

2012

Greenhouse gas emissions and nutrients dynamics in restored wetlands of the Mississippi River Basin

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GREENHOUSE GAS EMISSIONS AND NUTRIENTS DYNAMICS IN RESTORED
WETLANDS OF THE MISSISSIPPI RIVER BASIN

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 Department of Oceanography and Coastal Sciences

By
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May 2012

ACKNOWLEDGEMENTS

I wish to express my gratitude first to Dr. John W. Day, Jr., my mentor and advisor. John provided me with opportunities to excel, new avenues of exploration, and timely encouragement. I am a better scientist and person after working with John.

I wish to thank the individual members of my committee for their contributions to this work. For guidance and insight into statistical analyses, I thank Drs. Jay Geaghan and Gary Shaffer. I thank Dr. Ron DeLaune for always making time to answer my questions regarding diffusion chambers. For her instruction regarding hydrodynamics and her willingness to remain on my committee after relocating, I thank Dr. Jaye Cable. Special thanks belong to Dr. Marwa Hassan, who was willing to serve as a substitute outside committee member, and who provided helpful comments and guidance.

Many people outside of my committee assisted with this effort: Dr. Rob Lane, Matthew Moerschbaeche and Rhine Perrin provided helping hands and entertaining conversation in the field in Louisiana; University of Memphis's Dr. Reza Pezeshki and his students, including Melissa Koontz, Lyndsay Saunders, Burton Kirk, James Moore, and Samuel Pierce, served as mediators between myself and landowners at Memphis, as well as assistance in the field; Darrel Van Vickle operated the boats used during Memphis sampling; Gaynell Gibbs provided much appreciated assistance in paperwork and departmental procedures; and Dr. Syam Dodla provided his gas chromatograph for greenhouse gas analysis and assistance in flux calculations.

I wish to thank those individuals who offered stimulating exchange of ideas, camaraderie and much-needed stress relief in the form of frequent basketball games: Frank Rohwer, Richard Avent, Rob Mann, Robb Brumfield, David Chicoine, Prosanta Chakrabarty, Kenneth Rose, Rodd Naquin, Joshua Dara and A.D. Stevenson.

I wish to thank my mother, Pearl, and my brothers, Mike and Jonathan, from whom I received love and encouragement.

Finally, I wish to thank my loving wife and dearest friend Andrea, who offered patience, tolerance, support and humor when they were most needed. Thanks to my two young sons, Liam and Finn, who offered hugs and laughs in abundance. My family serves as my daily source of inspiration, and I thank them.

PREFACE

This dissertation details the results of research investigating greenhouse gas emissions and nutrient dynamics in wetlands restored with the purpose of reducing nitrogen loading from the Mississippi Basin that fuels coastal eutrophication in the Gulf of Mexico. This introductory chapter provides background information on wetland loss, coastal eutrophication and greenhouse gas emissions in wetlands and outlines the objectives of this research. Chapter 2 compares the greenhouse gas emissions of two different restored wetlands within the Mississippi River Basin (MRB): a riparian wetland under restored flood pulsing at Memphis, Tennessee, and a river diversion wetland located at Caernarvon in coastal Louisiana. Chapter 3 describes the nutrient dynamics of the restored riparian wetland, as well as the adjacent Loosahatchie Chute, which is a secondary shipping channel at Memphis. Chapter 4 details the analysis of a multi-year dataset of water quality sampling within the Breton Sound estuary, which receives freshwater input from the Mississippi River via the Caernarvon river diversion control structure. Results and conclusions from previous chapters are summarized in Chapter 5. The data from Chapter 4 represents the synthesis and analysis of data from several studies, whereas the research from Chapters 2 and 3 were undertaken as part of a larger collaborative effort to study the effects of reducing nutrient loading to the Gulf of Mexico. The research presented herein represents a portion of a larger research effort investigating the effects of using wetlands for reducing nutrient export to the northern Gulf of Mexico. The overall effort involves greenhouse gas and water quality sampling at the Olentangy River Wetland Research Park in Ohio, USA in addition to Caernarvon, LA and Memphis, TN.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
PREFACE.....	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	viii
 1 INTRODUCTION: GREENHOUSE GAS EMISSIONS AND NUTRIENTS IN THE MISSISSIPPI RIVER BASIN	 1
Introduction	1
Study Areas	5
Objectives	7
Literature Cited	7
 2 GREENHOUSE GAS EMISSIONS IN RESTORED WETLANDS AT FLOODPLAIN AND DELTAIC SITES IN THE MISSISSIPPI RIVER BASIN	 15
Introduction	15
Study Areas	17
Methods	20
Results.....	21
Discussion	29
Literature Cited	33
 3 SPATIAL AND TEMPORAL VARIATIONS IN NUTRIENTS AND WATER QUALITY PARAMETERS IN THE DIVERSION-IMPACTED BRETON SOUND ESTUARY	 48
Introduction	48
Study Areas	49
Methods	49
Results.....	52
Discussion	63
Literature Cited	65
 4 NUTRIENT LOADING RATES AND REMOVAL EFFICIENCY IN RIPARIAN WETLANDS UNDER RESTORED HYDROLOGY	 69
Introduction	69
Study Areas	70
Methods	71
Results.....	72

