1998) because the source for groundwater nitrate can be mineralized soil organic matter (Deutsch *et al*., 2006). A water balance analysis (Xu, 2006a) suggests that the basin is a groundwater discharge zone during late summer to early fall. Also considering the reduced discharge found during late summer, after the spring peak from snowmelt upriver, groundwater may be a contributing source in late summer for both rivers.

During typical flow patterns, our data indicate that there is no clear difference in nitrate processing between the two rivers. There is seasonality in isotope values in both the Atchafalaya River and Mississippi River, which reflects changes in the shared source from the upper Mississippi River. These conditions are applicable for average conditions, but not for extreme events as discussed below.

2.4.2 Flood and Hurricane Impacts on River Water Chemistry

During the 2-year study period, two extreme events occurred: the Mississippi River Spring Flood in April 2008 and two major hurricanes in September 2008. The Mississippi River crested 13.1 m at Baton Rouge on April 23, 2008, which is among the historical top ten crests during the 80+ years of river stage monitoring at this location. Hurricane Gustav was a Category 2 storm, which resulted in high rainfall variation from south-central to northern Louisiana. For instance, rainfall for September 1st, 2008 totaled 51.5 mm at Baton Rouge. In New Iberia, near the west bank of the southern Atchafalaya Basin, 130 mm of rain fell on September 1st followed by 104 mm of rain on September 2nd (NOAA). Hurricane Ike made landfall at Galveston, Texas on September 13, 2008. Although it was a category 2 in wind speed, the large breadth of the storm resulted in large-scale effects in both wind and precipitation. Because sampling occurred

prior to both hurricanes at the end of August and the day after Hurricane Ike passed by southeast Louisiana, this study cannot separate the effects of the individual storms.

The 2008 Mississippi River Spring Flood reflects what happens when additional water is directed into the Atchafalaya Basin. This important event can help with management strategies to determine how nitrate dynamics are impacted by increased flow to the Atchafalaya River. Although N concentrations were lower during the flood event than historical values, increased discharge contributes to significantly higher N-loadings to the upper Mississippi River (Hubbard *et al.,* 2011). We also observed this in the Atchafalaya River and Lower Mississippi River where nitrate flux was high. In a study of five German rivers, nitrification was the main source with soil leaching as the main transport of nitrate during spring flood (Johannsen*et al*., 2008). During the flood the nitrate isotopic signal was that of soil nitrate, but this is not a dramatically different signal than was found during the rest of the year.

When flooding occurs,hydrological connectivity of a river and its floodplain increases, providing the opportunity for the nitrate to be assimilated or transformed. Denitrification is likely to occur in small streams and backwater areas that have more interaction with soil as well as favorable conditions such as anoxic conditions, availability of carbon, and interaction with soil (Chang *et al*., 2002). There is accordingly lower nitrate removal with increasing stream order (Alexander *et al.,* 2000). The Atchafalaya Basin cypress swamp has high denitrification potential, especially at higher temperatures as has been determined through lab soil microcosm experiments (Lindau*et al.,* 2008). Wetland diversions can remove large amounts of nitrate from rivers, for example the CaenarvonDiversion that receives water from the Mississippi River in southern Louisiana results in the loss of 46 g-nitrate-m^{-2} per year (Mitsch*et al.,* 2005). However, these conditions do notexist in the main channel of large rivers. The main channel's high flow

results in virtually zero residence time and dilution of the isotope signal from the relatively small fraction of nitrate that may undergo denitrification.

Periods following flooding may have increased residence time, which allows for more turnover and results in greater variation in $\delta^{18}O_{NO3}$values. Typically, it takes water 36 hours to travel from the diversion to the outlets in the Atchafalaya River. After flooding, transport time in the Atchafalaya River may be longer; therefore, comparing values from the Atchafalaya to Mississippi River for the same date may be inappropriate following periods of flooding.

The 2008 Spring Flood likely reached a threshold in which water from the main stem of the Atchafalaya was reaching backwater areas. Denitrificationrates reported are high in these backwaters (DeLaune*et al*., 2005) and if the remaining nitrate were flushed back into the main channel during the receding limb, there should be higher$\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values in the Atchafalaya River. Therefore, the difference in isotope values between the two rivers may be the result ofdenitrification. The difference was only $4^{o}/_{oo}$, despite an expected fractionation factor of $10\text{-}30^{o}/_{oo}$ for denitrification (Mariotti*et al.,* 1981; Kellman and Hillaire-Marcel, 1998; Sebilo*et al.,* 2003). However, the portion of the nitrate denitrified is likely a small fraction, resulting in only a modest increase. This difference was not seen in summer 2007 probably because the river discharge did not reach the threshold required to inundate backwater swamps based on the estimate by Allen *et al.* (2008).If the Atchafalaya River were to be managed for nitrate reduction, multiple high discharge pulses above this threshold would be necessary each year to allow river water onto the floodplains and backwater areas.

High amounts of precipitation from hurricanes can wash nitrate from soils to surface and groundwater. Nitrate in streams in Puerto Rico increased 182% and remained high after Hurricane Hugo in 1989 (Schaefer *et al*., 2000). Because small streams are affected the most,

the backwater areas of the Atchafalaya could be expected to have increased in nitrate. Brulandet *al.*(2008) found thatafter Hurricanes Francis and Jeane in September 2004, NO_3-N in the soil was significantly lower.The researchers concluded that the intense precipitation flushednitrate from the soil into surface water and groundwater. As a result, nitrate isotope signature should be that of soil nitrate ($\delta^{15}N_{NO3}$: ~5$^{o}/_{oo}$ - 10$^{o}/_{oo}$) after a large rainfall event such as a hurricane.However, this was not the case in our study. On September 13, 2008 after the rainstorm from Hurricane Ike both the Atchafalaya and Mississippi Rivers had lighter signals ($\delta^{15}N_{NO3}$: 3.0$^{o}/_{oo}$ at Atchafalaya and 3.4$^{o}/_{oo}$ at Mississippi),suggesting nitrified ammonium fertilizer source.Comparing these values to those observed in the prior year (8.2 $^{o}/_{oo}$ to 10.3 $^{o}/_{oo}$), expected values during the fall are probably on the higher end of the range measured in 2008 (~10 $^{o}/_{oo}$) rather than the lower end (3.4$^{o}/_{oo}$). Thissuggeststhat the lower value was potentially a result from Hurricanes Gustav and Ike.Strong winds and storm surge brought detritus into waterways while mixing detritus throughout the water column. After Hurricane Gustav, the Atchafalaya Basin experienced an increased input of green leaves, an unusual nitrogen source, which also resulted in low DO (Atchafalaya Basinkeeper, 2008) which may have contributed to the lower isotope value and wide range observed (3.4$^{o}/_{oo}$ to 11.8 $^{o}/_{oo}\delta^{15}N_{NO3}$ for back to back sampling events).

2.4.3 Nitrate Source to Mississippi-Atchafalaya River Basin

In terms of nitrogen source, no clear division in the nitrate isotope signal between the Atchafalaya River and the Mississippi River can be made. Although the Mississippi River has a slightly heavier $\delta^{15}N_{NO3}$ than the Atchafalaya, both signals fall within the same source group (Figures2.2 and 2.6). Soil nitrate is the dominant signal; however, it is difficult to discern it from other overlapping sources including synthetic nitrate fertilizer and human and animal wastes (Kendall, 1998). A crossplot of nitrate $\delta^{18}O$ versus $\delta^{15}N$ falls close to the 0.5 line (slope= 0.45)

suggesting that the nitrate was affected by some degree of denitrification (Figure 2.8). Since it is observed in both systems, this transformation likely occurred well upriver prior to the Atchafalaya River diversion and in the Mississippi River headwaters. This indicates that the Atchafalaya River is not significantly different from the Lower Mississippi River when it comes to nitrate processing during the study period. Like the Lower Mississippi River, the Atchafalaya transports nitrate with little change in concentration or processing during typical flow patterns.The Red River, which flows directly into the Atchafalaya River, is a source typically not considered as a significant contributor of nitrate, but it may contribute to the Atchafalaya River's slightly lower $\delta^{15}N_{NO3}$ values. Land use in the Red River watershed is predominantly forest (42%), pasture (33%) and agricultural cropland (12%). Thus, the Red River may contribute additional organic nitrogen and ammonium to the Atchafalaya River as a source for nitrification in the well-oxygenated channel. This would yield the moderately lower $\delta^{15}N_{NO3}$ measured in the Atchafalaya River as compared with the Mississippi River. A difference was already found in the $\delta^{18}O$ of water between the Atchafalaya and Mississippi Rivers suggesting an influence from the Red River. Wagner and Slowey (2011) noted that the $\delta^{18}O_{H2O}$ is higher in the Atchafalaya River (-7.2 $^{o}/_{oo}$ to -3.7 $^{o}/_{oo}$) than the Mississippi River (-8.6 $^{o}/_{oo}$ to -5$^{o}/_{oo}$). Longing and Haggard (2010) found a wide range of total nitrogen (<0.02 mg L^{-1} to 20.2 mg L^{-1}) in the sub-watershedsof the Red River basin, with the 25th percentile in the lower range (0.37 mg L^{-1} to 0.88 mg L^{-1}).

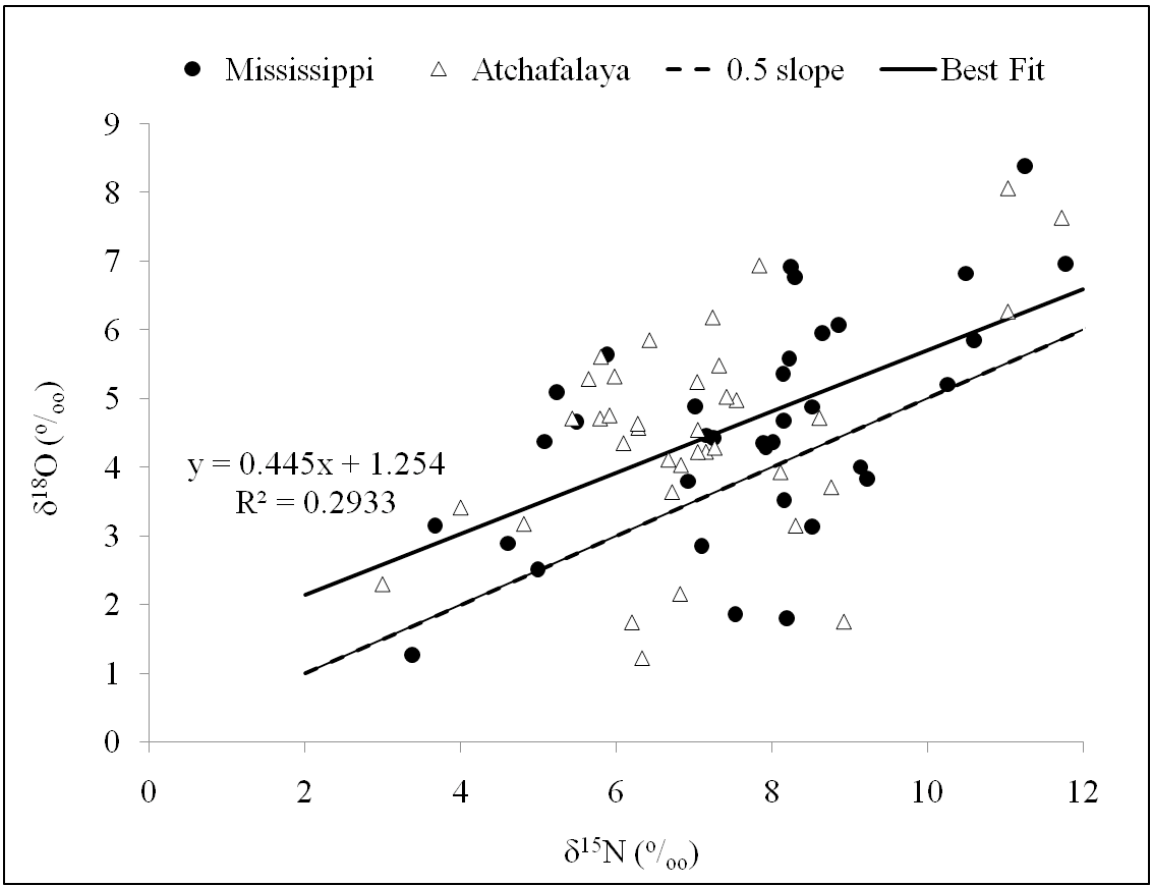


Figure 2.8. $\delta^{18}O_{NO3}$versus $\delta^{15}N_{NO3}$ of nitrate in the Atchafalaya and Mississippi Rivers. Dotted line with slope of 0.5 represents expected transformation. Black line is best fit line to data.

The relative contribution of flow from the Red River and Mississippi River into the Atchafalaya River varies depending on season. In spring when flow is high, the majority of flow in the Atchafalaya River is from the Mississippi River while during low flow periods in late summer the Red River fraction is larger than during other periods (Bratkovich*et al.,* 1994; Xu and BryantMason, 2011). Althoughnitrate isotope values are not available for the Red River, nitrate concentrations in the Red River during the study period averaged 0.15 mg L^{-1} (Xu and BryantMason, 2011), much lower than that in the Mississippi River;hence, the Red River likely has a dilution effect on the resulting nitrate concentrations in the Atchafalaya River. A closer examination of the Red River nitrogen inputs to the Atchafalaya River is necessary.

2.5 Summary and Conclusions

This study investigated nitrate isotopes in the Atchafalaya River that carries the entire flow of the Red River as well as approximately 30% of the Mississippi River's flow into the Northern Gulf of Mexico. It is the first comprehensive assessment on riverine isotopic signature of the lower Mississippi-Atchafalaya River system. During this study the Atchafalaya's discharge was on average 43% of the Mississippi River at Baton Rouge discharge. The Atchafalaya River had higher water temperatures and lower DO, which is attributed to backwater areas in the Atchafalaya Basin that are slower moving and shallower allowing water to heat up. The Atchafalaya River is exporting over 265,000 tonnes of nitrate a year to the Gulf of Mexico with a flux weighted average $\delta^{15}N_{NO3}$ of 6.5$^{o}/_{oo}$.

Overall, isotopic compositions are similar in both the Mississippi and Atchafalaya River reflecting a similar source and processing. The Mississippi River, however, has a consistently higher $\delta^{15}N_{NO3}$value. The Atchafalaya River's lower $\delta^{15}N_{NO3}$values may instead be the result of the Red River, a source that is typically not considered as a significant contributor. Examining the mass input and nitrate isotope values from the Red River may reveal potential inputs.

At first glance, the Atchafalaya with its braided channels would seem ideal for removal of nitrate; however, the results from this study suggest that the system is similar to the confined Mississippi River main stem in its effectiveness in removing nitrate. The lack of variation between the nitrate isotopic compositions of the Atchafalaya and Mississippi River indicates the majority of nitrate transported through the Atchafalaya River is not processed significantly more than the Mississippi River. Isotope results from extreme flood pulses (i.e. spring 2008) suggest

that these large pulses may be the only opportunity for nitrate removal. Management strategies for nitrate removal should consider these events to allow floodplain inundation.

CHAPTER 3. NITRATE REMOVAL POTENTIAL OF THE ATCHAFALAYA RIVER BASIN DURING A MAJOR FLOOD EVENT

3.1 Introduction

The Mississippi River (MR), draining 41% of the continental United States, delivers each year approximately 953,000 megagrams (Mg) nitrate-nitrogen (referred to as nitrate or NO_3N from here on) (Goolsby and Battaglin, 2001) into the Northern Gulf of Mexico (NGOM). About 174,600 Mg of the nearly 1 million Mg of nitrate input is discharged from the MR's largest distributary, the Atchafalaya River Basin that has extensive floodplains and backwater swamps (Xu, 2006b). The excess nitrogen is one of the major causes of the hypoxic dead zone (a condition when dissolved oxygen concentration in the deepwater is below 2 mg L^{-1}) occurring in NGOM during late spring and summer for the past two decades (Rabalais et al., 2007; Turner et al., 2008). Ecologically and economically, the hypoxic dead zone can have large reaching effects (O'Connor and Whitall, 2007; Diaz and Rosen, 2011). Rabalais and colleagues (2010) found that the extent of hypoxia in July averaged 13,500 km^2 from 1985 to 2009, with a range from negligible in 1988 to 22,000 km^2 in 2002. The fluctuation of the hypoxic dead zone has been found to be partially dependent on nitrogen load from the Upper Mississippi River (UMR) (Wang and Justic, 2009), especially during May and June (e.g., Rabalais et al. 1996) when river flow is normally high. To reduce the large nitrogen input to NGOM, several options were suggested in the action plan released in 2008 by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (MR/GOMWNTF, 2008), including diversion of the nitrogen-rich Mississippi water into floodplain wetland systems.

Many studies have found that riverine corridor wetland systems have the capability of reducing nitrogen loading to downstream areas (e.g. DeLaune et al., 2005; Noe and Hupp, 2009).

Floodplain systems have been reported to be effective sinks for riverine nutrients through removal mechanisms including denitrification, assimilation, and subsurface transport (Lindau et al., 1994; Tockner et al., 1999; Forshay and Stanley, 2005). However, it has also been reported that denitrification in river sediments is rather low because of unfavorable conditions (e.g. Hill, 1979; Alexander et al., 2000). Conditions that favor denitrification include high concentrations of nitrate and organic carbon with high water temperatures under anoxic conditions (Pina-Ochoa and Alvarez-Cobelas, 2006). Of these conditions, nitrate concentration in the overlying water was determined as the dominant control on denitrification potential followed by the thickness of the soil oxic surface layer (Christensen et al., 1990). Racchetti et al. (2011) argued that riverine wetlands increase interaction surface for denitrification while supplying nitrate constantly and therefore, encourage higher rates of nitrogen removal.

Channels of most rivers today are confined by levees for flood control and navigation purposes. The confinement separates the rivers from their natural floodplains, limiting or eliminating element exchange between water and terrestrial systems. This is particularly the case with large river systems, such as the MR, whose current path is estimated to cover only 10% of its once vast floodplain. Alexander et al. (2000) reported that nitrogen loss by denitrification decreases with increasing channel size; therefore despite the Atchafalaya River's potential for denitrification, it will occur when the channel water interacts with its extensive floodplain. According to our previous sampling from the Atchafalaya (BryantMason et al., 2012), this may be limited to very high flood stages, higher than typically seen in the yearly spring floods. With little progress made in reducing nitrate transport in the Mississippi River and in some locations nitrate increasing (Sprague et al., 2011), determining nitrate reduction techniques, especially during high flow events is vital.

