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**THE EFFECT OF HABITAT CHANGE ON NUTRIENT REMOVAL IN THE
ATCHAFALAYA RIVER BASIN, LOUISIANA**

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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August 2011

DEDICATION

To the people of the Atchafalaya:

Their love of, and connection with, the land never ceases to inspire and amaze me.

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During the course of my tenure at LSU I was supported by more friends and colleagues than I can list on a single page. I am grateful to all of them, but especially to:

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ABSTRACT

The Mississippi and Atchafalaya rivers are the major sources of freshwater and nutrients to the Gulf of Mexico. Increased nutrient loads from these rivers exacerbate eutrophication in coastal receiving waters and contribute to the large area of hypoxia that develops seasonally in the Gulf. Levees along the Mississippi River have reduced contact between the river and the historic floodplain; this limits the ability of floodplain wetlands to naturally mitigate excess nutrients. However, the Atchafalaya River diverges from the Mississippi 217 km from the Gulf and enters a large river floodplain with a widely spaced levee system. This enhances the ability of the Atchafalaya River Basin to remove and sequester nutrients, potentially reducing downstream eutrophication. Overbank flow spreads river-water and sediment across the floodplain. Over time, sedimentation has filled in many of the open water areas on the floodplain, such that lakes are transitioning to baldcypress swamps and bottomland hardwood forests. These habitats differ in their available nutrient reservoirs and the rates at which they transform and store nutrients.

This dissertation investigated the major retention and removal mechanisms for carbon, nitrogen, and phosphorus within bottomland hardwood forests, baldcypress swamps, and lakes of the Atchafalaya River Basin. These reservoirs include denitrification, sedimentation, and assimilation by aboveground biomass. Results estimate that nutrient retention and removal within bottomland hardwood forests ranges from 1,177,605—1,561,805 t C yr⁻¹, 46,049—47,603 t N yr⁻¹ and 20,040—20,175 t P yr⁻¹. Within baldcypress swamps, rates range from 493,953—600,180 t C yr⁻¹, 21,821—22,364 t N yr⁻¹ and 2,168—2,202 t P yr⁻¹. Rates in the lakes were 57,490 t C yr⁻¹, 5,140—5,390 t N yr⁻¹ and 2,550 t P yr⁻¹. Total retention and removal for

the entire basin is on the order of 1,177,605—1,561,805 t C yr⁻¹, 46,049—47,603 t N yr⁻¹, and 20,040—20,175 t P yr⁻¹. Rates varied by habitat, highlighting the need to consider habitat change when developing management strategies to improve water quality. Data from this dissertation can be used to parameterize nutrient models for the Atchafalaya River Basin, as well as for river diversions and floodplains with similar habitat types.

CHAPTER 1.

GENERAL INTRODUCTION

BACKGROUND

The Mississippi River Basin is responsible for draining over 3 million square acres of land, establishing a watershed that covers 40% of the land area of the continental United States (Mitsch 2001). Agriculture is one of the primary land uses in this watershed. Since the discovery of the Haber-Bosch process in 1908, which conveniently produces a synthetic fertilizer, the rate of nitrogen fertilizer application has continued to rise. For example, the flux of nitrate delivered to the Gulf of Mexico tripled between the 1950s and the 1990s (Goolsby 2001). Applying fertilizer to agricultural crops stimulates production and increases overall crop yields. However, once maximum plant productivity is attained, additional fertilizer application will have no effect. Much of the excess nitrogen and phosphorus will leave the agricultural system via surface runoff or subsurface groundwater flow, eventually discharging to coastal receiving waters.

The seasonal formation of a large area of hypoxia in the Gulf of Mexico (dissolved oxygen levels below 2 mg L^{-1}) is primarily attributed to nitrogen loading from the Mississippi and Atchafalaya Rivers (Rabalais et al. 2002). Nitrate, an inorganic form of nitrogen, is highly mobile and even localized applications can influence a large area. While nitrogen is an essential nutrient for primary production, increased nitrogen loading to coastal areas, which are generally adapted to nitrogen limitations, can alter dominant species, lower overall biodiversity, and stimulate the growth of phytoplankton (Tilman 1987; Vitousek and Howarth

1991; Rabalais 2001). Eutrophication can then lead to secondary effects such as harmful algal blooms, and hypoxia (Rabalais 2001).

Fortunately, natural processes that occur on floodplains and in coastal wetlands can offset high nutrient loads through biogeochemical transformations and sequestration. A strong linear correlation between nitrogen inputs and outputs indicates that, on average, N flux from rivers is only ¼ of the original anthropogenic-N inputs (Howarth 1996). Opportunities for retention and removal include denitrification, sedimentation, and assimilation into aboveground biomass on the floodplain.

A system of levees has reduced contact between the Mississippi River and its floodplain, decreasing the potential for the floodplain to mitigate excess nutrients before they discharge to coastal receiving waters. However, the Mississippi River diverts up to 30% of its flow to the Atchafalaya River before it reaches the Gulf of Mexico. This diversion was initiated as a natural event when the Atchafalaya River began to capture the Mississippi River. The Old River Control Structure, completed in 1963, was built to prevent the Mississippi from altering its course when nearly 50% of its flow had diverted to the Atchafalaya River Basin (ARB) (Sparks 1992). The ARB is now used to mitigate high water on the Mississippi River to prevent downstream flooding; levees are set back from the river to increase the size of the floodplain, and channels are dredged to prevent sedimentation (Sparks 1992; Xu 2006).

Despite the existence of levees, the ARB maintains a wide floodplain and is ranked as the largest deepwater swamp in North America. Habitats within the ARB are dynamic and in a constant state of transition; sediment deposition over the last century has transformed open water areas on the floodplain into baldcypress swamps, and eventually into bottomland

hardwood forests (Coleman 1988). All three of these habitat types currently exist in the ARB, but continued sedimentation is reducing the extent of open water in favor of forested habitats. Attempts to reduce the loss of backwater swamps in the ARB have involved channel training and bank shaving to reduce sediment deposition on the floodplain during high water. However, these attempts are aimed at slowing the transition to bottomland hardwood forests, and do not intend to restore backwater swamps (Sparks 1992). As a result, habitat change in the ARB is on a trajectory towards 100% bottomland hardwood forest.

Xu (2006) reported that 14% of the total nitrogen entering the ARB does not discharge into the Gulf of Mexico. While the precise fate of this nitrogen is unclear, we do know that denitrification, sedimentation, and assimilation into aboveground biomass are the major processes responsible for transformation, retention, and removal of carbon (C), nitrogen (N), and phosphorus (P) on floodplains. As river water leaves the channel and inundates the floodplain, the development of anaerobic conditions stimulates the denitrification reaction, resulting in a permanent removal of N from the system. Where water slows it deposits sediment on the floodplain, which binds P and traps C and N for long term storage. Aboveground biomass on the floodplain assimilates N and P during production; nutrients sequestered in woody biomass can be stored over the life of a tree, while nutrients stored in foliage may have a shorter storage life. Reduction of nitrate via denitrification permanently removes nitrogen from the system, thus we define nitrogen transformation via denitrification as “removal.” Sedimentation and biomass assimilation have the capacity for long-term storage of C, N, and P, thus we define these as “retention” pathways.

Any study that attempts to quantify nutrient retention and removal by storage reservoir in the ARB is complicated by the fact that habitat change is occurring. As a result, spatial variability of retention and removal processes across the ARB is expected to be high. This makes it difficult to develop management plans and to predict the outcome of restoration activities that aim to restore habitat cover and water quality. Proposed ideas to improve poor water quality along coastal Louisiana and in the Gulf of Mexico include improvements in fertilizer use efficiency, upstream wetlands creation, and river diversions. Hence, the potential for nutrient retention and removal in the ARB is increasingly being recognized by scientists and coastal managers. However, there is insufficient data available to compare the relative effects of natural succession and management activities with the ARB on subsequent nutrient discharge to the Gulf of Mexico. In order to build a model capable of predicting nutrient retention and removal within the ARB over time, data must first be collected from the ARB.

RESEARCH OBJECTIVES

This dissertation intends to quantify and compare the major pathways for nutrient retention and removal in the ARB. Data collection will focus on the potential for nutrient removal via denitrification (N), and nutrient retention via sedimentation (C, N, P) and biomass assimilation (C, N, P). We intend to answer the following research questions:

1. What are the major sinks for nutrients in the Atchafalaya River Basin?
2. Do storage reservoirs for C, N, and P differ among the major habitats of the ARB?
3. Do rates of nutrient retention/removal differ among the major habitats of the ARB?
4. How will nutrient retention and removal in the ARB respond to habitat change?

We expect our results to highlight the fate of nutrients that enter the ARB, and predict how habitat succession will affect nutrient cycling within the ARB.

STUDY AREA

The Atchafalaya River flows 217 km from its origin at the confluence of the Red and Mississippi Rivers, to the Gulf where it discharges at Wax Lake Outlet and Atchafalaya Bay. The floodplain for the Atchafalaya River is referred to as the ARB, which covers approximately 5,000 km² in south-central Louisiana. The ARB is bounded to the east and west by protection levees to prevent flooding of agricultural areas and towns; these levees reduce the size of the historic floodplain, but are significantly wider than the levees on the Mississippi River. The ARB can accommodate a flow rate of approximately 42,000 m³ s⁻¹ and still maintain the integrity of the levee system (Atchafalaya Basin Floodway System Louisiana Project, State Master Plan 1998). The Atchafalaya River has a high sediment load, transporting around 84 x 10⁶ metric tons (t) of sediment annually. Over the last century, the natural hydrology of the system was disrupted for flood control, pipeline and highway construction, navigation, and timber removal. Most of the cypress trees in the ARB are second growth; extensive harvests in the 1920s removed most of the original forest cover (Atchafalaya Basin Floodway System Louisiana Project, State Master Plan 1998). These barriers to flow remain in place today, but despite a long history of hydrologic alteration, the ARB remains a largely undeveloped wilderness.

Field Sites

We classified the ARB into three main habitat types; bottomland hardwood forest, baldcypress swamp, and lake. Nine sites were identified throughout the basin (3 in each habitat type) using a pseudo-random approach (Table 1). All sites are located on public land

and are accessible by boat or on foot throughout the year, regardless of water level fluctuations.

Table 1: Location and habitat type of field sites within the ARB.

Habitat type	Name	UTM east	UTM north
Bottomland Hardwood	Lake Long	15R 0634607	3342482
BLHW	Jake's Bayou	15R 0642301	3339353
BLHW	Bayou Chene Cut	15R 0641707	3336760
Swamp	Bayou Cowan	15R 0652424	3323317
Swamp	Bee Bayou	15R 0665505	3329455
Swamp	Murphy Lake Canal	15R 0655397	3332996
Lake	Flat Lake	15R 0674621	3293731
Lake	Duck Lake South	15R 0661845	3295485
Lake	Duck Lake North	15R 0664328	3298293

SYNOPSIS OF CHAPTERS

All five research chapters in this dissertation were designed to investigate nutrient retention and removal in the Atchafalaya River Basin (ARB) via denitrification, sedimentation, and biomass assimilation. This is reflected in the order of chapters. The first three chapters describe denitrification characteristics for sediments across the Atchafalaya River Basin for the purpose of modeling changes in nitrogen removal in response to habitat change. Chapter 2 examines spatial variability of denitrification potential across the Atchafalaya River Basin and attempts to account for factors influencing variation in rates. Chapter 3 takes this one step further by identifying habitat type as a distinguishing feature for sediments in the Atchafalaya River Basin, and compares denitrification rates among the major habitat types. Chapter 4 attempts to disentangle the roles of flooding and habitat type in determining the type of gaseous emissions from ARB sediments. Chapter 5 investigates an opportunity for nitrogen retention in the sediments: the role of vertical accretion. Data from suspended sediment samples and soil cores provide information on water movement, sedimentation rates, and

nitrogen retention. Chapter 6 reflects a literature review of nutrient content prediction equations and attempts to estimate the total amount of nitrogen stored in aboveground woody biomass in the ARB. Chapter 7 ties together all five research chapters, and discusses how the results contained herein may be used by scientists and managers to model nutrient cycling in the ARB.

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CHAPTER 2.

SPATIAL VARIABILITY OF SEDIMENT DENITRIFICATION ACROSS THE ATCHAFALAYA RIVER BASIN, LOUISIANA, USA¹

INTRODUCTION

Floodplains are frequently identified as important sites for nutrient retention and removal (Brinson et al. 1984; Craft and Casey 2000; Gergel et al. 2005; Forshay and Stanley 2005; Noe and Hupp 2009). Denitrification in particular has the potential to remove significant amounts of nitrogen (N) from floodplains, as seasonal river inundation establishes anaerobic soil conditions, delivers nitrate, and preserves carbon (C). However, these conditions vary across both large and small scales, resulting in spatial heterogeneity of soils and spatial variability of biogeochemical reactions. Aspects of spatial variability have often been neglected when studying denitrification (Pina-Ochoa 2006).

Floodplains on the Coastal Plain of the Southeastern USA often provide the last opportunity for sediment storage and biogeochemical cycling before rivers discharge into estuaries (Hupp 2000). Sediment deposition within the bottomlands of the Coastal Plain generally results in a net elevation gain (Hupp 2000). Because sedimentation facilitates nutrient sequestration, suspended sediments are usually associated with adsorbed nutrients (Hupp 2000). Hence, an intact or restored floodplain can function as a long term sink for nutrients. Conversely, when elevation gain is such that the floodplain becomes isolated from floodwaters, the potential for storage of river-borne nutrients is diminished. Soil conditions on a floodplain are largely influenced by the hydrologic conditions of the adjacent river. However,

¹ Reprinted by permission of "Wetlands."

many rivers have seen significant hydrologic alteration due to the construction of dams, levees, and navigation channels.

The Atchafalaya River is the largest tributary of the Mississippi River. Attempts by the Mississippi to flow into the Atchafalaya were thwarted by the construction of the Old River Control Structure in 1963. Today, flow of Mississippi water down the Atchafalaya River is limited to approximately 30% of the total volume of the Mississippi. The Atchafalaya River flows 217 km from its origin at the confluence of the Red and Mississippi Rivers, to the Gulf where it discharges into Atchafalaya Bay via the main stem of the river and the Wax Lake Outlet. Within the Atchafalaya River Basin (ARB), the reworking of sediments has resulted in variation in the conditions that are seen throughout the floodplain. Due to sedimentation, some areas of the floodplain are elevated such that they never have contact with river water. Other areas receive intermittent inundation, and some locations are permanently flooded. Wetlands on the floodplain of the Atchafalaya River function as water retention basins when river stage is high and as discharge areas when river stage is low (Xu 2010). Analysis of total suspended sediment samples collected across the Basin in the spring of 2008 (a high water year) suggests that only 21% of the floodwaters deposited sediments in the baldcypress region of the ARB (Scaroni, unpublished data). The retention of water on the floodplain has implications for downstream water quality; N transformations and removal generally occur where hydraulic residence time is increased (Cirimo and McDonnell 1997).

The formation of a large area of hypoxia (dissolved oxygen levels $< 2 \text{ mg L}^{-1}$) in the Gulf of Mexico is attributed to N loading from the Mississippi and Atchafalaya Rivers (Rabalais et al. 2002). Recent studies indicate that 14% of the total nitrogen (TN) that enters the ARB does not

discharge into the Gulf of Mexico; this is equivalent to 50,544 t TN annually sequestered or removed within the ARB (Xu 2006). Sedimentation and plant uptake are the major processes contributing to nitrogen retention, while the denitrification pathway is considered a permanent removal of N from the system. Nutrient retention studies tend to calculate a mass balance of N outputs from N inputs; quantifying the contribution of each of these three processes to total N retention and removal are not common, and are generally restricted to lakes (Saunders and Kalff 2001). However, Saunders and Kalff (2001) have shown that certain wetlands retain twice as much N as lakes at a given N load. Because the ARB contains a variety of habitats, including lakes, wetland areas, and bottomland hardwood forests, it is likely that there is considerable variability in N retention and removal rates across the Basin. Our goal was to examine spatial variability as well as look for trends in denitrification across the ARB.

STUDY AREA

The ARB is located in south-central Louisiana, and covers approximately 5,000 km². The floodplain consists of three major habitat types: bottomland hardwood forests, baldcypress swamps, and lakes. These tend to follow a north to south gradient, with the northern ARB dominated by bottomland hardwoods, and the southern ARB predominately lakes. The ARB is bounded to the east and west by protection levees to prevent flooding of adjacent agricultural areas and towns; however, these levees reduce the size of the floodplain for the Atchafalaya River. The river itself has a high sediment load, and transports around 84×10^6 t of sediment annually (Allison et al. 2000). While much of this sediment discharges into Atchafalaya Bay, contributing to delta formation (Roberts 1998), a portion is deposited on the floodplain within the ARB. This deposition leads to natural habitat succession, and is transitioning the ARB from

a lake-dominated ecosystem to a predominately bottomland hardwood forest ecosystem. As sedimentation continues there will be a further reduction in the total area of the ARB that has contact with floodwaters. In addition to alteration for flood control, the natural hydrology of the system has been further disrupted for pipeline and highway construction, navigation, and timber removal. However, despite this history of human intervention, the Atchafalaya Basin still contains large areas of uninhabited wilderness that provide extensive natural resources for fish and wildlife habitat.

METHODS

Sample Collection

Bulk sediment samples were collected from 10 sites throughout the ARB during May 2007 (Figure 1). Sites were haphazardly selected based on accessibility and proximity to public land, and were separated by at least 3 km but not more than 63 km. Samples were sealed in 4-L wide-mouth heavy duty polyethylene (HDPE) bottles, put on ice during transport to the laboratory, and then stored at 2°C. Subsamples were analyzed for N and C using a Leco C-N Analyzer (Leco Corp., St. Joseph, MI, USA). Extractable nitrate and ammonium were analyzed colorimetrically (Method 365.4, USEPA 1983). Particle size was determined by the Hydrometer Method (Gee and Bauder 1986). A conductivity meter was used to analyze samples for conductivity and salinity. A pH meter was used to determine the pH of samples. Samples were weighed before and after they were dried in an oven to determine moisture content. To increase spatial variability in our study, we included sediment samples that were collected during the prior growing season (August 2006) from 9 additional sites (Figure 1). Sites were separated by at least 5 km but not more than 74 km. These samples had been frozen and

stored in the laboratory since collection. Subsamples were analyzed for C and N shortly after they were collected in 2006. While the long storage time of the previously collected samples is a concern, Stenberg et al. (1998) saw less of an effect on microbial biomass and activity in soils that had been frozen, as opposed to refrigerated. Another study investigating the response of denitrifying bacteria to freeze/thaw cycles did not observe a decrease in microbial biomass as a result of freezing (Sharma et al. 2006). Sharma et al. (2006) observed a burst of N₂O emissions immediately following thawing, so before we began the experiment we let the sediment samples equilibrate after thawing. Denitrification experiments were then carried out at room temperature.

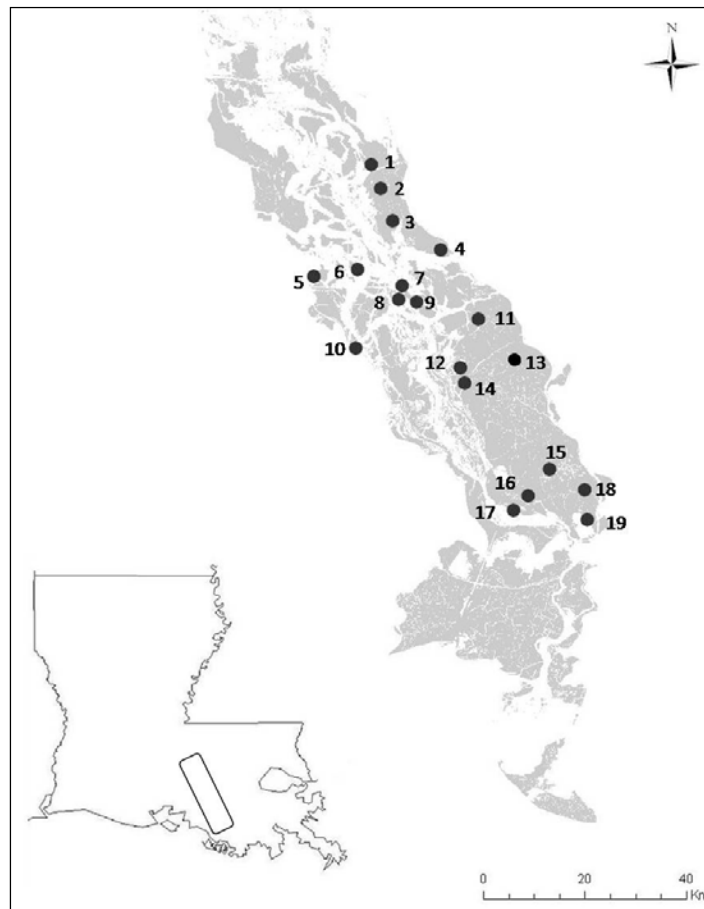


Figure 1: Location of sampling sites in the Atchafalaya River Basin.

We used the indirect acetylene block technique (Groffman 1994) to estimate denitrification rates. This technique is subject to criticism as it systematically underestimates denitrification rates (Groffman et al. 2006). Acetylene blocks the reduction of nitrous oxide to N_2 gas; however, incomplete inhibition can occur over longer time periods. Acetylene also inhibits nitrification, which can mask the importance of denitrification in systems with low external nitrate, where denitrification is primarily supported by internal nitrification. However, over short terms this is generally less of a problem (Ryden and Dawson 1982).

Background Denitrification

Duplicate microcosms were established for each site ($n=19$) by adding approximately 10 g of wet sediment to 40-ml glass vials capped with rubber septum tops. Following sediment addition, 10-ml of deionized water (no nitrate added) was added to all vials ($n=38$), which were subsequently agitated with a vortex mixer. Sealed vials were purged with ultra high pure N_2 gas for 1 minute to remove O_2 . A 2-ml gas tight syringe was used to remove 4-mL of gaseous headspace from all vials, which was then replaced by 4-ml purified acetylene (15% v/v C_2H_2 /air). Vials were again agitated by the vortex mixer, and left undisturbed for 24 hours in the dark. Gas samples were collected, at time 0 and at 24 hours, with a syringe and injected into a Shimadzu GC-14A gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA) fitted with a 1-ml sampling loop, Poropak Q 1.8 m ss column, electron capture detector (ECD) and calibrated with certified N_2O gas standards (Scott Specialty Gases, Inc., Plumsteadville, PA, USA). Ultra high pure N_2 was the carrier gas and the instrument operated at temperatures of 40, 100, and 290°C for the oven, injector, and ECD detector, respectively (Lindau et al. 1998).

Potential Denitrification

We replicated the methodology used for the background denitrification experiment to determine denitrification potential. However, the addition of 10-ml of deionized water was replaced by addition of 10-ml of 100 mg L⁻¹ NO₃-N solution. This high nitrate concentration was used to ensure that nitrate was not limiting denitrification.

Statistical Methods

Background denitrification and potential denitrification rates were analyzed using PROC MIXED in SAS to characterize denitrification within and across habitats (SAS Institute 2006). Correlations between N₂O emissions and soil components (N, C, NO₃⁻, and NH₄⁺) were tested using the PROC CORR function in SAS (SAS Institute 2006). The PROC REG function in SAS was used to test for a relationship between denitrification rates and site coordinates (recorded using the Universal Transverse Mercator projection, zone reference 15R), expressed as UTM east and UTM north (SAS Institute 2006).

RESULTS

Total N in the soil samples ranged from 0.1–1.4%. Total C ranged from 1.12–22.6%. Soil nitrate ranged from a minimum value of 0.07 mg kg⁻¹ to a maximum value of 98.3 mg kg⁻¹. Soil ammonium values ranged from 1.1 mg kg⁻¹ to 487.4 mg kg⁻¹ (Table 2).

Background denitrification rates and potential denitrification rates differed among sites ($p < 0.0001$ and $p = 0.0005$, respectively), and also differed from each other ($p < 0.0001$).

Background denitrification rates showed a positive correlation ($r = 0.74$, $p < 0.0001$) with soil nitrate, and negative correlations with soil C ($r = -0.38$, $p = 0.0183$) and soil N ($r = -0.32$, $p = 0.0475$). Potential denitrification rate showed no correlations with any of the soil parameters

Table 2: Sediment characteristics of samples collected from the Atchafalaya River Basin, LA.

Site	Total C (%)	Total N (%)	NO ₃ -N mg kg ⁻¹	NH ₄ -N mg kg ⁻¹	Flooded	pH	EC (mS/cm)	Salinity (ppt)	Moisture (%)	Sand (%)	Silt (%)	Clay (%)
1	14.5	0.8	0.2	89.8	Yes	5.5	0.6	0.3	83.4	22.6	11.2	66.2
2	22.6	1.4	0.6	91.0	Yes	5.4	0.6	0.3	90.0	30.2	16.8	53
3	9.1	0.7	1.1	77.1	Yes	6.0	0.2	0.1	58.6	13.3	14.7	72
4	2.7	0.2	0.4	137.5	Yes	6.3	0.6	0.3	66.6	5.7	43.9	50.4
5	1.2	0.1	3.7	6.9	No	5.6	0.0	0	18.8	65.3	23.7	11
6	1.7	0.1	6.2	8.7	Yes	6.4	0.2	0.1	35.0	2.5	48.4	49.1
7	1.6	0.1	2.1	11.0	Yes	5.6	0.3	0.2	42.0	1.8	28.5	69.7
8	3.1	0.2	40.6	1.3	No	7.0	0.4	0.2	32.7	9.5	58.9	31.6
9	13.3	0.9	1.7	27.4	Yes	5.9	0.4	0.2	78.3	17.9	15.2	66.9
10	2.4	0.2	12.6	1.1	No	6.0	0.3	0.1	37.7	2.8	32.4	64.8
11	1.9	0.2	66.0	9.9	No	7.0	0.4	0.2	24.0	58.2	31.5	10.3
12	1.1	0.1	32.8	1.1	No	6.6	0.2	0.1	17.4	78.5	14.2	7.3
13	2.3	0.2	34.8	2.3	No	7.1	0.4	0.2	27.3	15.4	66.6	18
14	7.8	0.8	0.1	487.4	No	4.4	1.9	1	71.6	10.5	15.5	74
15	9.1	0.8	4.9	105.0	No	4.7	1.4	0.7	70.7	12	28.5	59.5
16	3.2	0.3	98.3	27.1	No	5.6	0.8	0.4	48.8	4.1	34	61.9
17	1.4	0.2	1.2	2.7	Yes	6.7	0.8	0.4	48.3	16.3	60.4	23.3
18	2.7	0.3	0.1	24.3	Yes	6.9	1.8	0.9	71.3	3	41.5	55.5
19	3.3	0.3	1.0	35.2	Yes	7.0	1.9	1	71.4	3.4	31.6	65

tested. Soil N showed positive correlations with soil C ($p < 0.0001$) and soil ammonium ($p = 0.0035$). Background denitrification rates ranged from 0-1.35 $\mu\text{g N g}^{-1} \text{d}^{-1}$ and potential rates ranged from 26.72-710.47 $\mu\text{g N g}^{-1} \text{d}^{-1}$. Average denitrification rates for each site, and ranges, are shown in Table 3.

Table 3: Background and potential denitrification rates ($\mu\text{g N g}^{-1} \text{d}^{-1}$).