Discussion	75
Literature Cited	82
5 SUMMARY AND CONCLUSIONS	97
Objectives	97
Greenhouse Gas Fluxes	97
Nutrient Concentrations and Removal Efficiency.....	98
APPENDIX: PERMISSION TO USE COPYRIGHTED CONTENT	100
VITA	105

LIST OF TABLES

2.1 Literature values for wetland methane fluxes	32
2.2 Literature values for wetland nitrous oxide fluxes	33
3.1 Pearson correlation coefficients for water quality parameters.....	54
3.2 Nitrate loading rate and removal efficiency adjusted for mixing with saline Gulf waters.....	62
3.3 Nitrate removal efficiency at varying distances from the diversion	62
4.1 Loading rate and removal efficiency of nutrients sampled at Loosahatchie Chute	79
4.2 Seasonal mean loading rate and removal efficiency of nitrate sampled at Caernarvon	80
4.3 Mean loading rate and removal efficiency of nitrate in upper and lower Caernarvon.....	80
4.4 Mean loading rate and removal efficiency of nitrate at high and low discharge	80

LIST OF FIGURES

1.1 Aerial images of the study areas	6
2.1 Greenhouse gas sampling sites at Caernarvon, LA.....	19
2.2 Greenhouse gas sampling sites at Memphis, TN	20
2.3 Gage stage at Caernarvon during the study period	24
2.4 Discharge at Caernarvon during the study period	24
2.5 River stage at Memphis during the study period	25
2.6 Mean CH ₄ and CO ₂ fluxes	26
2.7 Seasonal differences of mean CH ₄ and CO ₂ fluxes	27
2.8 Site-specific differences in CH ₄ and CO ₂ fluxes	28
2.9 Fluxes of CH ₄ and CO ₂ with variations in water depth.....	29
3.1 Water quality sampling sites in Breton Sound, LA.....	52
3.2 Instantaneous daily discharge at the Caernarvon river diversion	54
3.3 Seasonal variation in mean concentrations of water quality parameters.....	55
3.4 Relationship between N- and P-containing water quality parameters and distance	56
3.5 Relationship between SiO ₄ , CHLa, salinity and TSS and distance.....	57
3.6 Concentrations of NO _x , PO ₄ , NH ₄ , TP and TN in relation to discharge	58
3.7 Concentrations of SiO ₄ , CHLa, TSS and salinity in relation to discharge	59
3.8 Salinity mixing diagrams	60
3.9 Relationship between nitrate loading rate and removal efficiency in the Breton Sound	63
4.1 Water sampling transects at Loosahatchie Chute.....	74
4.2 Mississippi River stage at Memphis, TN.....	75
4.3 Mean seasonal concentrations of NO _x , NH ₄ , TN, PO ₄ , TP, SiO ₄ , DO and chl <i>a</i>	78
4.4 Nitrate loading rate and removal efficiency at two locations	82
4.5 Variations in nitrate loading rate-removal relationship.....	83

ABSTRACT

Greenhouse gases were sampled during spring and summer months in 2010 and 2011 at two sites in the Mississippi River Basin: a riparian forested wetland under restored flood pulsing near Memphis, TN and a coastal estuarine marsh complex impacted by a river diversion at Caernarvon, LA. Mean methane fluxes at Caernarvon ($-0.09 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$) were lower than those at Memphis ($0.53 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$), and did not differ between seasons. Nitrous oxide fluxes were generally below detection limits. Fluxes were uncorrelated with water depth, soil temperature, and ambient air temperature, though sampling occurred over a narrow range of these variables due to limitations in site accessibility.