Although the Atchafalaya River would appear to be an ideal area to reduce nitrate loading from the MR, it does not do so under average conditions when examining the annual NO_3N budget (Xu, 2006b; Turner et al., 2007). A significant flooding event should in theory allow the river to leave the channel to interact with high denitrification-potential hotspots found in the basin by Scaroni et al. (2010). The 2011 major Mississippi River flood provided a unique opportunity for us to conduct a rapid sampling to test the hypothesis that floodplains function as a significant sink for nitrate during an extreme flood event. Combined with mass balance data, paired isotope technique can determine removal processes such as assimilation and denitrification(e.g. Wassenaar, 1995; Cohen et al., 2012). We also aimed to assess what role the timing of the flood later in the season played in nitrate removal. During normal river flow conditions, there is low denitrification potential resulting in nitrate loads, $\delta^{15}N_{NO3}$, and $\delta^{18}O_{NO3}$ values being equal at the input and output (BryantMason et al., 2012). We hypothesize that during extreme flood events, overbank flow occurs and the river water interacts with the floodplain where there is higher denitrification potential. As a result the nitrate loads will be lower at the output and the $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ will be higher at the output reflecting denitrification.

3.2 Methods

3.2.1 Study Area

The Atchafalaya River is formed by the entire Red River flow from western Texas combined with approximately 30% of the Mississippi River's latitudinal flow. The diversion of the Mississippi River flow into the Atchafalaya is controlled by a structural complex, the Old River Control structure that was completed in 1963 to restrict the increasing proportion of the Mississippi shifting to the Atchafalaya. Because of the shorter path to the Gulf of Mexico, the

Atchafalaya would capture the flow of the Mississippi without intervention resulting in drastic economic effects on the large number of ports in the lower Mississippi River (e.g. Roberts, 1998; Ford and Nyman, 2011). The Atchafalaya River flows southwards approximately 200 kilometers from Simmesport, Louisiana (30°59'00" N, 91°48'00" W) into the Gulf of Mexico via two outlets, Morgan City (29°41'35" N, 91°12'43" W) and Wax Lake Outlet (29°41'55" N, 91°22'24" W), Louisiana (Figure 3.1). The river is confined by levees on the east and west, in a distance varying from several kilometers in the north to approximately 35 kilometers in the south, creating a wide floodplain basin for a more natural lowland system (Ford and Nyman, 2011). In its first 110 kilometers south of the Mississippi River diversion, the Atchafalaya River flows in a well-confined channel. Afterwards, it becomes a series of braided channels that are highly connected with the surrounding landscape. The sediment rich water from the Mississippi River has resulted in filling in of the basin, converting many of the open water regions in the Atchafalaya River Basin to bottomland hardwood forests especially in the northern part of the basin (Coleman, 1988; Roberts, 1998) reducing connectivity of the river except during high floods.

The Atchafalaya River Basin is about 4,678 km^2 and composes predominantly wooded lowland and cypress-tupelo surface flow swamp with some freshwater marshes in the lower basin area. The river is channelized to allow for navigation and the basin as a whole is managed as a flood control basin. The basin serves as a major floodway for the Mississippi River floodwaters; therefore, more of the Mississippi River water can be directed into the basin from the Morganza Spillway during extremely high flow periods to reduce flooding potential for downriver cities such as Baton Rouge and New Orleans.

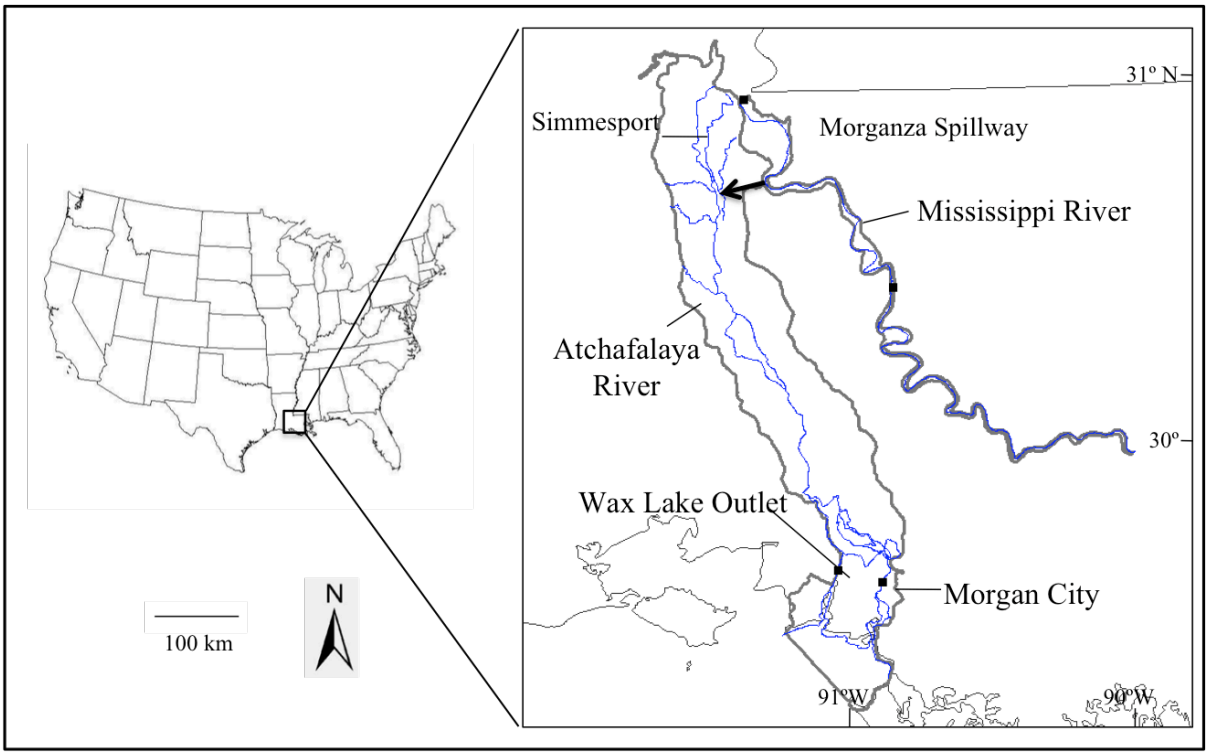


Figure 3.1. Sampling locations on the Atchafalaya River (Simmesport, Wax Lake, and Morgan City) during the 2011 Mississippi River Spring Flood. The Morganza Spillway was opened during the peak flood weeks.

In spring 2011, the lower Mississippi River rose rapidly. The river stage at Baton Rouge began increasing in early March. By 9 May river discharge was steadily increasing (Figure 3.3) and stage reached 12.4 m, 0.2 m higher than its major flood stage. To protect the cities of Baton Rouge and New Orleans, the U.S. Army Corp of Engineers began opening the Morganza Floodway on 14 May (Figure 3.2). On 18 May the maximum number of bays for this flood event was opened, diverting 3,228 m^3s^{-1} of water into the Atchafalaya River Basin (U.S. Army Corps of Engineers, 2011). Additional protection was also needed for the cities of Morgan City and Berwick, so the river side protection walls were closed to block the river water which left its channel from reaching the nearby structures.

Figure 3.2. Photos of the Morganza Spillway at Highway 90 taken on (A) May 14, between 2:00 pm and 2:30 pm, just a few hours before the gates were opened,and (B) May 22, between 1:30 pm and 2:30 pm, 8 days after the initial opening (Photos courtesy of Y. Jun Xu).

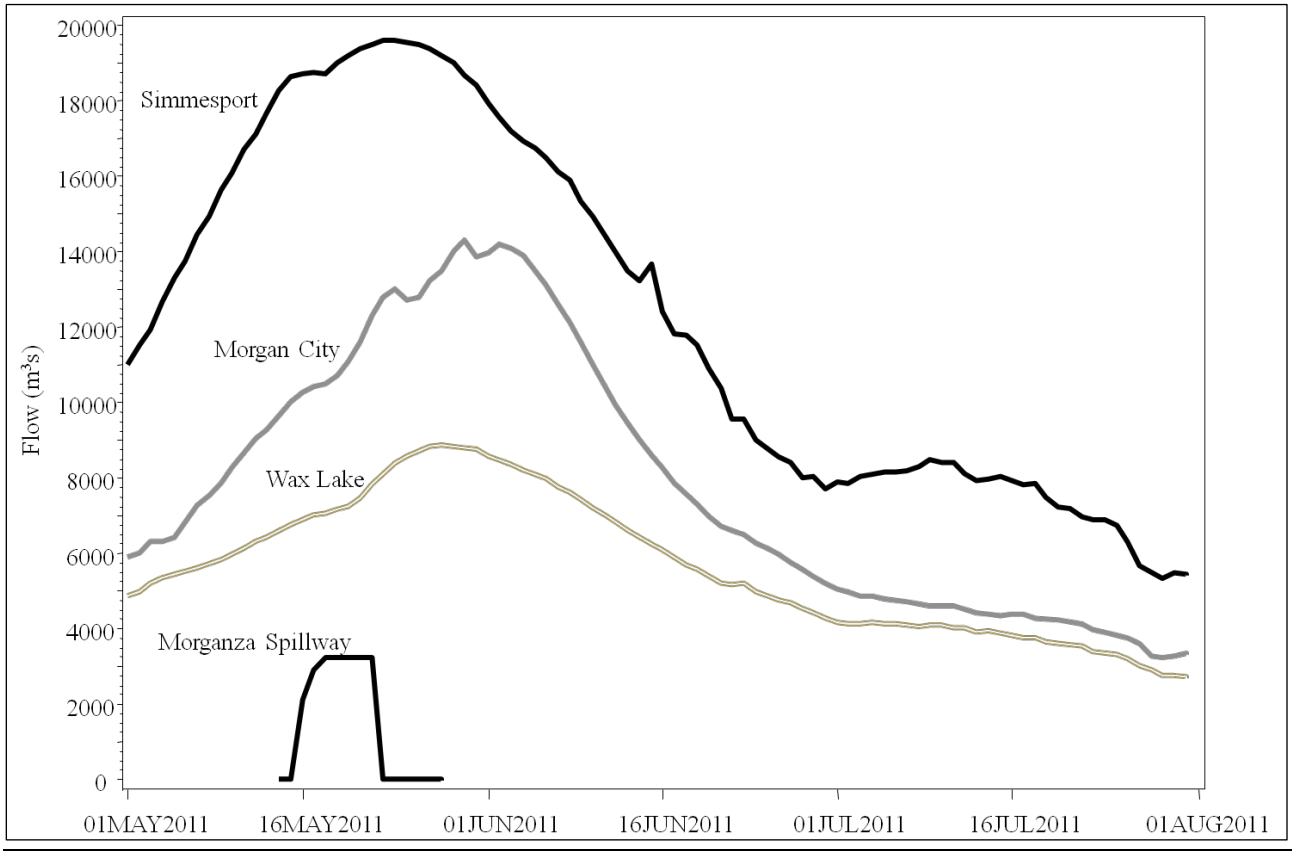


Figure 3.3. Discharge at the input (Simmesport, Morganza Spillway) and output (Wax Lake and Morgan City) during the 2011 Mississippi River Spring Flood.

3.2.2 Sampling Design

During the 10-week high flow period from 14 May 2011 to 20 July 2011, we collected water samples at three locations on the Atchafalaya: Simmesport (considered as input), and Wax Lake Outlet and Morgan City (together considered output). Each sampling effort was completed in a single day with sample frequency ranging from twice to once per week depending on how quickly river stage was changing. Composite grab samples were collected from shore. In fast flowing main channels, the chemical constituents are uniformly mixed making the sample representative of the entire water channel (e.g. Fry and Allen, 2003). Samples collected were filtered through a GF/F glass fiber filter (Whatman International Ltd., Maidstone, England). Samples were preserved with 25% hydrochloric acid, lowering the pH to 2, and kept at 4 ºCuntil analysis.

To determine ambient conditions at the sampling time, insitu measurements including river water temperature, dissolved oxygen, and specific conductance were also made at the three sampling locations. Daily average river discharge was obtained from three gauging stations: Simmesport (United States Army Corps of Engineers (USACE) station #03045), Wax Lake (United States Geological Survey (USGS) #07381590), Morgan City (USGS #07381600), and an USACE temporary gauge at the Morganza Spillway. Standard error for river discharge ranges from 3% to 6% (Sauer and Meyer, 1992).

3.2.3 Isotope Analysis

Nitrate isotope values ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) were measured using the azide method of McIlvin and Altabet(2005). Briefly, this method reduces nitrate first to nitrite with cadmium and then to nitrous oxide in a sealed 20 mL vial with azide/acetic acid buffer. Analysis of the resulting nitrous gas was performed with an Isoprime mass spectrometer (GV Instruments,

Manchester, England) in the Biogeochemistry Laboratory at the University of Massachusetts-Dartmouth. Delta values are expressed relative to atmospheric nitrogen for $d^{15}N_{NO3}$ and to Vienna standard mean ocean water (VSMOW) for $d^{18}O_{NO3}$. Ratios are used to represent the abundance of heavy to light isotope, as in the case of nitrogen isotope ratio (R_N):

$$R_N = {}^{15}N/{}^{14}N \quad (1)$$

Isotopic composition is presented in delta (δ) notation:

$$\delta A = [(R_A - R_{St})/ R_{St}] * 1000(‰) \quad (2)$$

where R_A is the isotope ($^{15}N/^{14}N$ or $^{18}O/^{16}O$) ratio measurement of sample A and R_{St} is the isotope ratio measurement of the standard. Analytical reproducibility ranged from $0.2^{o}/_{oo}$ - $0.4^{o}/_{oo}$. In addition, flood samples were analyzed for nitrate concentration using the vanadium method on a SmartChem 200 discrete analyzer (Westco Scientific Instruments, Inc., Brookfield, CT). Nitrate concentrations are presented as mg L^{-1} of nitrate-nitrogen.

3.2.4 Mass Load Estimation and Statistical Analyses

Daily NO_3N mass loads for the three sampling locations were computed by multiplying daily discharge and the nitrate concentrations measured at the locations. To estimate nitrate mass input from the Morgaza Spillway during the opening (14 May to 7 July), the nitrate concentration measured at Simmesport, was assumed to be representative of the Morganza Spillway because the low Red River flow during the MR flood made little effect on the water chemistry at Simmesport. Estimated mass loads for Simmesport and Morgaza Spillway were summed up to represent total nitrate input into the Atchafalaya, and the sum of the estimated mass loads for Morgan City and Wax Lake Outlet was used as total nitrate output from the basin.

The mass balance for the basin (ΔNO_3N) is therefore the difference between the input and output given as below:

$$\Delta NO_3N=[(Q_{Sim}C_{Sim})+ (Q_MC_{Sim})] - [(Q_{MC}C_{MC})+ (Q_{WL}C_{WL})] \quad (3)$$

whereQ_{Sim}, Q_M, Q_{MC}, and Q_{WL} are the discharge at Simmesport, Morgaza Spillway, Morgan City, Wax Lake, respectively, and C_{sim}, C_{MC}, and C_{WL} represent nitrate concentrations of the accordingly locations. A water budget is the difference between inflow (i.e., sum of the discharges at Simmesport and Morganza Spillway) and outflow (i.e., sum of the discharges at Morgan City and Wax Lake Outlet) as given below:

$$\Delta W= (Q_{Sim} + Q_M) - (Q_{MC} + Q_{WL}) \quad (4)$$

Where Q_{Sim}, Q_M, are the surface flows into the basin at Simmesport (Q_{Sim}) and the Morganza Spillway (Q_M). Q_{MC}, and Q_{WL} are the surface flows out of the basin at Morgan City and Wax Lake (Q_{MC} and Q_{WL}). Input from rainfall during the 10-week study period is considered to be negligible when compared to the amount of water and nitrate inputted from the Mississippi River.

Based on discharge, data were separated by rising and receding flow condition. Dates of peak discharge varied at all three sites, with receding flow beginning on 28 May at Simmesport, 1 June at Wax Lake, and 3 June at Morgan City. A two-way ANOVA test was used to evaluate significance in difference in insitu water quality variables (i.e. river water temperature, dissolved oxygen (DO), and specific conductance), nitrate concentrations, and isotope values among sites and flow conditions, with nesting of date within limb. An alpha value of 0.05 was used. Statistical analyses were performed with Proc Mixed on SAS 9.2 software (SAS Institute 2008). When there was no significant difference among sites, data were pooled by flow condition.

Interrelationship of measured parameters was investigated using Pearson product moment correlation analysis.

3.3 Results

3.3.1 Ambient Conditions During 2011 Spring Flood

During the 10-week high flow period, river water temperature increased from 19.1 ºCto 30 ºC with an average of 26 ºC. The temperature increase was sharp during the first four weeks and continued slowly for the remaining measured weeks (Figure 3.4). All sampling sites had relatively well-oxygenated water throughout the high flow period with DO levels mostly above 5 mg L^{-1}. Because insitu measurements were limited at Morgan City to after June 14th, DO was skewed to an overall lower mean (4.2 mg L^{-1}). Specific conductance during this flood period averaged 0.360 mS cm^{-1}, ranging from 0.239 mS cm^{-1} to 0.458 mS cm^{-1}. Water temperature and specific conductance were positively related, though neither varied largely among the sampling sites. During the flood recession river water temperature increased on average nearly 7 ºC in the receding flow, while DO decreased 1.6 mg L^{-1} (Table 3.1).

3.3.2 Mass Transport

During the 10-week flood period, a total of 89,634 Mg NO_3N entered the basin and a total of 83,158 Mg NO_3N exited the basin from the two outlets, showing a nitrate mass reduction of 6,476 Mg, or a retention rate of 7%. Error for calculated nitrate mass was 5% at Simmesport, 6% at Wax Lake, and 7% at Morgan City. Nitrate retention was highest during the week of 15 May (Figure 3.4). Nitrate concentrations from the three sampling locations averaged 1.3 mg L^{-1}, varying from 0.7 mg L^{-1} to 2.3 mg L^{-1}, with one of the downriver locations (Morgan City) slightly lower than the upriver location ($f=3.67$; $p=0.02$; Table 3.1; Figure 3.5A). Lowest nitrate concentrations were observed at the flood peak and the highest concentrations occurred during

the flood recession. Weekly nitrate load peaked at 14,822 Mg for Simmesport (input) and 10,702 Mg combined for Morgan City & Wax Lake Outlet (output), and then decreased to 7,587 Mg at the input and to 8,048 Mg at the output. The concentration change was inversely correlated with the flood discharge (Pearson's r = -0.50; p=0.001), with the lowest nitrate concentration occurring at the peak flow and the highest concentration occurred approximately one month later as the river flow receded.

3.3.3 Isotope Values

Similar to the nitrate concentration, $\delta^{15}N_{NO3}$ values also increased during the flood recession (Table 3.1; Figure 3.6). There was larger variation in the $\delta^{15}N_{NO3}$ values from late June through July, but there was no significant delay in values measured downriver to those measured in the upper Atchafalaya River ($p>0.10$). There was a significant difference between the outlets ($t=-2.71$; $p=0.01$). $\delta^{15}N_{NO3}$ values in the receding flow were significantly higher than those in the rising flow ($f=113.45$; $p<0.0001$; Table 1), coincidentally in a positive relationship with temperature and specific conductance (Table 3.2).