Site	Mean	Std Dev	Min	Max	Mean	Std Dev	Min	Max
	Background				Potential			
1	0.51	0.15	0.40	0.62	68.55	65.58	22.17	114.92
2	0.40	0.05	0.36	0.43	26.72	13.65	17.06	36.37
3	1.04	0.16	0.92	1.15	159.54	12.23	150.89	168.19
4	0.08	0.07	0.03	0.13	332.24	354.32	81.69	582.78
5	0.45	0.09	0.38	0.52	72.08	53.46	34.27	109.88
6	1.03	0.06	0.99	1.07	369.00	40.50	340.36	397.63
7	0.74	0.02	0.73	0.75	271.53	6.99	266.59	276.47
8	0.65	0.02	0.64	0.67	250.10	25.29	232.22	267.98
9	0.31	0.00	0.31	0.31	90.52	15.97	79.23	101.81
10	0.00	0.00	0.00	0.00	336.08	216.03	183.32	488.83
11	0.11	0.05	0.08	0.14	256.11	28.95	235.64	276.58
12	1.35	0.02	1.33	1.37	250.97	4.39	247.86	254.07
13	1.35	0.02	1.34	1.36	257.68	1.00	256.97	258.39
14	0.00	0.00	0.00	0.00	710.47	22.68	694.43	726.50
15	0.00	0.00	0.00	0.00	309.55	70.11	259.97	359.12
16	0.18	0.24	0.01	0.35	133.91	30.69	112.21	155.61
17	0.35	0.36	0.09	0.60	249.15	6.96	244.23	254.07
18	0.04	0.03	0.02	0.06	44.83	7.79	39.32	50.34
19	0.45	0.01	0.44	0.45	128.46	0.54	128.08	128.84
Mean	0.48	0.45	0.00	1.37	227.23	172.08	17.06	726.50

Simple linear regression between spatial coordinates of our sites and corresponding denitrification rates did not detect a relationship for background denitrification rates ($R^2 = 0.10$, $p = 0.31$), suggesting that patterns of spatial variability in background denitrification rates across the ARB are lacking. However, a significant relationship existed between spatial coordinates

and denitrification potential ($R^2=0.32$, $p=0.004$). In general the highest rates were found in the southeast, downstream area of the ARB (Figure 2). Soil nitrate did not show a spatial relationship across the ARB ($R^2=0.19$, $p=0.23$), but soil C was related to location ($R^2=0.32$, $p=0.004$). Soil C levels were highest in the north-central (upstream) and southeast (downstream) areas of the ARB (Figure 3).

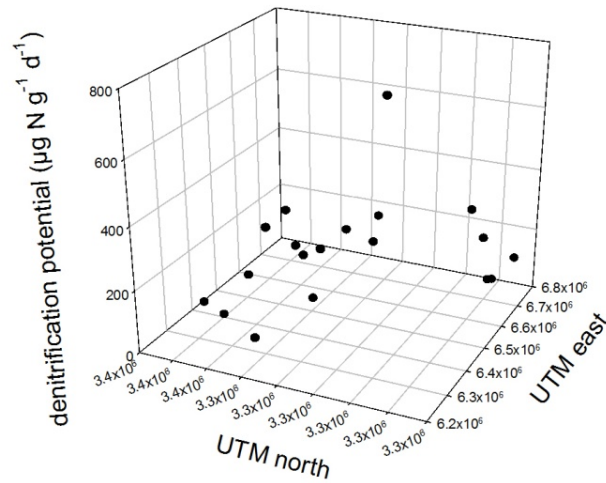


Figure 2: Denitrification potential ($\mu\text{g N g}^{-1} \text{d}^{-1}$) vs. spatial coordinates (UTM) showing a general trend of increasing denitrification rates along a northwest to southeast trajectory.

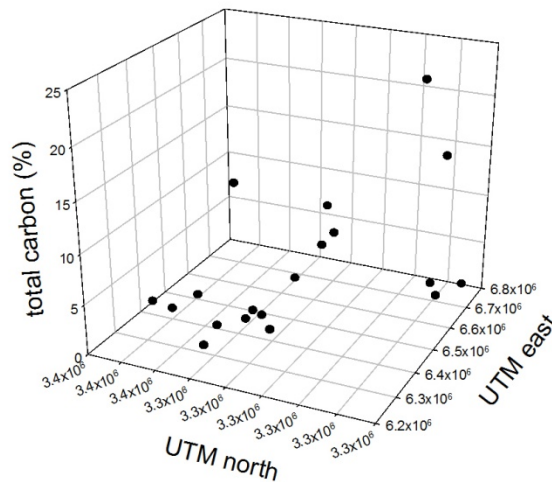


Figure 3: Total carbon vs. spatial coordinates (UTM) showing an increase in total carbon along a northwest to southeast trajectory.

DISCUSSION

Riparian soils flood more often than their upland counterparts, which can lead to anaerobic conditions in the soil and subsequent buildup of organic matter (Schipper et al. 1993). Through decomposition, this supply of C becomes available to fuel denitrifying bacteria; hence a positive correlation is often seen between soil organic C and denitrification potential (Gale et al. 1993; D'Angelo and Reddy 1999). While soil C and potential denitrification were not correlated, we observed a negative correlation between soil C and background denitrification. Plant communities differ across the ARB, thus the bioavailability of C will differ as well. Habitat types, hydrologic conditions, or quality of organic matter may be stronger predictors of denitrification potential than C. Schipper et al. (1993) indicated that in anaerobic and organic C-rich environments, denitrifying bacteria will have a competitive advantage for organic C and nutrients. However, when comparing soils across habitat types other variables could be more important than organic C concentrations.

Pina-Ochoa (2006) found that annual in-situ denitrification rates were highest in rivers and lakes, followed by coastal systems, and estuaries. These findings highlight the concept that environmental variability at scales of habitat and ecosystem level are often confounded and may explain inconsistencies between controlling variables (such as C) and denitrification rate. Pina-Ochoa (2006) corroborated our observation of a correlation between background denitrification and soil nitrate; they also found that nitrate concentration was the best explanatory variable for differences in denitrification rates across ecosystem types. In our experiment samples that received nitrate additions were spiked with non-limiting quantities ($100 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$), and because all other limiting factors besides C were controlled for, we

expected to see C as the factor most limiting denitrification rates. The lack of a statistical correlation between C and potential denitrification might be attributed to the failure to fractionate organic matter and determine what percent of soil organic C was labile, and thus bioavailable to denitrifiers.

In our study, a number of possible reasons exist for total C in the system failing to correlate with denitrification potential. Because plant communities differ across the ARB, the quality of organic matter probably differs as well. The recalcitrant nature of baldcypress needles could explain why some sites with adequate soil C content did not show a significant relationship between soil C and denitrification potential. We sampled from the top 10-cm of the soil profile, which is the area where denitrifying organisms are most prevalent. In habitats experiencing rapid sedimentation, labile organic C could be buried at deeper depths in the soil profile. Dodla et al. (2008) estimated labile organic C during a study of potential denitrification rates across forest swamp, freshwater marsh, and saline marsh in Southeast Louisiana and found that labile organic C had a positive correlation with potential denitrification rates.

The lack of a trend in spatial variability for background denitrification rates and soil nitrate in the ARB could also be due to the fact that plant communities and water levels do not strictly conform to a distinct north-south or east-west gradient. A category that encompasses a number of these variables influencing denitrification, such as habitat type, may better explain differences in biogeochemical cycling. However, trends in spatial variability for potential denitrification rates and soil C observed in this study suggest that C may be more limiting of denitrification potential at the landscape scale.

Adding to the difficulty in distinguishing the contributions of denitrification to ecosystem-scale N removal is the fact that biogeochemical cycling can vary over small scales and short time periods (Seitzinger 2006). “Hot spots” and “hot moments” result when key elements in the denitrification pathway are brought together in a particular place, or after an episodic water release re-activates accumulated reactants (McClain et al. 2003). Within the ARB specifically, reactants accumulate in the soil during dry periods when the river is not in contact with the floodplain. Litterfall primes the system with C from decaying organic matter, and N is introduced from nitrification during aerobic periods. This sets up a system where anaerobic conditions limit the denitrification reaction. When water transports additional nutrients across the floodplain, newly induced anaerobic conditions enhance reaction rates (McClain et al. 2003), leading to a hot moment for denitrification. Because some of our samples were collected dry (Table 1), we might have measured a temporal hot moment at some sites. This could have affected our analysis, which indicated that denitrification potential is related to landscape position. Future experiments will measure denitrification rates from these dry sites with and without flooding in the laboratory.

We observed a significant relationship between location and potential denitrification rates, with greater potential downstream than upstream, but not between location and background rates. This suggests that landscape scale studies should include additional qualifiers, such as habitat type and organic matter quality, for more reliable estimates of denitrification rates.

Brief 24-hour studies such as this one cannot elucidate denitrification dynamics over time. Actual peak denitrification rates for soil types that take more than one day to reach

maximum emissions might have been missed. Pulses of nitrate that enter the ARB seasonally or following storms will not be considered; these could lead to spikes in denitrification rates. Fluctuating water levels can accelerate denitrification rates (Bowden 1987), so sites should be sampled before and after floods to better understand patterns in denitrification. Additional studies are needed to determine the role of organic matter quality and habitat classification in predicting potential denitrification rates in the ARB.

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CHAPTER 3.

COMPARISON OF DENITRIFICATION CHARACTERISTICS AMONG THREE HABITAT TYPES OF A LARGE RIVER FLOODPLAIN; ATCHAFALAYA RIVER BASIN, LOUISIANA²

INTRODUCTION

Humans have altered the nitrogen cycle in such a way that levels of reactive nitrogen released into the environment are degrading air, soil, and water quality worldwide (Kulkarni et al. 2008). Nitrogen has been identified as a key limiting nutrient for biomass production. Consequently, the rate of nitrogen fertilizer application has been on the rise over the past century. While human manipulation of the nitrogen cycle has provided many benefits, a host of unintended problems have resulted. Consequences of increased nitrogen levels in the environment include eutrophication (Rabalais et al. 1996), and loss of ecosystem services (Tilman et al. 2001). Because of the highly mobile nature of nitrate-nitrogen, environmental problems extend beyond the area of application; adverse effects generally are seen downstream of the source. A prime example is the Mississippi River Basin (MRB) in the United States.

The MRB drains over 1.2 million ha of land, which constitutes 40% of the land area of the continental United States (Mitsch et al. 2001). Agriculture is one of the major land uses in this watershed. As a result, nitrogen loading to the MRB has increased substantially in comparison to a pre-industrial baseline (Howarth et al. 1996). This watershed is the primary source of freshwater and nutrients to the Gulf of Mexico (80 and 90% respectively), and the last 30 years have seen a tripling in the flux of nitrate to the Gulf (Goolsby et al. 2001).

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Increased nitrogen loadings to nitrogen-limited marine ecosystems can alter species composition, lower biodiversity, and stimulate biological productivity causing harmful algal blooms and hypoxia (Rabalais 2001). The formation of a large area of hypoxia (oxygen < 2 mg L⁻¹) in the Gulf is primarily attributed to nitrogen loading from the Mississippi and Atchafalaya Rivers (Rabalais et al. 2002). While there is evidence of natural hypoxic events before artificial fertilizers were used in the Upper MRB, hypoxic conditions have intensified since the 1940s and the extent and persistence of hypoxia are growing (Rabalais et al. 2002). Mitsch et al. (2001) recommend a combination of several best practices for reducing nitrogen loading to the Gulf; these include improvements in fertilizer-use efficiency, upstream wetland creation, and Mississippi River diversions.

Before the Mississippi River reaches the Gulf of Mexico, approximately 30% of the flow diverts through the Old River Control Structure where it joins with the Red River to form the Atchafalaya River. The control structure was built in 1962 to prevent the Atchafalaya River from capturing the Mississippi River (Sparks, 1992). With an average annual discharge of 6,228 m³ s⁻¹ (Xu 2006a), the 226-km Atchafalaya River is the fifth largest river in North America by volume. A combination of sedimentation, control structures, and levees ultimately reduce contact between floodwaters and floodplain sediments in the Atchafalaya River Basin (ARB). Once a river- and lake-dominated system, the ARB is now nearly 70% forested (Hupp et al. 2008), and the floodplain continues to fill in with sediment. As surface elevations increase, this will reduce connectivity between the river and sites that currently experience seasonal flooding. The ARB itself is a system in transition; habitats continue to change in response to hydrologic conditions and sediment loads.

The ARB removes 14%, or 50,544 t, of the total nitrogen that enters the system via the Atchafalaya River (Xu, 2006a). Processes responsible for removal include storage in the sediments, biomass uptake, and denitrification. The relative contribution of each of these processes is currently unknown for the ARB. Denitrification, the reduction of nitrate to dinitrogen gas, is the only permanent removal process and is likely the dominant process for removal of river-borne nitrogen (Howarth et al. 1996). Reviews have compared denitrification rates among different wetland types (Groffman, 1994) and across terrestrial, freshwater, and marine systems (Seitzinger et al. 2006). Denitrification characteristics have been estimated in Louisiana freshwater lakes (Lindau et al. 2009), baldcypress swamps (Lindau et al. 2008), and bottomland hardwood forests (Hunter et al. 2008). However, individual studies use different methodologies for measuring denitrification. This makes habitat comparison difficult and limits their use in models to predict the effects of habitat change on denitrification at the floodplain scale. A previous study (Scaroni et al. 2010) identified trends in spatial variability by geographic position across the ARB, with increasing potential denitrification rates along a northwest—southeast trajectory. We hypothesize that this variability can be explained, in part, by habitat type. The objective of this study was to determine whether there are significant differences in denitrification potential among the major habitat types of the ARB using the acetylene block technique. This will contribute to our understanding of the spatial distribution of denitrification rates in the ARB, and the effects of habitat change on nitrogen removal in the ARB. A secondary aim was to generate estimates of denitrification characteristics from these three habitats that could be used in models of denitrification at the floodplain scale.

METHODS

Sample Collection

We identified bottomland hardwood (BLHW), baldcypress swamp, and lake as the three major habitat types in the ARB, and selected three sites within each habitat type based on accessibility and proximity to public land ($n = 9$) (Figure 4). Sites within habitat type were considered replicates used to estimate variability in denitrification within habitats.

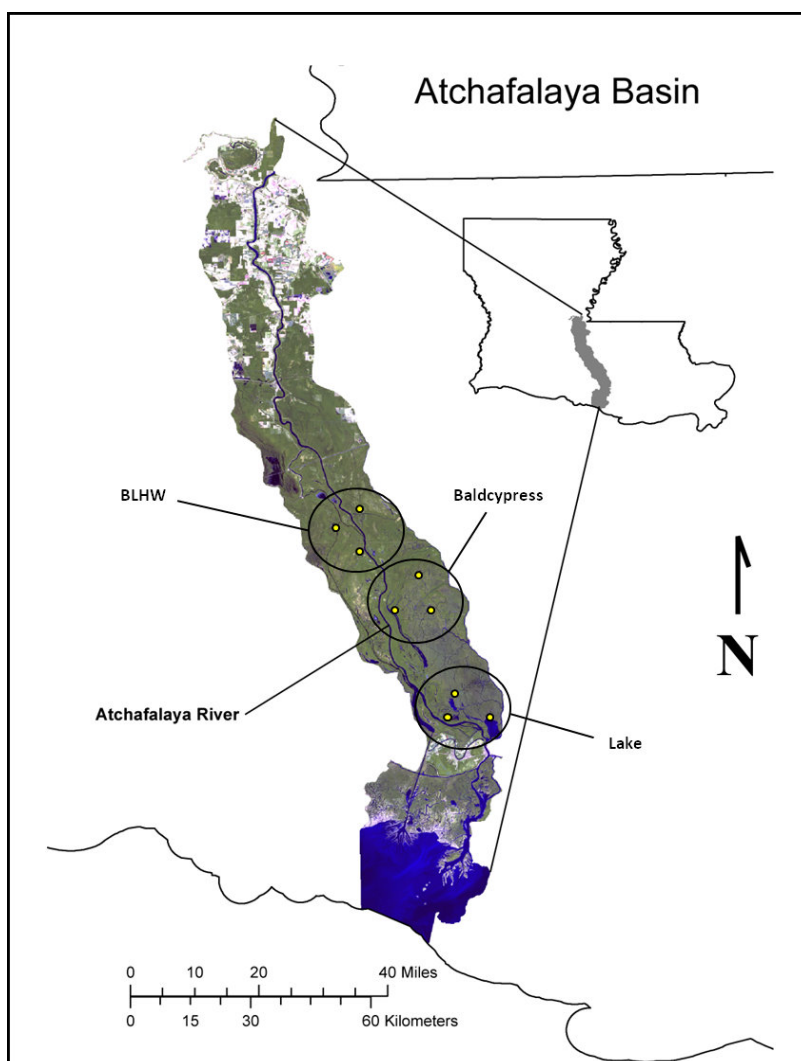


Figure 4: Location of sampling sites in the Atchafalaya River Basin, Louisiana.

It is important to note that there is considerable spatial and temporal variability both within and between habitats in respect to hydrology, and resulting biogeochemical properties of the sediment. The BLHW and baldcypress sites were not flooded during sampling, which reflects the seasonal nature of flooding in these areas. The three lake sites were flooded during sampling, which reflects their typical condition throughout the year. Water monitoring stations located in the main channel indicate that the seasonal range in water levels is 9.5 m at the upstream end of the Atchafalaya Basin but only 0.9 m at the downstream end of the basin (Ford and Nyman, in press). However, soil elevation data are unavailable, and even then water levels in forests and swamps may differ behind spoil banks and natural levees, wherein the majority of our sites were located.

Bulk sediment samples were collected (0—15 cm depth) between June and August 2006. All samples were sealed in 4-L wide-mouth heavy duty polyethylene (HDPE) bottles, put on ice, transported to the laboratory, and stored at 2° C for 1 month. Despite extensive disturbance during extraction and transport of cores, prior work has shown good agreement between in situ and laboratory denitrification studies (Well et al. 2003). Subsamples were removed and analyzed for bulk density. We analyzed nitrogen (N) and carbon (C) content with a Leco C—N Analyzer (Leco Corp., St. Joseph, MI, USA).

Denitrification Experiments

Sediments were mixed to homogenize samples. Duplicate microcosms were established for each site by adding approximately 576 g (5 cm) of wet sediment to the bottom of a 9-cm (circumference) glass incubation jar ($n = 18$). Sediments were compacted to remove excess gas. Final bulk densities ranged from 0.243 to 0.500 g cm⁻³. Sediments were then flooded with 240

ml (4 cm) of nitrate-free deionized water. Jars were encased in foil and loosely covered with tissue paper to discourage growth of plants. The microcosms equilibrated for approximately 1 week to allow for the development of a thin oxidized layer at the sediment—water interface as was observed in the field. This setup was repeated for each level of nitrate added.

We used the acetylene block technique (Groffman 1994) to measure background levels of denitrification. Nitrous oxide (N_2O) emissions were measured from the microcosms with no nitrate added (day zero). To simulate low, slightly elevated, and high nitrate loading rates, microcosms were amended with 2 mL of 1, 5, and 50 mg $\text{NO}_3\text{-N L}^{-1}$ solution, respectively. Nitrate concentrations in the Atchafalaya River ranged from 0.31 to 2.80 mg N L^{-1} over the last 25 years (Xu, 2006b).

Acetylene was added directly into the headspace ($\sim 10\%$ v/v) and floodwater of each microcosm on each day denitrification was measured, which was capped to prevent gaseous exchange with the atmosphere. Gas samples were collected via a rubber septum in the lid with a 2-ml gas tight syringe at 2h and 4h (for the 50 mg L^{-1} addition), or 2 and 6h (for the 1 and 5 mg L^{-1} additions). Samples were injected into a Shimadzu GC-14A gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA) fitted with a 1-ml sampling loop, Porapak Q 1.8-m ss column, electron capture detector (ECD) and calibrated with certified N_2O gas standards (Scott Specialty Gases, Inc., Plumsteadville, PA, USA). Ultra high-purity nitrogen was the carrier gas, and the instrument operated at temperatures of 40, 100, and 290°C for the oven, injector, and ECD detector, respectively (Lindau et al. 1998).

Denitrification rates were measured until they began to decrease: 0—9 days (1 mg L^{-1} $\text{NO}_3\text{-N}$), 0—13 days (5 mg L^{-1} $\text{NO}_3\text{-N}$), and 0—29 days (50 mg L^{-1} $\text{NO}_3\text{-N}$) following nitrate

additions. This ensured that the system had sufficient time to respond to the nitrate loading and reach maximum rates. Microcosms were sealed only during 4—6 hour incubations each measurement day. The highest rate of denitrification over time was defined as the “maximum denitrification rate,” and the time elapsed between nitrate additions and maximum denitrification rate was defined as “time to reach maximum emissions.” All tests were run at 22°C.

Calculations were performed using the Bunsen absorption coefficient (which corrects for solubility of N₂O in water) to determine N₂O—N that was recovered in the headspace and floodwater (Tiedje 1982). We used the closed chamber equation of Rolston (1986) to calculate final N₂O flux, reported as g N ha⁻¹ day⁻¹.

Statistical Analysis

Maximum N₂O emissions and time to reach maximum N₂O emission rates were analyzed to characterize denitrification for each habitat type and each level of nitrate added. Data were analyzed using PROC MIXED in SAS (SAS Institute 2006). The experimental design was completely randomized with nesting of site in habitat type to test the hypothesis that denitrification characteristics vary among habitat types and with nitrate level. We performed pair-wise comparisons with a Tukey adjustment (SAS Institute 2006). We estimated relationships between denitrification rates and nitrate levels for both initial (24 h following nitrate addition) and maximum emissions using the PROC REG function in SAS (SAS Institute 2006). For both regressions, background rates observed were subtracted from initial and maximum rates to force the regression lines through the origin (Nielsen 1992). Associations

between N_2O emissions and soil components (N, C) were tested using the PROC CORR function in SAS (SAS Institute 2006).

RESULTS

Background Denitrification Rates

Background denitrification rates were highest for the BLHW sites ($5.4 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=0.72$) followed by baldcypress ($3.9 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=0.52$), and lake sites ($1.4 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=0.52$) (Figure 5a). BLHW and lake sites differed ($P = 0.0077$), as did lake and baldcypress sites ($P = 0.0462$). BLHW and baldcypress sites did not differ ($P = 0.2023$).

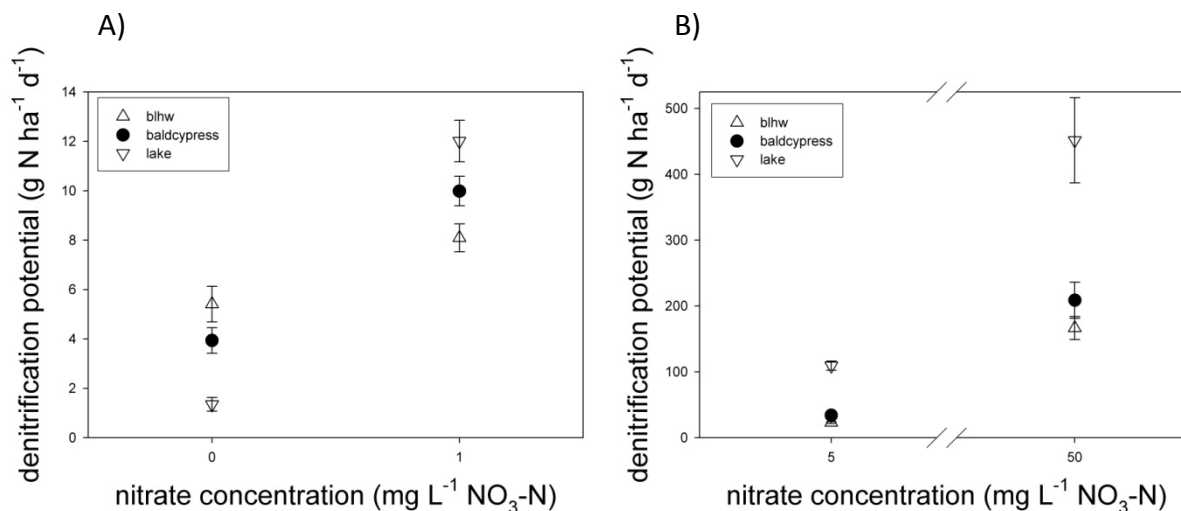


Figure 5: Denitrification rates for 3 habitat types in the Atchafalaya River Basin, Louisiana following A) 0 and 1 mg L⁻¹ NO₃-N nitrate additions, and B) 5 and 50 mg L⁻¹ NO₃-N nitrate additions. Graphs show Least Squares Means and Least Squares Standard Error bars.

Potential Denitrification Rates

The three habitats responded differently to nitrate addition, and the ranking differed from that observed in background denitrification. Upon addition of 1 mg L⁻¹ NO₃⁻-N,

denitrification rates were highest for lakes ($12.0 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=0.84$), followed by baldcypress ($10.0 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=0.60$) and BLHW sites ($8.1 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=0.57$) (Figure 5a). These rates differed among each of the habitats ($p=0.0395$), but only BLHW and lake differed from each other ($p=0.0143$). When amended with $5 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$, the same pattern was seen as with the 1 mg L^{-1} addition ($p=0.0002$); however, denitrification rates were higher (lake = $109.4 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=6.81$; baldcypress = $34.1 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=4.43$; BLHW = $23.0 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=1.29$) (Figure 5b). Once again, BLHW and baldcypress did not differ ($p=0.5247$). With a $50 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ addition, lake sediments showed the highest rates of denitrification ($451.6 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=64.62$), followed by baldcypress ($208.8 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=27.38$), and BLHW ($166.6 \text{ g N ha}^{-1} \text{ d}^{-1}$, $\text{SE}=17.51$) (Figure 5b). There were significant differences among all comparisons except BLHW and baldcypress sites ($p=0.8426$).

Response Time to Nitrate Loading

With a $1 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ addition, denitrification in the lakes peaked in 1.0 day ($\text{SE}=0.00$), while baldcypress took 1.6 days ($\text{SE}=0.42$) and BLHW sites took 3.0 days ($\text{SE}=0.00$) (Figure 6a). After addition of $5 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$, lakes peaked in 0.5 days ($\text{SE}=0.00$), baldcypress took 2.1 days ($\text{SE}=0.61$), and BLHW took 3.8 days ($\text{SE}=0.42$) (Figure 6b). After a $50 \text{ mg L}^{-1} \text{ NO}_3^- \text{-N}$ addition, it took 2.2 ($\text{SE}=0.42$), 3.0 ($\text{SE}=0.72$), and 7.5 days ($\text{SE}=1.63$) for lakes, baldcypress, and BLHW, respectively, to reach maximum emission rates (Figure 6c). We did not sample multiple times per day, and acknowledge that peak emissions may have occurred between samples.

Relationship Between Nitrate and Denitrification

When we regressed maximum N_2O emissions on nitrate, without accounting for habitat differences, there was a significant linear relationship between nitrate and N_2O , but the

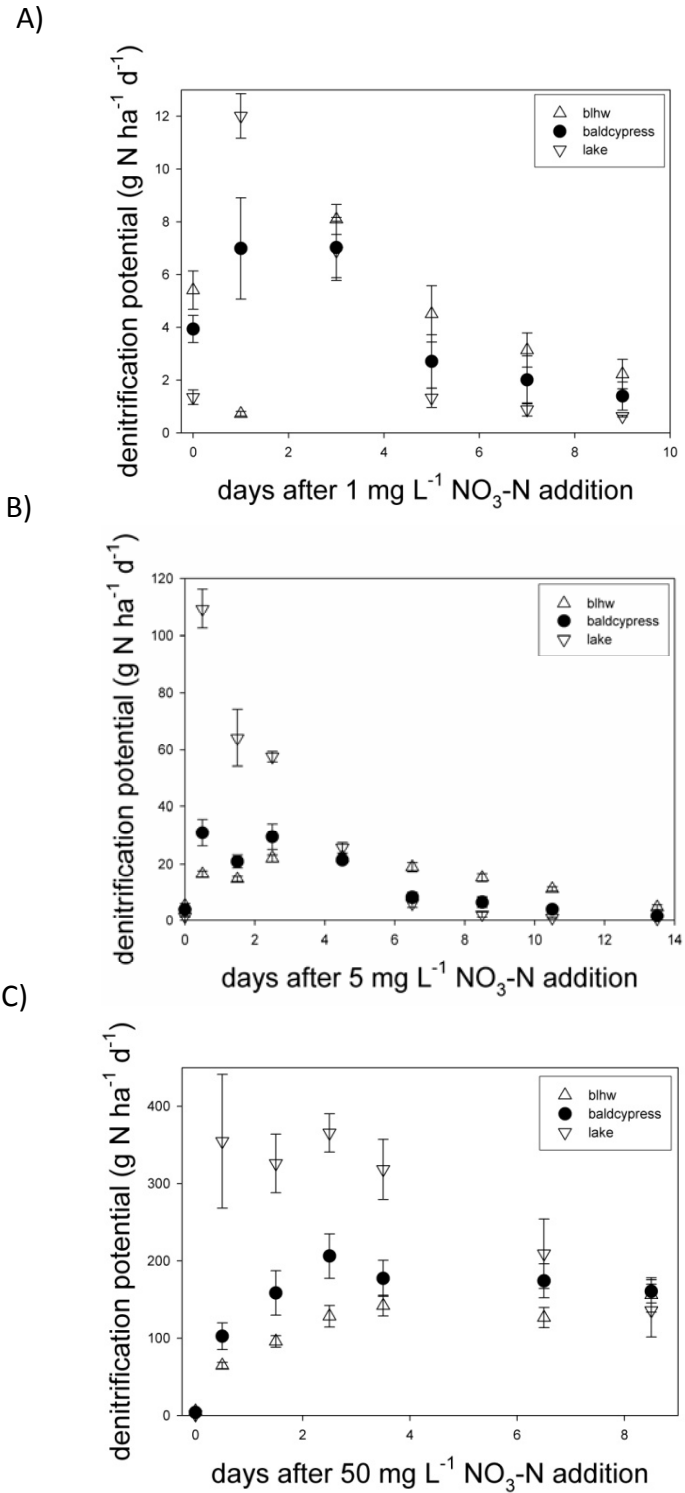


Figure 6: Temporal dynamics of denitrification potential after additions of A) $1 \text{ mg L}^{-1} \text{NO}_3\text{-N}$ nitrate, B) $5 \text{ mg L}^{-1} \text{NO}_3\text{-N}$ nitrate and C) $50 \text{ mg L}^{-1} \text{NO}_3\text{-N}$ nitrate to microcosms of each habitat type.

r-squared value was only 0.73 (slope= 5.49). When we ran this regression separately for each habitat, each of the habitat types proved to have a significant linear relationship between nitrate and maximum N₂O emissions, and more of the variation was explained (BLHW R²=0.94; baldcypress R²=0.91; lake R²=0.89). We then repeated separate regressions for each habitat using initial (24 h after nitrate addition) instead of maximum N₂O emissions. For both regressions, background rates observed were subtracted from initial and maximum rates to force the regression lines through the origin (Nielsen 1992). These regressions all underestimated the true response of denitrification to nitrate loading (Table 4).