A water quality dataset spanning 8 years of monthly sampling was analyzed to determine long-term spatial and temporal patterns in nutrient concentrations at Caernarvon. The estuary served as a source of ammonium, and chlorophyll *a* and a sink for nitrate, total nitrogen and total suspended sediments. Classification of the estuary as a source or sink for phosphate, total phosphorus and silicate changed with the seasons. Nitrate removal efficiency varied seasonally, with efficiency highest in the fall (98%), summer (92%) and spring (87%) and lowest in the winter (74%). Removal efficiency was inversely related to loading rate.

Water quality samples were collected at Memphis in a secondary channel of the Mississippi River under restored hydrology during spring and summer 2010-2011. Seasonal variations existed in concentrations of nitrate, total nitrogen, total phosphorus and total suspended solids, but not ammonium, phosphate, silicate, dissolved oxygen and chlorophyll *a*. No parameters varied longitudinally or laterally within the channel. Nitrate loading rate was high and removal efficiency was low, especially in comparison with Caernarvon and other study sites within the Mississippi River Basin, due to the limited size of the receiving wetland.

CHAPTER 1

INTRODUCTION: GREENHOUSE GAS EMISSIONS AND NUTRIENTS IN THE MISSISSIPPI RIVER BASIN

Introduction

The Mississippi River drainage basin covers an area of 3.22 million km², representing nearly 40% of the continental United States. The Mississippi River flows southward from its origin at Lake Itasca, Minnesota and empties into the Gulf of Mexico south of New Orleans, Louisiana. Major tributaries include the Ohio, Missouri, Arkansas and Red Rivers, among which the Ohio provides the most freshwater input and the Missouri provides the most sediment input (Turner & Rabalais, 2004). The Mississippi River Basin (MRB) covers most of the area between the Rocky Mountains in the west and Appalachian Mountains to the east, and accounts for 90% of the freshwater input to the northern Gulf of Mexico (Rabalais et al., 1996).

The MRB alluvial and deltaic wetlands have been described as under the most anthropogenic disturbance among the world's largest wetland systems (Keddy et al., 2009). Clear-cutting of bottomland hardwood forests in the MRB for timber and agricultural use began shortly after the arrival of American settlers from east of the Appalachians during the 1850s (Turner & Rabalais, 2003). Wetland loss continued in the MRB, due primarily to agricultural development (Hefner & Brown, 1984; Wilen & Frayer, 1990). During the 20th century, approximately 30 million ha of land within the upper MRB were drained, primarily for agricultural use (Mitsch et al., 2001).

Wetland loss also has occurred in the MRB deltaic wetlands on a large scale. The lower Mississippi River experienced episodic delta switching during the Holocene, which led to delta formation over the last 6000-7000 years as a result of the depositional activities at overlapping deltaic lobes (Roberts, 1997). There was a net increase in wetland area in the Mississippi River deltaic plain (MRDP) during that time, though localized wetland loss occurred within abandoned delta lobes. Deltaic wetlands were enhanced and stabilized by sediment input from seasonal river floods, hurricanes, tides and delta switching (Day et al., 2000). The trend of wetland growth continued until the beginning of the 20th century, after which large-scale wetland loss commenced, resulting in a loss of over 4500 km² of deltaic wetlands (Barras et al., 2003), with loss rates reaching over 100 km² per year from 1956-1978 (Barras et al., 2008). This reversal in trend is due to a number of natural and anthropogenic factors.