Variability in $\delta^{18}O_{NO3}$ values existed among the sites and during the study period (Figure 4). Average $\delta^{18}O_{NO3}$ was 3.4‰ with a fairly narrow range of 2.0 ‰ to 5.0 ‰. $\delta^{18}O_{NO3}$ was significantly lower at Morgan City than at Simmesport ($t=3.96$; 0.0006) or Wax Lake Outlet ($t=5.01$; <0.0001). The crossplots of $\delta^{18}O_{NO3}$ values versus $\delta^{15}N_{NO3}$ values do not reflect any significant transformation (Figure 3.6). Although the slope is higher on the crossplot for Simmesport (0.51) as compared to the outlets (~0.37), a single point low $\delta^{18}O_{NO3}$ value on 30 May is affecting the slope at Simmesport. When this point is removed, the slope (0.3807) is similar to the outlets.

Table 3.1. Average values of water temperature (Water temp), dissolved oxygen (DO), specific conductance (Sp Cond), and nitrate isotope values ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) for sites on the Atchafalaya River separated by flow condition during the 2011 Mississippi River flood. Asterisk indicates significant difference at p>0.05. Insitu data were not available for Morgan City during the rising flow condition.

Flow Condition	N	Site	Date Range	Nitrate	Temp	DO	SpCond	d15N	d18O
Rising	2	Simmesport	May 15-May 27	1.1 ± 0	19.5 ± 0.35	6.8 ± 0.05	0.268 ± 0	5.76 ± 0.06	3 ± 0.8
	3	Wax Lake	May 15-May 31	1 ± 0.1	21.5 ± 1.03	6.3 ± 0.93	0.265 ± 0.01	5.75 ± 0.05	3.3 ± 0.2
	2	Morgan City	May 15-June 2	0.9 ± 0.1					2.4 ± 0.2
		All Sites		1.0 ± 0	20.7 ± 0.76	6.5 ± 0.52	0.266 ± 0.01	5.8 ± 0.06	3 ± 0.3
Receding	10	Simmesport	May 28-July 20	1.5 ± 0.1	26.8 ± 0.59	5.2 ± 0.13	0.367 ± 0.02	7.4 ± 0.18	3.6 ± 0.2
	7	Wax Lake	June 1-July 20	1.5 ± 0.2	27.5 ± 0.45	4.9 ± 0.17	0.377 ± 0.02	7.3 ± 0.21	3.7 ± 0.2
	9	Morgan City	June 3-July 20	1.3 ± 0.1	28.4 ± 0.24	4.2 ± 0.19	0.386 ± 0.01	7.8 ± 0.14	3.1 ± 0.1
		All Sites		1.4 ± 0.1	27.5 ± 0.30	4.8 ± 0.12	0.375 ± 0.01	7.5 ± 0.10	3.5 ± 0.1
Rising versus Receding		p-value		* 0.04	* <0.001	* <0.001	* <0.001	* <0.001	0.09

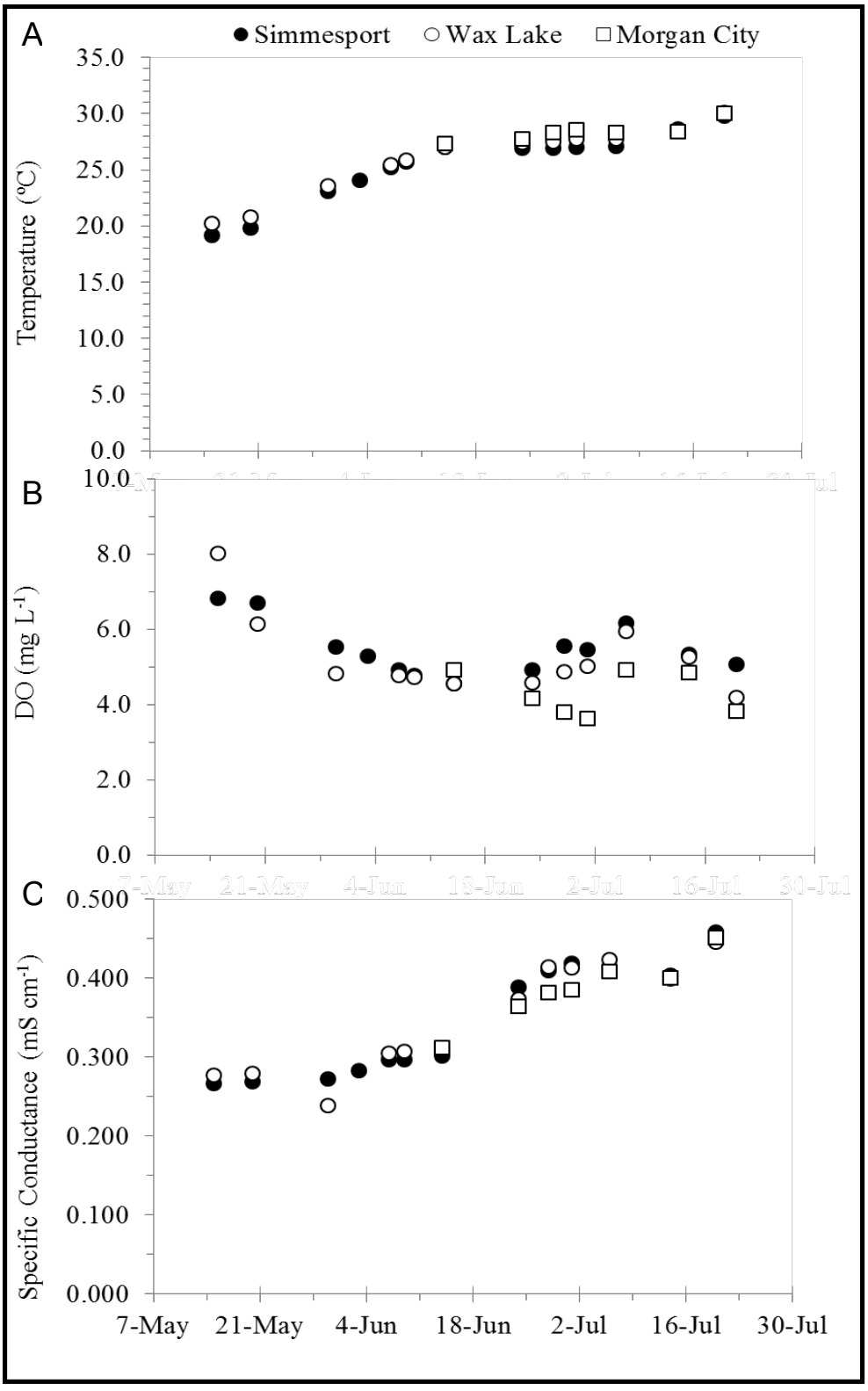


Figure 3.4. Measured: (A) temperature, (B) dissolved oxygen (DO), and (C) specific conductance in the Atchafalaya River during the 2011 Mississippi River Spring Flood.

Table 3.2. Pearson product moment correlation coefficients for water quality parameters in the Atchafalaya River. Significant correlation coefficient is bolded (for r> 0.37; p<0.01). "Sp. Cond." represents specific conductance.

	Temperature	SpCond	DO	d15N	d18O
SpCond	**0.83**				
DO	**-0.72**	-0.35			
d15N	**0.79**	**0.68**	**-0.62**		
d18O	0.21	0.19	0.09	0.36	
NO3N	**0.53**	**0.81**	-0.07	0.35	0.21

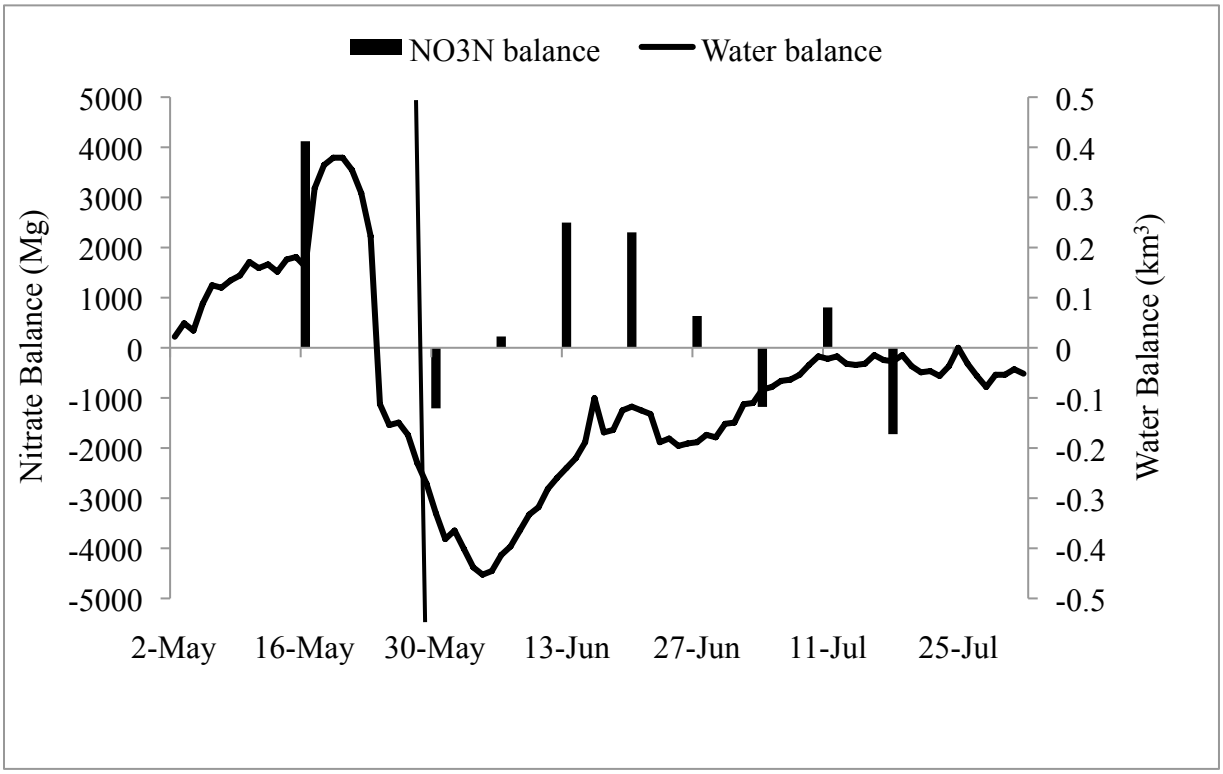


Figure 3.5. Water and nitrate balance in the Atchafalaya River during the 2011 Mississippi River Spring Flood. Solid line represents water flow (L per day) and bars represent total weekly nitrate (Mg). Positive values indicate basin retention, whereas negative values indicate basin release. Vertical line notes the starting day (28 May 2011) of the flood recession at Simmesport.

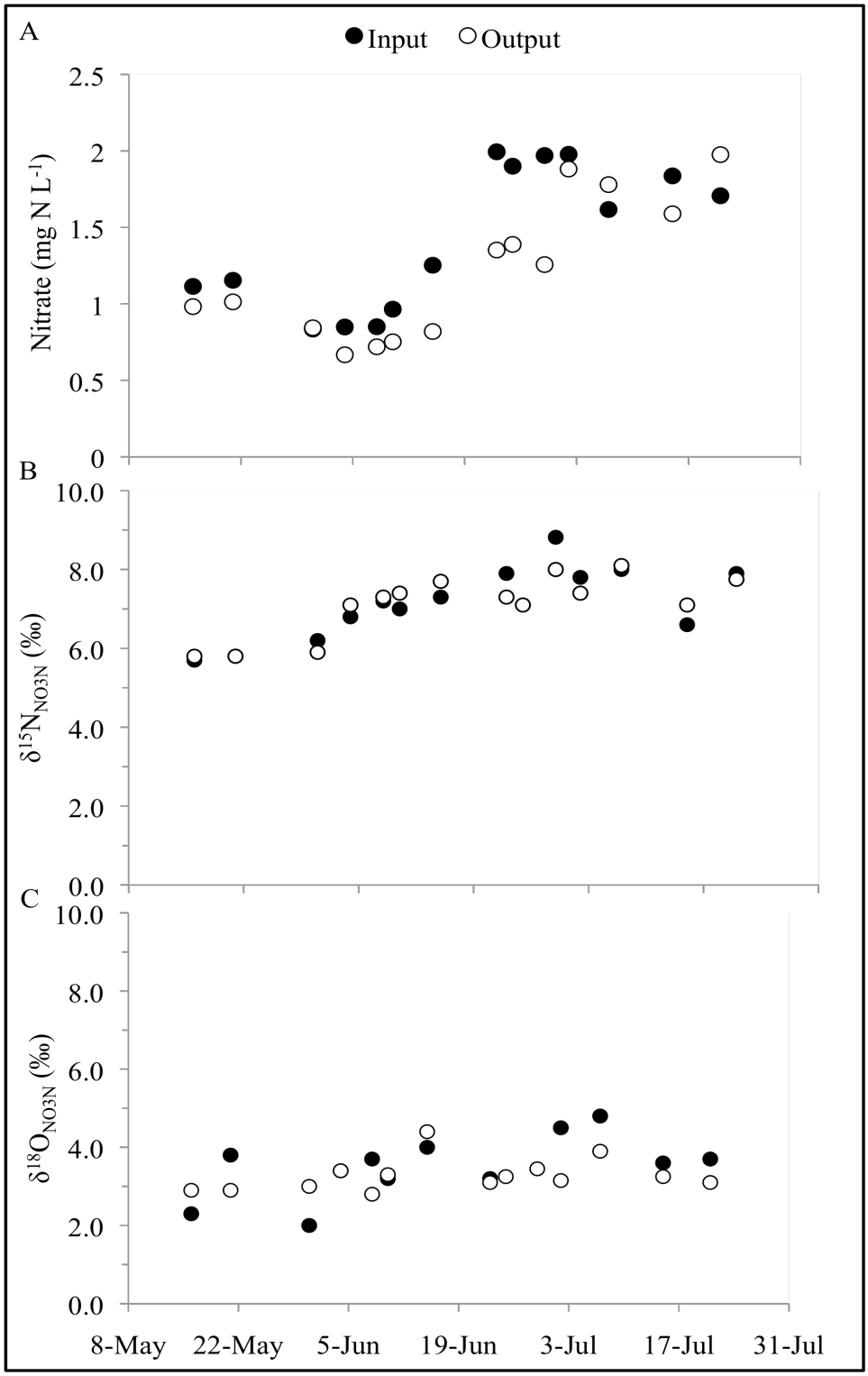


Figure 3.6. (A) Nitrate concentration (B) δ^{15}N-NO_3N and (C) δ^{18}O-NO_3N values on the Atchafalaya River during the 2011 Mississippi River Spring Flood.

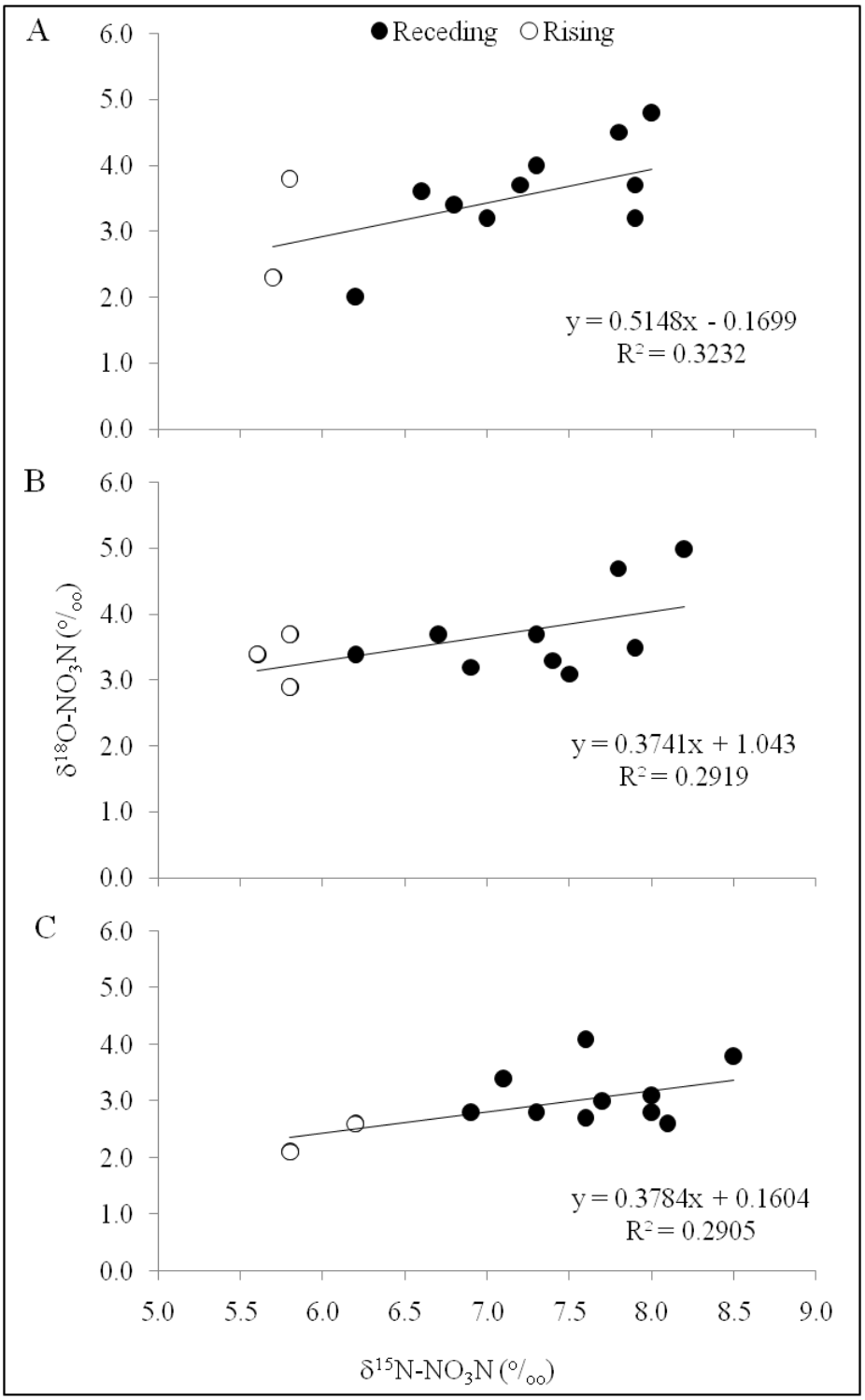


Figure 3.7. Crossplots of δ 18O-NO3N and δ 15N-NO3N values on the Atchafalaya River at (A) Simmesport, (B) Wax Lake Outlet, and (C) Morgan City during the 2011 Mississippi River Spring Flood.