Table 4: Slope of the regression line (g N ha⁻¹ d⁻¹/nitrate mg L⁻¹) for initial (24 hours after nitrate addition) N₂O emissions vs. nitrate, and maximum N₂O emissions vs. nitrate, by habitat type. Background N₂O emissions were subtracted from both initial and maximum emissions to force the regression line through the origin.

	Initial N ₂ O emissions	Max N ₂ O emissions
BLHW	1.2	3.2
Baldcypress	2.0	4.1
Lake	7.2	9.1

Associations with Soil Composition

Total C and N content of the sediments differed among habitat types ($P = 0.0171$, $P = 0.0146$, respectively). BLHW sediments contained 1.8% C (SE=0.36) and 0.18% N (SE=0.03). Baldcypress swamp sediments contained 6.7% total carbon (SE=1.8) and 0.66% total nitrogen (SE=0.16). Lake sediments contained 2.4% total carbon (SE=0.55) and 0.27% total nitrogen (SE=0.06). However, neither total carbon nor total nitrogen content were significantly correlated with denitrification rate ($P = 0.98$, $P = 0.95$, respectively).

DISCUSSION

While denitrification can remove a considerable amount of nitrate from floodwaters, it only occurs under anaerobic conditions. Areas of the floodplain exposed to different flooding regimes thus differ in their anaerobic conditions, and their ability to denitrify. Intermittently wet and dry sediments, such as those found in BLHW forests, respond differently to flooding than sediments that are always submerged, such as those found in lakes (Wijler and Delwiche 1954). With submerged sediments, flooding will likely bring in additional nutrients and an increased carbon supply. Nitrate does not accumulate, thus increased nitrate levels will stimulate denitrification. These sediments are primed to denitrify, so nitrate can become limiting to denitrifiers, and background rates may remain low. The rate of N mineralization probably controls the background rate of denitrification in these habitats, as has been shown in other habitats (Seitzinger et al. 2006). With bottomland sediments, dry periods allow for nitrogen mineralization, increased carbon preservation, and nitrate accumulation. This sets the stage for a pulse of denitrification upon rewetting, as previously observed by Groffman (1994) and Baldwin and Mitchell (2000). Our results agree with this scenario; the rewetted BLHW sediments showed the highest rate of background denitrification, while the highly anaerobic lake sediments showed the highest rates of denitrification in response to nitrate additions. Lake sediments also reached their maximum denitrification rates more quickly than the other habitats when nitrate was added. Because anaerobic conditions were limiting denitrification in the field-dry sediments, we likely measured a hot moment (McClain et al. 2003), or reactivation of reactants necessary for denitrification, upon flooding them in the lab.

It is important to note, however, that the BLHW sites in this study rarely receive flooding from the Atchafalaya River. This would decrease the ability to remove inorganic nitrogen flowing in from the Atchafalaya River, and indicates that the background denitrification rate is stimulated by internal nitrogen cycling. These results do suggest that seasonal diversions through spoil banks and natural levees could increase the capacity of the basin to remove nitrogen as sedimentation continues. BLHW and baldcypress sediments did not differ in their denitrification rates at any of the nitrate levels. Within the Atchafalaya Basin, both of these habitats are exposed to intermittent wet and dry cycles throughout the year, and probably maintain similar redox conditions in the sediment. Ongoing studies are attempting to determine background denitrification rates from unflooded BLHW sediments using unflooded microcosms; this also has implications for N₂O emissions from these areas.

Unlike Seitzinger et al. (1993), who observed no background denitrification from lake sediments when using the acetylene block technique, we observed significant background denitrification in all three habitats. Instead, our results were more similar to those of Groffman and Tiedje (1989), who observed significant background denitrification in forest soils when using this technique. These comparisons are consistent with our observation that background denitrification rates were higher in forest sediments than in lake sediments. Nonetheless, the acetylene block technique probably underestimated denitrification in the three habitats, especially the background estimates when there was no nitrate in the overlying water and only decomposing organic matter to supply nitrate (Groffman et al. 2006). Although acetylene inhibits nitrification, which can mask the importance of denitrification in systems with low

external nitrate loading that rely on nitrification as a source of nitrate, this is less of a problem over the short term (Ryden and Dawson 1982).

Gardner et al. (2010) quantified denitrification potential in a Louisiana freshwater marsh receiving diverted Mississippi River water (estimated loading rate of $2 \text{ mg NO}_3^- \text{ L}^{-1}$) and their rates fell in between our denitrification rates in response to our 1 and $5 \text{ mg NO}_3^- \text{ L}^{-1}$ additions. Lindau et al. (2008) recently published denitrification rates (0 and $100 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ additions) for the same baldcypress swamp sites used in this study. Our background rates were similar to their background rates at 22° C . Our potential rates were similar, although slightly lower, because our highest addition was $50 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$.

According to our results, denitrification increased linearly with nitrate concentrations, agreeing with previous research showing that denitrification in terrestrial and aquatic ecosystems can be estimated with first-order reaction rates (Boyer et al. 2006). Our results indicate that a linear relationship between denitrification rates and nitrate concentration was fairly strong across habitat types, and even stronger within habitat type.

The time required for denitrification to respond to nitrate loading differed among habitat types. This suggests that future measurements of denitrification potential that include more than one habitat type should avoid measuring at an arbitrary time after adding nitrate. Failure to account for differences in time to reach maximum denitrification rates could inaccurately estimate relationships between denitrification and nitrate concentrations. In this study, BLHW sediments took up to 7 days to reach maximum emissions. This peak would have been undetected in a common 24-h study, and would have misrepresented the differences among habitat types.

A carbon source is a necessary prerequisite for the denitrification process. We detected a difference in total carbon among our habitat types, with baldcypress sites showing the highest C content. However, C and denitrification were not correlated. The lack of a correlation suggests that differences in denitrification among habitat types are not due to C limitation. We did not measure the proportion of C that was labile, and the fairly recalcitrant nature of baldcypress needles could explain why the habitat with the highest C content did not exhibit the highest rates of denitrification. N and C content were correlated with each other, suggesting that much of the N in the soil is bound up in organic matter and is not bioavailable until remineralized by decomposers.

CONCLUSION

The Atchafalaya River functions as a natural diversion of the Mississippi, and the large floodplain has been shown to remove C, N, and P from floodwaters (Xu 2006b). Results from this study could be used to guide future planning efforts for diversions. We showed that lake habitats in the Basin differ from forested habitats in their ability to remove nitrate. The transition from lake to baldcypress and BLHW habitat is changing the overall dynamic within the ARB, potentially altering the fate of nutrients flowing toward the Gulf of Mexico. Our results indicate that denitrification responds to nitrate in the floodwater differently across habitat types, and modeling efforts addressing watersheds containing these habitats should model denitrification separately for each habitat. Models specific to the ARB should use background N₂O emissions for the intercept of a regression line, and maximum N₂O emissions from each habitat type for the slope of a regression line.

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CHAPTER 4.

EFFECT OF HABITAT TYPE ON N₂O AND N₂ EMISSIONS FROM THE ATCHAFALAYA RIVER BASIN, LOUISIANA, USA

INTRODUCTION

A review of the literature finds a large number of denitrification studies and review papers emphasizing the ability of denitrifying microorganisms to remove excess nutrients from water (Seitzinger 1988; Pina-Ochoa and Alvarez-Cobelas 2006; Rivera-Monroy et al. 2010). Past research has advanced our understanding of factors leading to spatial variability in denitrification rates, as well as provided estimates for actual and potential denitrification in treatment wetlands, freshwater ecosystems, estuaries, groundwater, and even the ocean. Denitrification is not the sole process mitigating excess nitrogen in a floodplain; sedimentation and biomass assimilation also remove nitrogen from water and soil. However, denitrification (the reduction of nitrate to nitrogen gas) is the only permanent removal process and is likely the dominant process for removal of river-borne nitrogen (Howarth et al. 1996).

The denitrification reaction occurs under anaerobic conditions in the presence of a carbon source and a supply of nitrate. When nitrate diffuses into the anaerobic zone in the sediment, it can be incrementally reduced to nitrogen gas via the denitrification pathway ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$). However, environmental conditions are not always conducive to completion of the pathway. Incomplete denitrification releases N₂O, which is favorably produced in well drained, aerated sites with coarse textured soils (Groffman 1991). Low temperature, low pH, and the presence of O₂ all favor the production of N₂O relative to N₂ (Knowles 1982; Granli and Bockman 1994; Stevens et al. 1998). Alternating wet and dry cycles, commonly seen on floodplains, tend to produce higher N₂O emissions (Granli and Bockman

1994). Because flooding affects these soil characteristics, soil moisture and soil management schemes will affect emission ratios (Ullah et al. 2005). At the ecosystem scale, the emission ratio of $\text{N}_2:\text{N}_2\text{O}$ is of concern because riparian wetlands can produce substantial quantities of N_2O (Burt et al. 1999; Kroeze et al. 2005). N_2O is a gas with a high global warming potential (IPCC 2007), so understanding the factors controlling N_2 vs. N_2O emissions is essential to minimizing greenhouse gas emissions from natural and restored freshwater wetlands.

Despite this extensive body of knowledge for the denitrification process, differing methodologies and analytical techniques can make it difficult to compare individual results to those of prior studies in comparable habitats. Also, there are few comparative studies on N_2O emissions across habitat types. Current attempts to model nitrogen removal in the Atchafalaya River Basin (ARB) necessitate measurement of local denitrification rates, as well as proportion of N_2O emissions. Such work will aid in modeling the effectiveness of river diversions as a tool for water quality improvement, and add to the pool of data on N_2 and N_2O emissions from riparian ecosystems.

The ARB in South Louisiana is a large 5000 km² floodplain that includes three major habitats: forested bottomlands, baldcypress swamps, and lakes. Continued influx of sediment is driving rapid habitat succession, such that open water areas are giving rise to seasonally flooded swamps and higher elevation forests that have minimal contact with the Atchafalaya River. Continued influx of nutrients derived from upstream activities, namely agriculture, is exacerbating a seasonal area of hypoxia downstream in the Gulf of Mexico. Attempts to model the possible outcomes of different water management regimes have been limited by lack of site-specific data and lack of comparative data in similar systems in the southeast U.S.

Recent work indicates that the ARB retains up to 14% of the total nitrogen entering the system from the Mississippi and Red Rivers (Xu 2006). While the pathways for N removal are well understood, the relative proportion of removal by each of the ARB's major habitats is less clear. Scaroni et al. (2011) showed that the 3 major habitats differ in their effectiveness at nitrogen removal via denitrification. Notably, intermittently flooded habitats had lower rates of denitrification potential than permanently flooded habitats. Differences in degree of inundation leads to differences in both the potential of sediments to denitrify, and the ratio of $N_2:N_2O$ produced. We hypothesized that intermittently flooded habitats would release more N_2O relative to N_2 , i.e. have lower $N_2:N_2O$ ratios. We designed an experiment to determine (1) if incomplete nitrate reduction is a significant source of N_2O , and (2) if the amount of N_2O emitted differs among habitat types. This baseline data will inform managers of the magnitude of potential N_2O emissions from the three habitat types in the ARB. These data may also serve as proxy estimates of denitrification and N_2O emissions for similar floodplains on the coastal plain of the southeast U.S.

STUDY SITE

The ARB is the largest deepwater swamp in North America. Considered the largest distributary of the Mississippi River, the Atchafalaya River is fed by the entirety of the Red River, and a controlled diversion of approximately 1/3 of the flow of the Mississippi River. As the river enters the ARB, the distance between levees increases to at least 24 km, which widens the floodplain and provides increased opportunity for nutrient transformation and removal. The hydroperiod varies greatly across the floodplain; some areas rarely, if ever flood, while others are constantly inundated. Once a river and lake dominated system, the ARB is now

nearly 70% forested, and sedimentation continues to convert aquatic habitats into forested bottomlands (Hupp et al. 2008). As surface elevations increase, connectivity between the river and floodplain is reduced.

Despite areas of extensive wilderness, the ARB is a highly altered and managed system. Management relies upon a partnership between the Louisiana Department of Natural Resources and the Army Corps of Engineers (FY2011 Atchafalaya Annual Basin Plan). Originally managed for flood control and navigation, water management projects now aim to improve water quality and internal circulation, and address sediment reduction, removal and diversion (FY2011 Atchafalaya Annual Basin Plan). These restoration goals are not unique to the ARB; neither is the rapid sedimentation occurring within the levees constricting the floodplain. Increasing our understanding of biogeochemical cycling in the ARB, and the response of these cycles to habitat succession, will lead to more effective management plans for both the ARB and other floodplains and freshwater wetlands throughout the coastal plain of the southeast U.S.

METHODS

Sample Collection

Bottomland hardwood forests (BLHW), baldcypress swamps, and lakes were identified with aerial maps as the three major habitat types in the Atchafalaya River Basin. To compare $N_2:N_2O$ emission ratios throughout the ARB, we selected three sites within each of these three habitat designations to estimate variability in emission ratios within and among habitats (Figure 7). Samples were collected from these nine sites throughout the ARB during June, 2009. The BLHW sites we selected were flooded by uncharacteristically high water. We returned to

sample these BLHW sites on July 31, 2009, when the water had dropped to typical levels and the BLHW sites were unflooded.

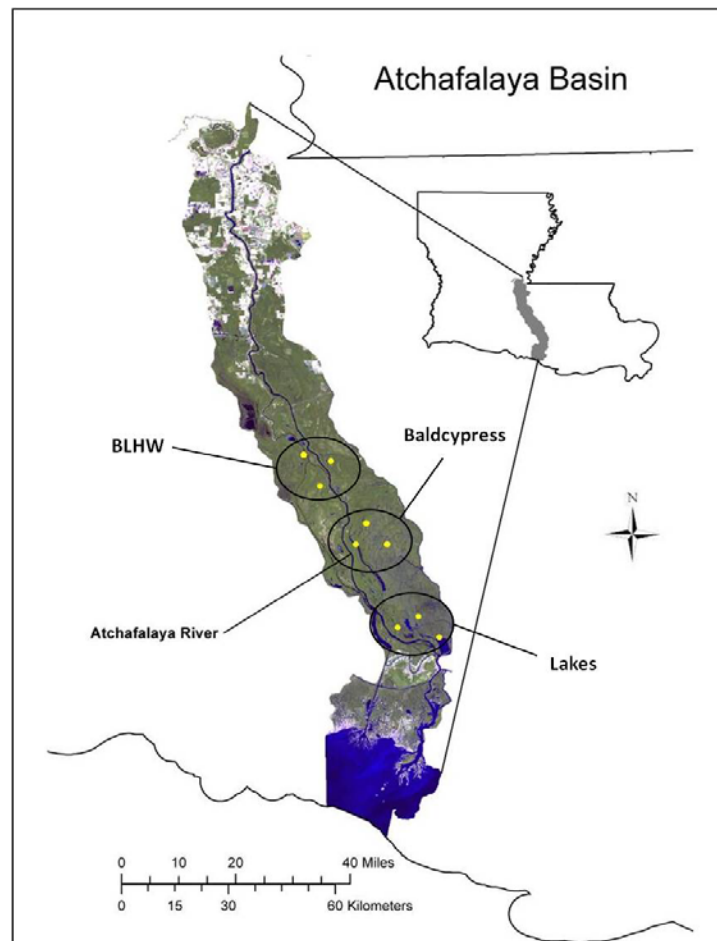


Figure 7: Atchafalaya Basin and location of sampling sites.

The BLHW sites were approximately 75 km upstream from the mouth of the Atchafalaya River, the baldcypress swamp sites were approximately 40 km upstream, and the lake sites were approximately 25 km upstream. We randomly selected three sites within each habitat type during a previous denitrification study (Scaroni et al. 2011), and selected those sites again for this study. Sites within habitats were separated by at least 2.7 km but not more than 14.5 km.

Sediment samples were collected (0-15cm depth) using either a hand shovel (dry sites) or an Eckman Dredge (flooded sites). Samples were sealed in 4-L wide-mouth heavy duty polyethylene (HDPE) bottles, put on ice, transported to the laboratory, and stored at 2°C. Subsamples were removed and analyzed for total nitrogen (N) and total carbon (C), using a Leco C-N Analyzer (Leco Corp., St. Joseph, MI, USA), particle size using the Hydrometer Method (Gee and Bauder 1986), salts using a conductivity meter, pH using a pH meter, and P using an ICP spectrophotometer (Table 5).

Denitrification (background and potential) was characterized using the indirect acetylene block technique (Groffman 1994). Despite its popularity, there are a number of disadvantages associated with this technique. For example, the use of acetylene tends to underestimate denitrification, because in addition to inhibiting the final step in the denitrification pathway, acetylene also inhibits nitrification (Hynes and Knowles 1978). Underestimation of rates can also occur if N_2O reduction to N_2 is not completely blocked. Another concern is microbes will use acetylene as an energy source during longer incubations when labile carbon has been consumed. However, research shows that these are less of a concern over the short term (Ryden and Dawson 1982),

Background Denitrification

Four microcosms were established for each site by adding approximately 576 g (5 cm) of wet sediment to a glass incubation jar (9 cm diameter). Sediments were compacted in the incubation jars to vent entrapped gas. Microcosms were flooded with approximately 240 ml (4 cm) of nitrate-free deionized water, except for replicates of sediments collected dry in the field.

Table 5: Sediment characteristics from 9 sites sampled in the Atchafalaya River Basin.

Site	Habitat	Total C (%)	Total N (%)	OM %	P (ppm)	Salts (ppm)	pH	Sand %	Silt %	Clay %	% Moisture
1	BLHW	1.8	0.1	3.4	14.5	330.2	6.7	39.4	50	10.6	16.7
2	BLHW	3.5	0.2	4.9	19.2	632.3	7.4	31.5	52.9	15.6	27.5
3	BLHW	3.1	0.2	4.4	44.4	468.5	6.6	26.5	60.7	12.8	24.7
4	CYP	8.9	0.6	7.6	15.7	673.3	6	13.3	29.5	57.2	68.9
5	CYP	9.3	0.6	7.5	14.3	963.8	5.7	14.8	23.1	62.1	76.9
6	CYP	8.7	0.5	7.4	19.8	585	6.4	12.6	32.2	55.2	68.5
7	LAKE	2	0.1	3.2	91	410.9	7.3	6.8	70.4	22.8	46.1
8	LAKE	4.2	0.3	6.3	39.9	839.7	7.3	8.9	48.8	42.3	58.5
9	LAKE	8.8	0.4	7.5	55.6	960	6.5	13.8	37.1	49.1	71.6

Jars were wrapped in foil and covered with tissue paper to discourage growth of plants and microbes. The microcosms sat for approximately 2 weeks under these conditions to allow for equilibration; flooded sediments developed an oxidized layer at the sediment-water interface as was seen in the field. Initial soil moisture content (for the unflooded cores) was maintained throughout the experiment. Despite unavoidable disturbance to cores in the lab, prior research has shown good agreement between results from in situ and laboratory denitrification studies (Well et al. 2003).

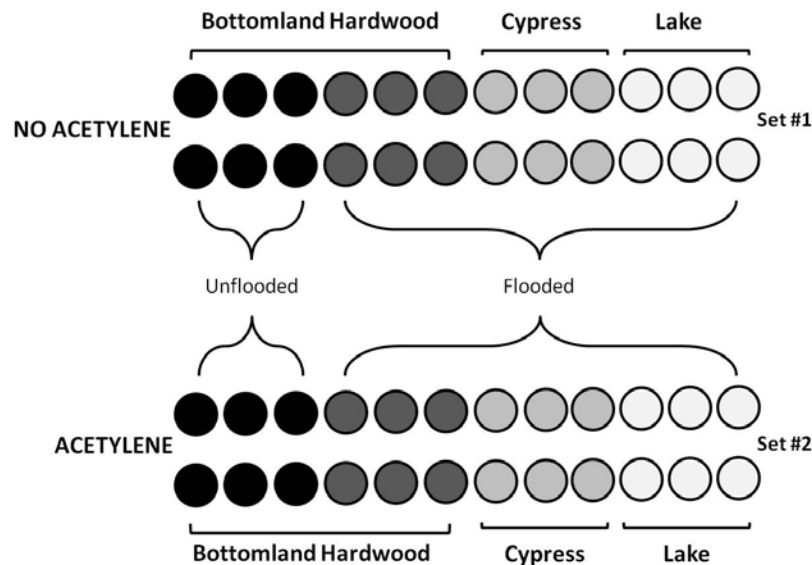


Figure 8: Laboratory experimental setup.

Our sampling scheme involved setting up 2 sets of duplicate microcosms (Figure 8). Within each set, the BLHW sites were divided into 2 sets of duplicates. One set ($n=2$) was flooded, while the other set ($n=2$) was not flooded, to simulate field conditions upon collection, and to account for the pulse of denitrification generally seen upon rewetting. Acetylene was

added to set #2 (n=24), but not to microcosms in set #1 (n=24). N₂O emissions were determined from set #1 (no acetylene), and N₂ + N₂O emissions were determined from set #2 (with acetylene). To simulate background loading rates, no nitrate was added. To simulate slightly elevated nitrate loading rates, microcosms were amended with 3 and 5 mg NO₃-N L⁻¹, respectively. This laboratory setup was repeated for each level of nitrate added.

Emissions rates were measured at 0, 1, 3, and 7 days after nitrate additions. Previous work in the ARB indicates that these habitats reach peak emission rates at different times (Scaroni et al. 2011) so sampling continued until day 7, when emissions from all sites at all nitrate concentrations returned to background levels. All tests were run at 22°C. For temperature effects on denitrification at these same baldcypress sites, see Lindau et al. (2008).

Acetylene was added directly to the headspace and floodwater of jars in set #2 (~10% v/v), which were then capped to prevent gaseous exchange with the atmosphere. Gas samples were collected via a rubber septum sealed in the lid with a 2-ml gas tight syringe at 0 and 24 hours (set #1) and 2 and 6 hours (set #2) after nitrate addition, to determine the linear rate of N₂O buildup in the headspace. Samples were injected into a Shimadzu GC-14A gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA) fitted with a 1-ml sampling loop, Porapak Q 1.8m ss column, electron capture detector (ECD) and calibrated with certified N₂O gas standards (Scott Specialty Gases, Inc., Plumsteadville, PA, USA). Ultra high purity nitrogen was the carrier gas and the instrument operated at temperatures of 40, 100 and 290°C for the oven, injector, and ECD detector, respectively (Lindau et al. 1988). Calculations were performed using the Bunsen absorption coefficient (which corrects for solubility of N₂O in water) to determine N₂O-N that was recovered in both the headspace and floodwater (Tiedje

1982). The closed chamber equation of Rolston (1986) was used to calculate final N₂O flux, which we reported as g N ha⁻¹ d⁻¹.

Statistical Analysis

Background (0 mg NO₃-N L⁻¹ addition) and potential (3, 5 mg NO₃-N L⁻¹ additions) N₂O and N₂O plus N₂ emissions were measured to characterize denitrification. Total N₂ emissions were then estimated by calculating the difference between these direct measurements from each set (Ryden et al. 1979). N₂:N₂O ratios were also calculated using this approach. Data were analyzed using PROC MIXED and PROC REG in SAS (SAS Institute 2006). Correlations between emissions and soil components (C, N, P, organic matter content, pH, sand, silt and clay content) were tested using the PROC CORR function in SAS (SAS Institute 2006). Regression coefficients relating N₂ and N₂O emissions to nitrate concentrations were estimated using PROC REG when appropriate. Results are reported for both peak emissions and means of emissions averaged over the entire sampling period.

RESULTS

N₂O Emission Rates

Background levels of N₂O were below detection limits (<0.4 g N ha⁻¹ d⁻¹) at time zero. Unflooded BLHW sediment N₂O-N fluxes remained below detection levels throughout the course of the experiment for all nitrate levels (0, 3, and 5 mg NO₃-N L⁻¹). Flooded BLHW sediments had greatest N₂O emissions on day 1 (1.46 g N₂O-N ha⁻¹ d⁻¹) with the addition of 5 mg NO₃-N L⁻¹, but averaged approximately 0.60 g N₂O-N ha⁻¹ d⁻¹ (SE=0.21, n=18) over the three sampling days (Figure 9). Emissions of N₂O-N from the flooded BLHW sediment cores treated with 3 mg NO₃-N L⁻¹ were significantly lower and averaged 0.14 g N₂O-N ha⁻¹ d⁻¹ (SE=0.02, n=18)

on days 1 and 3; on day 7 emissions were below the detection limit. Baldcypress and lake sediments peak N_2O emission rates (day 1) after 3 mg $\text{NO}_3\text{-N L}^{-1}$ additions were 1.35 (SE=0.23, n=18) and 0.29 (SE=0.05, n=18) g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, respectively. After addition of 5 mg $\text{NO}_3\text{-N L}^{-1}$, peak emissions were 2.31 (SE=0.30, n=18) and 0.61 (SE=0.09, n=18) g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$, respectively. Over the three sampling dates, baldcypress sediment core N_2O emissions averaged 0.65 g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (SE=0.23, n=18) (3 mg $\text{NO}_3\text{-N L}^{-1}$ addition) and 1.39 g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (SE=0.30, n=18) (5 mg $\text{NO}_3\text{-N L}^{-1}$ addition), while lakes averaged 0.15 g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (SE=0.05, n=18) (3 mg $\text{NO}_3\text{-N L}^{-1}$ addition) and 0.27 g $\text{N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ (SE=0.09, n=18) (5 mg $\text{NO}_3\text{-N L}^{-1}$ addition).

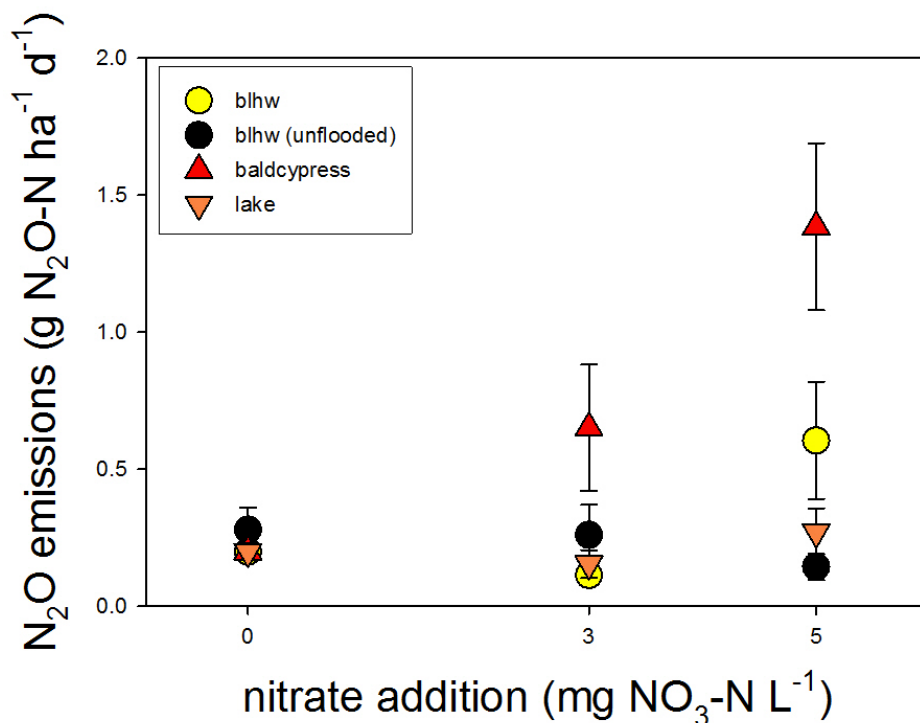


Figure 9: Mean N_2O emission rates averaged over 3 sampling dates for 3 habitat types in the Atchafalaya River Basin, Louisiana; background, 3, and 5 mg $\text{NO}_3\text{-N L}^{-1}$ addition. Graph shows Least Squares Means and Least Squares Standard Error bars.