After extensive levee construction on the Mississippi River prevented seasonal floods, isolating the delta wetlands from its primary source of sediment, eustatic sea level rise and subsidence began to outpace delta-building processes in the Mississippi deltaic plain (Day et al., 2000). Additionally, all but two Mississippi River distributaries (the lower Mississippi River and the Atchafalaya River, which receives 30% of the main channel flow) were closed and the main channel was dredged to enhance navigation, enhancing loss of riverine sediments to the Gulf of Mexico. Dam construction within the MRB during the mid 20th century resulted in a 50%

reduction in sediment load (Blum & Roberts, 2009). This isolation of the wetlands from their primary source of sediment prohibited the accretion that historically offset subsidence. Subsidence is a complex process of sediment compaction resulting in decreased elevation (Yuill et al., 2009) and is occurring at a high rate ($> 10 \text{ mm yr}^{-1}$) in coastal Louisiana (Tornqvist et al., 2008). Over the past century, the aggradation rate of the Mississippi deltaic plain has decreased from 2.0 to 0.3 mm yr^{-1} , which represents an 85% decrease in sediment input (Syvitski et al., 2009). Additionally, altered hydrology due to canal construction, especially for the petroleum industry, has contributed to deltaic wetland loss. Canal construction is a major cause of wetland loss in coastal Louisiana, especially in conjunction with other factors (Day et al., 2000).

Since the 1950s, nitrate export to the Gulf of Mexico in the Mississippi River has doubled to nearly one million tonnes (t) per year and concentrations have doubled to $1.45 \text{ g N liter}^{-1}$ (Goolsby & Battaglin, 2001). This increase is a result of increased fertilizer application, an increase in surface water runoff and an expansion in soybean and corn production (Howarth et al., 2002; Donner et al., 2004; Zhang & Schilling, 2006), as well as domestic wastewater discharge and surface runoff from agricultural feedlots (Mitsch et al., 2001). Within the Basin, nitrogen fertilizer use has increased seven-fold (Goolsby et al., 2000). Additionally, the construction of artificial levees prevented seasonal flooding in the Mississippi River alluvial floodplain and delta, isolating the river from its floodplain wetlands, which serve as nitrogen sinks (Day et al., 2000; Day et al., 2003b). By preventing riverine floodwaters from reaching wetlands or reducing the retention time of surface water in wetlands, an important sink for nitrate has been minimized. The elevated riverine nitrate levels have resulted in increasing extent and severity of hypoxic zones in the Gulf.

Hypoxic zones, or low-oxygen conditions in bottom waters of the Gulf of Mexico on the continental shelf off the Louisiana coast, began occurring in isolated areas early in the 20th century, though large seasonal hypoxic zones began by the 1960s (Osterman et al., 2009). Hypoxic zones typically form when high nutrient loads from freshwater inputs fuel large phytoplankton blooms. Decomposition of the resulting organic matter depletes bottom water of oxygen, and the strength of the pycnocline during stratification prevents the downward diffusion of oxygen from the well-mixed surface layer. The extent of the hypoxic zone at times may exceed $20,000 \text{ km}^2$ (Turner et al., 2008). Factors influencing the severity and extent of this “dead zone” are numerous and complex (Bianchi et al., 2010), but the link between nitrate export in the MRB and phytoplankton productivity in the Gulf is well-established (Justic et al., 1995; Rabalais et al., 1996; Rabalais et al., 2002a; Lohrenz et al., 2008).

Wetland restoration efforts and changes in agricultural practices are required to reduce the severity and extent of hypoxia in the Gulf (Mitsch et al., 2001). From 1968 to 1998, a 12% reduction in fertilizer application would have reduced the nitrate flux in the Mississippi River while having minimal impact on agricultural yields (McIsaac et al., 2001). Wetlands have been shown to effectively remove nutrients and ameliorate water quality (Kadlec & Wallace, 2008). Reducing the nitrogen export to the Gulf requires the creation and restoration of riparian

wetlands to intercept agricultural runoff and river diversions that divert nutrient-rich flood waters to wetlands (Mitsch et al., 2001; Mitsch & Day, 2006).

Several river diversions are currently operating in the MRDP with the goal of promoting wetland development and regeneration. River diversions in the MRDP have been shown to effectively promote vertical accretion and marsh development (DeLaune et al., 2003; Lane et al., 2006), which may minimize damage from hurricanes and other storms, as wetlands provide buffers for wind and storm surge activity (Day et al., 2007), though there is evidence that diversions may make wetlands more susceptible to erosion (Howes et al., 2010). Diversions also have been shown to be effective sinks for riverine nutrients and sediments (Lane et al., 1999; Lane et al., 2001; Lane et al., 2007). River diversions are therefore considered a partial solution to Gulf eutrophication and coastal wetland loss. However, there has been concern expressed over the potential of river diversions, and wetland restoration in general, to increase greenhouse gas production in wetlands, which would exacerbate global climate change (Freeman et al., 1997; Bridgham et al., 2006).