3.4 Discussion

3.4.1 Nitrate Removal by River Corridor Wetlands

Floodplain systems have been reported to be effective sinks for riverine nutrients through removal mechanisms including denitrification, assimilation, and subsurface transport (Lindau et al., 1994; Tockner et al., 1999; Forshay and Stanley, 2005). Therefore, we assumed that significant nitrate removal could occur during a river flood through overbank flow. However, our result indicates that such a removal potential for nitrate through flow-through wetlands may be very limited. The 7% reduction in nitrate found in the Atchafalaya River during the major 2011 Mississippi River flood is much lower than we expected. In addition to the limited change in nitrate load, we did not observe a change in the nitrate isotopic signature between the upbasin and downbasin locations. These findings strongly suggest that no additional nitrate transformations occurred within the main river channel. Furthermore, specific conductance did not change from upriver to downriver, indicating that backwaters had little effect on the main river water chemistry. Collectively, these findings indicate that the majority of nitrate is transported through the basin unprocessed, and that floodplains and corridor wetlands in the basin play insignificant roles in riverine nitrate removal during floods as commonly assumed. Therefore, substantial modifications may be required to make the flow-through river corridor wetland an effective sink for nitrate. This may be similar for other riverine floodplain systems, which have nitrate enrichment problems such as the Coastal Plain Rivers in the Chesapeake Bay Watershed (e.g., Noe and Hupp, 2009) and Baltic Sea Catchment (e.g., Voss et al., 2006).

The paired process of nitrification and denitrification can potentially underestimate nitrate removal because it would result in no change in the mass balance. In riverine wetlands of Northern Italy, denitrification from water column nitrate was 60%-100% of total denitrification

while denitrification from nitrified nitrate was limited (Racchetti et al., 2011). In a bottomland hardwood wetland, Delaune et al. (1996) determined that nitrification made up 5%-12% of the total nitrate reduced in the floodwaters. If nitrate is readily available in the overlying water, as would be the case in areas connected with the nitrate rich Atchafalaya River water, nitrified ammonia sources are not a dominant control of denitrification(Christensen et al., 1990). Our nitrate isotope values did not show any change from the upriver to the downriver location, suggesting that paired nitrification and denitrification was below detection limits.

Only 7% of NO_3N was removed during this flood event, which can limit the detection of the removal process. However, considering that the isotope values from the upper Atchafalaya and the outlets followed each other closely, additional input from draining of the backwater areas in the basin does not appear to have occurred. This small nitrate removal was likely hydrologic transport (water removed from channel) or assimilation (biological uptake), which has minimal change in isotope value. Assimilation can be responsible for a large portion of nitrate removal (Arrango et al., 2008; James, 2010), especially during summer (Gardner et al., 2011). Although Kreiling et al. (2011) determined that denitrification was the dominant removal mechanism for an UMR backwater; they also acknowledge that they may have underestimated assimilation.

The Atchafalaya exported a large quantity of NO_3N during this short flood period. The 83,158 Mg exported represents nearly 48% of the long-term annual average nitrate export (174,600 Mg Xu, 2006b). While the amount of nutrients loaded into a system can limit retention (Hopkinson, 1992), with higher nitrate load suggesting lower possible retention, other factors may have also contributed to the low retention rate. Alexander et al. (2000) and Boyer et al.(2006) reported that nitrogen loss by denitrification decreases with increasing streamflow, water depth, and hydraulic load. Shortened residence time in the basin likely affected nitrate

removal. In a study of a freshwater marsh receiving Mississippi River water, denitrification in the receiving wetland was mainly determined by discharge and resulting retention times, with lower retention time (i.e. 1 day) having lower denitrification rates (Yu et al., 2006). Removal efficiency reached 95% with a 5-day retention period, more than double the removal efficiency of the lowest retention period (1 day). Caernarvon, which diverts freshwater from the Mississippi River to the Brenton Sound, has high removal efficiency of nitrate (88%-97%); however, the residence time is longer and loading rate is a fraction of the Atchafalaya River Basin (Lane et al., 1999). In a study of a Southeastern U.S. treatment wetland, effective nitrate removal (90%) by denitrification could be achieved with a retention time of 3 days as long as there was sufficient carbon source (Misiti et al., 2011). Nitrate removal by a natural tropical riverine wetland system was found to be negligible because of short residence time (6 hours) and high flow, conditions unfavorable to denitrification(McJannet et al., 2012). During average conditions, it takes approximately 36 hours for water to travel from the inlet near Simmesport to the outlets. We speculate that during the flood, it may have been shorter as the insitu measurements followed each other closely at all sites during the sampling period. Additionally, the Atchafalaya Basin can be divided in "compartments" based on water management units (WMU) or subunits (WMS), with the lower basin containing more compartments. During the 2011 flood, these compartments likely filled and then may have acted as a hydrologic dam. This may also explain the limited variation in the in-situ measurements observed from upriver to downriver. Although the flood provided a pulse of water, it was also traveling quickly leaving little time for denitrification to occur effectively.

In a constructed wetland in Korea, nitrate retention was least effective at 25 $\pm$ 17% among nutrients including phosphate, ammonium, and total phosphorus (Maniquiz et al., 2012).

In flow-thru systems, the water is transported faster than immobilization or storage can occur (i.e. Hopkinson, 1992). Artificial wetlands are successful in retaining nutrients such as nitrate because flow through the wetland can be largely controlled to encourage low flow and high residence time. When comparing open systems like riparian floodplains to a closed system in Okefenokee Swamp, less than 5% of the inorganic nutrients were retained in the open system compared to more than 90% in the closed system (Hopkinson, 1992). The results from our study are in agreement with those findings, and they imply that the Atchafalaya River Basin cannot become an effective nitrate sink unless substantial modification has taken place to the wetlands for allowing longer residence time.

3.4.2 Flow ConditionEffect on Nitrate

Although a "first flush" would be expected for a flood event, a recent study (Kato et al., 2009) observed that nitrate had the lowest strength of first-flushes among eight species of phosphorus and nitrogen. Peak flow in the Mississippi-Atchafalaya system occurs every spring from both rainfall and snowmelt in the Upper Mississippi River Basin, as is this extreme flood event, which may explain why we observed a delay in peak nitrate at Simmesport, Wax Lake, and Morgan City. Highest nitrate concentrations were also consistently found in the falling stage about two months after the peak discharge during the ten-year period of 1995-2005 on the Mississippi River (Duan et al. 2010). This suggests that subsurface flow in the UMR is a dominant source of nitrate to the Mississippi-Atchafalaya River system in the spring flood pulse, which is also supported by the isotope values reflecting that of soil nitrate ($\delta^{15}N_{NO3}$: ~5$^{o}/_{oo}$ - 10$^{o}/_{oo}$; Kendall, 1998).

Highest retention occurred during the rising flood condition, in which more than half of the total retention occurred. This period also had lower nitrate concentration, which can result in

higher percent removal (Hopkinson, 1992). Additionally, this was the period that had water storage in the basin, which may have resulted in removal by hydrologic transport, rather than through more stable removal mechanisms like denitrification or assimilation.

There was a significant difference in $\delta^{15}N_{NO3}$ from the rising to the receding flow condition likely impacted by seasonality of the nitrate source rather than the flood. Voss et al. (2006) observed decreased $\delta^{15}N_{NO3}$ from winter to spring and then increased $\delta^{15}N_{NO3}$ from spring to summer with variations ranging from 3 $^{o}/_{oo}$ to 8 $^{o}/_{oo}$ depending on the river. Knapp et al. (2010) noted seasonality of nitrate isotope values in precipitation (with higher values in the spring). Duan et al. (2010) determined that seasonality of concentrations in the Lower Mississippi River was attributed to conservative mixing of the primary tributaries (Ohio/Arkansas Rivers and UMR/Missouri). These tributaries also likely control the seasonality in isotope values we observed in this study.

3.5 Summary and Conclusions

The 2011 Mississippi River Spring flood transported a large quantity of nitrate-rich water into the Atchafalaya River Basin, which has extensive floodplains and corridor wetlands. We hypothesized that a large amount of the riverine nitrate would be removed through denitrification, which would be reflected in decreased nitrate load and increased nitrate isotope values downriver sites on the Atchafalaya River. However, our results from this rapid sampling study show little processing of nitrate despite the high connectivity during the major flood in the Atchafalaya River, rejecting the initial hypothesis. The river waters moved quickly through the basin leaving little or no residence time for denitrification. Based on our findings, we conclude that this system may not be a significant sink for nitrate-nitrogen, while we acknowledge that future studies are needed to verify the result gained from this one flood event. Furthermore, this

study found higher isotope values in conjunction with peak nitrate concentrations during the flood recession, indicating that a change of nitrate sources occurred in the Upper Mississippi River from surface to subsurface leaching in the post-flood period.

CHAPTER 4. CARBON EXPORT BY THE ATCHAFALAYA RIVER AND ITS RELATIONSHIP TO NITRATE

4.1 Introduction

The pathway of terrestrial organic carbon to oceans is via rivers; however, rivers are more than conduits to the ocean. Rivers receive carbon sources from land and can release it to the atmosphere, contribute to accumulation in the geosphere, and transport it to the ocean (Aufdenkampe et al., 2011). The dominant carbon sources to the oceans are from rivers in the humid tropics (46%) and temperate forest and grassland (31%) (Meybeck, 1993).Rivers can also act as a considerable source of CO_2 to the atmosphere (i.e. Cole et al., 2007; Tranvick et al., 2009). Dissolved inorganic carbon (DIC)comprises 45% and dissolved organic carbon (DOC) is 37% of the total atmospheric carbon to oceans from rivers (Meybeck 1993). Rivers serve as an important influx of carbon to the estuary balance, fueling net ecosystem metabolism, and affects biogeochemical processes in estuarine sediments (Meiggs and Taillefert, 2011).

In estuarine systems with large riverine inputs like the Mississippi-Atchafalaya River System, rivers may have even greater impact. Because of the lower latitude location of the Gulf of Mexico, there is greater importance as low latitudes (0º to 30º) were found to be sources of CO_2 to the atmosphere. These low latitude areas release a total of 0.11 Picograms (Pg) C yr^{-1} because of warm water temperatures and high terrestrial organic carbon input (Cai et al., 2006). However in the Amazon River discharge, Ternon et al. (2000) found a portion of the outflow into the ocean acting as a sink for CO_2 while the central and eastern parts of the plume are sources for atmospheric CO_2. They demonstrate that nutrient rich river water enhances the biological pump resulting in the CO_2 sink. This is clearly an important process to investigate; however, Lohrenz

et al. (2010) note that there are few observations of low salinity waters in the northern Gulf of Mexico from the riverine sources.

In some cases riverine sources can bypass estuaries going directly into oceans (i.e. Cai et al. 2011), which makes quantification a significant part of the carbon budgeting. It is important to fully know the freshwater end member, especially during a high flow event when the river flow is dominant in the plume. This is especially true for a river-dominated system like the Gulf of Mexico near the Mississippi-Atchafalaya outflow. Furthermore, the Atchafalaya with its wide floodplains can potentially have different carbon export than the well-confined Mississippi River. These differences may further influence biological communities that establish in the plumes (i.e. Pakulski et al. 2000).

As the Mississippi and Atchafalaya Rivers are the 1st and 5th largest ocean discharging rivers in North America, respectively, it is critical to understand the dissolved carbon export. In this study, we aimed to: (1) Determine the respective riverine end member andquantify the dissolved organic and inorganic carbon exported from the Atchafalaya and Mississippi River,(2) Investigate Mississippi and Atchafalaya Rivers as potential CO_2 sinks or sources to the atmosphere, and (3) Explore how carbon in the Atchafalaya relates to potential nitrate removal.

4.2 Methods

4.2.1 Study Area

The Mississippi River is the longest river in North America and the fourth longest in the world, draining about 3,230,000 km^2. Just north of Simmesport, La (30°59'00" N, 91°48'00" W), 30% of the Mississippi's lateral flow is diverted into the Atchafalaya River. The Atchafalaya River flows through south Louisiana from just north of Simmesport, Louisiana into

the Gulf of Mexico via Morgan City (29°41'35" N, 91°12'43" W) and Wax Lake Outlet (29°41'55" N, 91°22'24" W). The Atchafalaya also serves as a distributary of the 2190 km long Red River and 480 km long Black River. Wide floodplains (25-35km wide) with levees on both east and west create a unique environment with a level of natural processes not seen in any other North American river (Ford and Nyman, 2011). In its first 110 kilometers south of the Mississippi River diversion, the Atchafalaya River flows in a well-confined channel. Afterwards, it becomes a series of braided channels that are highly connected with the surrounding landscape. The 4,678 km^2 Atchafalaya River Basin is predominantly wooded lowland and cypress-tupelo surface flow swamp with some freshwater marshes in the lower distributary area. The drainage basin serves as a major floodway for the Mississippi River floodwaters.

This subtropical region is often impacted by tropical systems. During the study period there two major storms: Hurricanes Gustav and Ike. Hurricane Gustav, a Category 2 storm, made landfall near Cocodrie, Louisiana on September 1st, 2008. It resulted in high rainfall variation from south-central to northern Louisiana. For instance, rainfall for September 1st, 2008 totaled 51.5 mm at Baton Rouge. In New Iberia, near the west bank of the southern Atchafalaya Basin, 130 mm of rain fell on September 1st followed by 104 mm of rain on September 2nd (NOAA). Hurricane Ike made landfall at Galveston, Texas on September 13, 2008. Although it was a category 2 in wind speed, the large breadth of the storm resulted in large-scale effects in both wind and precipitation for the Lower Mississippi River and Atchafalaya River Basin. Both storms pushed storm surge inland with oxygen-depleted waters from the Northern Gulf of Mexico.

4.2.2 River Water Sampling and Analysis

Composite water samples were collected from the surface at three sites along the Atchafalaya River (Simmesport, Wax Lake Outlet, and Morgan City) and one on the Mississippi River (Baton Rouge). In fast flowing, main channels, the physical factors and chemical constituents are uniformly mixed making the sample representative of the entire water channel as demonstrated in a study on the Atchafalaya River (U.S. Department of Interior 1969 cited in Lambou and Hern 1983) as well as in the Mississippi River at Baton Rouge (Fry and Allen, 2003). Water samples were filtered through a GF/F filter (Whatman International Ltd, Maidstone, England) and preserved with hydrochloric acid.Water samples were analyzed for nitrate with the cadmium reduction method.

Water samples were analyzed for dissolved organic carbon with a Shimadzu Total Organic Carbon Analyzer (TOC-V CSN Shimadzu Corporation, Kyoto, Japan) using the combustion/non-dispersive infrared gas analysis method. The laboratory measurements were conducted in the Wetland Biogeochemistry Institute, Louisiana State University. Dissolved inorganic carbon is reported as bicarbonate-C concentrations from USGS (nwis.waterdata.usgs.gov) locations Melville (07381495), Morgan City (07381600), and Baton Rouge (07374000). Because the neutral pH in the Lower Mississippi-Atchafalaya System, most of the inorganic carbon is in the bicarbonate form. pH ranged from 7.3 to 8.1 at the Atchafalaya inlet, 7.4 to 8.2 at the Atchafalaya outlet, and 7.7 to 8.4 on the Mississippi River at Baton Rouge. Melville (30° 41' 26.00" N -91° 44' 9.99" W) is 39.6 km south of Simmesport, however both sites are well leveed so are comparable in water quantity and quality. Simmesport and Melville are considered the "input" in reported DOC and DIC concentrations, respectively, and Morgan City and Wax Lake are considered the "output" for the Atchafalaya River. DIC concentrations

were only available at Morgan City, so this site represents the output for the Atchafalaya River, while both Morgan City and Wax Lake DOC concentrations are reported for the Atchafalaya River output.

4.2.3 Data Analysis

Carbon loading was determined from daily flow measurements from USGS and US Army Corps sites (Simmesport, Wax Lake, Morgan City, and Baton Rouge) times measured carbon concentration. The measured carbon concentration measured on one day was assumed to be representative of the entire month. If sampling occurred more than once in a month, the mean concentration was used to represent the month. Although this introduces some error into loading calculations, the frequency of measurements reduces some of this error. DIC concentrations were only available for Morgan City, therefore in order to calculate output loading, the concentration at Morgan City was assumed to be representative of the concentration at Wax Lake.

Values of pCO_2 can be calculated according to the method shown by Cai and Wang (1998), which uses measured pH and DIC data in the equation:

$$pCO_2 = [CO_2]/K_H = \frac{C_T\{H\}^2}{(\{H\}^2 + \{H\}K_1 + K_1K_2)K_H}$$

where C_T is the DIC value, $\{H\} = 10^{-pH}$, K_H is the solubility constant (Weiss, 1974), and K_1 and K_2 are the dissociation constants of carbonic acid. As the waters we sampled were freshwater with salinity measurements less than 0.2, we used K_1 and K_2 of Harned and Davis (1943) and Harned and Scholes (1941), respectively for salinities near 0. These were also validated by Millero et al. (2006) for higher salinity and temperatures ranging from 0 to 50 ºC. K_H, K_1 and K_2 are adjusted for absolute temperature.

A two-way ANOVA test was used to evaluate significance in difference in DOC, DIC, and pCO2 among sites and seasons, with nesting of season within date. An alpha value of 0.05 was used. Statistical analyses were performed with Proc Mixed on SAS 9.2 software (SAS Institute 2008). Seasons were divided by: Spring (March to May), Summer (June to August), Fall (September to November), and Winter (December to February).

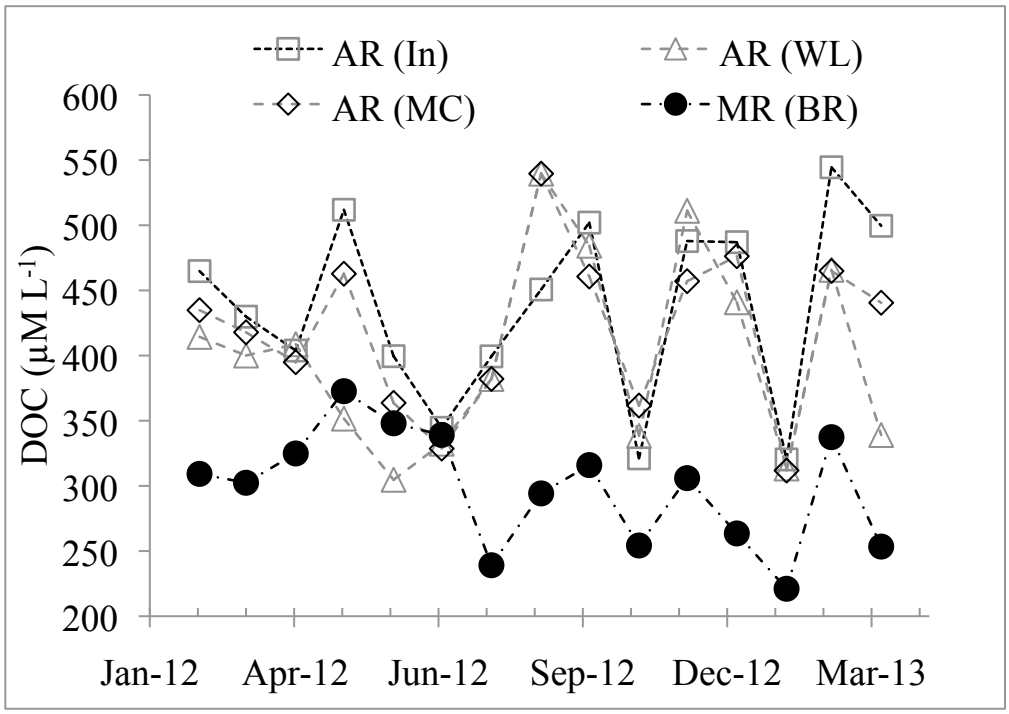
4.3 Results

4.3.1. Temporal Variation of Riverine Carbon Concentrations

From February 2008 to April 2009, DOC concentrations on the Atchafalaya River averaged 436±15.0 μM at Simmesport, 394±16.9 μM at Wax Lake, and 412±14.3 μM at Morgan City. The concentrations fluctuated largely from 350 μMto 550 μM (Figure 4.1), witha significant seasonal difference ($f=7.16$; $p=0.0004$). There were no significant differences among the Atchafalaya sites ($f=1.73$, $p=0.17$). When compared with the Atchafalaya, average DOC on the Mississippi River (311±9.6 μM) was significantly lower ($p<0.0001$). The Atchafalaya had consistently higher DOC than the Mississippi River except May 2008-July 2008 in which concentrations from both rivers overlapped.