Table 6: N₂ was positively correlated with C, N, organic matter content, pH, clay content, and moisture content, and negatively correlated with P and sand content. For each correlation, top number is correlation coefficient and bottom number is p-value.

	N₂O	N₂O+N₂	N₂	ratio	C	N	P	OM	pH	Sand	Silt	Clay
N₂O	1	0.41925 0.0002	0.37743 0.0011	-0.25062 0.0337	0.40133 0.0005	0.4527 <.0001	-0.23185 0.05	0.33897 0.0036	-0.5227 <.0001	-0.15024 0.2078	-0.4406 0.0001	0.38596 0.0008
N₂O+N₂		1	0.99896 <.0001	0.47184 <.0001	0.31854 0.0064	0.26876 0.0224	0.31727 0.0066	0.31625 0.0068	-0.1619 0.1742	-0.51417 <.0001	-0.17305 0.146	0.40899 0.0004
N₂			1	0.49388 <.0001	0.30474 0.0092	0.25138 0.0332	0.33528 0.004	0.30552 0.0091	-0.13888 0.2446	-0.51691 <.0001	-0.15437 0.1954	0.39777 0.0005
Ratio				1	-0.18115 0.1278	-0.18348 0.1229	0.52131 <.0001	-0.14097 0.2376	0.30773 0.0085	-0.34464 0.003	0.3387 0.0036	-0.03648 0.761

There was a significant three way interaction between nitrate, day and habitat ($p=0.02$). Baldcypress sites showed the greatest spike in N_2O emissions after nitrate addition, but all habitats peaked after 24 hours. N_2O was positively correlated with C, N, organic matter content, clay content, and moisture content, and negatively correlated with pH, P, and silt content (Table 6).

N_2 Emission Rates

Unflooded BLHW sediments reached their peak N_2 emissions on day 7 ($1.44 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$) following $3 \text{ mg NO}_3\text{-N L}^{-1}$ addition, and on day 1 ($2.12 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$) following a $5 \text{ mg NO}_3\text{-N L}^{-1}$ addition. Unflooded core mean N_2 emissions over the seven day incubation averaged 1.35 ($SE=0.43$, $n=18$) ($3 \text{ mg NO}_3\text{-N L}^{-1}$) and 2.08 ($SE=0.64$, $n=18$) ($5 \text{ mg NO}_3\text{-N L}^{-1}$) $\text{g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$ (Figure 10). Flooded BLHW sediments also saw a spike in N_2 emissions, but maximum emissions were seen on day 1 with a $5 \text{ mg NO}_3\text{-N L}^{-1}$ nitrate addition ($22.23 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$), and on day 3 with a $3 \text{ mg NO}_3\text{-N L}^{-1}$ nitrate addition ($11.94 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$). N_2 emissions averaged 13.07 ($SE=2.35$, $n=18$) and 5.75 ($SE=1.58$, $n=18$) $\text{g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$, respectively, over the sampling period. Baldcypress sediments saw peak N_2 emissions on day 3 with $3 \text{ mg NO}_3\text{-N L}^{-1}$ addition ($20.4 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$), and on day 1 with $5 \text{ mg NO}_3\text{-N L}^{-1}$ addition ($41.9 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$). Over the seven day incubation, N_2 emissions from the baldcypress cores averaged 13.03 ($SE=2.31$, $n=18$) and 21.97 ($SE=4.32$, $n=18$) $\text{g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$ for the 3 and $5 \text{ mg NO}_3\text{-N L}^{-1}$ treatments, respectively. Lake sediments also peaked on day 3 with a $3 \text{ mg NO}_3\text{-N L}^{-1}$ nitrate addition ($20.48 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$), and on day 1 with a $5 \text{ mg NO}_3\text{-N L}^{-1}$ addition ($53.68 \text{ g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$), and averaged 12.34 ($SE=2.10$, $n=18$) and 31.41 ($SE=5.31$, $n=18$) $\text{g } N_2\text{-N ha}^{-1} \text{ d}^{-1}$, respectively over the entire incubation period.

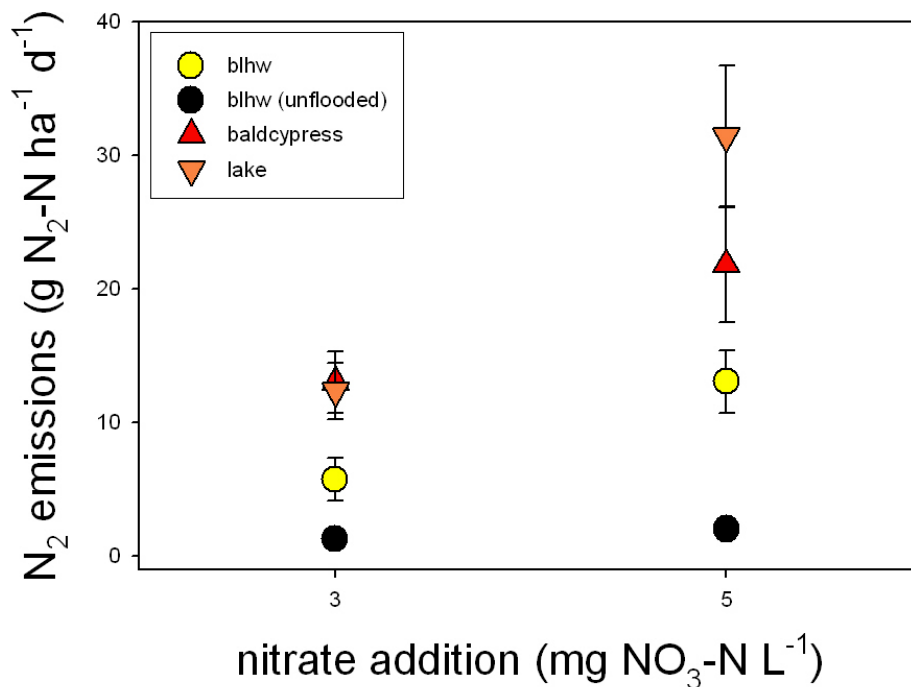


Figure 10: Calculated mean N₂ emission rates averaged over 3 sampling dates for 3 habitat types in the Atchafalaya River Basin, Louisiana; 3 and 5 mg NO₃-N L⁻¹ addition. Graph shows Least Squares Means and Least Squares Standard Error bars.

There was a significant three way interaction between nitrate, day and habitat ($p < 0.0001$). At the low concentration of nitrate (3 mg NO₃-N L⁻¹) emissions didn't peak until day 3 (for all but unflooded BLHW, which stayed at background levels despite nitrate addition), whereas N₂ emissions were highest on day 1 following 5 mg NO₃-N L⁻¹ nitrate addition. N₂ was positively correlated with C, N, organic matter content, pH, clay content, and moisture content, and negatively correlated with P and sand content (Table 6).

N₂:N₂O

Ratios of N₂:N₂O were highly variable across habitat type and between replicates (Figure 11). After addition of 3 mg NO₃-N L⁻¹ to the BLHW sediment cores, peak N₂:N₂O ratios occurred

on day 3 for the flooded (123.5) and unflooded (19.2) treatments. $N_2:N_2O$ ratios averaged over the 3 sampling dates were approximately 62.4 (SE=18.01, n=18) (flooded) and 17.4 (SE=6.19, n=18) (unflooded). This indicates that N_2 emissions were 3.6 times higher from the flooded sites. Only one sediment core collected from the unflooded BLHW sites displayed $N_2:N_2O$ ratios less than one (0.5) indicating N_2O emissions were greater than N_2 fluxes over the seven day incubation. After 5 mg $NO_3-N\ L^{-1}$ addition, $N_2:N_2O$ emission ratios from the BLHW cores were comparable to the 3 mg $NO_3-N\ L^{-1}$ treatment. Peak $N_2:N_2O$ also occurred on day 3 (119.8-flooded, 24.8-unflooded) and averaged (over seven days) 80.7 (SE=23.95, n=18) and 25.2 (SE=9.42, n=18) for flooded and unflooded cores, respectively.

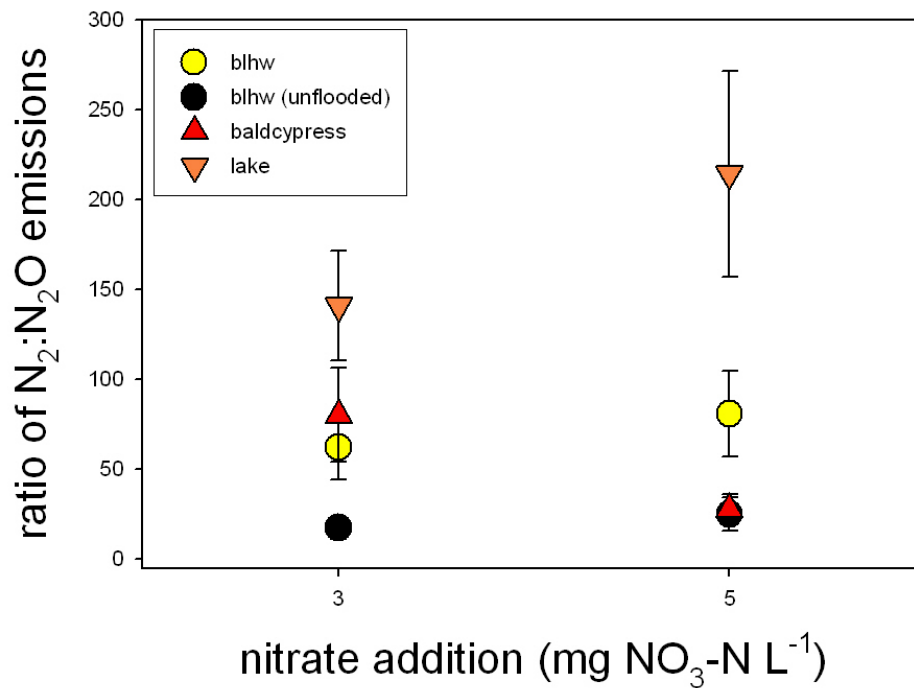


Figure 11: Ratio of $N_2:N_2O$ emission rates averaged over 3 sampling dates for 3 habitat types in the Atchafalaya River Basin, Louisiana; 3 and 5 mg $NO_3-N\ L^{-1}$ addition. Graph shows Least Squares Means and Least Squares Standard Error bars.

Emission ratios of $\text{N}_2:\text{N}_2\text{O}$ from the baldcypress sediments peaked on day 3 (135.9) and on day 1 (141.8) after 3 and 5 mg $\text{NO}_3\text{-N L}^{-1}$ additions, respectively. Ratios dropped sharply on day 7 (averaging 8.7 across both $\text{NO}_3\text{-N}$ treatments). Over the incubation period, $\text{N}_2:\text{N}_2\text{O}$ ratios averaged 80.2 for the 3 mg $\text{NO}_3\text{-N L}^{-1}$ treatment, and 27.7 for the 5 mg $\text{NO}_3\text{-N L}^{-1}$.

Highest $\text{N}_2:\text{N}_2\text{O}$ gas flux ratios were observed from the lake sediment cores (Figure 11). Maximum $\text{N}_2:\text{N}_2\text{O}$ emission ratios of 239.2 and 373.8 were observed on day 3 and averaged 140.9 (SE=30.36, n=18) and 214.4 (SE=57.19, n=18) over the three incubation times after application of 3 and 5 mg $\text{NO}_3\text{-N L}^{-1}$, respectively. At day 7 $\text{N}_2:\text{N}_2\text{O}$ ratios dropped sharply to 18.7 (3 mg $\text{NO}_3\text{-N L}^{-1}$) and 43.9 (5 mg $\text{NO}_3\text{-N L}^{-1}$).

The ratio of $\text{N}_2:\text{N}_2\text{O}$ differed among the habitats, but in different ways, as indicated by the two way interaction between nitrate and habitat ($p=0.02$). The ratio increased with increasing nitrate concentration for lake habitats, decreased with increasing nitrate concentration for baldcypress habitats, and remained the same for both flooded and unflooded BLHW habitats when nitrate increased. The ratio of $\text{N}_2:\text{N}_2\text{O}$ was positively correlated with P, pH, and silt content, and negatively correlated with sand content (Table 6).

Relationship Between Nitrate and Denitrification

We regressed N_2O emissions on nitrate for each habitat type, and there was a significant linear relationship between nitrate and nitrous oxide for BLHW ($p=0.07$) and baldcypress ($p=0.002$) habitats, but the r-squared values were only 0.07 and 0.18 respectively. The relationship between nitrate and N_2O was not significant for unflooded BLHW habitat ($p=0.28$) or lake habitats ($p=0.48$), thus it was appropriate to use the overall means to predict emission rates (Table 7).

Table 7: Regression coefficients (for habitats with a significant linear relationship between nitrate and N₂O or N₂) or overall means with standard deviations of emissions from all levels of nitrate additions (for habitats without a significant linear relationship between nitrate and N₂O or N₂).

Habitat	N ₂ O (g N ₂ O-N ha ⁻¹ d ⁻¹)	N ₂ (g N ₂ -N ha ⁻¹ d ⁻¹)
BLHW	N ₂ O = 0.0767 + 0.081 (NO ₃ -N)	N ₂ = -5.2519 + 3.6653 (NO ₃ -N)
BLHW unflooded	<0.4 g N ₂ O-N ha ⁻¹ d ⁻¹ ± 0.3	1.66 g N ₂ O-N ha ⁻¹ d ⁻¹ ± 2.3
BCS	N ₂ O = 0.1048 + 0.2365 (NO ₃ -N)	17.42 g N ₂ O-N ha ⁻¹ d ⁻¹ ± 15.1
LAKE	0.21 g N ₂ O-N ha ⁻¹ d ⁻¹ ± 0.3	N ₂ = -16.218 + 9.5256 (NO ₃ -N)

When we regressed nitrate on N₂ for each habitat type, there was a significant linear relationship between nitrate and N₂ for BLHW (p=0.01) and lake (p=0.002) habitats, but the r-squared values were only 0.16 and 0.25 respectively. Baldcypress (p=0.08) and unflooded BLHW (p=0.33) were not significant at a 95% confidence level, so it is appropriate to use the overall mean to estimate emission rates for these habitats.

DISCUSSION

Background levels of denitrification were below detection limits in nearly all jars. This was surprising considering that sediments collected from the same locations for a previous study measured background levels of denitrification ranging from (1.4 g N₂-N ha⁻¹ d⁻¹ to 5.4 g N₂-N ha⁻¹ d⁻¹) (Scaroni et al. 2011). We attribute this to the high degree of spatial and temporal variability in denitrification rates within habitats and to differences in soil organic nitrogen associated with seasonal differences in plant growth and senescence. Lindau et al. (1988) also measured non-detectable levels of background N₂O emissions from a Louisiana baldcypress swamp, and then similarly saw an increase upon amendment with nitrate. Our northern BLHW sites have either indirect or no contact with the Atchafalaya River, thus external nitrate-loading

to these sites may be lower than expected, resulting in lower background emissions of N_2O and N_2 . Our southern lake sites are directly connected to the Atchafalaya River; however, they receive river water after it has travelled a considerable distance through the ARB with ample opportunities for nitrate removal via sedimentation, biomass uptake, and denitrification.

N_2O emissions responded to nitrate additions, but our potential rates were similar to background rates reported by DeLaune et al. (1989) from a Louisiana freshwater marsh ($1.5 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$), Lindau and DeLaune (1991) from a Louisiana salt marsh ($2\text{-}3 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$), Hernandez and Mitsch (2006) from an Ohio freshwater marsh ($1.6 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$), and Smith et al. (1983) from a Louisiana freshwater marsh ($1.5 \text{ g N}_2\text{O-N ha}^{-1}$). DeLaune et al. (1998) reported higher background N_2O fluxes from soil water columns ($9.4 \text{ g N ha}^{-1} \text{ d}^{-1}$); however, that swamp forest was receiving direct runoff from sugarcane fields.

A review of N_2O emissions from treatment wetlands reported an average rate of emission of $40 \text{ g N}_2\text{O-N ha}^{-1} \text{ d}^{-1}$ across 15 wetlands (Kaldec and Wallace 2008). This amounted to a removal of approximately 2.2% of the nitrogen load in the wetlands. These elevated rates were in response to a higher external nitrate loading. The ‘elevated’ nitrate loads we applied to our microcosms in the laboratory ($3 \text{ and } 5 \text{ mg NO}_3\text{-N L}^{-1}$) were more than double the concentration introduced by the Atchafalaya River, and still saw N_2O emissions of less than 6% of the average from the treatment wetlands mentioned above (Kaldec and Wallace 2008). Because the majority of the ARB is BLHW, we do not expect increasing river access to the lake and baldcypress habitats to produce a large spike in N_2O emissions.

Increasing the concentration of nitrate from 0 to 3 to $5 \text{ mg NO}_3\text{-N L}^{-1}$ stimulated denitrification rates, as expected. The significant interaction between nitrate and habitat with

denitrification rates indicates the importance of considering habitat type when estimating denitrification rates across a spatially variable system. We also recommend consideration of habitat type when modeling ecosystem-scale nitrous oxide emissions, as the habitats in this study did not all respond with linear increases to increasing nitrate additions.

It appears that differences in soil moisture and texture were driving differences in gas emissions among habitat types. Water filled pore space is one of the best predictors of N_2O emissions (relative to N_2 emissions), so it follows that soils with a high clay content and a high percentage of water filled pore space would realize higher emissions up to a certain threshold. N_2O emissions generally increase with increasing soil water content, as this reduces O_2 availability and increases Eh (Granli and Bockman 1994). However, at a certain point the soil becomes saturated, and highly anaerobic, causing N_2O emissions to decrease in favor of N_2 emissions. Alternating wet and dry cycles, commonly seen in the BLHW habitats of the ARB, tend to produce higher N_2O emissions (Granli and Bockman 1994). Although our flooded BLHW sediments exhibited higher N_2O emission rates than the unflooded BLHW sediments, these rates were still less than emissions from lake sediments. BLHW sediments in the ARB have a higher sand content, whereas the texture of lake sediments is predominately silt and clay. These lake soils have higher water content, lower Eh, and exhibit higher denitrification rates. The flooded BLHW sediments had higher denitrification rates than the unflooded BLHW sediments; it appears that the moisture content of unflooded sediments was too low to denitrify. This was corroborated by the positive correlation between soil moisture and nitrous oxide emissions ($p=0.005$), and between soil moisture and N_2 emissions ($p<0.0001$). Without flooding, there was adequate gas exchange between the sediment and the atmosphere,

prohibiting the formation of an anaerobic layer necessary for the denitrification reaction. Weitz et al. (2001) reported an increase in N_2O production following precipitation, i.e. with an increase in soil moisture. We found a similar pattern; when the BLHW sediments were flooded and spiked with nitrate in the laboratory N_2O emissions increased compared to the unflooded, spiked BLHW cores.

The negative correlations we saw between P and N_2 , and P and N_2O , indirectly result from the negative correlation between P and organic matter content. The P in the system is primarily associated with mineral sediment, whereas the C in the system is associated with organic sediment. A carbon source is required for denitrification; more organic matter and bioavailable C stimulates denitrification (Dolda et al. 2008), whereas more P indicates there is less C available to stimulate denitrifiers. This is corroborated by the positive correlation between N_2 (and N_2O) with C, N, and organic matter.

A longer duration of flooding increases pH in wetland sediments and reduces Eh. Therefore, as pH increases, the ratio of $\text{N}_2:\text{N}_2\text{O}$ emissions increases. It follows that we also saw a positive correlation between pH and N_2 emissions. The negative correlation between pH and N_2O emissions agrees with previous studies. Low pH tends to favor a higher proportion of N_2O emissions relative to N_2 (Knowles 1982).

CONCLUSION

Our results indicate that when attempting to quantify nitrogen retention and removal in a floodplain, regardless of location, it is necessary to sample each habitat separately to account for differences in spatial variability across the floodplain. In this study we classified habitats based on the dominant vegetation, because vegetation controls soil organic matter. While the

data we obtained will not be applicable to all floodplains, the procedure we used is applicable everywhere. We recommend that all large scale denitrification studies account for habitat type in the experimental design, maintain in the laboratory similar soil moisture regimes as observed in the field, and continue sampling gas emissions from microcosm until they return to background levels.

We found that background N_2O emissions were low compared to N_2 , with a slight increase in response to nitrate additions when anaerobic conditions were maintained. This suggests that increases in external nitrate loading to isolated areas in the ARB will not produce emissions on par with those from treatment wetlands, or from areas directly in the path of agricultural runoff. Diverting water across the floodplain in the ARB is being considered to combat anoxic conditions in backwater swamps. Our results suggest that introducing river water to seasonally dry areas will not stimulate drastic increases in N_2O emissions. Many BLHW areas in the ARB will remain dry, in spite of diversions, due to their higher elevation. Thus, diverting water will not result in uniform flooding, but will instead allow a higher percentage of river water to access areas with a higher potential for nitrogen retention and removal (such as baldcypress swamps). Because field conditions in these areas are generally anaerobic, we expect that N_2O emissions will remain low.

The tradeoffs between water pollution (high nitrate loading) and air pollution (high N_2O emissions) should be considered when making management decisions that will redirect the flow of water, impact water retention time, or alter the rate of habitat change resulting from sedimentation. Creating river diversions via gaps in spoil banks and natural levees appears to be a viable option for removing nutrients and minimizing nitrogen loading to receiving waters,

as demonstrated by this work in the ARB. Similar diversions in Louisiana and across the coastal plain should consider using these results as proxy data for comparable systems until site-specific data is collected. Future in situ experiments to monitor denitrification following water diversions could enhance our understanding of nutrient dynamics in the ARB. In the meantime, these data comparing habitats in the ARB are sufficient to inform nutrient models, and to predict the outcome of various management strategies.

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CHAPTER 5.

SEDIMENT AND NITROGEN RETENTION IN A COASTAL FLOODPLAIN

INTRODUCTION

Floodplains have long been identified as important sites for nutrient transformation and removal (Brinson et al. 1984; Craft and Casey 2000; Kaye et al. 2003; Noe and Hupp 2009; Schramm et al. 2009; Spink et al. 1998). Their geomorphic setting allows for periodic inundation by river overflow (Junk 1989); consequently, floodplains can act as sinks for water-borne sediments and nutrients (Hupp 2000). Riparian zones and larger floodplain areas often intercept nutrient runoff from agricultural and urban watersheds, naturally mitigating these additions before they reach estuaries and coastal waters. A substance entering a wetland or floodplain can be stored, transformed, and/or discharged (Johnston 1991). In the case of nitrogen, storage occurs as deposition within accreting mineral sediments, or as organic nitrogen in biomass. Nitrogen that is not retained within a basin will be discharged to receiving waters, where it may stimulate eutrophication (Rabalais et al. 2002).

Modern floodplains in the coastal plain of the Southeastern United States are largely a result of fluvial processes during the last low-stand of global sea level about 16,000 years ago, and the subsequent rapid oceanic transgression that persisted until about 4,000 years ago (Hupp 2000). Over time, delivery of sediments to receiving waters in the Gulf of Mexico has built thick layers of alluvial, deltaic, shelf, slope and basinal deposits (Coleman 1988) extending the shoreline outward. Recent river control measures, such as levees and canals, have reversed this trend along much of the Gulf Coast such that approximately 65 km² of coastal wetlands are lost annually (Boesch et al. 1994).

Habitat abundance changes in coastal floodplains when either (a) sedimentation is insufficient to counter subsidence and global sea-level rise, or (b) sedimentation exceeds subsidence and global sea-level rise. The former situation favors conversion to more flooded habitats, such as lakes, and probably predominated along the Gulf Coast of the U.S. until about 4,000 years ago. The latter situation favors conversion to less flooded habitats, such as bottomland hardwood forests (BLHW), and has been more common for the last 4,000 years on the Gulf Coast (Williams et al. 1999). The Atchafalaya River Basin (ARB) in south-central Louisiana is an example of a coastal floodplain where sedimentation is increasing the area of less flood-tolerant habitats at the expense of more flood-tolerant habitats (Coleman 1988). However, Xu (2010) suggests that the ARB may have silted in and reached equilibrium, as data over the last 10 years show a significant decrease in the disparity between inflow and outflow suspended sediment concentrations.

We studied sedimentation on the floodplain of the Atchafalaya River, the largest tributary of the Mississippi River (Ford and Nyman 2011). The Atchafalaya River is approximately 220 km long and 25 km wide, with a floodplain of approximately 5,000 km². The Atchafalaya River has an average annual discharge of 6228 m³ s⁻¹ (Xu 2006), transports approximately 84 x 10⁶ t of sediment annually (Allison et al. 2000), and is the fifth largest river in North America by discharge. Inflow to the Atchafalaya River from the Mississippi River has been managed daily since 1963 at the Old River Control Structure such that the Atchafalaya River receives approximately 30% of the flow from the Mississippi River. Control of these flows prevents the Atchafalaya River from capturing the flow of the Mississippi River. The

Atchafalaya River discharges to the Gulf of Mexico via two channels that have growing deltas: the Wax Lake Outlet Delta and Atchafalaya River Delta (Roberts 1998).

The Atchafalaya River is dredged to accelerate self-induced enlarging and deepening (Xu 2006; Sparks 1992). Natural and managed channel deepening has reduced contact between the river and its floodplain by lowering flood levels (Sparks 1992) primarily in the upper half of the Basin. At the downstream end of the ARB, flood levels have gradually increased because of global sea-level rise and local subsidence (Keim et al. 2006). Habitats within the ARB are changing in an undesirable manner; over the last century sedimentation associated with the delta lobe cycle has transformed lake areas into baldcypress swamps, and baldcypress swamps into BLHW forests (Coleman 1988; Reuss 2004). With this habitat change, contact between the river and its floodplain decreases because BLHW forests flood less than baldcypress swamps, which flood less than lakes. Efforts to accelerate channel enlargement by closing 22 distributaries has also reduced contact between the river and its floodplain (Sparks 1992). Sparks (1992) estimated that by 2030 as many as 50,000 hectares of baldcypress swamp and BLHW that flooded seasonally will no longer flood. In addition to habitat change and reduced flooding, hypoxic waters regularly develop in parts of the Basin where back flooding is more important than unidirectional flow (Sparks 1992).

The ARB functions as a sink for sediment and nutrients, specifically nitrogen. Estimates of annual sediment retention rates range from 5,000,000 Mg yr⁻¹ (Hupp et al. 2008) to 6,000,000 Mg yr⁻¹ (Xu 2010), while total nitrogen retained annually is on the order of 50,544 Mg, or 14% of the total annual load entering the ARB (Xu 2006). Notably, Xu (2006) reported a 2.3% increase in nitrate-nitrogen discharging from the ARB. This study focused on comparing

long-term sedimentation rates and N accumulation rates of these sediments among BLHW forests, baldcypress swamps, and lakes of the Atchafalaya River floodplain. We measured total suspended solids in the ARB during a high water year to investigate patterns of flooding and water movement across the floodplain. We also collected sediment cores from each habitat to determine whether vertical accretion depended upon mineral sediments or organic matter. We hypothesized that vertical accretion rates would be lowest in the BLHW, and would increase in the baldcypress and lake habitats. We expected to see highest levels of suspended sediments in the upstream region of the ARB (BLHW habitat), with decreasing concentrations along a southern trajectory (towards the lake habitat).