Global climate change has been described as one of the most severe threats facing human society today (King, 2004). The mean global surface temperature has risen by 0.74° C from 1906 to 2005 (Trenberth et al., 2007). Mean global surface temperature is positively correlated with the concentration of atmospheric greenhouse gases. Since the Industrial Revolution, the concentrations of three of the main greenhouse gases (GHGs) – carbon dioxide, methane and nitrous oxide – have increased significantly when compared to previous centuries (Forster et al., 2007). Anthropogenic sources of GHGs include fossil fuel consumption, land-use change, and agriculture. Effects of climate change on ecological systems already have been observed, including shifts in distributions of terrestrial (Parmesan & Yohe, 2003; Karban & Strauss, 2004; Thomas, 2010) and marine (Perry et al., 2005; Dulvy et al., 2008) species, accelerated sea-level rise (Trenberth et al., 2007), decreases in glacial coverage (Kaser et al., 2004), local decreases in species richness (Wilson et al., 2007), coral bleaching (McWilliams et al., 2005), and altered migratory behavior. Additionally, climate change has negatively impacted human health (McMichael et al., 2006) and is expected to adversely affect the global economy. Technologies and practices that decrease the amount of greenhouse gases to the atmosphere and maximize carbon removal are needed to minimize the future effects of climate change.

Depending on water, soil and other environmental conditions, wetlands may serve as a source or sink for greenhouse gases. Oxygen diffusion in wetland soils decreases as pore space is filled with water. Once oxygen is depleted, the microbial community must utilize alternate terminal electron acceptors (ATEAs) for respiration. The main ATEAs include nitrate (NO_3^-), manganese dioxide (MnO_2), iron (III) oxide (Fe_2O_3), sulfate (SO_4^{2-}) and carbon dioxide (CO_2). These alternate electron acceptors are sequentially reduced by the anaerobic microbial community (Ponnamperuma, 1972), and yield sequentially less energy per mole of organic matter oxidized relative to oxygen (Reddy & DeLaune, 2008). This results in decreased efficiency and rates of

decomposition in anaerobic soils, causing organic matter to accumulate in wetlands, sequestering carbon that would otherwise undergo respiration and be emitted to the atmosphere as CO₂.

However, wetlands also may emit greenhouse gases. In strongly-reducing soils, CO₂, carbonate (CO₃²⁻) or bicarbonate (HCO₃⁻) may be reduced to methane (CH₄) as organic matter is oxidized anaerobically (Ponnamperuma, 1972). Once produced in flooded soils, CH₄ may be oxidized by methanotrophic bacteria or emitted into the atmosphere by diffusion, by ebullition, or by exchange via aerenchyma – air spaces in root and shoot structures of flood-adapted vascular plants (Schutz et al., 1991). Under aerobic conditions, methanotrophy has the potential to consume most of the methane produced in wetlands (Boon & Lee, 1997). Greenhouse gas transport has been observed in both herbaceous and woody wetland plants (Sebacher et al., 1985; Rusch & Rennenberg, 1998). Methane has a lifetime of 12 years in the atmosphere, after which it is oxidized with hydroxyl radicals. Methane's global warming potential (GWP), which is a measure of how much heat a given GHG traps in the atmosphere relative to CO₂, is 25 over a 100-year period (Forster et al., 2007), indicating that a given amount of CH₄ will trap 25 times more heat than the same amount of CO₂ over a 100-year period.