Average DIC (Bicarbonate) was significantly higher ($p=0.0004$; $f=8.73$) on the Mississippi River (2220±120 μM) than the Atchafalaya River, at the inflow (1879±88 μM); however the outflow (1944±112 μM) was not significantly different from either site. At all locations DIC concentrations were low in March and increased steadily until November when concentrations decreased again (Figure 4.1). Seasonally, concentrations were lowest in the spring (1770±56 μM) and highest in the fall (2219±102 μM). Additionally, there was a negative correlation between bicarbonate concentrations and discharge at the respective sites (Figure 4.2). Specific conductance was also inversely related to discharge; however the best relationship was

on the Mississippi River (Figure 4.3), while the Atchafalaya River at Simmesport had the weakest relationship (Figure 4.4).



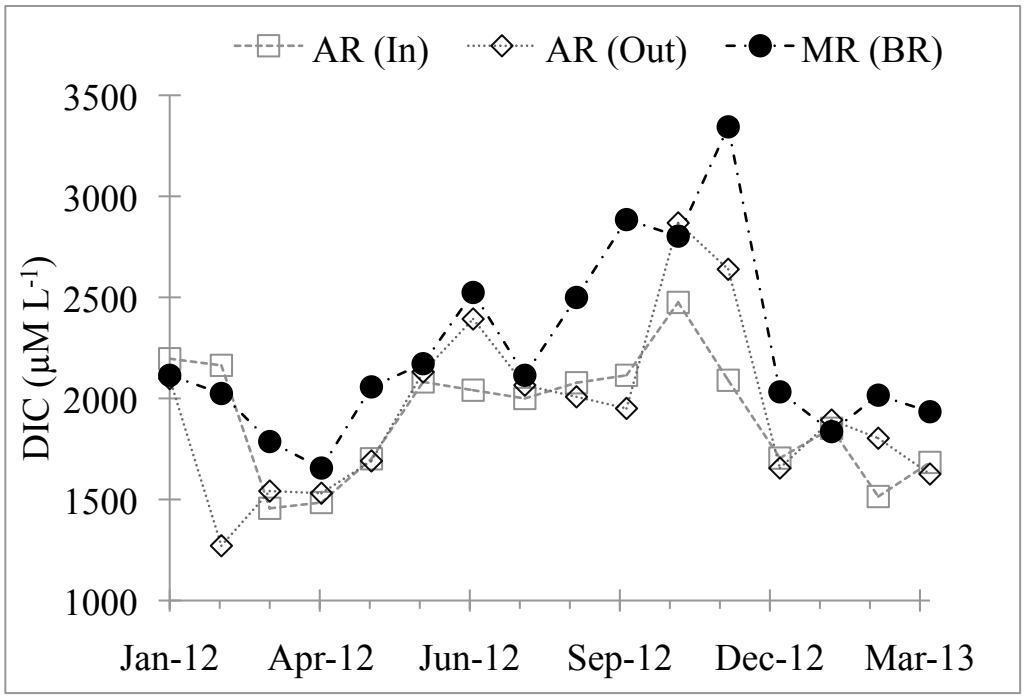


Figure 4.1. (A) Dissolved organic carbon and (B) dissolved inorganic carbon concentrations in the Atchafalaya (AR) and Mississippi (MR) Rivers from February 2008 to April 2009. AR(WL) is Atchafalaya River at Wax Lake Outlet; AR(MC) is Atchafalaya River at Morgan City, AR(In) represents the inflow and AR(Out) represents the outflow for the Atchafalaya River.

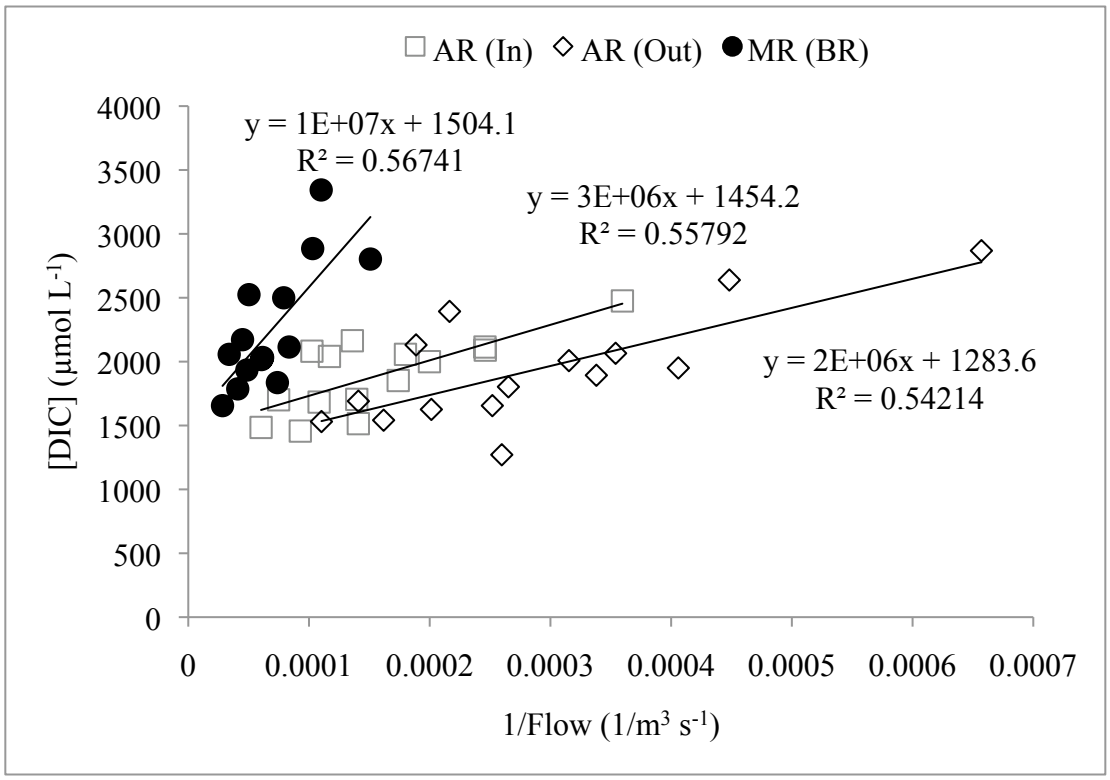


Figure 4.2 Inverse relationship between dissolved inorganic carbon concentration and discharge on the Atchafalaya River (AR) and Mississippi River (MR).

4.3.2. Riverine Carbon Mass Export and CO_2 Emission

In 2008 the Atchafalaya River exported 1,230,000 tonnes of DOC and 5,550,000 tonnes of DIC; and the Mississippi River exported 2,150,000 tonnes of DOC and 14,440,000 tonnes of DIC (Table 1). The combined dissolved carbon export to the Gulf of Mexico was 23,370,000 tonnes, with DIC comprising nearly 20,000,000 tonnes. The Atchafalaya DOC fraction totals 36% (WL: 15.2%; MC: 20.1%), while the Atchafalaya transports 28% of the DIC fraction delivered to the coastal margin. Approximately 80,000 tonnes of DOC was retained in the basin in 2008, but there was negligible retention of DIC.

Table 4.1. Organic and inorganic carbon mass loads for January 2008 through April 2009 in the Atchafalaya River (AR) and Lower Mississippi River at Baton Rouge (MR).

	DIC (*10^3) tonnes C			DOC (*10^3) tonnes C			
	AR (In)	AR (Out)	MR (BR)	AR (In)	AR (Out-WL)	AR (Out-MC)	AR (BR)
Jan-08	413	393	889				
Feb-08	479	271	996	103	402	504	152
Mar-08	505	542	1402	149	610	831	237
Apr-08	767	735	1817	209	810	111	367
May-08	731	710	1952	220	674	106	354
Jun-08	633	655	1503	121	448	62	249
Jul-08	561	666	1623	94.8	414	47.3	210
Aug-08	322	341	814	64.3	283	34.7	92
Sep-08	359	364	984	78	446	53.3	116
Oct-08	277	278	900	65.7	307	36.5	98.6
Nov-08	214	248	578	27.8	133	17.1	52.4
Dec-08	273	344	977	63.8	300	32.8	89.4
Jan-09	393	397	1062	112	493	60.8	138
Feb-09	309	310	723	53.5	243	26.8	87
Mar-09	346	413	857	124	527	582	150
Apr-09	483	472	1238	144	446	658	157
Mean	442	446	1145	109	436	211	170

All sites were supersaturated with respect to the atmosphere during the entire sampling period. Values of pCO2 ranged from 764 μatm to 3908 μatm with no significant differences among sites ($p>0.05$) (Figure 4.5). Seasonal trends in pCO2 differed from that observed in DIC concentrations with the lowest pCO2 in the winter (1264±94 μatm) and higher pCO2 in the fall (1419±171 μatm), and spring (1701±150 μatm). pCO2 was significantly higher ($p=0.0003$; $F=8.01$; $df=42$) in the summer months (2621± 334 μatm).

4.3.3. Relationship Between Riverine Carbon and Nitrate

There was a significant inverse relationship between nitrate and DOC at the Atchafalaya Outlets ($p=0.0013$; $F=16.77$; $R^2=0.56$). Although not significant ($p=0.15$; $F=2.39$, $R^2=0.16$), there was a positive trend on the Mississippi River (Figure 4.6). Nitrate at the Atchafalaya River input ranged from 41.7 µM to 112 µM. The Atchafalaya outputs had a slightly lower range: 23.9 µM to 103 µM. Nitrate on the Mississippi River ranged from 38.3 µM to 140 µM.

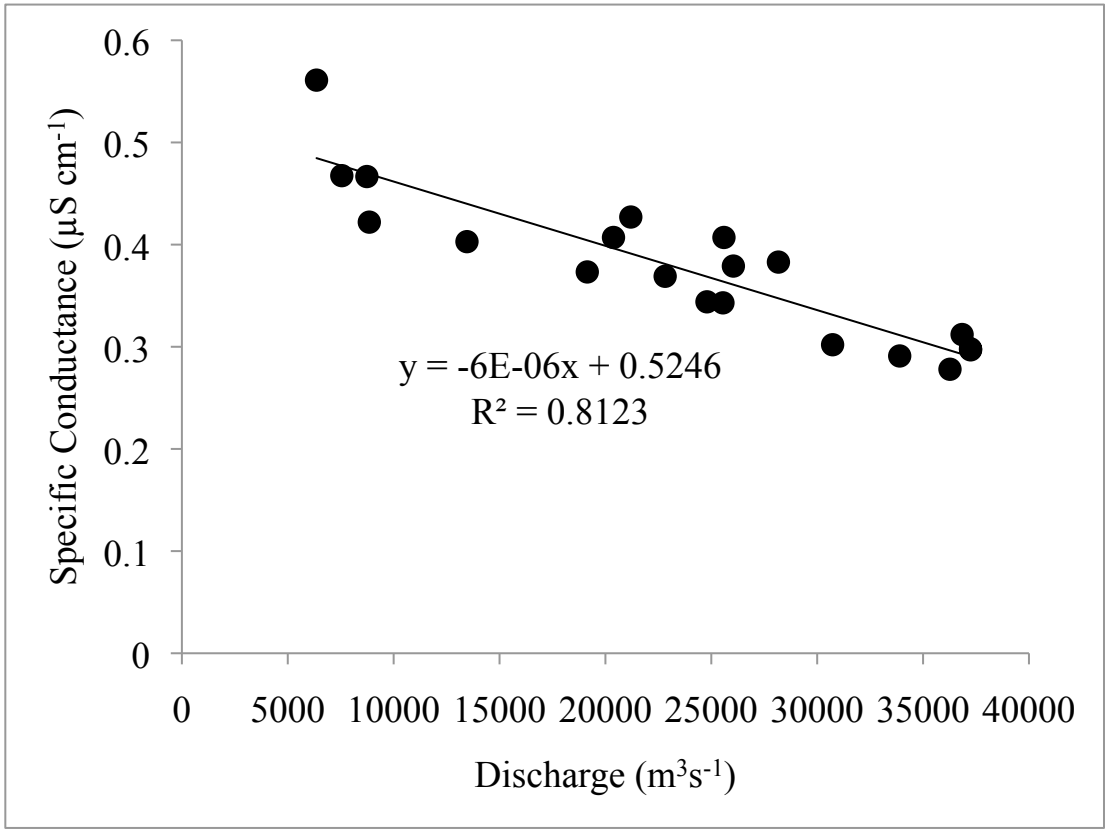


Figure 4.3. Relationship between specific conductance and discharge on the Mississippi River at Baton Rouge.

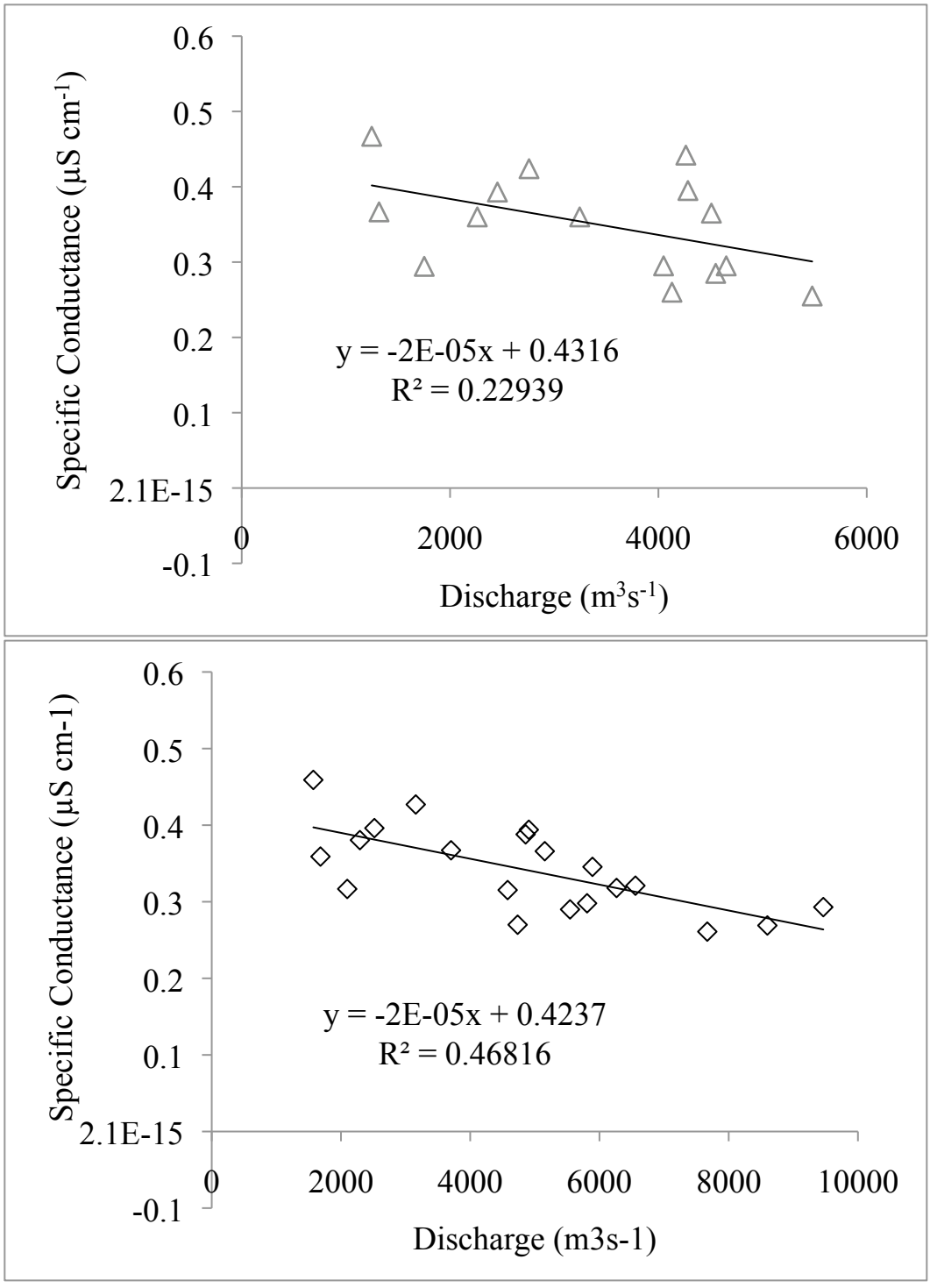


Figure 4.4. Relationship between specific conductance and discharge on the Atchafalaya River at A. Wax Lake Outlet (open triangles) and B. Morgan City (open diamonds).