METHODS

Sediment Accretion

Sediment cores were collected between August 2006 and December 2009 (Figure 12). Three sets of duplicate cores ($n = 6$) were collected from each of the three major habitat types in the ARB ($n = 18$), and an additional 6 cores were collected from the baldcypress habitat ($n = 24$). Cores from BLHW sites were taken from unflooded areas using sharpened iron pipes (radius = 7.5 cm), which were pounded in the ground to break through tree roots. Cypress cores were collected from shallowly flooded sites using aluminum tubes pushed into the ground (radius = 7.6 cm). Lake cores were taken using clear PVC tubes (radius = 3.2 cm) that were pushed into the lake bottom.

Cores were capped on both ends and transported to the laboratory. There, cores were cut into 2-cm sections for the first 18 cm and 3-cm sections thereafter, and air dried at 80° C. Soil bulk density (g cm^{-3}) of each section was determined from the oven-dried mass and the

volume of the section; section volume was estimated from the diameter and thickness via the relationship $V = (\pi r^2 h)$. Samples were ground, to homogenize the sediment, using a Wiley Mill.

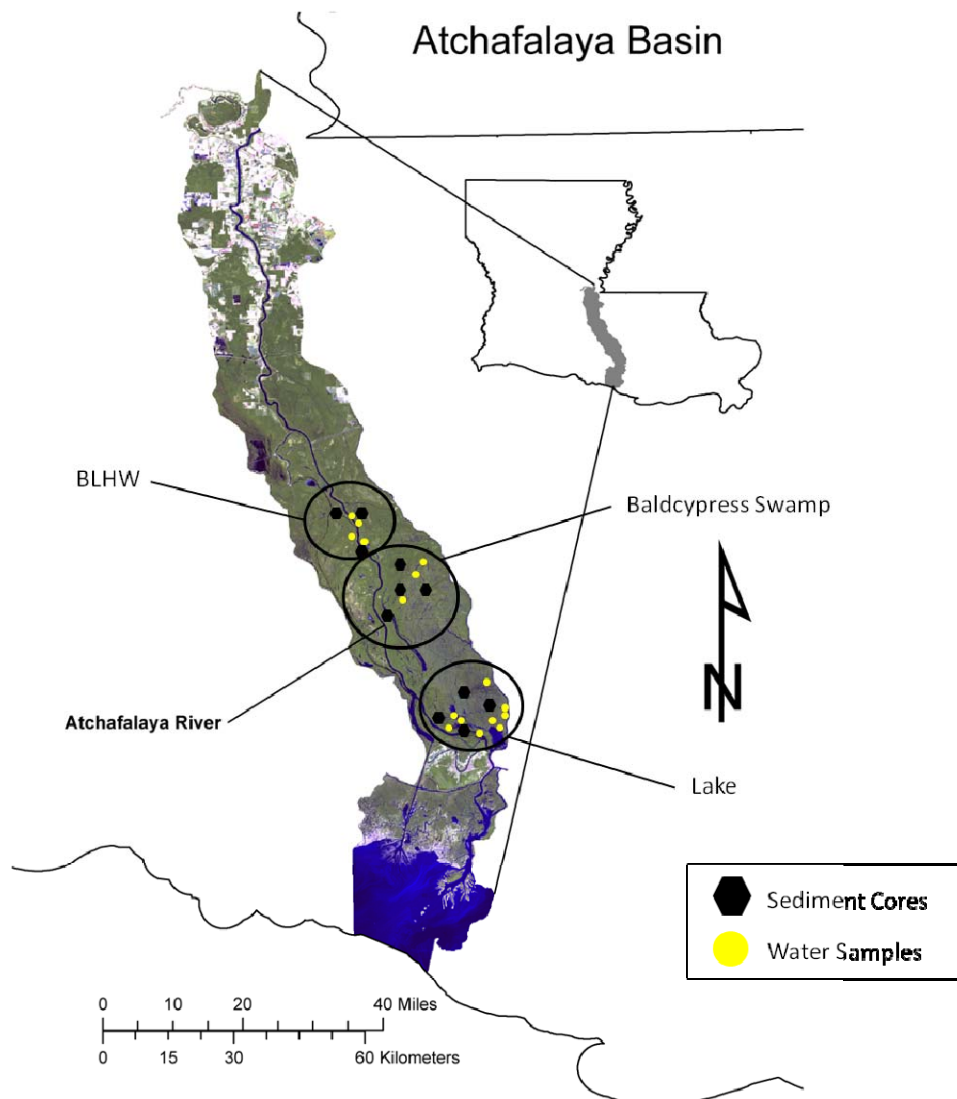


Figure 12: Map showing location of sediment cores ($n = 24$) and water samples ($n = 21$) collected in the Atchafalaya River Basin, LA.

Nitrogen (N) and carbon (C) content were analyzed with a Leco C-N Analyzer (Leco Corp., St. Joseph, MI, USA) at the LSU Soil and Plant Testing and Analysis Lab. Particle size was determined by the Hydrometer Method (Gee and Bauder 1986) using samples collected from

these sites for a denitrification study (Chapter 4). We determined percent organic and mineral matter of each section using the Loss on Ignition method (Ball 1964) with a few minor adjustments. Approximately 10g of each sample was heated to 400° C (Ben-dor and Banin 1989) for >8 hours to ensure that we combusted the more humified part of the organic matter (Boyle 2004) but did not release structural water in the clay matrix (Ball 1964). Sample weights were recorded pre- and post-burn, and the loss on ignition was equated to the mass of organic matter in the sample.

All sections were counted for ^{137}Cs . ^{137}Cs dating has been used to measure vertical accretion in reducing environments including freshwater wetlands in the fluctuation zone of lakes, baldcypress swamps, tidal freshwater marshes, and tidal saline wetlands (Ritchie and McHenry 1990). The ^{137}Cs dating technique was used to estimate vertical accretion (cm yr^{-1}) at all sites. ^{137}Cs does not occur naturally but atmospheric deposition peaked throughout the northern hemisphere in 1963 when atmospheric testing of nuclear weapons peaked. This technique exposes heavily shielded, highly sensitive gamma ray detectors to soil increments for three to eight hours depending upon ^{137}Cs concentrations.

After locating the 1963 peak, the C, N, and P concentrations were determined in subsamples of all increments using an ICP after sample digestion. The C, N and P content of each section (g m^{-2}) was estimated from the soil bulk density and the soil concentration of C, N, and P of each section. Accretion rates ($\text{g m}^{-2} \text{yr}^{-1}$) of C, N, and P were estimated from the sum of all C, N, and P above the 1963 surface and the number of years since that surface was deposited.

Suspended Sediments

Spring of 2008 was an unusually high water year for the Mississippi, as evidenced by only the 9th opening of the Bonne Carre Spillway in 77 years of operation. The spillway is designed to prevent downstream flooding in New Orleans, LA. The ARB also functions as a natural spillway for the Mississippi, which piqued our interest in sampling during this event. In May, 2008 we measured suspended sediment concentrations at 21 sites in the ARB classified as being in the BLHW forest region (upstream), baldcypress swamp region (midstream), or lake region (downstream) (Figure 12). In the upstream region, sediment concentrations were measured in distributary channels because there was too little water in adjacent BLHW forests. During the period of sampling river discharge at Simmesport, Louisiana, which is at the upstream end of ARB, averaged $13,400 \text{ m}^3 \text{ sec}^{-1}$ (data from: http://toxics.usgs.gov/hypoxia/mississippi/flux_estimates/delivery/index.html). The average flow at Simmesport (since 1975) averages $6500 \text{ m}^3 \text{ s}^{-1}$ (Xu 2010). Samples were collected from the river using rubber tubing and a syringe. Water samples were filtered in the field using $0.45 \mu\text{m}$ nylon filters (Watman) to separate sediment from water. Filters were put on ice and transported back to the laboratory, where they were weighed, dried, and weighed again. The average mass of 10 clean, oven-dried filters was subtracted from each final filter weight to estimate the mass of sediments in each water sample. Soil elevation was inferred from the difference between the water depth at the closest water level recorder and the water depth at the location where the sample was collected. A simplistic estimation was made of proportions of sediment-rich river water and sediment-poor baldcypress water needed to create the intermediate levels of sediment observed in the lake water samples: $[Bx + C(1-x) = L]$ where $B =$

[TSS] in river water at BLHW region, C = [TSS] in baldcypress backwater swamps, and L = [TSS] in lakes.

Statistical Analysis

Bulk density (g cm^{-3}), bulk accumulation (g m^{-2}), and mineral and organic content (percent) were determined to characterize vertical accretion. The experimental design was completely randomized analysis of variance with replication. The treatment effect was “habitat” and the replicate cores were the sampling units. Data were analyzed using PROC MIXED for analysis of variance and PROC REG for regression analysis in SAS (SAS Institute 2006). Correlations between accretion rates (vertical, bulk, mineral and organic accretion rates) and soil components (C, N, P, organic matter content, sand, silt, and clay content) were tested using the PROC CORR function in SAS (SAS Institute 2006). Regression coefficients relating the contributions of bulk, mineral and organic accretion rates to vertical accretion rates were estimated using PROC REG.

RESULTS

Sediment Composition

Habitats in the ARB differed in the mineral ($P < 0.0001$) and organic ($P < 0.0001$) matter content of their sediments (Figure 13). BLHW sediments were on average 93% mineral (SE = 0.01), and 7% organic (SE = 0.01). Baldcypress sediments averaged 81% mineral and 19% organic (SE = 0.01, SE = 0.01, respectively). Lake sediments averaged 91% mineral (SE = 0.01) and 9% organic (SE = 0.01). BLHW and lake were not significantly different in either their mineral ($P = 0.74$) or organic ($P = 0.74$) matter content.

The BLHW habitat was highest in sand and lowest in clay, while sediments from the baldcypress habitat showed the highest clay content (Figure 14).

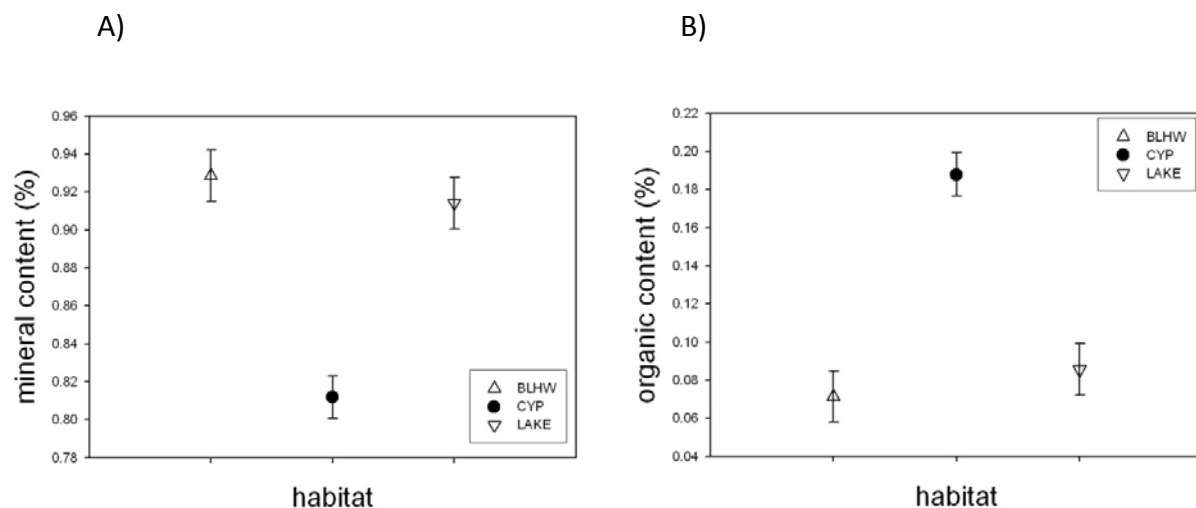


Figure 13: A) Mineral and B) organic matter content (%) of sediments collected from 3 habitat types in the Atchafalaya River Basin, Louisiana, USA: bottomland hardwood forests (BLHW), baldcypress swamps (CYP), and lake. Graph shows Least Squares Means (BLHW $n = 7$, CYP $n = 10$, LAKE $n = 7$), and Least Squares Standard Error bars.

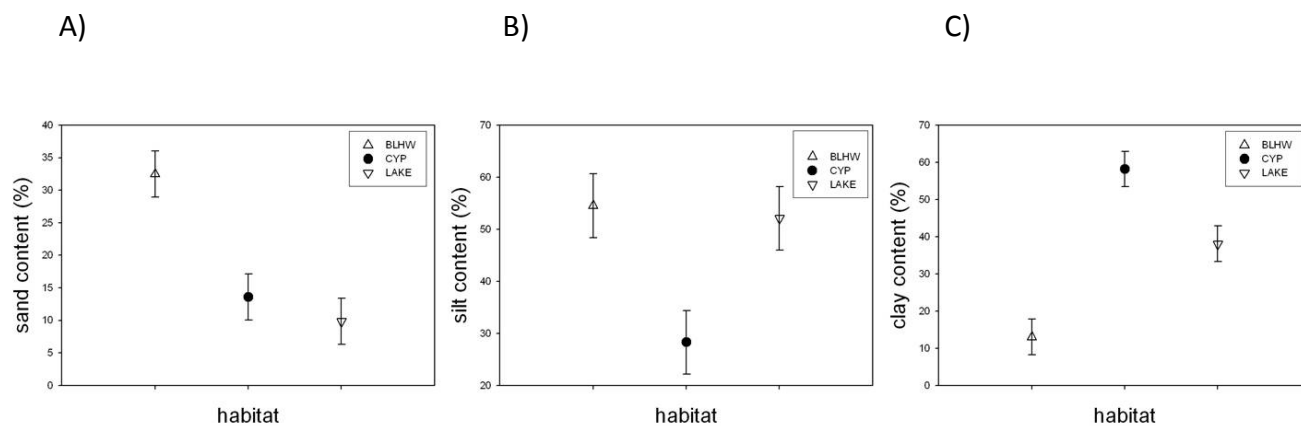
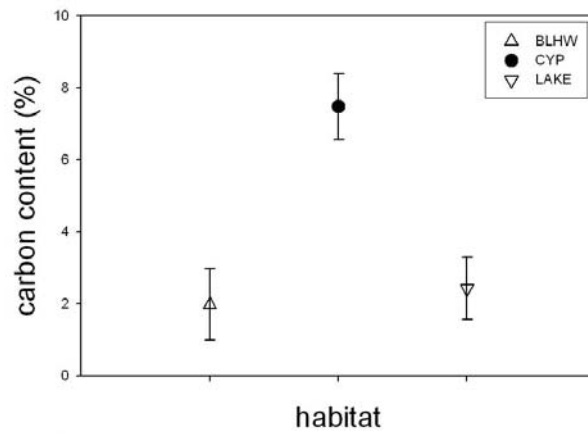
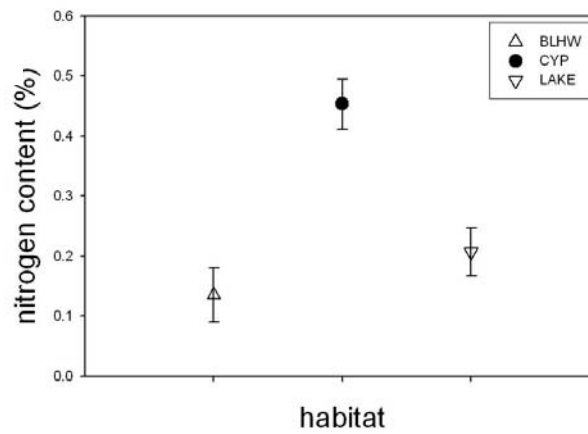


Figure 14: Particle size analysis showing A) sand content, B) silt content, and C) clay content of sediments collected from three habitats in the Atchafalaya River Basin, Louisiana, USA: bottomland hardwood forests (BLHW), baldcypress swamps (CYP), and lake. Graphs show Least Squares Means (BLHW $n = 3$, CYP $n = 3$, LAKE $n = 3$), and Least Squares Standard Error bars.

A)



B)



C)

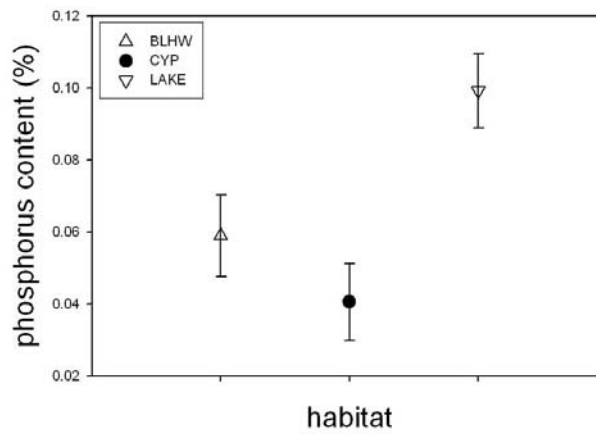


Figure 15: A) Carbon B) Nitrogen and C) Phosphorus content of sediments collected from three habitat types in the Atchafalaya River Basin, Louisiana, USA: bottomland hardwood forests (BLWH), baldcypress swamps (CYP), and lake. Graphs show Least Squares Means (BLHW $n = 7$, CYP $n = 10$, LAKE $n = 7$), and Least Squares Standard Error bars.

Carbon content of the sediments differed among habitats in the ARB ($P = 0.0001$) (Figure 15a). This difference was significant for all comparisons except BLHW and lake sediments ($P = 0.93$). Carbon content averaged 1.97%, 7.19%, and 2.4% for BLHW, baldcypress, and lake sediments, respectively. Nitrogen content also differed among the three habitats ($P < 0.0001$) (Figure 15b). Once again, BLHW and baldcypress differed ($P < 0.0001$), baldcypress and lake differed ($P = 0.0006$), but BLHW and lake sediments did not differ ($P = 0.4344$). Phosphorus content differed among habitats in the ARB ($P = 0.0022$) (Figure 15c); however, BLHW and baldcypress sediments did not differ ($P = 0.5646$).

Sediment Accretion

Bulk density differed across habitat types ($P < 0.0001$) (Figure 16). Specifically, BLHW sediments differed from baldcypress sediments ($P < 0.0001$) and lake sediments ($P < 0.0001$), but baldcypress and lake sediments did not differ ($P = 0.9613$). Soil bulk density averaged 1.23 g cm^{-3} (SE= 0.07) at BLHW sites, 0.51 g cm^{-3} at baldcypress sites (SE=0.05), and 0.53 g cm^{-3} (SE=0.07) at lake sites. Bulk density ranged from $0.85\text{--}1.39 \text{ g cm}^{-3}$ (BLHW), $0.27\text{--}0.70$ (baldcypress), and $0.36\text{--}0.80$ (lake) (Table 8).

Bulk accumulation rates differed across habitat types ($P = 0.0026$) (Figure 17a). Once again, BLHW differed from baldcypress ($P = 0.0072$) and lake ($P = 0.0045$) sediments, but baldcypress and lake sediments did not differ ($P = 0.8649$). Bulk accumulation rates averaged $8,280 \text{ g m}^{-2} \text{ yr}^{-1}$ at BLHW sites (SE = 839.3), and ranged from $4,654\text{--}11,041 \text{ g m}^{-2} \text{ yr}^{-1}$. At the baldcypress sites, rates averaged $4,557 \text{ g m}^{-2} \text{ yr}^{-1}$ (SE = 709.2), and ranged from $1,695\text{--}7,891 \text{ g m}^{-2} \text{ yr}^{-1}$. Finally, the lake sites averaged $3,993 \text{ g m}^{-2} \text{ yr}^{-1}$ (SE = 839.5), and ranged from $2,102\text{--}6,670 \text{ g m}^{-2} \text{ yr}^{-1}$ (Table 8).

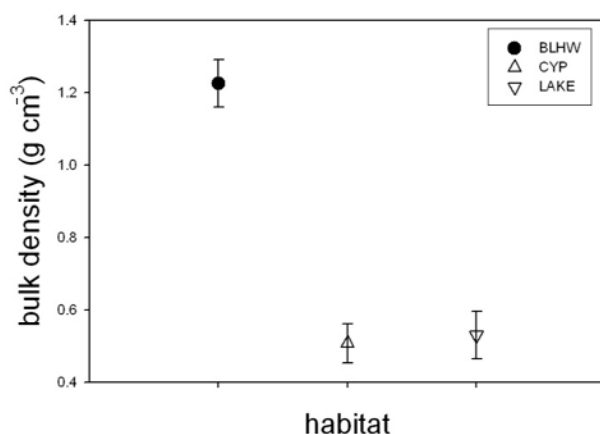


Figure 16: Bulk density (g cm^{-3}) of sediments collected at three habitat types in the Atchafalaya River Basin, Louisiana, USA: bottomland hardwood forests (BLWH), baldcypress swamps (CYP), and lake. Graph shows Least Squares Means (BLHW $n = 7$, CYP $n = 10$, LAKE $n = 7$), and Least Squares Standard Error bars.

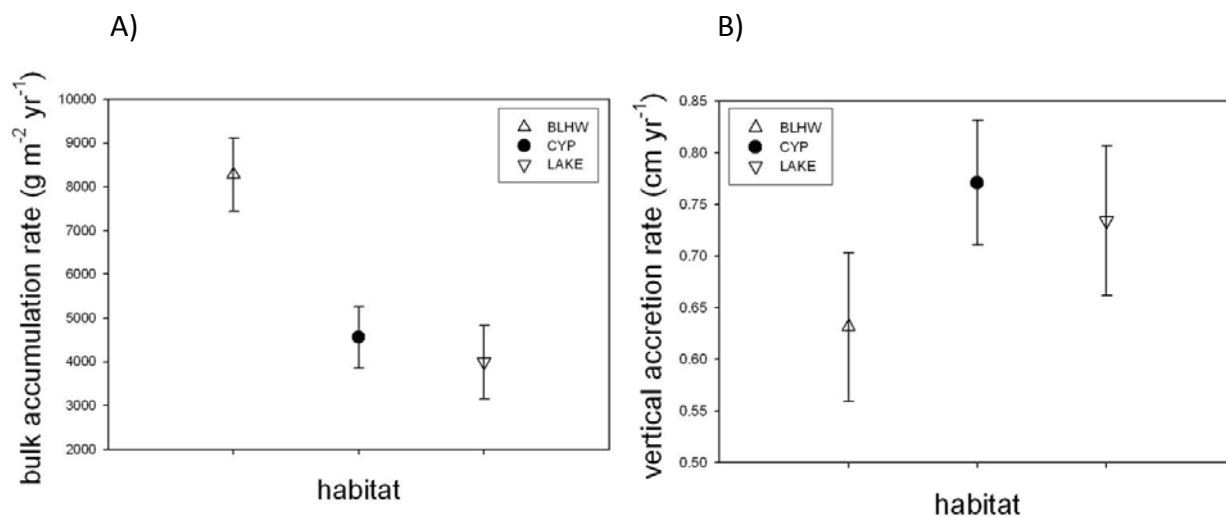


Figure 17: A) Bulk accumulation rate ($\text{g m}^{-2} \text{yr}^{-1}$) and B) vertical accretion rate (cm yr^{-1}) since 1963 of sediments at three habitat types in the Atchafalaya River Basin, Louisiana, USA: bottomland hardwood forests (BLWH), baldcypress swamps (CYP), and lake. Graphs show Least Squares Means (BLHW $n = 7$, CYP $n = 10$, LAKE $n = 7$), and Least Squares Standard Error bars.

Vertical accretion rates did not differ among habitat types ($p=0.3419$) (Figure 17b).

Vertical accretion rates ranged from 0.37—0.88 cm yr^{-1} at BLHW sites, to 0.50—1.06 cm yr^{-1} at baldcypress sites, and 0.54—1.10 cm yr^{-1} at lake sites. Baldcypress cores averaged 0.77 cm yr^{-1}

(SE=0.06) of accretion, followed by lake (0.73 cm yr⁻¹, SE=0.07), and BLHW cores (0.63 cm yr⁻¹, SE=0.07), respectively (Table 8).

Despite the fact that vertical accretion did not differ among habitats, mineral and organic matter accretion rates differed among habitats ($P = 0.0012$ and $P = 0.0023$, respectively) (Figure 18). Tukey comparisons indicate that mineral accretion rates of BLHW rates differed from those of baldcypress ($P = 0.0022$) and lakes ($P = 0.0039$), but baldcypress and lake did not differ from each other ($P = 0.9976$). For organic accretion rates, baldcypress and lake were the only two habitats that differed ($P = 0.0017$).

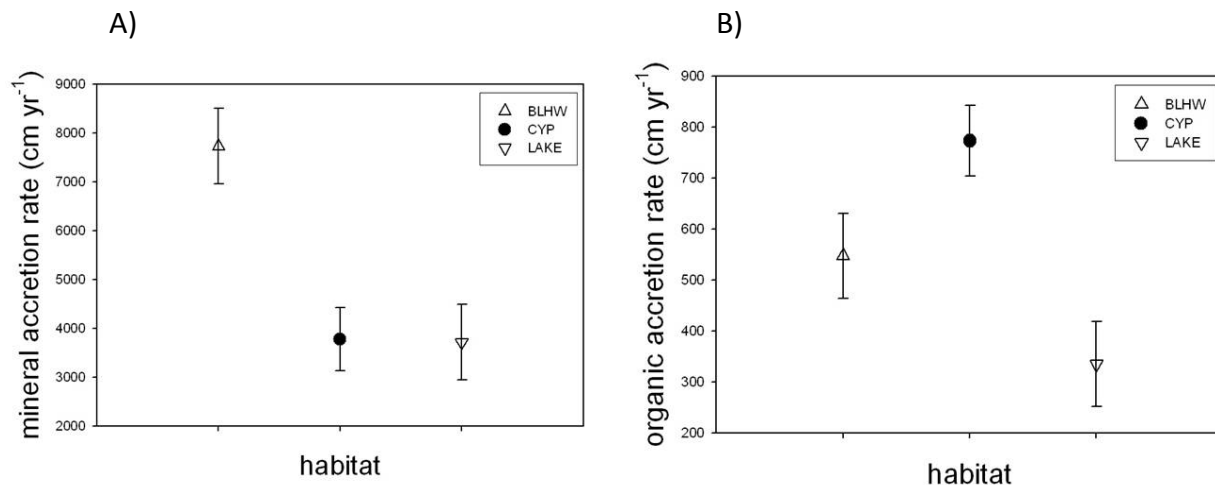


Figure 18: A) Mineral and B) organic accretion rates among habitats in the Atchafalaya River Basin, Louisiana, USA: bottomland hardwood forests (BLWH), baldcypress swamps (CYP), and lake. Graphs show Least Squares Means (BLHW $n = 7$, CYP $n = 10$, LAKE $n = 7$), and Least Squares Standard Error bars.

Bulk accumulation rates were correlated with mineral ($P < 0.0001$) and organic ($P = 0.022$) accretion rates. Vertical accretion rate was correlated with organic accumulation rate ($P = 0.003$). Notably, percent organic content was not correlated with organic accumulation (Tables 9 and 10).