Wetlands also may emit another greenhouse gas, nitrous oxide. Nitrous oxide (N₂O) may be emitted as a product of denitrification. Under anaerobic conditions, NO₃⁻ is utilized as an ATEA for denitrifying bacteria that results in the gaseous end product nitrogen gas (N₂). Nitrous oxide is an intermediate in denitrification (Firestone et al., 1980), though transformation to N₂ may not be complete. The average ratio of N₂ to N₂O produced has been estimated at 22 to 1 (Schlesinger, 1997), though this varies depending on residence time of N₂O in the soil. Nitrous oxide may also be produced as a by-product of nitrification. Nitrification is a two-step biological process by which *Nitrosomonas* bacteria species convert ammonium (NH₄) to nitrite (NO₂⁻), which is converted to NO₃⁻ by *Nitrobacter* species. Unlike denitrification, nitrification requires oxygen and thus occurs in the aerobic water column and aerobic-anaerobic soil interface, as well as in oxidized root zones of wetland plants. Once produced, N₂O diffuses upward into the atmosphere, sometimes through aerenchyma (Reddy et al., 1989). Nitrous oxide has a lifetime of 114 years and a GWP of 298 over a 100-year period, due to its high relative heat absorption (Forster et al., 2007). The fate of atmospheric N₂O is photolysis, or photodegradation.

The production and consumption of greenhouse gases in the soil is dependent on various edaphic, hydrologic and biological factors (Smith et al., 2003). Nitrous oxide emissions generally increase in response to flooding (Kasimir-Klmedtsson et al., 1997; Hernandez & Mitsch, 2006), whereas draining wetlands may result in up to a 95% decrease in N₂O emissions (Freeman et al., 1997). Likewise, CH₄ emissions may be inhibited under a pulsing hydrologic regime relative to a steady-state hydrology (Altor & Mitsch, 2006). Methane production has been shown to be inhibited by NO₃⁻ addition, due to the increase in redox potential (Jugsujinda et al., 1995), whereas NO₃⁻ addition increases the proportion N₂O: N₂ (Firestone et al., 1980). Yu et al. (2001) suggest that both N₂O and CH₄ can be minimized through management practices that maintain redox values between +120 and -170 mV. The presence of other ATEAs,

especially sulfate, inhibits CH₄ emissions (Crozier & DeLaune, 1996). The presence of vegetation also effects N₂O emissions in wetlands, with vegetated soil emitting more N₂O than non-vegetated soil, likely due to increased gas transport through aerenchyma tissue under inundated conditions (Hernandez & Mitsch, 2006). Biological factors that may influence wetland GHG emissions include plant and microbial community composition, above- and belowground macrophyte biomass, functional group richness and net primary productivity (Wang et al., 2008; Andrews et al., 2010; Nahlik & Mitsch, 2010; Sutton-Grier & Megonigal, 2011).

The purpose of this study is to determine the effects of reintroduction of riverine water to riparian wetlands, via river diversions or restored hydrology, on greenhouse gas production and nutrient dynamics. This study is part of a larger proposal investigating nutrient dynamics and greenhouse gas production in wetlands within the upper, central and lower Mississippi River Basin. This study focuses on the latter two locations, with a riparian wetland near Memphis, TN representing the central MRB wetlands and the Caernarvon river diversion wetlands of southeast coast Louisiana representing the lower MRB wetlands. Studies at Ohio State University investigated wetlands in the upper MRB.

Study Areas

The Caernarvon freshwater diversion is located on the Mississippi River at river mile 81.5, south of New Orleans in St. Bernard Parish, Louisiana, USA. The control structure is a five-box culvert with vertical lift gates for managed flow. The diversion has been in operation since August 1991. Since discharge began, the control structure has discharged into the Breton Sound estuary, which contains 1100 km² of fresh, brackish and saline marshes. Breton Sound has an open connection to the Gulf of Mexico, and is bounded by the Mississippi River levee to the west, the natural levees of Bayou La Loutre to the north, and the spoil banks of the Mississippi River Gulf Outlet to the east. Wetlands within the Breton Sound were originally formed as part of the Plaquemines-St. Bernard delta lobes (Roberts, 1997). During the recent past, approximately half of the original wetlands have been lost due to subsidence and shoreline erosion (Penland et al., 1988). More detailed descriptions of this area can be found in Day et al. (2009b) and Lane et al (2007).