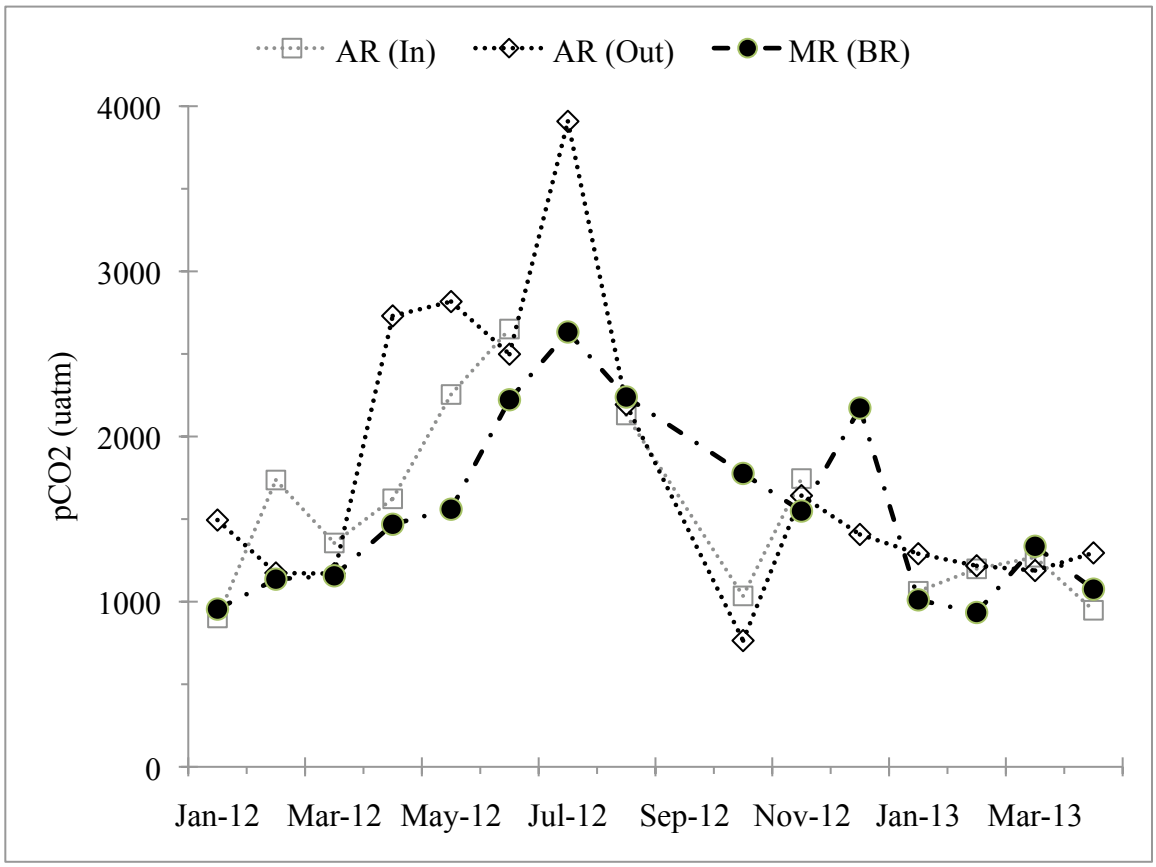


Figure 4.5. Monthly pCO2 values on the Atchafalaya River (AR) at the input (In) and output (Out), and Mississippi River (MR) at Baton Rouge (BR).

4.4 Discussion

4.4.1 Quantification of Riverine Carbon

Dissolved organic carbon outflow to the Gulf of Mexico totaled 3.4 x 10^6tonnes C $year^{-1}$ in 2008, which is 0.76 % of the global riverineorganic carbon flux. This is only about 10% and 26% of the total organic carbon exported by the largest riverine organic carbon exporters — the Amazon and Congo Rivers, respectively (compiled in Schlunz and Schneider, 2000). Annual discharge of total organic carbon from rivers to the Gulf of Mexico has been estimated at 3.6 x 10^6tonnes C $year^{-1}$ (compiled in Schlunz and Schneider, 2000). It is evident that the

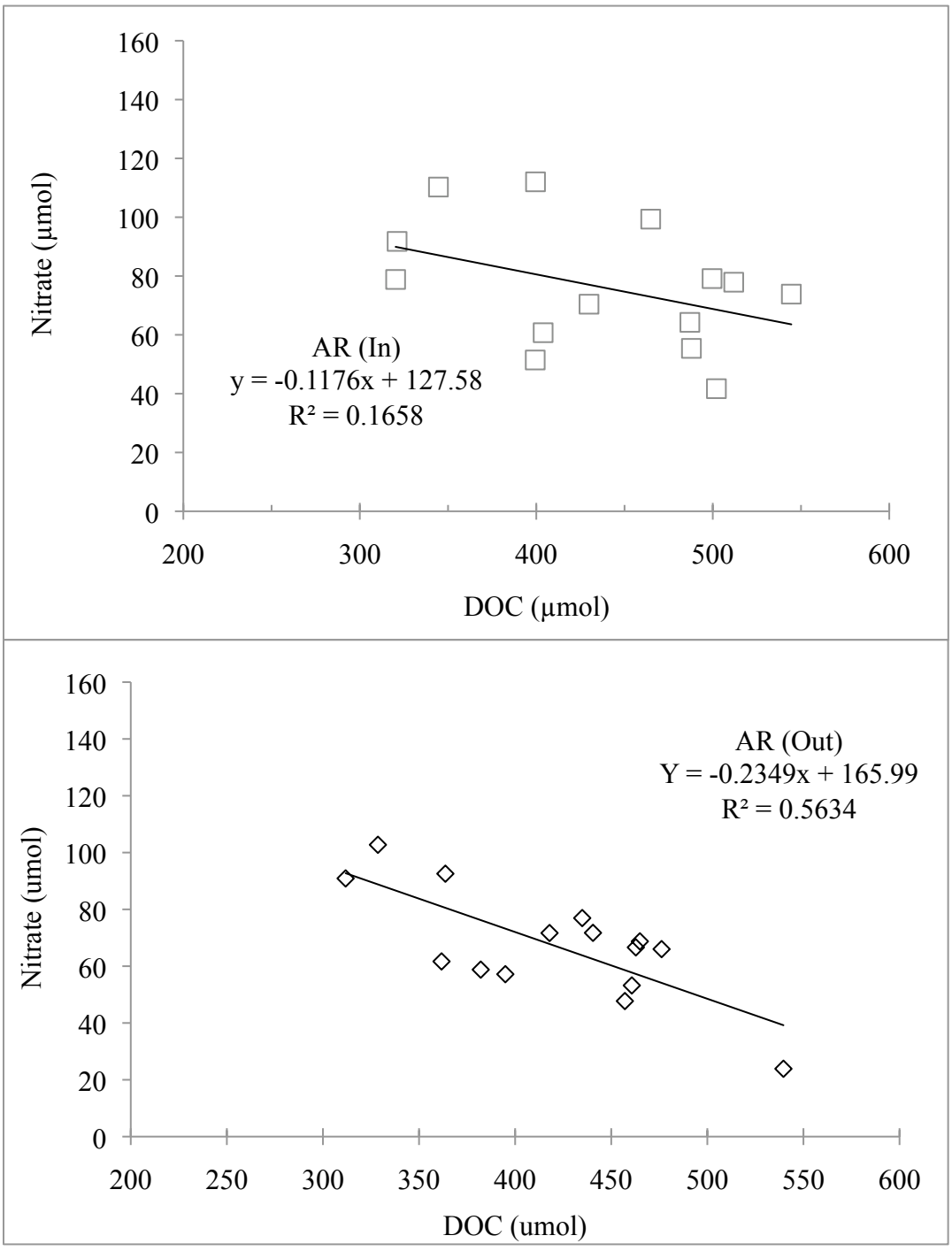


Figure 4.6. Relationship between nitrate and dissolved organic carbon (DOC) on the Atchafalaya River atA. Input- Simmesport (squares) and B. Output (diamonds).

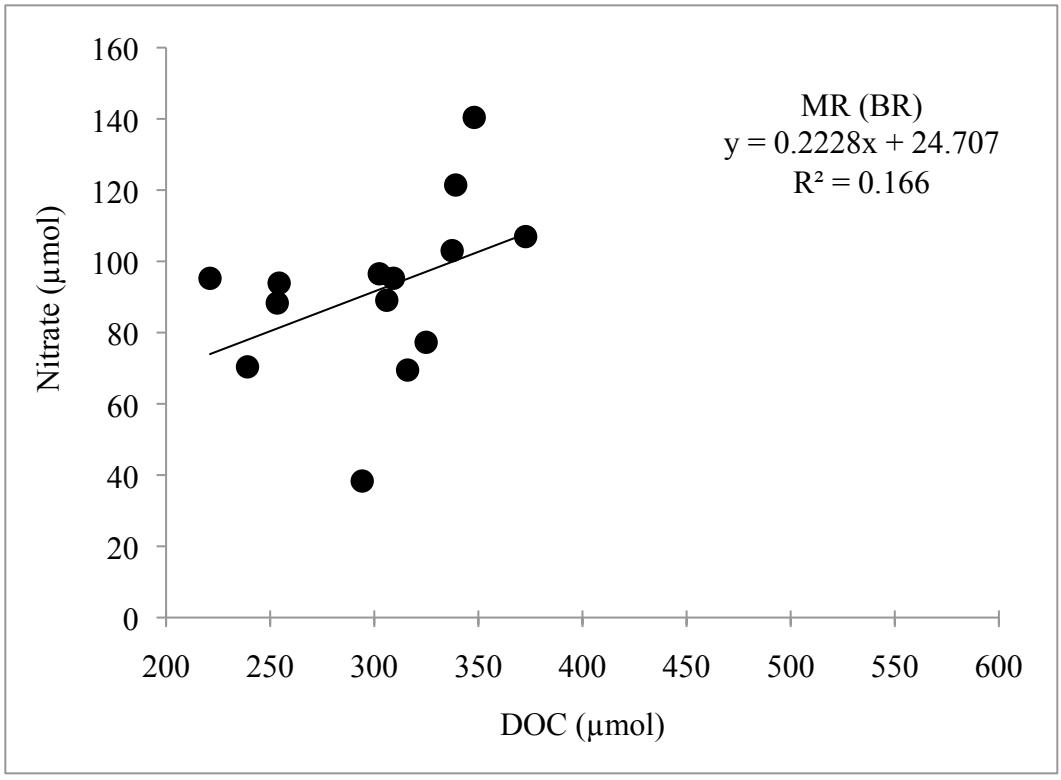


Figure 4.7. Relationship between nitrate and dissolved organic carbon (DOC) on the Mississippi River at Baton Rouge.

Mississippi-Atchafalaya system is responsible for most of the organic carbon export to the Gulf of Mexico. The yearly average (3.1 x10^6tonnes C $year^{-1}$) calculated for the Mississippi-Atchafalaya by Bianchi et al. (2004) is slightly lower than we found in 2008, but our higher value can be attributed to 2008 being a high flood year. Additionally, our estimates may be higher as Bianchi et al. (2004) utilized mean concentrations from the lower Mississippi River, which may underestimate actual export by the Atchafalaya River. We determined significantly higher concentrations of DOC on the Atchafalaya River which is in accordance withPakulski et al. (2000), who observed 35 µM higher DOC in the Atchafalaya River plume than the Mississippi River plume.

World DOC average has been reported as 5.75 mg L^{-1} (Meybeck, 1982), which is slightly higher than what we measured at all sites. Concentrations at Simmesport (5.2 mg L^{-1}) were

closest to the world DOC average, while concentrations measured on the Mississippi River were nearly 2 mg L^{-1} lower than the world DOC average (3.8 mg L^{-1}). The Mississippi-Atchafalaya system has half the DOC concentration of the second largest carbon exporter, the Congo River (10.7 mg L^{-1}) (Spencer et al., 2012). The Congo River drains a tropical forest, which accounts for 46% of the riverine carbon source to oceans.

Some researchers have examined the Mississippi River plume and assumed that the freshwater endmember represented the actual river value. Although it is difficult to compare directly from different years, we observed a lower DIC concentration than the range (2200µM - 2900µM) reported by Cai (2003). This may suggest that DIC concentration in the river is different than that found in the lowest salinity of the plume; however, it may simply be interannual variation. We found an inverse relationship between DIC concentration and discharge, so during high flow years like 2008, lower DIC concentrations are expected. Determining accurate biological uptake and cycling rates in the plume depends on precise freshwater end members.

4.4.2 Mechanisms Controlling Retention and Sources of Carbon

The Atchafalaya Basin has been determined to be a major sink for TOC (Lambou and Hern, 1983; 16% Xu and Patil 2006); however it is evidently not a sink for DOC as demonstrated from the limited retention observed in this study. The Atchafalaya appears to be a particulate organic carbon (POC) sink through physical sedimentation. Sedimentation occurs in the Atchafalaya Basin (i.e. Hupp et al., 2008). Lambou and Hern (1983) calculated an average POC sedimentation rate of 1.1 $x10^5$ kg km^{-2}, with higher sedimentation occurring in two overflow subunits. This mechanism was also observed with nitrogen, in which organic "particulate" nitrogen (TKN) had high rates of removal (27%) in the Basin (Xu, 2006a) while there is

negligible removal of "dissolved" nitrogen (nitrate) (e.g. Xu, 2006b; BryantMason et al. 2012); which requires more residence time for biochemical reactions to occur.

Much of riverine organic matter has terrestrial derived sources (i.e. Rhone River-Harmelin-Vivien et al., 2010; Congo River: Spencer et al., 2012), with approximately 430 $x10^{12}$ g of terrestrial organic carbon transported by rivers to oceans worldwide (Schlunz and Schneider, 2000). It is logical therefore; the landuse in the drainage basin would have the greatest impact on organic carbon concentrations. Rivers draining forests, particularly tropical forests typically have the highest organic carbon loads, impacting the estuaries and coastal environments they flow into (e.g. Meiggs and Taillefert, 2011). Different weathering intensities at various climate zones can result in varied inorganic carbon concentrations (Cai, 2003). Much of the Mississippi River flows through temperate region with agriculture as the dominant land use. Anthropogenic landuse changes have dominated TOC delivered by the Mississippi River to the continental margin, more so than natural events like hurricanes, which have an effect, but is not long lasting (Sampere et al., 2011).

Both rivers transported higher concentrations of inorganic carbon than organic carbon — 87% of the total dissolved carbon was DIC on the Mississippi River, and slightly lower fraction (82%) was found at the Atchafalaya Outlets. A similar trend was observed on the Yellow River, which has highly decomposed loess deposits and carbonate in its reach (Wang et al., 2012). Some of the thickest loess is found in the Mississippi River Alluvial Valley, specifically in Missouri River watershed (Bettis et al., 2003), which is the largest subwatershed in the Mississippi River. Additionally anthropogenic activities in the Mississippi River have resulted in a large increase of bicarbonate flux over the last 50 years (Raymond et al., 2008), which was also postulated by Cai (2003) in finding a 16% increase in DIC flux over the last 40 years.

Decreased DIC concentrations with increasing flow are expected as increased runoff results in increased organic export from soils. The inverse relationship between DIC concentration and flow is consistent at all sites; however, the lower concentrations converged, similar to what Waldron et al. (2007) observed in a headwater subcatchment in NE Scotland. Although the relationship explained less of the variability in the Mississippi-Atchafalaya system (R^2=0.54 to 0.59), it was a significant relationship and likely has additional variation because of the respective locations in the catchment (headwaters versus outlets). Additionally the convergence at the lower concentrations, and thus high discharge, reflect the shared source. Although DIC is significantly higher on the Mississippi River, the small difference in concentration (12%) suggests that both rivers the same DIC source material. In Coastal Georgia, the DIC concentration in the estuary of the Altamaha River was double that observed in Satilla and Savannah Rivers clearly delineating the source materials to the different rivers.

The Red and Black Riversmay potentially have a high impact on the Atchafalaya River, resulting in a separation between water quality in the Atchafalaya and Mississippi Rivers. As seen in Figure 4.6 the nitrate to DOC relationship in the Atchafalaya River appears to have a mixing effect, as there is a shift from a positive relationship on the Mississippi River to a negative relationship observed at the Atchafalaya River output. The relationship at the Atchafalaya input may reflect the shift of lower organic carbon in the Mississippi River to potentially higher organic carbon in the Red and Black Rivers, which flow only into the Atchafalaya River. The relative contribution of flow from the Red River and Mississippi River into the Atchafalaya River varies depending on season. In spring when flow is high, the majority of flow in the Atchafalaya River is from the Mississippi River while during low flow periods in

late summer the Red River fraction is larger than during other periods (Bratkovich*et al.,* 1994; Xu and BryantMason, 2011).

Conductivity can differentiate sources of dissolved constituents and determine flow paths. It is clear that the Mississippi River is well mixed with a consistent source and flow path as there is a simple inverse relationship between specific conductance and discharge. Although there is also decreasing trend on the Atchafalaya, there is more variation suggesting more complex flow paths, which is expected with the input of the Red River as well within basin flow path changes.

4.4.3 Atmosphere Linkage

The Mississippi and Atchafalaya Rivers are a source of CO_2 to the atmosphere as they were supersaturated with respect to the atmosphere during the entire sampling period. In the Amazon River plume, the fCO_2 (pCO_2 corrected for temperature) was highly correlated with salinity suggesting that the Amazon River acted as a sink for CO_2 (Ternon et al., 2000). However there was also some variation within the plume that was not from physical mixing between ocean and river waters that suggested biological activity contributed to decreased fCO_2 in the plume; which may not accurately reflect the actual riverine endmember. When comparing river dominated estuaries to marine dominated estuaries, large CO_2 loading in rivers can drive higher CO_2 degassing in the river-dominated estuaries (Jiang et al., 2008). With high activity and turnover in the coastal margins, knowing actual riverine endmembers is important in understanding global carbon cycling, not just in waterbodies, but also in the atmosphere.

There was a strong spatial gradient of pCO_2 observed in the Gulf of Mexico, with the highest values associated with areas influenced by the Mississippi River (Lohrenz et al., 2010). The strong biological pump found in the Gulf of Mexico in the late spring and early summer

(Lorrenz et al., 2010) is driven by the flux of carbon and nutrients from the Mississippi and Atchafalaya Rivers. Considering the clear seasonality in observed pCO_2 and peak river flow, it is important to consider seasonality of the freshwater endmembers when calculating biological uptake in the Northern Gulf of Mexico.

4.4.4 Organic Carbon: Implications for Nitrate

The continuum from terrestrial to headwater streams to rivers to marine environment represents a shift from N-limitation in a C-rich environment to C-limitation in an N-rich environment (Taylor and Townsend, 2010). The Atchafalaya likely fits in differently in this continuum than the Mississippi River because of its more natural floodplain as compared to the more closely leveed system in the Mississippi River. The Atchafalaya River can react more like an upper river/headwater system by receiving terrestrial inputs of carbon. In a review of various nitrate leaching studies over the last 15 years, Curtis et al. (2011) determined that maximum N-rentention and accumulation in soils occurred in carbon-rich systems while loss of nitrate through leaching to waterbodies occurred in carbon-poor systems.