Table 8: Accretion and accumulation rates (since 1963) determined using the ^{137}Cs technique (dating) and the LOI technique (OM content).

habitat	site	bulk density (g cm^{-3})	bulk accumulation (g m^{-2})	bulk accumulation rate ($\text{g m}^{-2} \text{yr}^{-1}$)	vertical accretion (cm)	vertical accretion rate (cm yr^{-1})	% Mineral	% Organic	Mineral Accretion (g m^{-2})	Organic Accretion (g m^{-2})	Mineral Accretion Rate ($\text{g m}^{-2} \text{yr}^{-1}$)	Organic Accretion Rate ($\text{g m}^{-2} \text{yr}^{-1}$)
BLHW	LL#1	0.85	209437	4654	22.5	0.50	0.88	0.12	184433	25004	4099	556
BLHW	LL#1a	1.32	486870	10584	34.5	0.75	0.95	0.05	460486	26384	10011	574
BLHW	LL#2a	1.26	488291	10615	37.5	0.82	0.94	0.06	459211	29080	9983	632
BLHW	BCH#1	1.39	385976	8391	25.5	0.55	0.94	0.06	364426	21550	7922	468
BLHW	BCH#2	1.24	339890	7389	25.5	0.55	0.91	0.09	310933	28957	6759	630
BLHW	JAB#1	1.18	507892	11041	40.5	0.88	0.93	0.07	474268	33625	10310	731
BLHW	JAB#2	1.34	241739	5255	17	0.37	0.95	0.05	230593	11146	5013	242
average		1.22	380014	8276	29.0	0.63	0.93	0.07	354907	25107	7728	548
Cypress	CO#1	0.27	76271	1695	25.5	0.57	0.73	0.27	55504	20767	1233	461
Cypress	CO#2	0.28	97111	2158	34.5	0.70	0.77	0.23	74380	22731	1653	505
Cypress	ML#1	0.70	304877	7090	42.5	0.99	0.82	0.18	250818	54059	5833	1257
Cypress	ML#2	0.69	235677	5481	33.5	0.78	0.82	0.18	193997	41679	4512	969
Cypress	ML#3	0.59	285577	6490	46.5	1.06	0.86	0.14	245704	39873	5584	906
Cypress	ML#4	0.56	234542	5331	40.5	0.91	0.86	0.14	200584	33958	4559	772
Cypress	BB#1	0.63	339316	7891	36.5	0.85	0.85	0.15	287813	51504	6693	1198
Cypress	BB#2	0.61	219267	5099	33.5	0.78	0.87	0.13	190120	29147	4421	678
Cypress	BC#1	0.35	94784	2204	24.5	0.57	0.77	0.23	73189	21595	1702	502
Cypress	BC#2	0.39	90439	2103	21.5	0.50	0.77	0.23	69664	20775	1620	483
average		0.51	197786	4554	33.9	0.77	0.81	0.19	164177	33609	3781	773
Lake	LSML	0.45	164445	3654	34.5	0.77	0.91	0.09	149811	14634	3329	325
Lake	FL#2	0.55	164895	3664	28.5	0.63	0.92	0.08	151125	13770	3358	306
Lake	FL#4	0.36	98790	2102	25.5	0.54	0.91	0.09	89517	9274	1905	197
Lake	DLS#2	0.37	126007	2800	31.5	0.70	0.89	0.11	112774	13232	2506	294
Lake	DLS#3	0.75	313468	6670	40.5	0.86	0.92	0.08	289099	24370	6151	519
Lake	DLN#2	0.43	218922	4865	49.5	1.10	0.92	0.08	200885	18037	4464	401
Lake	DLN#3	0.80	215818	4592	25.5	0.54	0.94	0.06	202360	13458	4306	286
average		0.49	181088	3959	35.0	0.77	0.92	0.08	170796	15553	3717	333

Regression Analysis

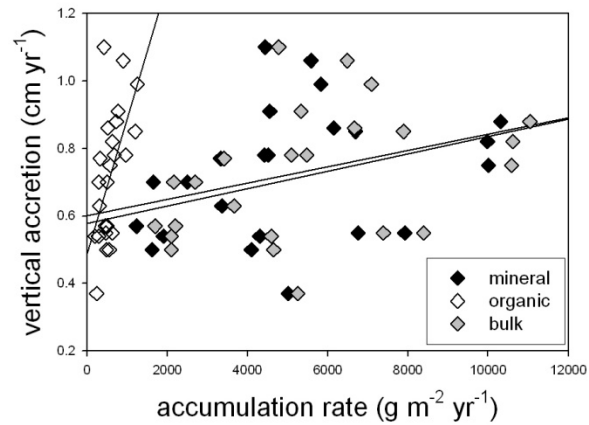
To determine which variables were associated with vertical accretion rates in the ARB we regressed mineral, organic, and bulk accretion rates ($\text{g m}^{-2} \text{yr}^{-1}$) on vertical accretion rate, without accounting for habitat types, and the model was significant ($P = 0.0025$, adjusted $R^2 = 0.43$) (Figure 19a). We also regressed mineral, organic, and bulk accretion rates on vertical accretion rates, with habitats included, and this model was significant as well ($P = 0.017$, adjusted $R^2=0.91$) (Figure 19b).

Because inclusion of habitats provided a better-fit model, we ran stepwise regressions for each habitat separately to determine which factors best predicted vertical accretion rates within each habitat. For BLHW habitat, we regressed mineral, organic, and bulk accretion rates on BLHW vertical accretion rate. The model was significant ($P = 0.0029$, $R^2 = 0.85$) and bulk accumulation rate was the only variable remaining in the model at a significance level of $\alpha = 0.05$ (Figure 20a). For baldcypress habitat, the model was significant ($P = 0.0012$, $R^2 = 0.75$) and mineral accretion rate was the only variable that remained in the model (Figure 20b). The model for lake habitat was significant ($P = 0.04$, $R^2 = 0.57$) and organic accretion rate was the only variable included in the final model (Figure 20c).

Nutrient Accretion

BLHW habitat accumulated approximately $11 \text{ g N m}^{-2} \text{yr}^{-1}$, $163 \text{ g C m}^{-2} \text{yr}^{-1}$, and $5 \text{ g P m}^{-2} \text{yr}^{-1}$. Baldcypress swamps accumulated approximately $20 \text{ g N m}^{-2} \text{yr}^{-1}$, $327 \text{ g C m}^{-2} \text{yr}^{-1}$, and $2 \text{ g P m}^{-2} \text{yr}^{-1}$. Lakes accumulated approximately $8 \text{ g N m}^{-2} \text{yr}^{-1}$, $90 \text{ g C m}^{-2} \text{yr}^{-1}$, and $4 \text{ g P m}^{-2} \text{yr}^{-1}$.

A)



B)

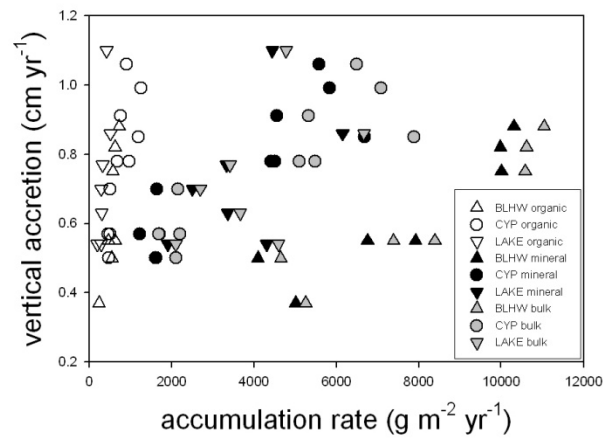
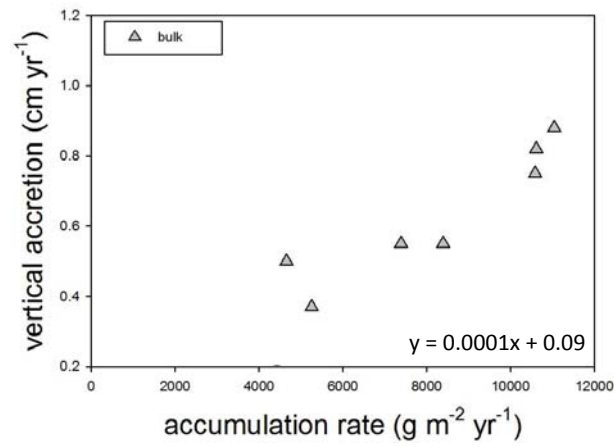
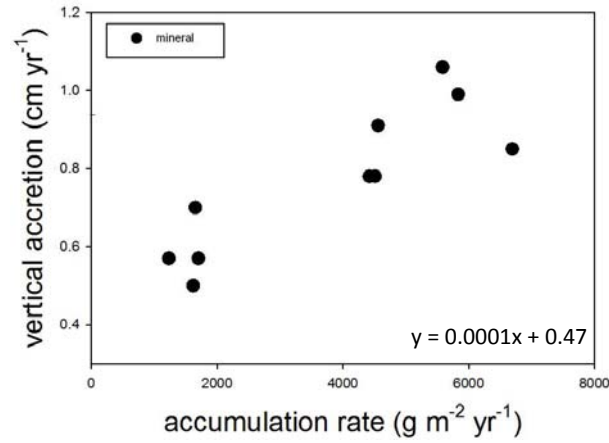


Figure 19: Multiple regression between vertical accretion rate ($\text{cm}^2 \text{yr}^{-1}$), and mineral, organic, and bulk accumulation rates ($\text{g m}^{-2} \text{yr}^{-1}$) A) without accounting for habitats and B) with accounting for habitats. Graph A shows separate regression lines for mineral, organic, and bulk accretion. All data collected from Atchafalaya River Basin, Louisiana, USA: bottomland hardwood forests (BLWH), baldcypress swamps (CYP), and lake sites.

A)



B)



C)

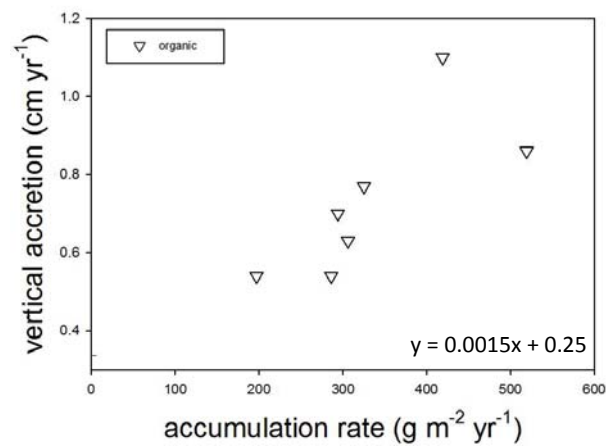


Figure 20: Multiple regression between vertical accretion rate (cm yr⁻¹) and organic, mineral, and bulk accumulation rates (g m⁻² yr⁻¹) for A) BLHW B) baldcypress, and C) lake sediments in the Atchafalaya River Basin, Louisiana, USA.

Table 9: Correlation table for sediment characteristics of samples collected from the Atchafalaya River Basin, Louisiana, USA. For each correlation, top number is correlation coefficient and bottom number is p-value.

	% C	% N	% P	Sand content (%)	Silt content (%)	Clay content (%)	Bulk Density (g cm ⁻³)	Vertical accretion (cm)	Bulk accumulation (g m ⁻²)	Mineral content (%)	Organic content (%)	Mineral accretion (g m ⁻²)	Organic accretion (g m ⁻²)
Carbon (%)	1	0.97841 <.0001	-0.32056 0.1809	-0.42745 0.0679	-0.74569 0.0002	0.67739 0.0014	-0.37046 0.1184	0.55626 0.0134	-0.12561 0.6084	-0.42607 0.0689	0.42607 0.0689	-0.19136 0.4326	0.70945 0.0007
Nitrogen (%)		1	-0.28167 0.2427	-0.53767 0.0176	-0.80404 <.0001	0.76803 0.0001	-0.4964 0.0306	0.47896 0.038	-0.26554 0.2719	-0.51743 0.0233	0.51743 0.0233	-0.32943 0.1684	0.63904 0.0032
Phosphorus (%)			1	-0.10291 0.6751	0.43349 0.0637	-0.22151 0.3621	0.05368 0.8272	-0.23766 0.3272	-0.03477 0.8876	0.43765 0.0609	-0.43765 0.0609	0.01099 0.9644	-0.53074 0.0194
Sand content (%)				1	0.46474 0.0221	-0.81048 <.0001	0.87556 <.0001	-0.25958 0.2206	0.67259 0.0003	0.41484 0.0438	-0.41484 0.0438	0.69022 0.0002	0.06802 0.7521
Silt content (%)					1	-0.89533 <.0001	0.55963 0.0045	-0.17054 0.4256	0.36947 0.0756	0.85097 <.0001	-0.85097 <.0001	0.44241 0.0304	-0.5381 0.0067
Clay (%)						1	-0.81066 <.0001	0.2434 0.2518	-0.58275 0.0028	-0.77163 <.0001	0.77163 <.0001	-0.63987 0.0008	0.32176 0.1252
Bulk Density (g cm ⁻³)							1	-0.12397 0.5638	0.8307 <.0001	0.67063 0.0003	-0.67063 0.0003	0.85107 <.0001	0.11521 0.5919
Vertical accretion (cm)								1	0.37205 0.0734	0.07125 0.7408	-0.07125 0.7408	0.34104 0.1029	0.52859 0.0079
Bulk accretion (g m ⁻²)									1	0.58432 0.0027	-0.58432 0.0027	0.99578 <.0001	0.45675 0.0249
Mineral content (%)										1	-1 <.0001	0.63892 0.0008	-0.26784 0.2057
Organic content (%)											1	-0.63892 0.0008	0.26784 0.2057
Mineral accretion (g m ⁻²)												1	0.37482 0.0711
Organic accretion (g m ⁻²)													1

Table 10: Correlation table for rates of sediment accretion measured from sediment cores collected in the Atchafalaya River Basin, Louisiana, USA. For each correlation, top number is correlation coefficient and bottom number is p-value.

	Vertical accretion rate (cm yr ⁻¹)	Bulk accretion rate (g m ⁻² yr ⁻¹)	Mineral accretion rate (g m ⁻² yr ⁻¹)	Organic accretion rate (g m ⁻² yr ⁻¹)
Vertical accretion rate (cm yr ⁻¹)	1	0.337709 0.0693	0.33775 0.1065	0.58391 0.0027
Bulk accretion rate (g m ⁻² yr ⁻¹)		1	0.99513 <0.0001	0.46515 0.022
Mineral accretion rate (g m ⁻² yr ⁻¹)			1	0.37722 0.0692
Organic accretion rate (g m ⁻² yr ⁻¹)				1

Suspended Sediments

Suspended sediment concentrations differed among habitats ($P = 0.009$) (Figure 21). Specifically, BLHW and baldcypress differed ($P = 0.01$), and baldcypress and lakes differed ($P = 0.03$) in their sediment concentrations. Suspended sediment concentrations were not significantly different between BLHW and lake samples ($P = 0.74$).

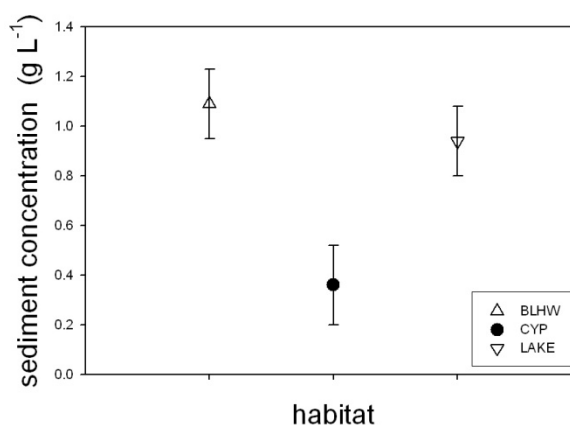


Figure 21: Suspended sediment concentrations of three habitat types in the Atchafalaya River Basin, Louisiana, USA collected during the flood of May, 2008. Graph shows Least Squares Means (BLHW $n = 10$, CYP $n = 6$, LAKE $n = 9$), and Least Squares Standard Error bars.

Highest suspended sediment concentrations were seen in the BLHW region (mean=1.09 g L⁻¹, SE=0.14), which also had the greatest water depth (mean = 6.29 m). Lowest suspended sediment concentrations occurred in the baldcypress region (mean = 0.36 g L⁻¹, SE=0.16), which had intermediate water depth (mean = 4.70 m). The lake region, which had the lowest water depth (mean = 0.74 m), had intermediate suspended sediment concentrations (mean = 0.94 g L⁻¹, SE=0.14) (Table 11). Publicly available satellite images indicate that lake water is a mixture of sediment-rich water from the main river channels and sediment-poor water from the baldcypress swamps. The pattern of suspended sediment concentrations observed in this study could be explained if lake water (0.94 g L⁻¹) represented a mixture of 52% water that had retained its sediments and remained in the channels (1.09 g L⁻¹) with 48% water that had lost much of its sediment as it passed through baldcypress swamps (0.36 g L⁻¹).

Table 11: Site characteristics for the suspended sediment samples where USGS water level recorders were in close proximity, Atchafalaya River Basin, Louisiana, USA.

Habitat	Site	Water Depth (ft)	Water Level Recorder (ft)	Soil Elevation (ft)
Lake	Flat Lake	1.08	2.42	1.34
Lake	Duck Lake South	1.48	2.42	0.94
Lake	Duck Lake South	1.54	2.42	0.88
Lake	Duck Lake North	1.51	2.42	0.91
Baldcypress	Murphy Lake	7.5	15.45	7.95
Baldcypress	Bee Bayou	6	15.45	9.45
Baldcypress	Bayou Cowan	7.5	15.45	7.95
BLHW	Bayou Chene Cut	0.5	20.63	20.13
BLHW	Jake's Bayou	1	20.63	19.63

DISCUSSION

Bulk accretion limited vertical accretion in BLHW habitat, mineral accretion limited vertical accretion in baldcypress swamps, and organic accretion limited vertical accretion in the

lakes. We expected to see mineral accumulation driving vertical accretion at all habitats, but results indicate that the situation in the ARB is more complicated than we expected. BLHW habitat is located in the upstream region of the floodplain, where the river first slows and sediments begin to fall out of suspension. Thus, the BLHW sediments had the highest sand content, and the lighter clay particles dominated farther downstream in the baldcypress swamps and lakes. This process of sedimentation created the BLHW habitat, as increasing elevation from sediment deposition allowed for colonization by less flood-tolerant species. However, mineral accretion rates in the BLHW were unrelated to vertical accretion rates there; instead, bulk accumulation rate was the factor most predictive of vertical accretion rates. This is probably because bulk accretion rate was very highly correlated with mineral accretion rate.

Vertical accretion in the baldcypress swamps of the ARB was related to mineral accretion. Vertical accretion rates in the baldcypress did not differ from that of the BLHW. BLHW sediments had higher bulk densities than baldcypress sediments, and the vegetation suggests that the BLHW sediments are more aerobic than the baldcypress sediments. The greater aeration should make sediments in the BLHW habitat more prone to auto-compaction (Kaye and Barghoorn 1964) or consolidation. The fact that BLHW are vertically accreting at similar rates to the rest of the ARB indicates that these areas have not reached equilibrium, as we expected. Instead, these areas apparently are continually consolidating, thus lowering their elevation, and continually vertically accreting, thus maintaining elevation.

Surprisingly, the rate of organic matter accretion was the best predictor of vertical accretion rate in the lakes of the ARB. Vertical accretion in many coastal marshes depends upon organic matter rather than mineral sediments (McCaffrey and Thomson 1980, Chmura et

al. 2004, Nyman et al. 2006, Newbauer 2008) but the process in those coastal marshes depends upon rooted, emergent vegetation which was lacking from our lake sites; thus the process by which organic matter caused the lake beds to vertically accrete must be different than organic-controlled accretion previously described.

The concentration of total suspended sediment at the lakes was higher than in the baldcypress sites. This implies limited connectivity between the baldcypress swamps and the main stem of the Atchafalaya River. It appears that river-borne sediment bypasses many backwater areas and instead deposits more fine sediment in the lakes. This would explain the spatial pattern in our suspended sediment concentrations, which suggest that only 48% of the floodwaters deposited sediments in the baldcypress region. Because allochthonous sediment carried by the river decreased in concentration in baldcypress habitat, the subsequent increase in concentration in the lakes could also suggest that within-basin erosion provides additional source of sediment here. Owens and Walling (2002) noted that erosion of channel banks can provide a substantial source of sediment, particularly during higher flows. However, water moves through much of the backwater areas in the ARB via low-energy channels (Sabo et al. 1999), so sediment contribution from erosion is likely minimal. The dynamic nature of water movement throughout the ARB was illustrated by Sabo et al. (1999), who showed that major lateral movement of water between the channel and floodplain occurs in a limited number of locations, which affects the speed and direction of water movement across the floodplain.

If upstream habitats were contributing sediment to downstream habitats, they were likely exporting organic matter (and associated nutrients) downstream as well. Prior work has shown that the ARB is a sink for 54,406 Mg of organic nitrogen annually while a source for

3,863 Mg of nitrate annually (Xu 2006). Within the ARB, the lakes are positioned to receive nutrients and sediment exported from upstream sources; namely the river channels, the baldcypress swamps and, in some cases, the BLHW forests. Lambou and Hern (1983) suggested that overflow areas on a floodplain are sinks for POC (associated with sedimentation), and sources of DOC (via decomposition of leaf litter). Hupp et al. (2008) identified a large amount of carbon trapping in the ARB. These ideas are consistent with our data for habitats in the ARB. Our results show that the baldcypress swamps, where vertical accretion was driven by mineral sedimentation, had the highest rates of carbon accumulation in the ARB. High levels of POC in the water column are likely driven by high levels of POC in the sediment, as well as by the periodic anaerobic conditions that slow decomposition of baldcypress biomass. Some of this dissolved carbon is likely exported to the lakes, via sheetflow through the baldcypress swamps along a southward trajectory, particularly during high flows. Water that reaches the lake habitats backs up and stagnates because of limited outlets; this would facilitate deposition of DOC, contributing to organic accretion, and hence vertical accretion, in the lakes. Anecdotally, we noticed considerable growth of floating and submerged aquatic vegetation while collecting our lake cores. Invasive water hyacinth (*Eichhornia crassipes*) and hydrilla (*Hydrilla verticillata*) frequently choked the entrances to, and edges of, these lakes. The use of an Eckman dredge at these sites to collect unconsolidated sediment (for a previous study) was often challenging because the surface of the lake bed was covered in a thick mat of decaying plant material. Because the lake sites are continuously flooded, sediments are generally anaerobic; this leads to slowed decomposition and long term preservation of organic matter. This localized accumulation of detritus provided a source of organic matter that ultimately contributed to

organic accretion rates driving total vertical accretion in the lakes. In terms of mineral deposition, lake sediments are predominately silty loams and clays. These fine sediments have less pore space, and are less susceptible to auto-compaction. This is consistent with the findings of Ross et al. (2004) who suggested that, within Coastal Plain floodplains, areas with the lowest elevation and highest duration of flooding will not necessarily have the highest deposition rates.

Vertical accretion at these sites ranged from 0.37—1.10 cm yr⁻¹. Our rates are within the range, although on the low end, of those reported by Hupp et al. (2008) for sites in the ARB (0.2 cm yr⁻¹ on high levees to 4.2 cm yr⁻¹ at lower elevation). Their measurements spanned three years, while ours were averaged over 45+ years and do not describe short term variability, and also include consolidation within the upper 50-cm. Our results were similar to those reported for other coastal plain floodplains and freshwater marshes, and generally higher than those reported for salt marshes (Table 12).

Our results for carbon, nitrogen and phosphorus accumulation (g m⁻² yr⁻¹) were comparable to other rates reported for the coastal plain (Table 12), although our P rates were slightly higher. Our suspended sediment concentrations for the Atchafalaya River were higher than the 0.310 g L⁻¹ average reported by Xu (2010). Our suspended sediment data is more indicative of the maximum suspended sediment concentrations seen during unusually high water years, while our accretion data provides a better profile of long term sediment dynamics in the ARB.

Table 12: Comparison of vertical accretion rates to other studies published in the literature.

Study	Site	Habitat	Time (yr)	Vertical Accretion (mm yr ⁻¹)	Carbon (g m ⁻² yr ⁻¹)	Nitrogen (g m ⁻² yr ⁻¹)	Phosphorus (g m ⁻² yr ⁻¹)	Bulk Density (g cm ⁻³)
Hatton et al 1982	Barataria Basin, LA	Freshwater	Cs137	10.6	477	16	1	0.11
	Barataria Basin, LA	Freshwater	Cs137	6.5	306	9	0.5	0.09
	Barataria Basin, LA	Intermediate	Cs137	13.5	797	28	1.5	0.18
	Barataria Basin, LA	Intermediate	Cs137	6.4	269	11	0.4	0.08
	Barataria Basin, LA	Brackish	Cs137	14	826	25	2.4	0.27
	Barataria Basin, LA	Brackish	Cs137	5.9	348	10	0.5	0.14
	Barataria Basin, LA	Salt	Cs137	7.5	435	11	1.1	0.29
Craft & Casey 2000	Georgia	Marsh	Cs137	--	0	0	0	1.42
	Georgia	Savannah	Cs137	--	31	2.2	0.11	1.21
	Georgia	Forested	Cs137	--	31	2.2	0.12	0.47
	Georgia	Floodplain Forested	Cs137	--	18	1.4	0.12	1.02
Lynch et al 1989	Rookery Bay, FL	Mangroves	Cs137	1.8	--	--	--	0.212-0.225
Orson et al 1990	Delaware River estuary	Tidal Freshwater marsh	Cs137	120	--	--	--	0.21
Thom 1992	Pacific NW USA	Intertidal Salt Marsh	Cs137	3.6	--	--	--	0.05-0.65**
Nyman et al 1990	Louisiana	Mississippi Deltaic Plain	Cs137	86	--	--	--	0.14
	Louisiana	Mississippi Deltaic Plain	Cs137	67	--	--	--	0.08
Reddy et al 1993	Florida Everglades	Sawgrass dominated	Cs137	25	86	5	0.11-0.25	--
	Florida Everglades	Cattail dominated	Cs137	110	163-387	11-24	0.54-1.14	--
Feijtel et al 1988	Barataria Basin, LA	Freshwater	Cs137	8.5	--	--	--	--
	Barataria Basin, LA	Brackish	Cs137	9.5	--	--	--	--
	Barataria Basin, LA	Saltmarsh	Cs137	10.5	--	--	--	--
DeLaune & Smith 1984	Barataria Basin, LA	Fresh	Cs137	85	254	--	--	0.9
	Barataria Basin, LA	Brackish	Cs137	95	296	--	--	0.8
DeLaune et al 1980	Barataria Basin, LA	Marsh	Cs137	--	--	21	1.7	--
DeLaune et al 1978	Barataria Basin, LA	Marsh	Cs137	135	--	--	--	--
DeLaune et al 1981	Barataria Basin, LA	Marsh	Cs137	135	393	21	1.7	0.25
	Barataria Basin, LA	Marsh	Cs137	75	237	13.4	0.8	0.2
	Barataria Basin, LA	Lake	Cs137	110	231	15.3	3.2	0.45-0.65
Neubauer et al 2002	SE Virginia	Freshwater Marsh	Cs137	8.5	224	--	--	0.324

*burned during experiment **estimated from graph

CONCLUSION

Current management goals for the ARB aim to maximize freshwater inflows to stagnant (hypoxic) areas and to minimize sedimentation. Attempts to slow sedimentation and reduce hypoxia involve plugging canals that admit large amounts of sediments during floods and creating gaps in spoil banks that hinder unidirectional flow (Sparks 1992). Increasing unidirectional flow also has the benefit of increasing nitrate retention in the ARB via denitrification (Scaroni et al. 2010) and sedimentation, thereby reduce nitrate inputs and the resulting hypoxia in the northern Gulf of Mexico.

The ARB has long been identified as a sink for sediments and nutrients; results of this study indicate that vertical accretion on the floodplain is complex and influenced by a number of factors. We were not able to identify all factors affecting accretion rates; however we determined whether bulk, mineral, or organic accumulation is most influential in driving vertical accretion within each habitat type. We also identified rates of nutrient retention and accretion across habitats in the ARB. This knowledge can inform managers seeking to minimize sedimentation while maximizing nutrient removal in particular areas. Despite the fact that habitats did not differ in their vertical accretion rates, improved r-squared values resulted from separate analysis of each habitat type. We recommend that large scale sedimentation studies account for habitat type in the experimental design, and model habitats separately.

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CHAPTER 6.

NUTRIENT STORAGE IN ABOVEGROUND WOODY BIOMASS OF THE ATCHAFALAYA RIVER BASIN, LOUISIANA.

INTRODUCTION

The coastal plain of the southeastern United States is covered by nearly 12.5 million hectares of wetland hardwood forests (Phillips et al. 1989). These lowland forests, which once covered the majority of the coastal plain, are in decline due to extensive conversion to agricultural land. Approximately 2.6 million hectares of bottomland hardwood forests remain in the Lower Mississippi Alluvial Valley (Gardiner and Oliver 2005), down from an estimated 10 million prior to land conversion (Schoenholtz et al. 2001). Bottomland hardwood forests are highly productive ecosystems, due in part to frequent inundation by adjacent rivers which provide freshwater and nutrients (Conner and Day 1976). Intact floodplain forests receive energy subsidies during the flood pulse, creating biogeochemical conditions on the floodplain distinct from those in the river, and facilitating nutrient transformation (Junk 1989). As a result, some coastal plain floodplains, such as the ARB, function as a sink for carbon, nitrogen, and phosphorus (Hupp and Noe 2006, Chapter 5). Management strategies to improve water quality often target coastal floodplains, as they often provide the last opportunity for filtration before rivers discharge into coastal receiving waters.

The degree of water exchange between the river and the floodplain is a major factor controlling the retention and removal of water-borne nutrients on the floodplain (Tockner et al. 1999). As water residence time increases, so does the potential for nutrients to be removed from flood water (Hill 1997). In the spring, snowmelt at higher altitudes drives high water

downstream. As floodwaters spread out across the floodplain, greater contact with soils and vegetation leads to greater removal of nutrients (Xu 2006). Because biogeochemical cycles in the floodplain differ from those in the main river channel (Junk 1989), it is necessary to consider *in situ* cycling of nutrients and organic matter along with lateral exchange of nutrients and organic material between the river and the floodplain.