The Loosahatchie Chute is located on the west bank of the Mississippi River in Crittenden county, Arkansas, USA across from Memphis, Tennessee between river miles 736.5 and 742.8. In the 1960s, the U.S. Army Corps of Engineers (USACE) constructed stone dikes measuring between 100 and 600 meters wide to divert flow from the Mississippi River away from the Loosahatchie Bar secondary shipping channel during periods of low flow. To restore hydrology in the Loosahatchie chute, twelve USACE –designed notches were constructed in nine existing dikes in 2008 according to the specification of the Lower Mississippi River Conservation Committee (LMRCC). Each notch measures 7.5-65 meters wide. These notches allow riverine water to flow into the Loosahatchie chute during periods of high flow. This effort was funded by



Figure 1.1: Aerial images of the study areas: the Caernarvon river diversion wetland in coastal Louisiana (top) and the Loosahatchie chute, a secondary channel located on the Mississippi River near Memphis, TN (bottom). Images are shown on the same scale to show the difference in spatial scales of the study areas. The box indicates the study area at the Memphis site.

the US Fish and Wildlife Service Fish Passage Program, Audubon Society and non-governmental conservation organizations to restore flow to habitats of two federally listed species (pallid sturgeon and least tern), as well as other wildlife.

The two study sites operate on different spatial scales (Figure 1.1). Riverine water moving through the Caernarvon study area travels approximately 39 km, whereas riverine water moving through the Loosahatchie chute travels approximately 5.6 km. This difference in scale is important to consider when interpreting the results of these studies.

Objectives

These restoration projects offer an opportunity to investigate how managing wetlands for nutrient reduction will affect greenhouse gas emissions. Specifically, this research will address the following:

- 1) How are methane and nitrous oxide emissions related to nutrient input in restored wetlands, and how do these emissions differ between riparian and coastal wetlands within the Mississippi River Basin? What are the spatial and temporal patterns of emissions in each site?
- 2) What are the long-term spatial and temporal nutrient patterns within the Breton Sound estuary? What are the nutrient uptake-loading relationships?
- 3) What are the nutrient dynamics within the Loosahatchie chute and its adjacent wetlands during flood pulsing?

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CHAPTER 2

GREENHOUSE GAS EMISSIONS IN RESTORED WETLANDS AT FLOODPLAIN AND DELTAIC SITES IN THE MISSISSIPPI RIVER BASIN

Introduction

The Mississippi River drainage basin encompasses 3.22 million km², representing over 40% of the contiguous United States. The Mississippi River accounts for over 90% of the freshwater input to the northern Gulf of Mexico (Rabalais et al., 1996) and is one of the world's most altered large rivers (Keddy et al., 2009). The upper basin experienced large-scale riparian wetland loss during the 20th century, primarily due to forest clearing and agricultural development (Hefner & Brown, 1984; Wilen & Frayer, 1990; Mitsch et al., 2001). Deltaic wetlands have also been lost on a large scale, with 4500km² lost during the 20th century (Barras et al., 2003). Eustatic sea level rise and subsidence began to outpace delta-building processes after extensive levee construction on the Mississippi River prevented seasonal floods (Day et al., 2000). The construction of upriver dams, levees along much of the lower river below Cairo IL, and the closing of coastal distributaries have further isolated floodplain and deltaic wetlands from sources of sediment. Without this sediment supply, coastal wetlands have been unable to offset the high rates of subsidence of up to 10 mm yr⁻¹ experienced in coastal Louisiana (Tornqvist et al., 2008).

Elevated nitrate levels in the Mississippi River resulted in increased severity and extent of hypoxia in the Gulf of Mexico. Hypoxic zones are areas of low oxygen conditions (<2 mg/l) in marine bottom waters. These hypoxic zones form when high nutrient loads from freshwater inputs fuel large phytoplankton blooms, and the decomposition of the resultant organic matter depletes bottom water of oxygen. The strength of the pycnocline during stratification prevents the downward diffusion of oxygen from the well-mixed surface layer. Large seasonal hypoxic zones began appearing on the continental shelf in the Gulf of Mexico in the 1960s (Osterman et al., 2009), coinciding with increased riverine nitrogen loads (Howarth et al., 2002; Donner et al., 2004). The extent of the hypoxic zone at times may exceed 20,000 km² (Turner et al., 2008). Factors influencing the severity and extent of this “dead zone” are numerous and complex (Bianchi et al., 2010), but the link between nitrate export in the Mississippi River Basin (MRB) and phytoplankton productivity in the Gulf is well-established (Justic et al., 1995; Rabalais et al., 1996; Rabalais et al., 2002a; Lohrenz et al., 2008).