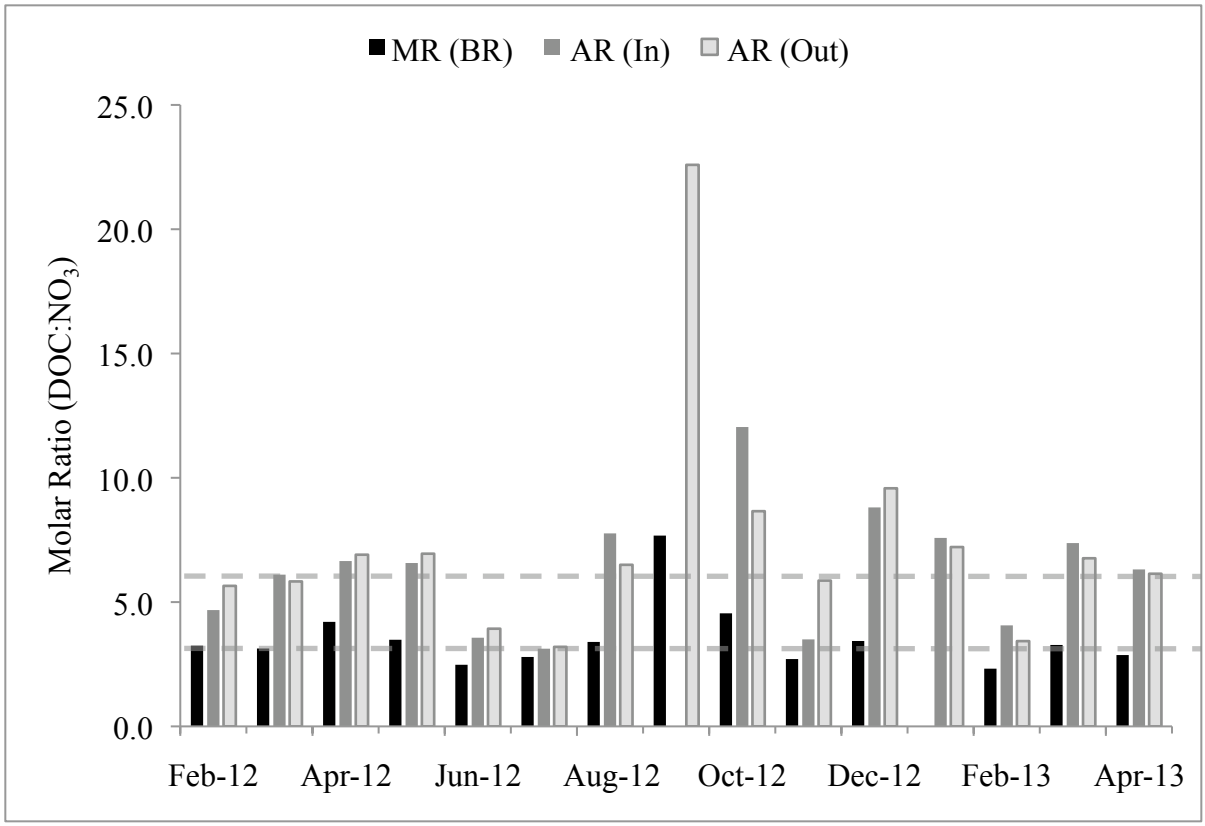


Figure 4.8. Molar ratio (dissolved organic carbon to nitrate) of the Mississippi River (MR) at Baton Rouge (BR), Atchafalaya River (AR) input, and Atchafalaya output. Dotted lines denote the 3 to 6 inflection point presented by Taylor and Townsend, 2010.

The inflection point of the DOC:NO3 in which the limitation shifts from organic carbon to nitrate is between 3 and 6 (Taylor and Townsend, 2010). Interestingly, this range alsoindicates the lowest relative nitrogen processing rate. DOC:NO3 higher than 6 represents the point of increasing N-assimilation, while DOC:NO3 of 1-2 indicates peak denitrification processing rate, and nitrification dominates below the inflection point (Taylor and Townsend, 2010). Much of the study period, the Mississippi River was within the inflection pointwhich suggests low nitrogen processing rate as expected for a fast moving, confined river (Figure 4.8). Although the Atchafalaya sites had higher DOC:NO3, most months were within the inflection point range (Figure 4.8). However, in September 2008 DOC:NO3 increased three-fold from the month prior at the Atchafalaya Outlet approaching a ratio that would be expected from a

terrestrial carbon source. This higher DOC:NO3 may suggest an increased source of DOC and/or increasing potential N-assimilation. In an Atchafalaya isotope study during the same period, $\delta^{15}N$ isotope values were low when compared to the prior year, which may indicate a nitrified ammonium source or an additional influx of nitrate (BryantMason et al., 2012). As this sampling was after Hurricane Gustav, it is likely the storm resulted in an additional source of organic carbon and nitrate. Hurricanes move significant organic carbon from forest canopies to headwaters; however, it may only have an ephemeral impact on overall nitrate dynamics as observed on the continental shelf (Sampere et al., 2011). Caution should be used in the extrapolation of the inflection point, as the quality of the organic carbon is unknown and may be inappropriate for these floodplain soils.

4.5 Summary and Conclusions

It is clear that the Atchafalaya and Mississippi River have different inputs of organic carbon. The Atchafalaya is the result of the merging of two different river systems (Red/Black and Mississippi Rivers), which causes a shift in the organic carbon to nitrate relationship. With higher DOC observed at Simmesport than on the Mississippi River, it suggests that the Red and Black Rivers serves as an organic source to the Atchafalaya River. An additional organic source appears to be hurricanes. Accurate freshwater end members are important in calculating biological uptake and global carbon cycling in the Northern Gulf of Mexico, as well as in other riverine dominated coastal margins. Differences between the Atchafalaya and Mississippi Rivers demonstrate the need for individual end members. The molar ratio of dissolved organic carbon and nitrate can provide important insight to potential nitrate processing and carbon source.

During most of the study period both the Mississippi and Atchafalaya Rivers had molar ratios suggesting limited potential nitrogen processing.

CHAPTER 5. SUMMARY AND CONCLUSIONS

This dissertation research examined nitrate and carbon in the Atchafalaya River to: (1) determine nitrate processing by a large river swamp basin under varied seasons, (2) investigate nitrate retention and processing in the river basin during an extreme flood event, and (3) assessthe relationship of nitrate with the dissolved organic and inorganic carbon exported from the Atchafalaya and Mississippi Rivers. Two main hypotheseswere made: (1) the Atchafalaya River acts a significant sink for nitrate nitrogen, especially during high flows when the river water interacts with its wide floodplain; and (2) there is a significant change in dissolved organic carbon in the Atchafalaya River due to denitrification processing.

The research treated the Atchafalaya River Basin as a closed system with the only inflow at Simmesport (the upper river location) and outflow occurring at Morgan City and Wax Lake Outlet (the lower river locations).Water samples were collected biweekly to monthly from April 2007 to April 2009 at the Atchafalaya River inflow and outflow locations. In addition, water samples were also collected on the Mississippi River at Baton Rouge during the same period. During the 2011 Mississippi River spring flood, water samples were collected twice to once per week at Simmesport, Wax Lake Outlet, and Morgan City from May 14th to July 20th. To determine ambient conditions at the time of sampling, in-situ measurements including river water temperature, dissolved oxygen, and specific conductance were also made during each sampling event at all sampling locations. All water samples were analyzed for nitrate concentrations and isotope values ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$). Samples from February 2008 to April 2009 were also analyzed for dissolved organic and inorganic carbon.

The Atchafalaya River discharge peaks from March to May, when the melting snowpack and spring rains in the upper Mississippi River causes increased river flows, while river

discharge was low from October to November. Combined discharge from Morgan City and Wax Lake Outlet on the Atchafalaya River averaged6,716 m^3s^{-1}, varying from 975 $m^3 s^{-1}$ in the summer of 2007 to a peak of 16,880 $m^3 s^{-1}$ during the 2008 Spring Flood. However, during the 2011 spring flood total discharge from the outlets peaked at 23,100 m^3s^{-1}, nearly four times the long-term average daily discharge. All sampling sites had relatively well-oxygenated water with DO levels mostly above 5 mg L^{-1}. Water temperatures were 1ºC higher on the Atchafalaya River than the Mississippi River, which is attributed to backwater areas in the Atchafalaya Basin that are slower moving and shallower allowing water to heat up.

In 2008, the Atchafalaya River exported over 265,000 Mg of nitrate-nitrogen (referred to as nitrate here on) per year to the Gulf of Mexico. Although this is higher than the long-term average, 2008 had a relatively high spring flood. The 2011 record spring flood demonstrated that the Atchafalaya is capable of exporting a large quantity of nitrate during a short time. The 83,158 Mg NO_3N exported represent nearly half (48%) of the long-term average annual nitrate export. Despite the high floodplain connectivity during this period, there were only 6,476 $MgNO_3N$ retained in the basin for a negligible retention rate of 7.2%.

During the study period of April 2007 to April 2009, flux weighted average $\delta^{15}N_{NO3}$was 6.5‰.The lack of variation during this time period between the nitrate isotopic compositions of the Atchafalaya and Mississippi River indicates the majority of nitrate transported through the Atchafalaya River is not processed significantly more than the Mississippi River. In the 2011 record flood, $\delta^{15}N_{NO3}$ values increased from 5.8 ‰ to 7.5 ‰ during the flood recession. Average $\delta^{18}O_{NO3}$ was 3.4$^{o}/_{oo}$ with a fairly narrow range of 2.0 $^{o}/_{oo}$ to 5.0 $^{o}/_{oo}$. There was little variation in the isotope values from the inflow and outflows reflecting little processing of nitrate.

The Mississippi-Atchafalaya River system exported nearly 20,000,000 Mg of dissolved inorganic carbon and 3,380,000 Mg of DOC. The Atchafalaya is responsible for about a third of the dissolved carbon export (DOC: 36%; DIC: 28%). The DOC:NO_3 molar ratio on the Mississippi River was consistently within the inflection point reported by (Taylor and Townsend, 2010) indicating the lowest relative nitrogen processing rate. Mean DOC:NO_3 on the Atchafalaya River was slightly higher than the inflection point suggesting the relative processing rate of N-assimilation was increasing as compared to the Mississippi River. However, it is clear that denitrification (~1 DOC:NO_3) does not occur in any significant role in either river.

Prior work has shown the Atchafalaya River Basin to be effective in retaining nutrients such as TKN (27%: Xu, 2006) and total organic carbon (16%: Xu and Patil, 2006); however, this appears to be mainly through physical processes such as sedimentation rather than biochemical processes such as denitrification. As a result, particulate forms are more likely to be stored whereas nitrate — a dissolved nitrogen species, the problematic species for hypoxia and eutrophication — is transported through the river unprocessed. Scaroni (2011) estimated total N removal for the Atchafalaya at 3,500 Mg yr^{-1} and 1,840 Mg yr^{-1} for biomass assimilation and maximum potential denitrification, respectively. This represents only 3% removal of the long-term yearly average nitrate load. Sedimentation, however, totaled 70,020 t yr^{-1}, which if represented as nitrate is 41% of the yearly average nitrate load. As these values are not for nitrate, but estimated for total nitrogen, my findings are in accordance. The residence time in the Atchafalaya is too short to effectively remove nitrate through denitrification. Although the Atchafalaya offers a number of important ecosystem functions, greatly reducing nitrate is not one as maximum nitrate retention was 7%. Addressing nitrate pollution closer to its source, prior to it reaching the Mississippi River would likely be more effective in reducing nitrate loads to the

Gulf of Mexico. This is an important finding as other similar flow-through systems also may not be significant dissolved nutrient sinks as previously assumed.

Although one of several options proposed by the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (MR/GOMWNTF, 2008) to reduce the hypoxic dead zone in the Gulf of Mexico included diversion of the nitrogen-rich Mississippi water into floodplain wetland systems, the Atchafalaya River Basin does not appear to be an effective diversion for such a purpose. Managing the Atchafalaya River Basin for nitrate removal would require a change in the Basin to encourage multiple flood pulses and drainage events. This can potentially conflict with the main purposes of navigation and flood control in the Atchafalaya. This research shows that as currently designed, dissolved nutrients like nitrate and DOC in the Atchafalaya are transported out of the basin with relatively little processing.

Future studies during flood events in both the ARB and other systems can help to confirm my finding that flow-through river floodplains are not a significant sink for riverine nitrate, but should consider residence time in the sampling design and also measure dissolved organic carbon. Examining DOC:NO_3 can provide important insight to stoichiometric controls on nitrate processing (Taylor and Townsend, 2010). Additionally, pairing DOC:NO3 with nitrate isotope values may aid in determining what process and relative rate of the process responsible for any nitrate retained in the system. Future research on the Atchafalaya River should consider the influence of the Red River.

CHAPTER 6. LITERATURE CITED

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APPENDIX A: ADDITIONAL NITRATE CONCENTRATION AND ISOTOPE RESULTS

Table A1. Average nitrate concentrations, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ in the Atchafalaya River at Simmesport (input), Melville, Butte La Rose (BLR), Wax Lake (WL), and Morgan City (MC) from April 2007 to April 2009.

	NO3N (mg L^{-1})	$\delta^{5}N$ (‰)	$\delta^{18}O$ (‰)
Simmesport	1.3 ± 0.07	7.0 ± 0.2	4.3 ± 0.2
Melville	1.3 ± 0.07	7.5 ± 0.3	4.6 ± 0.2
BLR	1.2 ± 0.07	7.2 ± 0.3	4.7 ± 0.3
WL	1.3 ± 0.07	6.9 ± 0.2	4.4 ± 0.2
MC	1.2 ± 0.06	7.2 ± 0.3	4.3 ± 0.3

[1]± standard error

Table A2. Nitrate concentrations and isotope values of rainwater samples collected from Louisiana State University Agricultural Center- Iberia Research Station in Jeanerette, Louisiana.

Date	Nitrate (μM)	$\delta^{15}N_{NO3}$ (‰)	$\delta^{18}O_{NO3}$ (‰)
3/31/2009	10.1	2.5	64.5
4/7/2009	21.4	0.2	62.6
4/14/2009	37.3	2.0	71.0

Table A3. Nitrate concentrations from river-water samples collected from the Atchafalaya River (Simmesport, Melville, Butte La Rose, Wax Lake Outlet, and Morgan City) and the Mississippi River (Baton Rouge).

	Nitrate (μM)					
	Simmesport	Melville	Butte La Rose	Wax Lake Outlet	Morgan City	Baton Rouge (MR)
Apr-07	126.7	140.4	132.0	132.8	128.3	NA
May-07	141.0	136.0	147.0	143.9	130.5	NA
Jun-07	137.7	136.0	123.5	134.4	129.9	175.3
Jul-07	73.3	81.1	74.4	75.1	77.3	145.7
Aug-07	26.5	24.7	22.4	22.1	25.8	43.3
Sep-07	62.5	67.6	71.9	58.4	58.2	106.7
Oct-07	77.6	67.6	75.1	68.9	68.6	87.0
Nov-07	163.9	180.4	148.2	142.5	134.1	172.4
Dec-07	127.7	114.0	118.8	131.1	112.6	118.3
Jan-08	98.1	122.4	120.4	119.6	111.9	126.0
Feb-08	99.4	83.8	109.1	84.4	76.9	95.3
Mar-08	70.4	77.4	78.2	66.9	71.7	96.5
Apr-08	60.7	64.1	67.9	61.4	57.2	77.3
May-08	77.9	83.3	83.1	NA	66.6	107.0
Jun-08	112.0	109.1	109.4	121.8	92.6	140.4
Jul-08	110.3	116.3	106.7	94.7	102.7	121.4
Aug-08	51.4	52.5	NA	NA	58.8	70.4
Sep-08	NA	NA	24.8	NA	23.9	38.3
Oct-08	41.7	44.7	41.5	49.6	53.2	69.5
Nov-08	91.8	83.2	77.4	66.6	61.7	93.9
Dec-08	55.4	56.9	57.2	50.9	47.7	89.1
Jan-09	64.2	70.6	68.4	65.5	66.0	NA
Feb-09	78.8	82.6	85.5	88.8	90.9	95.2

Table A3. Continued

	Nitrate (μM)					
	Simmesport	Melville	Butte La Rose	Wax Lake Outlet	Morgan City	Baton Rouge (MR)
Mar-09	73.8	76.4	66.9	72.5	68.7	103.0
Apr-09	79.1	76.3	67.0	75.2	71.7	88.3
May-11	73.8	86.2	NA	68.2	65.3	85.0
Jun-11	94.1	97.1	NA	82.8	74.4	127.7
Jul-11	126.2	117.1	NA	141.3	114.5	113.1

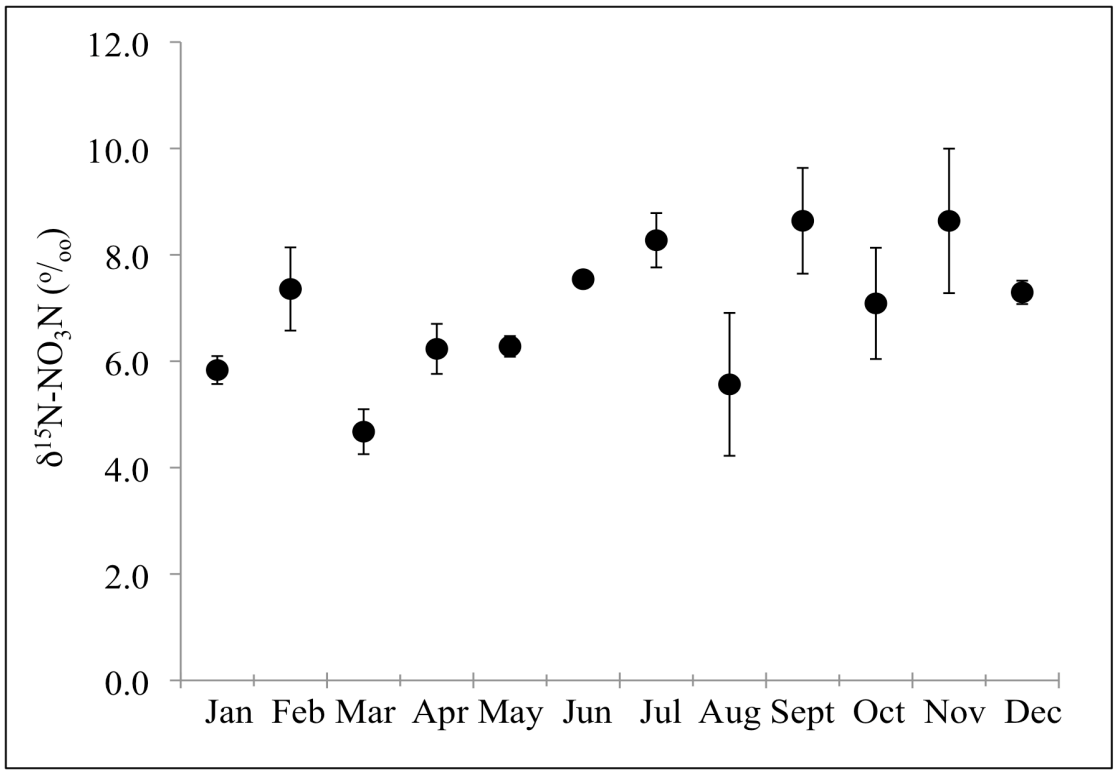

Figure A1. Monthly mean $\delta^{15}N_{NO3}$ values on the Atchafalaya River at Simmesport from April 2007 to April 2009 and during the 2011 record spring flood (May-July 2011). Error bars indicate standard error.