Floodplain connectivity is particularly important for the Atchafalaya River, which, along with the Mississippi River, transports a large amount of freshwater, nutrients, and sediment to the Gulf of Mexico (Xu 2006). Delivery of excess nutrients into the Gulf stimulates phytoplankton productivity and leads to a reduction in dissolved oxygen (Rabalais et al. 2002). This creates a seasonal area of hypoxia, extending up to 20,000 km², with dissolved oxygen concentrations less than 2 mg L⁻¹. River diversions and upstream wetlands creation and restoration have been suggested as options to mitigate river nutrient loads before they reach saltwater (Mitsch et al. 2001). With a large floodplain and wide set levees, flood pulses in the ARB allow the river to leave the channel and spread across the floodplain, thus promoting nutrient transformation and sediment deposition.

The ARB, located in south-central Louisiana, is the largest deepwater swamp in the United States. Covering approximately 5,000 km², the floodplain of the Atchafalaya River contains extensive lakes, baldcypress swamps, and the largest contiguous BLHW habitat in North America. Formed where the Red River meets approximately 30% of the diverted flow of the Mississippi River, the Atchafalaya River travels 226-km before it discharges into the Gulf of Mexico at the Wax Lake outlet and Atchafalaya Bay (Ford and Nyman 2011).

The ARB functions as a sink for sediment and nutrients, specifically nitrogen (Xu 2006). Initially derived from upstream sources, including agriculture, nutrients enter the Mississippi River and some are diverted to the Atchafalaya River. As water flows through the ARB, up to 50,544 t of total N, or 14% of the total load, is retained or removed before it reaches the Gulf of Mexico (Xu 2006). Conversely, there is a slight increase in nitrate exported (3,863 tons of nitrate) from the ARB, indicative of internal nutrient cycling (Xu 2006).

Sediment discharge from the ARB into the Gulf of Mexico has formed two prograding deltas at both river outlets (Roberts 1998). This delta building follows several centuries of sediment deposition in the ARB (Roberts et al. 1980). Initially, lacustrine deltas formed in many of the floodplain lakes; by the 1950s these lakes had filled in and river-borne sediment bypassed these areas, reaching the coast and forming the river deltas (Roberts 1997; Tye and Coleman 1989). Estimates of annual sediment retention rates in the ARB range from 5,000,000 Mg yr⁻¹ (Hupp et al. 2008) to 6,000,000 Mg yr⁻¹ (Xu 2010). As the ARB fills in with sediment, many of the aquatic habitats are transitioning into seasonal wetlands and even upland forests. Hupp et al. (2008) recently estimated that 70% (396,900 ha) of the ARB is now BLHW habitat, and that percentage is expected to increase as continued sedimentation drives habitat change. The remaining 30% is a combination of baldcypress swamps and lakes/freshwater marshes. Faulkner et al. (2009) used the National Wetlands Inventory classification system to estimate the total area of baldcypress-tupelo forests in the ARB at 106,227 ha.

As habitats in the ARB transition from lakes to baldcypress swamps and bottomland hardwood forests, contact between the river and its floodplain decreases because elevations increase with the accumulation of sediment (Table 13). Floodplain connectivity has been

further decreased by efforts to accelerate channel enlargement by closing 22 distributaries (Sparks 1992). In addition to habitat change and reduced flooding, hypoxic waters regularly develop in parts of the Basin where water stagnates in low energy channels (Sabo et al. 1999). Restoration in the basin is complicated because increasing unidirectional flow to reduce anoxia might also increase sedimentation and thus promote habitat change.

Table 13: Classification of habitats within coastal floodplains on a flooding gradient based dominant vegetation.

habitat	flooding	dominant plant species
bottomland hardwood	least	sweetgum (<i>Liquidambar styraciflua</i>), sugarberry (<i>Celtis laevigata</i>), oak (<i>Quercus</i> spp.), willow (<i>Salix</i> spp), elm (<i>Ulmus</i> spp.), ash (<i>Fraxinus</i> spp.), red maple (<i>Acer rubrum</i>)
baldcypress swamp	intermediate	baldcypress (<i>Taxodium distichum</i>), water tupelo (<i>Nyssa aquatica</i>)
open water	most	phytoplankton and submersed aquatic vegetation such as <i>Myriophyllum</i> spp., <i>Ceratophyllum demersum</i> , and <i>Valisneria americana</i>

Opportunities for nutrient retention and removal on the floodplain include loss via denitrification (N), storage in sediments (C, N, P), and assimilation into woody biomass (C, N, P). Nutrients and carbon are stored in soil as sediments accumulate and are stored in persistent woody biomass as forests develop following disturbance, such as the widespread harvesting of the late 1800's and early 1900's. Because of these extensive harvests, forest growth in the ARB is fairly young. Clearcuts were common until approximately 1930, after which time forests were either converted to agriculture or allowed to naturally regenerate (Keim et al. 2006). In addition to this regrowth, delta building creates new land in the ARB that has allowed establishment of forest stands where open water used to exist (Tye and Coleman 1989).

Growth and productivity of forests decline as they mature (Gower et al. 1996), thus nutrient accumulation rates decrease over time. However, intact forests continue to sequester nutrients that have already been assimilated; thus unharvested stands can function as long term sinks for nutrients. However, floodplain wetlands and aquatic environments can remove nitrogen from floodwater virtually indefinitely via denitrification, but C and P removal by floodplains is limited by storage in persistent biomass.

In addition to serving as potential indicators of differences in nutrient removal rates, habitats directly influence nutrient removal (e.g. Smialek et al. 2006). Plant communities reflect as well as affect many hydrogeomorphic processes (e.g., water velocity, sedimentation, sediment elevation); thus, the intrinsic character of habitats and geomorphological processes are partly the result of each other (Hupp 2000). For these reasons, it is imperative that efforts to understand floodplain biogeochemistry account for variability. Habitats might differ in nutrient removal processes such that submergence could decrease nutrient removal even as flooding increased if a more flood tolerant habitat removed nutrients slower than less a flood tolerant habitat. Conversely, submergence could increase nutrient removal non-linearly if a more flood tolerant habitat removed nutrients faster than a less flood tolerant habitat.

A baldcypress swamp in Florida demonstrated that immobilization of N by microbial assimilation was relatively insignificant as an N sink when compared with other processes (DeBusk and Reddy 1987). Similarly, Brinson et al. (1984) found that only 3.6% of nitrogen added to a swamp ends up being retained in tree wood. However, in a large floodplain such as the ARB, 3.6% of N inflow is the equivalent of $11,725 \text{ t yr}^{-1}$ ($1.1 \text{ billion kg yr}^{-1}$) (Xu 2005), which is a substantial amount of nitrogen potentially restricted from coastal waters.

We predicted the direction and magnitude of change in nutrient removal by floodplains in light of habitat change. First, we identified the major habitat types of the ARB, and the dominant nutrient removal processes in these habitats. Previous work in the ARB has investigated N removal via denitrification (Scaroni et al. 2011), and sedimentation (Chapter 5). The next step is to determine N storage in aboveground standing biomass stock in the ARB, and to estimate an annual rate of growth. These values can then parameterize models aiming to predict how habitat shifts within the ARB will affect nutrient discharge to the Gulf of Mexico.

METHODS

Estimates for biomass accumulation and nutrient uptake rates were already available for coastal plain bottomland hardwood and swamp species. We used the specific estimates for C, N, and P accumulation in BLHW and baldcypress swamp forests in the SE Coastal Plain of US by Messina et al. (1986) to estimate storage rates in aboveground woody biomass. Those estimates were made for the most prevalent coastal plain tree species from Virginia to the Louisiana/Mississippi border; however, we assumed that the plots were representative of the larger southeast coastal plain, and can thus be applied to the ARB in south-central Louisiana.

We made several adjustments to the estimates generated by Messina et al. (1986) to reflect the assumptions of our study. First, Messina et al. (1986) classified BLHW and wet flats as two distinct habitat types, while our BLHW designation includes wet flats. Therefore, we averaged the nutrient uptake values reported separately for BLWH and wet flats to estimate C, N, and P uptake in BLHW of the ARB.

Second, Messina et al. (1986) did not report C accumulation, but instead reported total biomass (dry weight). We assumed that the carbon fraction of the dry weight estimates was 50% of the total (Swift et al. 1979).

Third, Messina et al. (1986) estimated total aboveground biomass and nutrient content as the sum of all individual site pools for each habitat (foliage, branches, bole, saplings, understory-ground vegetation, forest floor). Because we wanted an estimate of storage in persistent wood biomass, we modified the reported estimates to include only the foliage, branches, and bole storage pools. Coarse woody debris can be an important pool of stored nutrients in forests (e.g., Fisk et al. 2002), but we assume that component was accounted for by sediment cores collected for another study (Chapter 5). We acknowledge that failure to include storage rates in saplings and understory-ground vegetation may lead to an underestimation of floodplain storage rates.

Fourth, Messina et al. (1986) estimated storage rates for 20, 40, and 60 year old stands. Stands in the ARB are probably closer to 80-120 years old (Conner and Toliver 1990). Because nutrient accumulation rates change over time, we compared the predicted carbon storage estimate for a 60 year old stand with estimates for 80 and 120 year old stands using the BLHW growth model of Shoch et al. (2009). Accumulation rates for 80 year old stands were 15% lower than those for 60 year old stands, and 120 year old stands had 42% lower carbon accumulation rates than 60 year old stands. We used these calculations of percent decrease over time to estimate ranges for the ARB based on predicted carbon accumulation rates for 60-120 year old stands. We acknowledge that the lower limit may underestimate current accumulation rates, and the upper limit likely overestimates current rates. Without similar

curves available for baldcypress swamps, or nitrogen and phosphorus, we used curves for carbon accumulation to estimate analogous decreases for the other nutrients (N and P), and the other forested habitat type (baldcypress swamp) in the ARB.

We then combined our adjusted estimates of nutrient uptake rates with the area of BLHW and baldcypress habitat in the ARB, for a basin-wide estimate of annual N, C, and P uptake in aboveground biomass.

Bottomland Hardwood Habitat

After adjusting the results of Messina et al. (1986) as described above, and extrapolating accumulation for 80—120 year old stands based on percent decrease in C content over time, we estimated that the accumulation rate of carbon in a BLHW stand is approximately 2,305 kg C ha⁻¹ yr⁻¹ at 60 years, 1,960 kg C ha⁻¹ yr⁻¹ at 80 years, and 1,337 kg C ha⁻¹ yr⁻¹ at 120 years.

Using the same adjustment for nitrogen accumulation rate, we estimated that BLHW stands accumulate approximately 6.98 kg N ha⁻¹ yr⁻¹ at 60 years, 5.93 kg N ha⁻¹ yr⁻¹ at 80 years, and 4.05 kg N ha⁻¹ yr⁻¹ at 120 years.

Finally, we estimated annual phosphorus accumulation rates for BLHW stands at 60, 80, and 120 years. These rates were approximately 0.82 kg P ha⁻¹ yr⁻¹, 0.70 kg P ha⁻¹ yr⁻¹, and 0.48 kg P ha⁻¹ yr⁻¹, respectively.

Baldcypress Swamp Habitat

Next, we estimated that baldcypress swamps in the ARB accumulate C at rates of 2,380 kg C ha⁻¹ yr⁻¹, 2,023 kg C ha⁻¹ yr⁻¹, and 1,380 kg C ha⁻¹ yr⁻¹, for 60, 80 and 120 year old stands, respectively. We estimated that baldcypress swamps accumulate approximately 6.83 kg N ha⁻¹ yr⁻¹ at 60 years, 5.80 kg N ha⁻¹ yr⁻¹ at 80 years, and 3.96 kg N ha⁻¹ yr⁻¹ at 120 years. And finally, P

accumulation rates were estimated at $0.77 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, $0.65 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, and $0.45 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, for 60, 80 and 120 year old stands, respectively.

RESULTS

Table 14: Removal rates ($\text{kg ha}^{-1} \text{ yr}^{-1}$) and total removal based on area (t yr^{-1}) for forested habitats in the Atchafalaya River Basin, Louisiana, USA. Total removal ranges from rates for 120 year old stand to 60 year old stand.

	Biomass assimilation ($\text{kg ha}^{-1} \text{ yr}^{-1}$)			Area in ARB (ha)	Total removal (t yr^{-1})
Stand age (yr)	60	80	120		60 - 120
<u>BLHW</u>					
C	2,305	1,960	1,337	396,900	530,655 - 914,855
N	6.98	5.93	4.05	396,900	1,607 - 2,770
P	0.82	0.70	0.48	396,900	190 - 325
<u>BALDCYPRESS</u>					
C	2,380	2,023	1,380	106,227	146,593 – 252,820
N	6.83	5.8	3.96	106,227	421 - 726
P	0.77	0.65	0.45	106,227	48 - 82

DISCUSSION

Previous work indicates that forest productivity is higher in seasonally flooded wetlands, as opposed to swamps with standing water (Mitsch 1991). Conner and Day (1976) reported that flowing water led to the highest productivity in swamp forests. The ARB includes continuously flooded and seasonally flooded swamps, which could explain why our estimated rates of annual nutrient uptake are similar between BLHW and baldcypress swamps. Generally, older trees exhibit lower productivity due to more efficient internal nutrient cycling (Messina et al. 1986). However, when comparing BLHW vs. baldcypress swamps across the coastal plain, Messina et al. (1986) did not observe obvious trends in nutrient concentrations across age and size classes, although basal area was higher in the baldcypress swamps.

Cole and Rapp (1981) reported an annual N uptake rate of $5.19 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ averaged across 22 worldwide temperate deciduous and coniferous forests. This is within the range we estimated for the ARB. Schlessinger (1978) estimated an annual uptake of $6.64 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from a baldcypress dominated swamp in Georgia. This value is at the upper end of our predicted range; however, Schlessinger also included all aboveground biomass (not just tree biomass). For P from the same swamp, Schlessinger (1978) estimated an annual uptake of $0.31 \text{ kg ha}^{-1} \text{ yr}^{-1}$, which is slightly lower than the range we predicted. Our carbon predictions were lower than others for BLHW ($13,740 \text{ kg C ha}^{-1} \text{ yr}^{-1}$: Conner and Day 1976) and baldcypress ($11,200 \text{ kg C ha}^{-1} \text{ yr}^{-1}$: Conner et al. 1981). Once again, this is likely because we only included persistent tree biomass in our estimate, and these published estimates accounted for all aboveground biomass. In general, comparison with other studies is consistent with the postulate of Messina et al. (1986) that the productivity and nutrient content of coastal plain hardwoods is generally higher than comparable stands elsewhere.

Our combined estimate of nutrient retention in biomass for both the BLHW and baldcypress swamps is on the order of $677,248\text{--}1,167,675 \text{ t C yr}^{-1}$, $2,028\text{--}3,496 \text{ t N yr}^{-1}$, and $238\text{--}407 \text{ t P yr}^{-1}$. Based on estimates of total N and P input into the Atchafalaya River from Goolsby et al. (1999), it appears that the ARB is removing between 0.60%—1.0 % of the annual N input from the river, and between 0.90%—1.5% of the annual P input, via accumulation in aboveground biomass. It is important to note that while BLHW and baldcypress habitat have similar rates of annual nutrient uptake on a per hectare basis, it is the transition from lake to forested habitat that has the greatest implication for nutrient retention in biomass.

This was the first attempt to quantify the magnitude of forest nutrient removal in the ARB. Our estimate is for current rates of removal based on recent stand age estimates. Models attempting to estimate nutrient assimilation rates in light of future habitat change must account for advancing stand age, lower productivity in older trees, and a subsequent change in nutrient accumulation rates.

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CHAPTER 7.

SUMMARY AND CONCLUSION

Previous work has indicated that the Atchafalaya River Basin, a natural diversion of the Mississippi River, can function as a sink for nutrients. However, few studies attempted to account for these lost nutrients, and no studies considered multiple pathways for removal within the ARB. This dissertation investigated the potential for nutrient removal and retention via denitrification (N), sedimentation (C, N, P), and biomass assimilation (C, N, P) across the three major habitats in the Atchafalaya River Basin. Determining retention and removal for each habitat type proved to be important, as each habitat differs in its storage reservoirs and biogeochemical processes.

First, I assessed the degree of spatial variability in denitrification potential in the ARB. This laboratory experiment demonstrated that denitrification is occurring in the ARB, and that it varies across spatial scales. Background and potential rates of denitrification differed from each other, illustrating the existence of hotspots of denitrification across the landscape. Background rates were related to soil characteristics (carbon, nitrogen, nitrate), but potential rates appeared to be related to landscape position (spatial coordinates). This suggests that landscape scale studies should include additional qualifiers, such as habitat type and quality of organic matter to reduce uncertainty in estimates of denitrification rates. Trends in the data indicated that spatial variability of potential rates was correlated with geographic position in the ARB. The increase in rates along a southwest to northeast trajectory suggested that differences in habitat type may account for the variability in these rates. This insight prompted further study to disentangle the role of habitat type in affecting denitrification potential.

Next, I explored the connection between differences in denitrification rates and habitat type. A microcosm experiment demonstrated that background and potential rates differed across habitat types. Background rates were highest in BLHW habitats, and lowest in the lakes. Potential rates were reversed and highest rates were seen in the lakes, while lowest rates were seen in the BLHW sediments. This reversal in rank suggests that continuous flooding leads to nitrate limitation; when I removed all limiting factors, the most flooded, and presumably most anaerobic, habitats had the highest potential for denitrification. Habitats also differed in the time it took to reach maximum denitrification rates following nitrate additions. From this experiment I concluded that large scale denitrification studies spanning more than one habitat type should model habitats separately. I also recommended that future researchers conduct experiments until maximum emissions are reached; brief 24 hour studies appear to be inadequate to characterize rates across habitats.

Concern over the potential for significant N_2O emissions from the ARB provided the impetus for a study to determine $\text{N}_2:\text{N}_2\text{O}$ emissions ratios. Results from this study indicated that, again, nitrate removal rates differed by habitat type. As seen in the previous study, lake habitats had the highest N_2 emissions rates; however, this time I showed that baldcypress habitats had the highest N_2O emissions. Overall $\text{N}_2:\text{N}_2\text{O}$ emissions were low across habitat types and increased N_2O emissions from additional flooding in the ARB does not appear to be a serious concern. Unflooded BLHW sediments had very low N_2 and N_2O emissions, indicating that unflooded areas in the ARB can become too dry for denitrification to occur. These results also suggest that management strategies aiming to improve water quality should consider each

habitat separately when modeling nitrogen removal within large river floodplains and those models will need to account for habitat change where it is occurring.

After investigating permanent removal processes, the next step was to consider long term storage opportunities in the ARB. To do this I collected and analyzed sediment cores collected from all three habitats to determine accretion rates and annual retention of C, N, and P in sediments. Surprisingly vertical accretion rates did not differ among habitats in the ARB. Vertical accretion in BLHW and baldcypress habitats was driven by bulk and mineral accretion, respectively. Organic accretion drove vertical accretion in the lake sites. Further analysis of the data indicated that the situation in the ARB is complicated, and will require a more in-depth understanding of the hydrology to truly understand sedimentation dynamics. The snapshot taken by the suspended sediment samples suggested that during high water only 48% of the river water left the channel and spilled over into the baldcypress swamps before rejoining sediment-rich water from channels in the lakes. Regardless, this still results in a large storage of sediments and associated nutrients throughout the ARB.

Lastly, I estimated assimilation rates by trees in the ARB to account for long term storage in aboveground biomass. BLHW and baldcypress appeared to have similar rates of annual uptake on a per hectare basis; however, the conversion from lake habitat to forested habitat will affect overall nutrient retention in aboveground biomass.

Rates of C, N, and P uptake from each chapter were compiled and total removal and retention for each habitat were calculated based on estimated area of each habitat in the ARB (Table 15). Finally, a basin-wide estimate of C, N, and P annual removal and retention was reported (Table 16). BLHW habitat area was estimated at 396,900 ha (Hupp et al. 2008),

baldcypress habitat area was estimated at 106,227 ha (Faulkner et al. 2009), and the remaining area, 63,873 ha, was attributed to lake habitat (Hupp et al. 2008). The range of removal estimates via denitrification was based on measured background rates and potential rates with a loading of $1 \text{ mg NO}_3\text{-N L}^{-1}$, which is comparable to, although slightly lower than, the current loading rate in the Mississippi River. The lower end of the range likely represents background rates in areas disconnected from the river, and the upper end of the range likely represents background rates under flooded conditions. Overall, our estimates of nutrient removal and retention likely underestimated the true values. Some of these “missing” nutrients could be casualties of our methodology; the acetylene block technique tends to underestimate denitrification rates, our biomass estimates only included the aboveground portion of persistent woody biomass, and our sample sizes were limited by time and money. Additional reservoirs for nutrients that I failed to account for include discharge to groundwater, deposition at depths below the reach of our cores during subsurface flow, and assimilation by biological organisms (such as crawfish) that are subsequently removed from the ARB in large quantities.

However, this work raises upper limit on estimates of N uptake in the ARB, as evidenced by the disparity between our estimated rates of annual N uptake in the ARB and the previous estimate of approximately $51,000 \text{ t N yr}^{-1}$ (Xu 2006). This is likely because Xu (2006) reported the amount of river-borne nitrogen that was sequestered or removed by the ARB. Our reported removal rates include removal of N derived from additional unspecified sources such as nitrogen fixation, atmospheric deposition or fertilizer use within the ARB.

Table 15: Removal rates ($\text{g ha}^{-1} \text{yr}^{-1}$) and total removal based on area (t yr^{-1}) for each major habitat in the ARB. The estimates for removal via biomass assimilation range from stand ages of 60—100 years. The estimates for removal via denitrification range from background (no nitrate added) to potential ($1 \text{ mg NO}_3\text{-N L}^{-1}$) emission rates.

	Area in ARB (ha)	Sedimentation ($\text{g ha}^{-1} \text{yr}^{-1}$)	(t yr^{-1})	Biomass assimilation ($\text{g ha}^{-1} \text{yr}^{-1}$)	(t yr^{-1})	Denitrification ($\text{g ha}^{-1} \text{yr}^{-1}$)	(t yr^{-1})	Total removal (t yr^{-1})
<u>BLHW</u>								
C	396,900	1,630,000	646,950	1,337,000—2,305,000	530,655—914,855	--	--	1,177,605—1,561,805
N	396,900	110,000	43,660	4,050—6,980	1,607—2,770	1,971—2,956	782—1,173	46,049—47,603
P	396,900	50,000	19,850	480—820	190—325	--	--	20,040—20,175
<u>CYPRESS</u>								
C	106,227	3,270,000	347,360	1,380,000—2,380,000	146,593—252,820	--	--	493,953—600,180
N	106,227	200,000	21,250	3,960—6,830	421—726	1,424—3,650	150—388	21,821—22,364
P	106,227	20,000	2,120	450—770	48—82	--	--	2,168—2,202
<u>LAKE</u>								
C	63,873	900,000	57,490	--	--	--	--	57,490
N	63,873	80,000	5,110	--	--	511—4,380	30—280	5,140—5,390
P	63,873	40,000	2,550	--	--	--	--	2,550

Table 16: Estimates of total C, N, and P removal (t yr^{-1}) by the ARB. Total removal rate consolidates individual habitat removal estimates for each nutrient.

	ARB Area (ha)	Total removal (t yr^{-1})
C	567,000	1,729,048—2,219,475
N	567,000	73,010—75,357
P	567,000	24,758—24,927

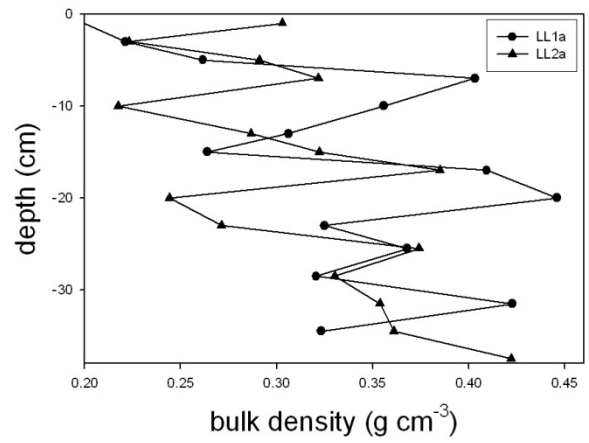
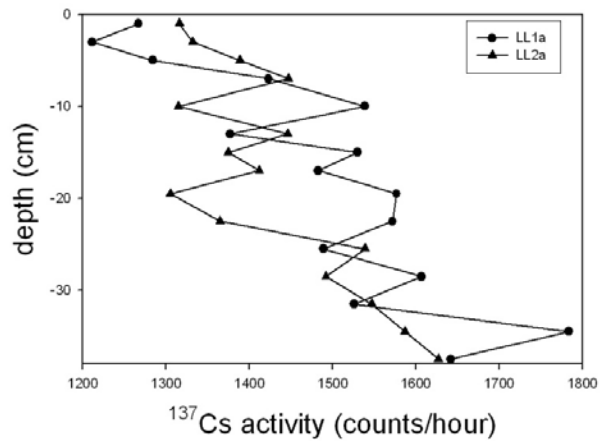
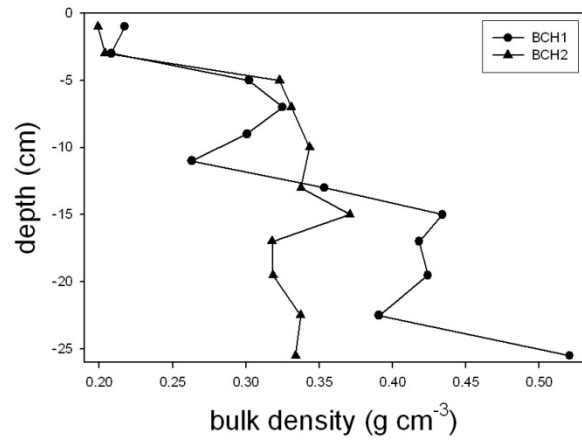
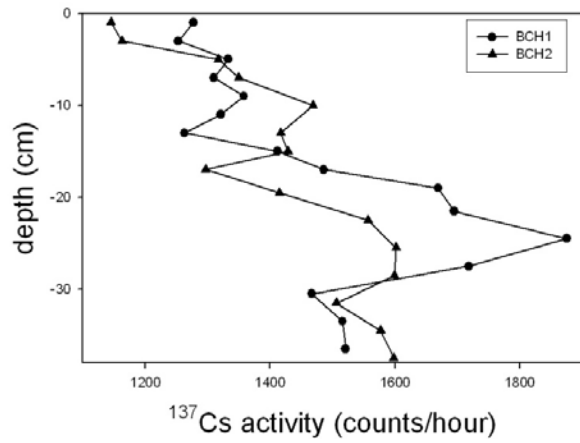
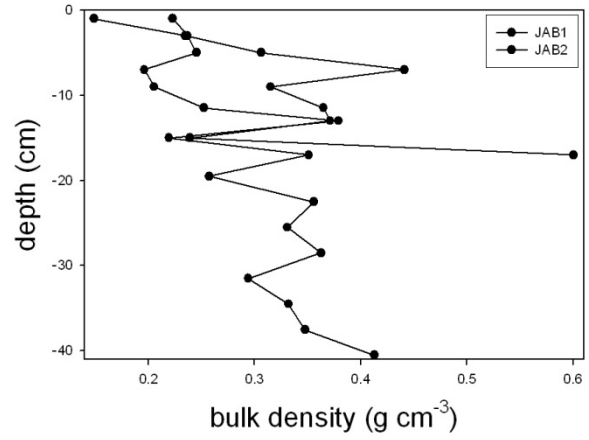
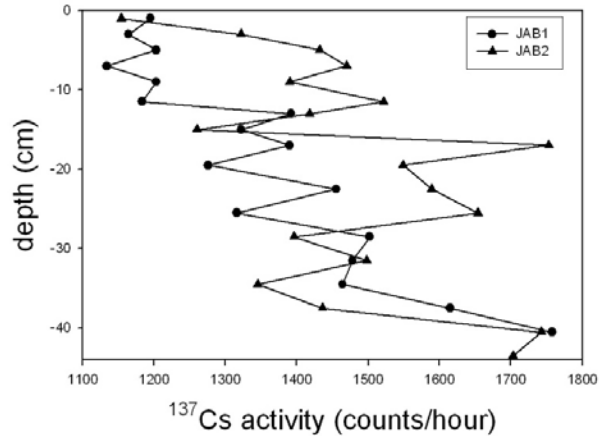
Degraded water quality in the Mississippi River and Gulf of Mexico is an ongoing problem without an easily identifiable solution. Many options are under consideration to combat nutrient loading and eutrophication, including river diversions and upstream wetlands creation. River diversions are gaining momentum in Louisiana; originally proposed to deliver sediment and freshwater to coastal wetlands, they can also function as sites of nutrient storage and transformation. The results of this dissertation indicate that the ARB is capable of removing large amounts of C, N, and P delivered by the river, and is efficient at cycling nutrients internally. It appears that the greatest barrier to removal is lack of connectivity between the river and the floodplain. While accreting sediments trap large amounts of C, N, and P, over time they impede flow between the river and the floodplain. I estimated that 48% of Atchafalaya River water leaves the channel to reach the baldcypress swamps on the floodplain. The remaining 52% has little to no contact with the floodplain, with limited opportunity to dispose of excess nutrients before discharging into the Gulf of Mexico. Creating opportunities for enhanced contact between the river and floodplain should be considered as a means of water quality improvement, but must be considered in light of possible habitat change resulting from increased sedimentation. Additional negative consequences of enhanced nutrient delivery to the floodplain could include increased algal blooms and subsequent hypoxia. Future work could incorporate these estimates into an ecosystem model to predict C, N, and P removal with the ability to adjust model parameters, such as degree of flooding, area of each habitat, forest basal area, etc. Such a model could then be used to predict the outcome of various management strategies.