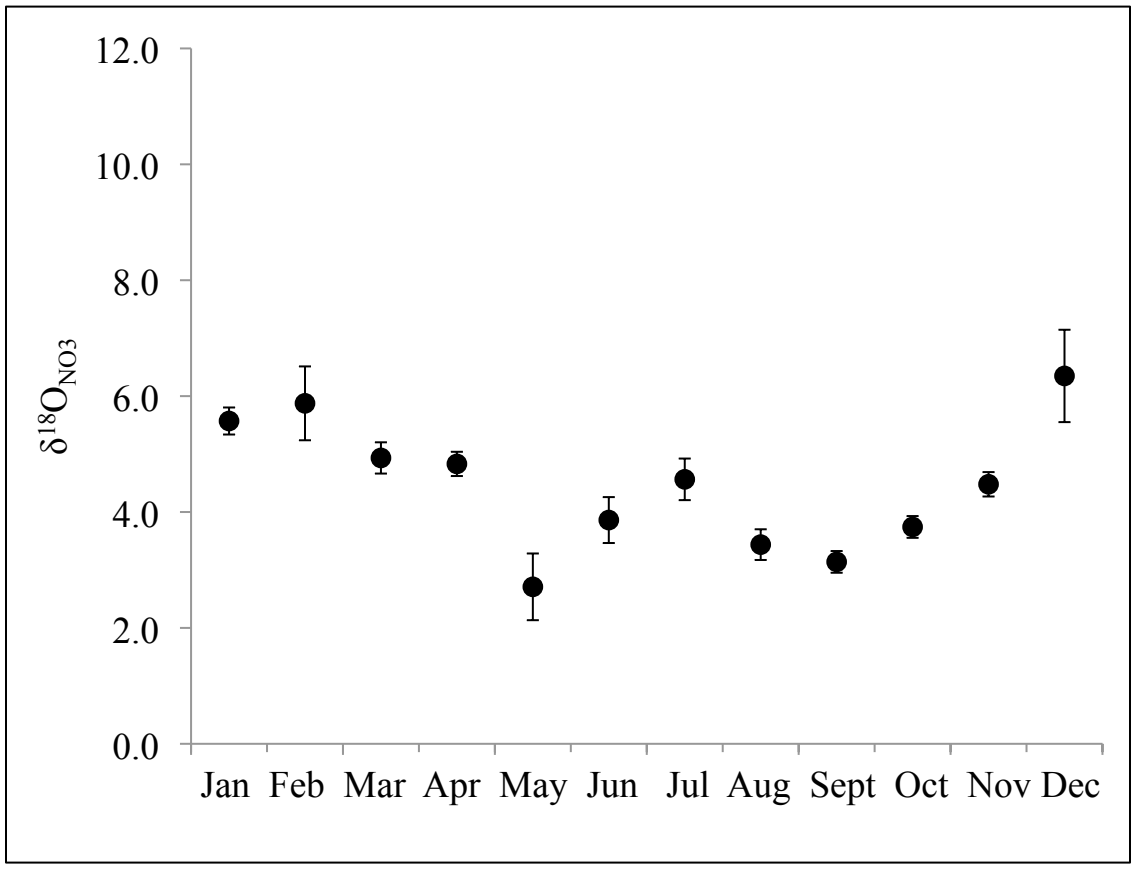

Figure A2. Monthly mean $\delta^{18}O_{NO3}$ values on the Atchafalaya River at Simmesport from April 2007 to April 2009 and during the 2011 record spring flood (May-July 2011). Error bars indicate standard error.

Table A4. Mean nitrate isotope values from river-water samples collected from the Atchafalaya River (Simmesport, Melville, Butte La Rose, Wax Lake Outlet, and Morgan City) and the Mississippi River (Baton Rouge) from April 2007 to April 2009 and May to July 2011. NA indicates data unavailable.

	$\delta^{15}N_{NO3}$(‰)						$\delta^{18}O_{NO3}$(‰)					
	Sim.	Melville	Butte La Rose	Wax Lake Outlet	Morgan City	Baton Rouge (MR)	Sim.	Melville	Butte La Rose	Wax Lake Outlet	Morgan City	Baton Rouge (MR)
Apr-07	6.8	6.6	6.7	7.0	7.1	NA	4.8	4.5	4.6	5.2	5.3	4.4
May-07	6.9	6.7	6.7	6.2	6.4	NA	5.0	5.1	4.6	4.6	4.6	6.1
Jun-07	7.3	7.8	7.7	7.5	7.6	8.0	5.0	5.9	6.2	5.7	4.3	1.9
Jul-07	NA	NA	NA	NA	NA	8.9	NA	NA	NA	NA	NA	3.5
Aug-07	6.9	7.4	6.4	NA	NA	7.5	3.2	3.9	3.0	NA	NA	4.2
Sep-07	8.6	8.1	8.5	8.6	8.5	8.2	3.1	2.3	3.0	3.4	2.3	5.2
Oct-07	8.1	8.9	8.8	8.3	8.5	9.4	3.8	3.3	4.0	3.6	5.0	5.6
Nov-07	7.3	8.0	7.5	6.4	8.0	8.4	4.4	4.4	4.8	3.7	4.8	5.4
Dec-07	7.1	7.9	6.6	7.3	6.6	7.8	5.6	4.3	3.8	4.4	3.8	4.4
Jan-08	5.8	6.1	6.2	6.0	6.0	5.6	5.6	5.5	4.9	4.9	5.9	4.9
Feb-08	8.1	7.7	6.4	5.3	7.8	5.1	5.2	5.2	3.9	4.0	6.3	5.1
Mar-08	5.1	4.4	4.8	6.4	5.4	7.0	4.7	3.3	4.4	5.8	3.7	2.9
Apr-08	6.5	7.8	7.3	7.1	7.2	8.1	5.1	5.9	5.4	5.5	4.9	4.2
May-08	6.6	7.0	7.4	NA	6.3	8.7	1.6	2.1	2.1	NA	1.2	6.8
Jun-08	8.0	8.7	8.5	10.1	8.8	8.1	4.3	5.6	5.4	6.4	6.9	2.9
Jul-08	9.9	14.1	9.6	9.5	10.3	10.5	5.8	7.6	5.7	5.2	6.6	1.3
Aug-08	4.2	4.9	NA	NA	4.8	4.6	3.7	3.6	NA	NA	3.2	5.8
Sep-08	NA	NA	3.7	NA	3.0	3.4	NA	NA	3.2	NA	2.3	7.0
Oct-08	5.1	4.9	11.1	6.7	6.9	10.6	3.6	2.4	7.0	2.6	1.7	8.4
Nov-08	11.3	10.4	11.4	10.5	11.6	11.8	4.6	5.1	6.8	5.6	7.0	NA
Dec-08	7.5	9.3	7.9	7.0	7.5	11.2	7.1	7.8	7.2	5.9	6.4	4.7
Jan-09	6.0	3.9	3.6	3.6	2.1	NA	5.6	3.2	5.8	6.2	4.1	3.4
Feb-09	6.6	6.1	5.9	5.8	5.1	5.5	6.5	5.8	5.0	5.0	4.4	3.5
Mar-09	4.3	4.9	3.4	4.6	5.4	6.4	5.2	3.8	4.0	4.2	4.6	2.9

Table A4. Continued

	$\delta^{15}N_{NO3}$(‰)						$\delta^{18}O_{NO3}$(‰)					
	Sim.	Melville	Butte La Rose	Wax Lake Outlet	Morgan City	Baton Rouge (MR)	Sim.	Melville	Butte La Rose	Wax Lake Outlet	Morgan City	Baton Rouge (MR)
Apr-09	5.4	7.7	6.9	6.1	6.3	5.3	4.4	5.3	4.9	4.1	4.9	4.1
May-11	5.9	5.8	NA	5.8	6.0	6.2	2.7	2.3	NA	3.3	2.4	4.0
Jun-11	7.3	7.3	NA	7.4	7.7	7.7	3.4	3.7	NA	3.6	3.3	NA
Jul-11	7.6	7.4	NA	7.3	7.9	7.5	4.1	4.0	NA	3.9	2.8	NA

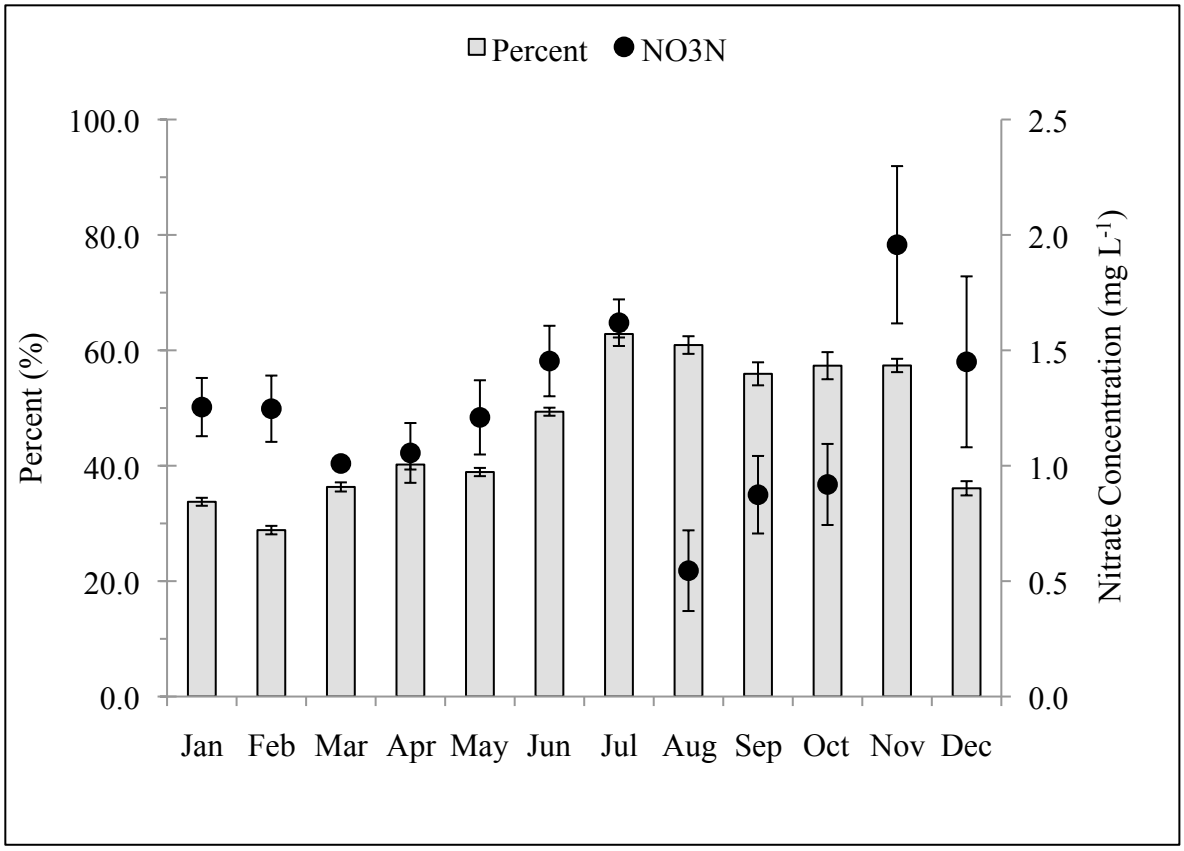

Figure A3. Monthly average nitrate concentration at Simmesport (dots) and proportion of flow at Simmesport from the Mississippi River at Thebes (bars) to show water source to the Atchafalaya in late summer.

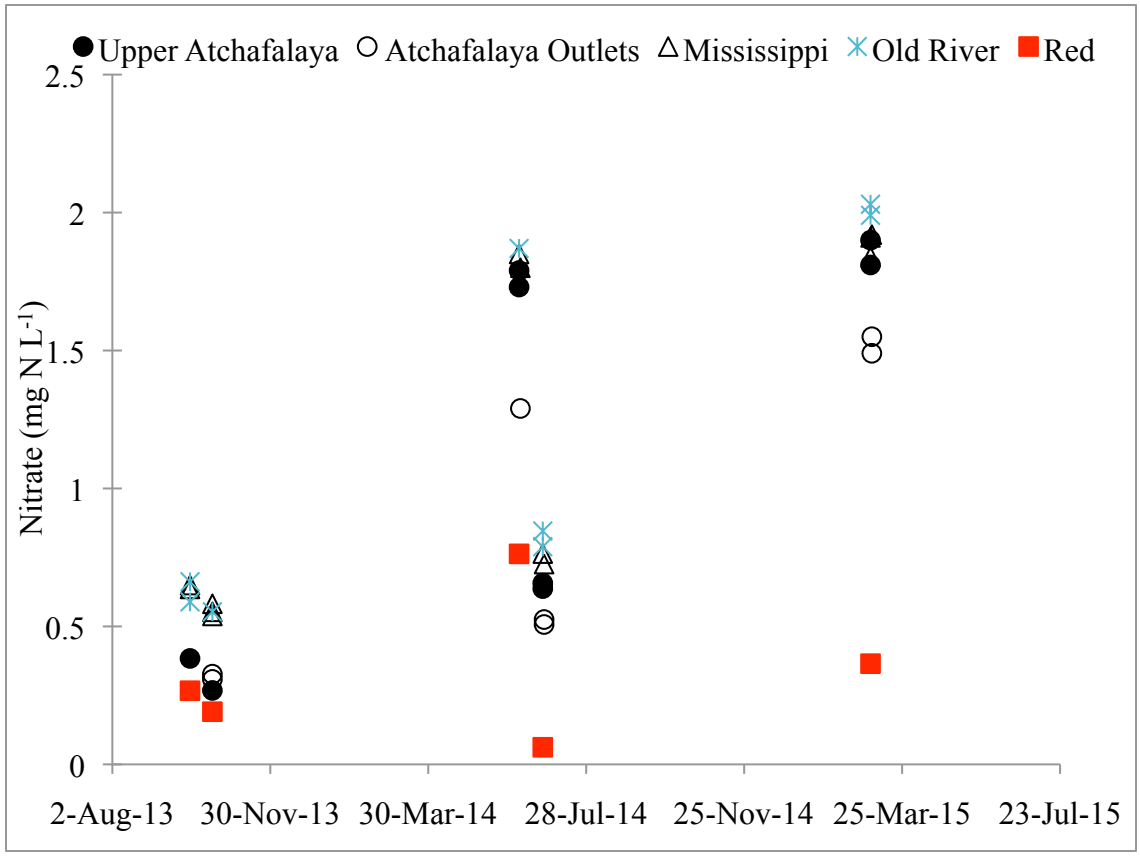

Figure A4. Nitrate concentration at sites on the Upper Atchafalaya River (Simmesport, Melville), Atchafalaya Outlets (Wax Lake Outlet, Morgan City), Mississippi River (Angola, Knox Landing, and Baton Rouge), and Red River.

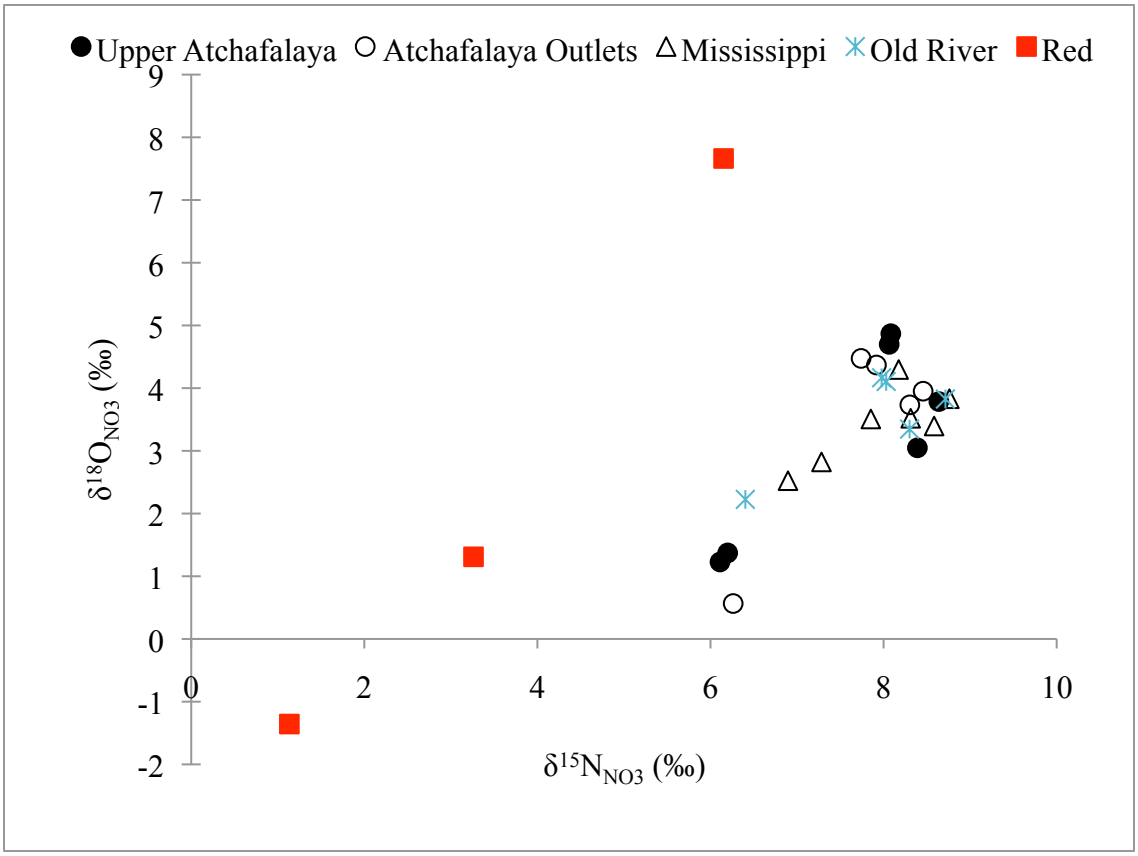

Figure A5. Isotope values at sites on the Upper Atchafalaya River (Simmesport, Melville), Atchafalaya Outlets (Wax Lake Outlet, Morgan City), Mississippi River (Angola, Knox Landing, and Baton Rouge), and Red River on June 6, 2010; June 24, 2010; and Februrary 28 2011.

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VITA

April BryantMason was born in April 1982 and grew up in Mechanicsville, Maryland. She graduated from St. Mary's College of Maryland in May 2004, earning her Bachelor of Arts degree in biology. After working at Chesapeake Biological Lab in 2004 as a Fisheries Technician and Maryland Department of Natural Resources in 2005 as a Natural Resources Technician, she relocated to Baton Rouge in August 2005 to attend Louisiana State University. She earned her master's degree in 2008. After earning her Ph.D., she would like to return to Maryland to apply her education to the Chesapeake Bay.