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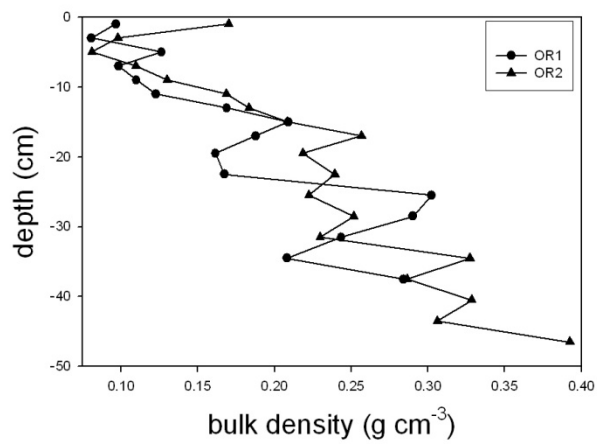
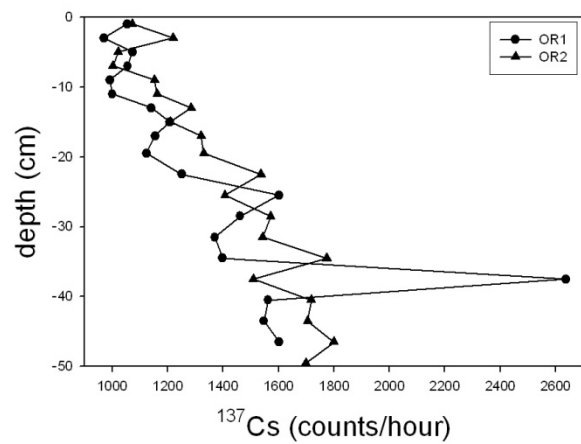
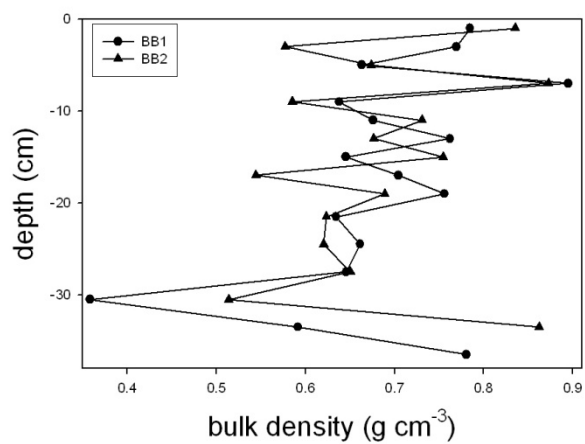
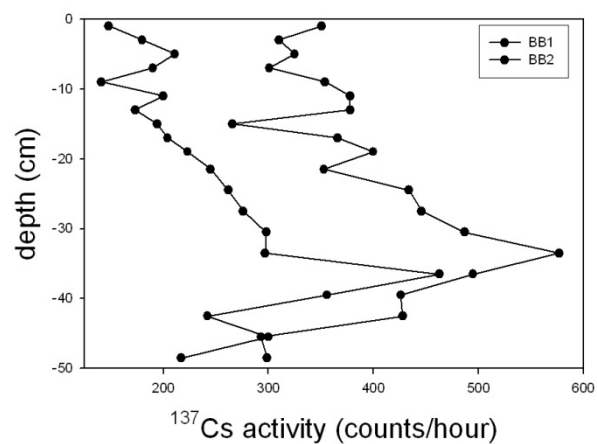
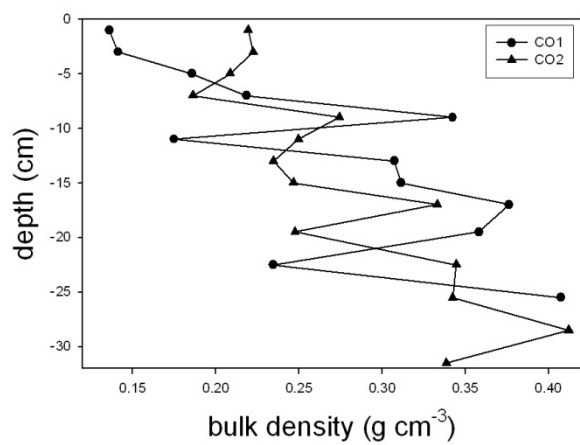
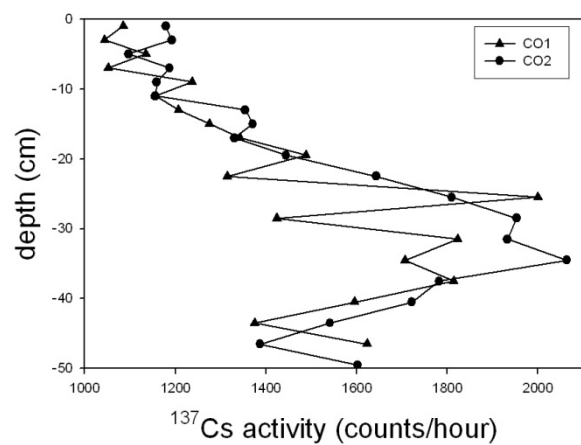
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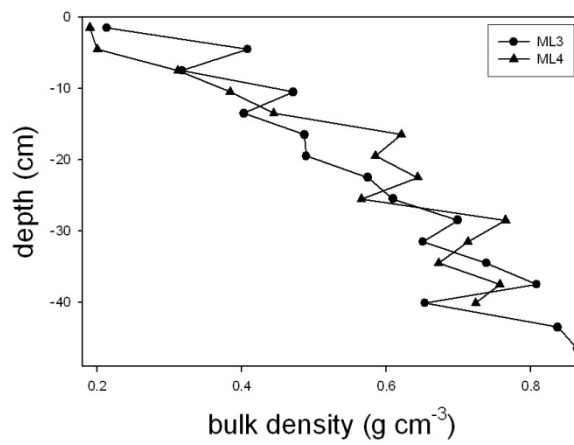
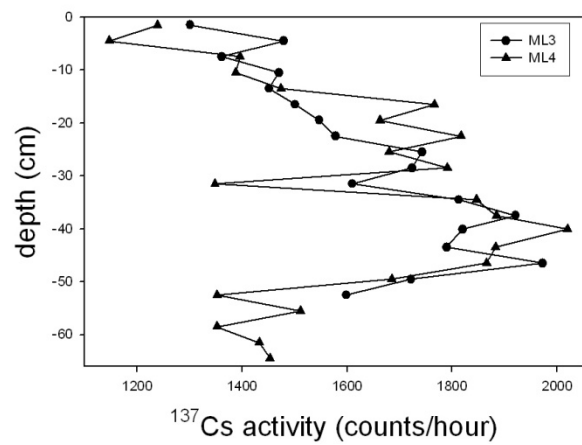
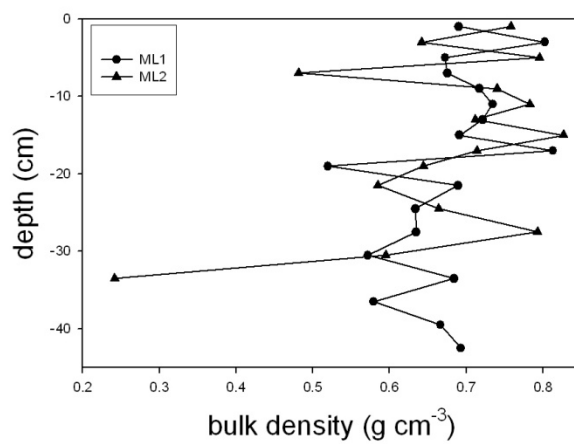
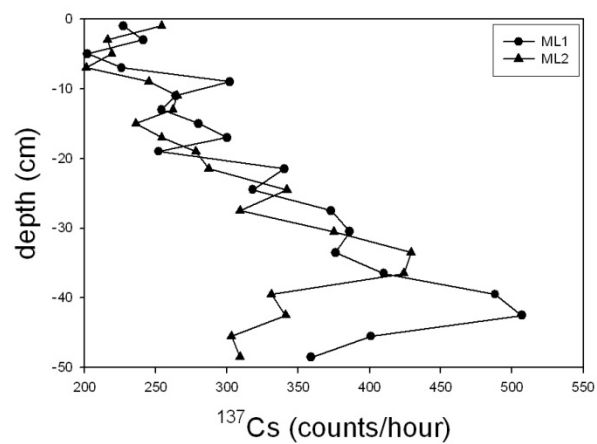
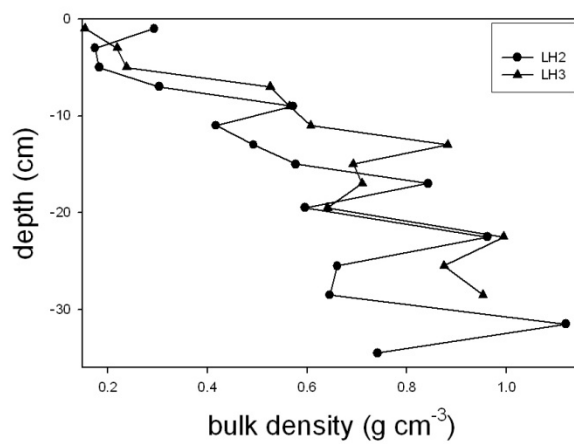
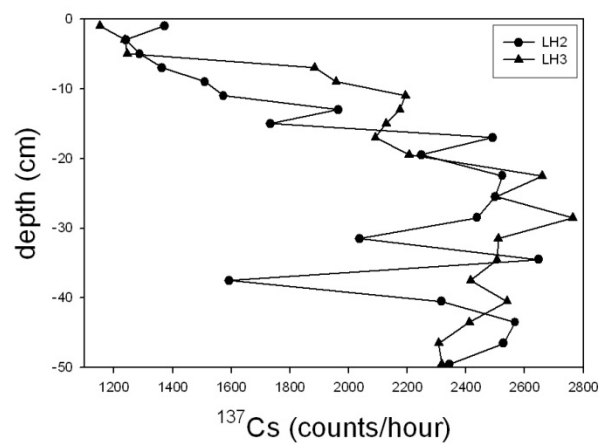
APPENDIX A: ^{137}Cs PROFILE AND BULK DENSITY RESULTS

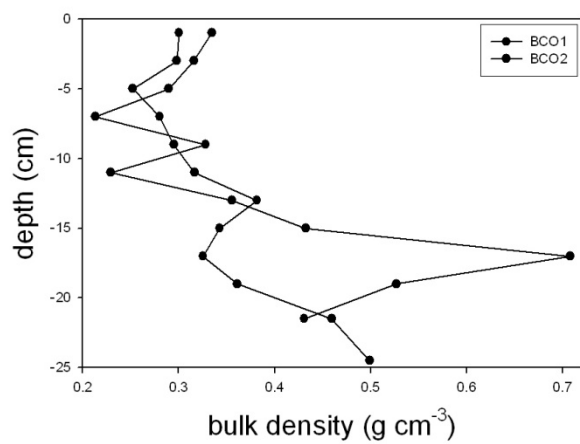
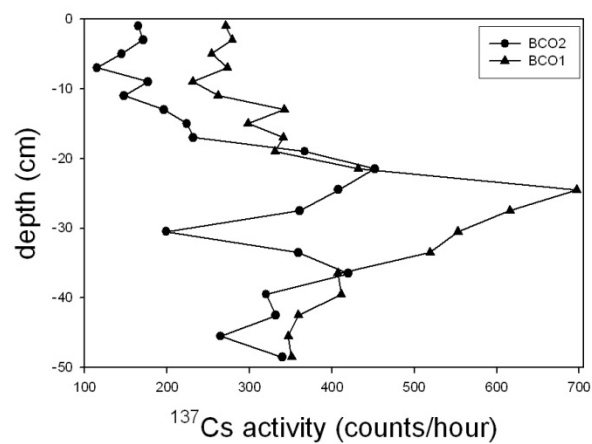
Bottomland Hardwood Sediment Cores



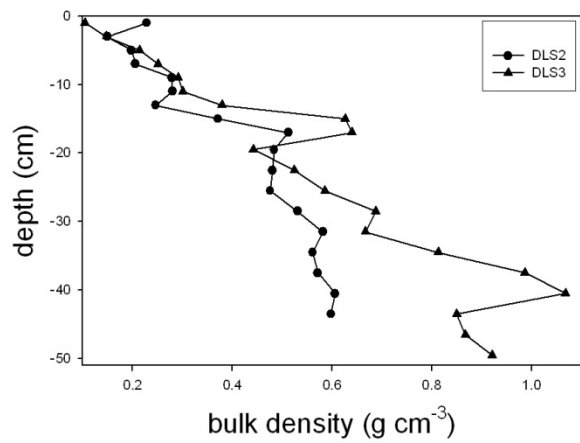
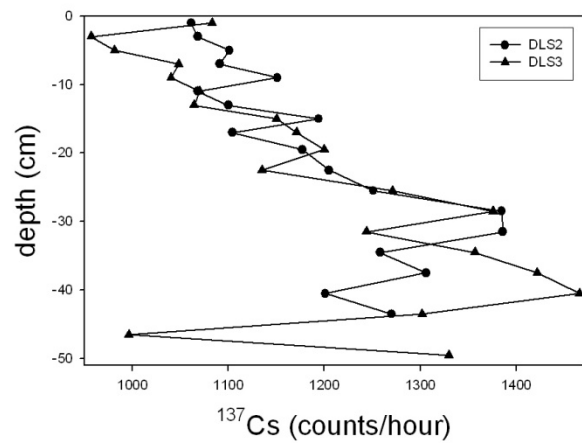
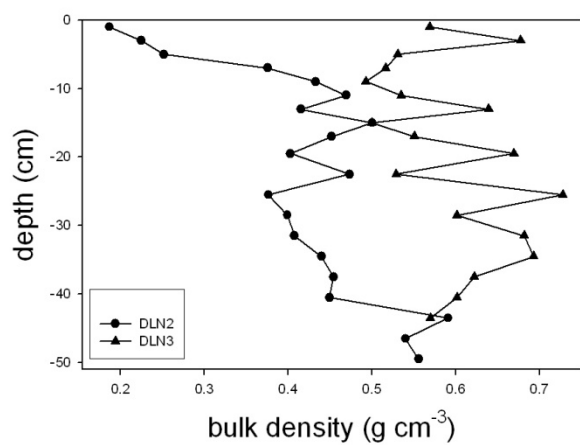
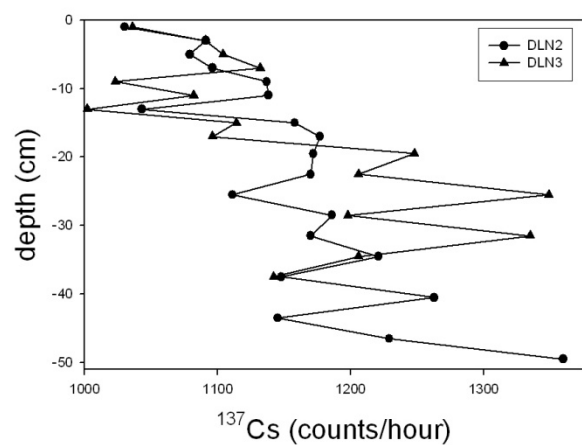
Baldcypress Sediment Cores

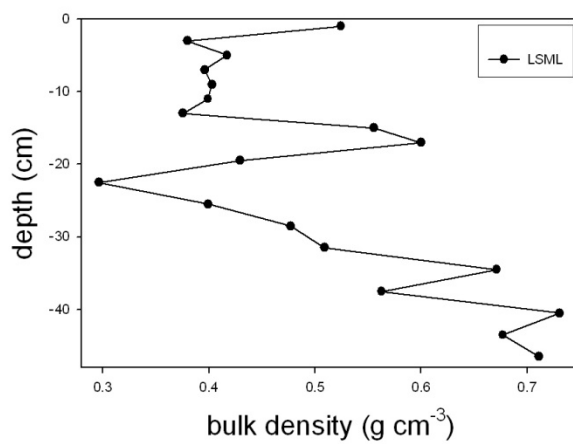
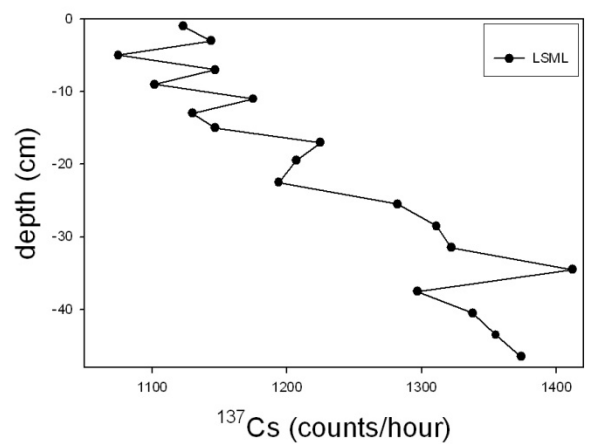
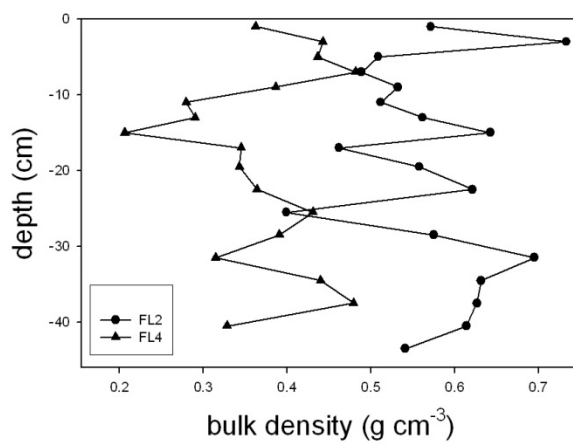
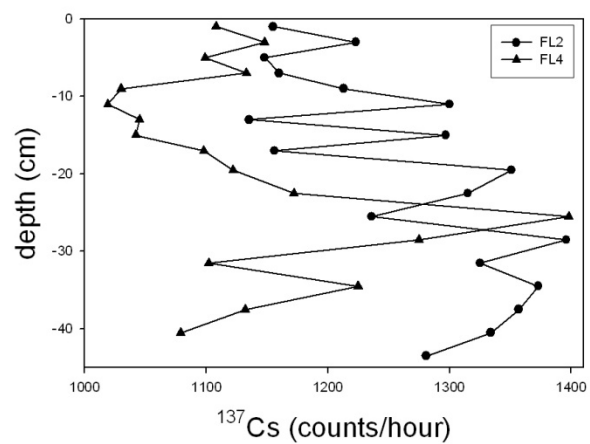






Lake Sediment Cores





APPENDIX B: PERMISSION TO REPRINT

CHAPTER 2

Scaroni AE, Lindau CW, Nyman JA (2010). Spatial Variability of Soil Denitrification across the Atchafalaya River Basin, Louisiana, USA. Wetlands 30: 949—955.

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My manuscript recently accepted by Wetlands "Spatial Variability of Soil Denitrification across the Atchafalaya River Basin, Louisiana, USA" (currently in press: DOI 10.1007/s13157-010-0091-1) is also one of the chapters of my dissertation. I am kindly requesting permission to include this manuscript in my dissertation, which will be ultimately available on the LSU Electronic Thesis and Dissertation database.

Thank you,

Amy Scaroni
PhD Candidate
Wetlands Ecology Lab
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Spatial Variability of Sediment Denitrification Across the Atchafalaya River Basin, Louisiana, USA

Amy E. Scaroni · Charles W. Lindau · John A. Nyman

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Abstract Ecosystem-wide denitrification estimates generally depend on the degree of spatial variability in the system, but spatial variability is rarely assessed. To model nitrogen removal rates in the Atchafalaya River Basin we first identified trends in background and potential denitrification across this large floodplain. We conducted a laboratory study to quantify background and potential denitrification rates. Background and potential denitrification rates were significantly different. Background rates ranged from 0–1.35 $\mu\text{gN g}^{-1} \text{d}^{-1}$ and potential rates ranged from 26.72–710.47 $\mu\text{gN g}^{-1} \text{d}^{-1}$, illustrating the existence of denitrification hotspots across the landscape. Background rates were related to soil characteristics (carbon, nitrogen, nitrate), but potential rates appeared to be related to landscape position (spatial coordinates). Background denitrification showed a strong positive correlation with soil nitrate, and a negative correlation with soil nitrogen and soil carbon. Potential denitrification rates showed no significant correlations with any parameters tested. We observed a significant relationship between location and potential denitrification rates, with greater potential downstream than upstream, but not

between location and background rates. This suggests that landscape scale studies should include additional qualifiers, such as habitat type and organic matter quality, for more reliable estimates of denitrification rates.

Keywords Acetylene block technique · Background denitrification · Nutrient removal · Potential denitrification · Wetlands

Introduction

Floodplains are frequently identified as important sites for nutrient retention and removal (Brinson et al. 1984; Craft and Casey 2000; Gergel et al. 2005; Forshay and Stanley 2005; Noe and Hupp 2009). Denitrification in particular has the potential to remove significant amounts of nitrogen (N) from floodplains, as seasonal river inundation establishes anaerobic soil conditions, delivers nitrate, and preserves carbon (C). However, these conditions vary across both large and small scales, resulting in spatial heterogeneity of soils and spatial variability of biogeochemical reactions. Aspects of spatial variability have often been neglected when studying denitrification (Pina-Ochoa and Alvarez-Cobelas 2006).

Floodplains on the Coastal Plain of the Southeastern USA often provide the last opportunity for sediment storage and biogeochemical cycling before rivers discharge into estuaries (Hupp 2000). Sediment deposition within the bottomlands of the Coastal Plain generally results in a net elevation gain (Hupp 2000). Because sedimentation facilitates nutrient sequestration, suspended sediments are usually associated with adsorbed nutrients (Hupp 2000). Hence, an intact or restored floodplain can function as a long term sink for nutrients. Conversely, when elevation gain is such that the floodplain becomes isolated from

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CHAPTER 3

Scaroni, AE, Lindau, CW, Nyman JA (2011). Comparison of Denitrification Characteristics Among Three Habitat Types of a Large River Floodplain; Atchafalaya River Basin, Louisiana, USA. *Hydrobiologia* 658: 17—25.

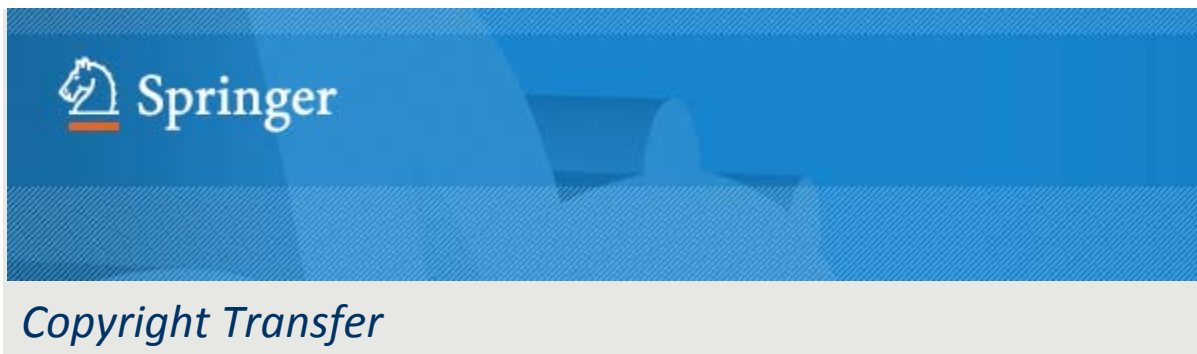
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Comparison of denitrification characteristics among three habitat types of a large river floodplain: Atchafalaya River Basin, Louisiana

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Abstract Mobile forms of nitrogen leach from upland environments into aquatic systems, often discharging to coastal zones. Addition of nitrogen to once N-limited systems results in a host of changes ranging from eutrophication to loss of biodiversity. Floodplains can ameliorate these changes by removing and sequestering nitrogen. In many coastal floodplains, sedimentation causes lakes to transition to baldcypress swamps, and ultimately to bottomland hardwood (BLHW) forests. These habitats differ in their contact with floodwater, which directly and indirectly affects their ability to process nutrients, but the effects of habitat change on denitrification at the floodplain scale cannot be predicted because of lack of suitable data. This study compared denitrification characteristics among the aforementioned habitats within the Atchafalaya River Basin (ARB). Microcosms were established in the laboratory, and the

acetylene block technique was used to estimate four denitrification characteristics: background denitrification rates, maximum rates, time to reach maximum rates, and the linear response of denitrification to nitrate concentration. There were significant differences in denitrification characteristics among the three habitat types; specifically, all habitats differed in the time required for denitrification to respond to nitrate in the overlying water, and denitrification in lake habitats differed from both BLHWs and baldcypress swamps. Landscape-scale models should account for different linear relationships between denitrification and nitrate concentrations, and different response times to nitrate concentrations for different habitats. Because denitrification characteristics differ across habitats within the ARB, continued habitat change within the floodplain will alter nutrient discharge to coastal waters.

Keywords Acetylene blockage technique · Eutrophication · Mississippi River · Nitrate removal · Succession · Wetlands

Guest editors: M. Ford & J.A. Nyman / Interactions among rivers, floodplains, and coastal areas examined at the Atchafalaya River

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Introduction

Humans have altered the nitrogen cycle in such a way that levels of reactive nitrogen released into the environment are degrading air, soil, and water quality worldwide (Kulkarni et al., 2008). Nitrogen has been

VITA

Amy Scaroni was born in the land-locked town of State College, Pennsylvania, to parents both hailing from the coast. She spent the first years of her life living in graduate housing on Penn State's campus. This, undoubtedly, prepped her from an early age for the rigorous life of a grad student. Life in "Happy Valley" was truly perfect until she discovered the ocean, and warm weather. Upon graduating from Penn State in 2002 with a bachelor of science in biology, she headed as far south as feasibly possible, to Sydney, Australia, where she could see the waves from her window. A return to the Appalachians (this time in South Carolina, then Georgia) piqued her interest in rivers, but contributed to her longing for coastal ecosystems. Several years of work as an environmental education instructor confirmed her interest in teaching, naturalizing, and most importantly, learning.

This led to a master's degree in environmental studies from the College of Charleston. Here, Amy fell in love with the lowcountry salt marsh, and decided to pursue a doctorate in wetlands ecology, that she might one day champion wetlands conservation and restoration efforts. Her doctoral experience at LSU created the perfect storm of rivers, swamps, coastal wetlands, and the ocean, not to mention a little culture and recreation on the side. Following completion of her dissertation, Amy will be moving to Washington, D.C., to work at the NOAA National Sea Grant office as a National Sea Grant College Program Dean John A. Knauss Marine Policy Fellow. She hopes to ultimately contribute her knowledge of wetland and water resources to the public health field, to ensure that all people have access to clean, safe drinking water.