Riverine nitrate export to the Gulf of Mexico has doubled since the 1950s due to increased fertilizer application, an increase in surface water runoff, and an expansion in soybean and corn production (Howarth et al., 2002; Donner et al., 2004; Zhang & Schilling, 2006), as well as domestic wastewater discharge and surface runoff from agricultural feedlots (Mitsch et al., 2001). Within the MRB, nitrogen fertilizer use has increased seven-fold since the 1950s (Goolsby et al., 2000). Additionally, artificial levee construction has prevented seasonal

flooding of the Mississippi River floodplain and deltaic wetlands, which serve as sinks for nitrogen (Day et al., 2000; Day et al., 2003b). By preventing riverine floodwaters from reaching wetlands or reducing the retention time of surface water in wetlands, an important sink for nitrate has been reduced. Wetland restoration efforts, as well as changes in agricultural practices, are required to reduce the severity and extent of hypoxia in the Gulf of Mexico (Mitsch et al., 2001). Reducing the nitrogen export to the Gulf can be accomplished by the creation and restoration of riparian wetlands to intercept agricultural runoff and river diversions to direct nutrient-rich flood waters to coastal wetlands (Mitsch et al., 2001; Mitsch & Day, 2006).

Concern exists over the potential of river diversions, and other wetland restoration techniques, to increase greenhouse gas emissions from wetlands, which would exacerbate global climate change (Freeman et al., 1997; Bridgham et al., 2006). Depending on climatic, hydrologic, and edaphic conditions, wetlands may serve as sources or sinks for specific greenhouse gases (Phillips & Beerli, 2008; Kayranli et al., 2010). Wetlands sequester carbon through the burial of organic matter under anaerobic conditions (Chmura et al., 2003; Mitra et al., 2005). Wetlands behave as greenhouse gas sources when nitrous oxide (N_2O) and methane (CH_4) are emitted (Whiting & Chanton, 2001). In strongly-reducing soils, CO_2 , carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-) may be reduced to CH_4 as organic matter is oxidized (Ponnamperuma, 1972). Once produced, CH_4 can be utilized by methanotrophs or emitted to the atmosphere via ebullition, diffusion at the water-atmosphere interface or exchange via aerenchyma tissue in some wetland macrophytes (Schutz et al., 1991). Nitrous oxide is produced as an intermediate end-product of denitrification and as a by-product of nitrification (Reddy & DeLaune, 2008). Transformation of the intermediate N_2O to nitrogen gas (N_2) during denitrification may be incomplete, though the ratio of N_2 to N_2O produced has been estimated at 22 to 1 (Schlesinger, 1997) and can decrease with increases in nitrate concentration and pH, and decreases in soil water content and available organic C (Weier et al., 1993; Cuhel et al., 2010). Once produced, N_2O diffuses upward through the water column into the atmosphere, sometimes through aerenchyma tissue (Reddy et al., 1989).

The flux of greenhouse gases in the soil is dependent on various edaphic, hydrologic and biological factors (Smith et al., 2003). Total nitrous oxide emissions generally increase in response to flooding (Kasimir-Klemetsson et al., 1997; Hernandez & Mitsch, 2006), nitrate addition (Firestone et al., 1980), and the presence of vegetation (Hernandez & Mitsch, 2006). Methane emissions are inhibited by a pulsing hydrologic regime (Altor & Mitsch, 2006), nitrate addition (Jugsujinda et al., 1995) and the presence of other alternate electron acceptors such as SO_4 (Crozier & DeLaune, 1996). Biological factors that influence wetland N_2O and CH_4 emissions include plant and microbial community composition, above- and belowground macrophyte biomass, functional group richness and net primary productivity (Wang et al., 2008; Andrews et al., 2010; Nahlik & Mitsch, 2010; Sutton-Grier & Megonigal, 2011).

The purpose of this study is to determine the effects of reintroduction of riverine water to wetlands, via river diversions or restored hydrology, on greenhouse gas production. This study

was part of a larger project investigating nutrient dynamics and greenhouse gas production in wetlands within the upper, central, and lower MRB. This study focuses on the latter two locations, with a riparian wetland near Memphis, TN representing the central MRB wetlands and the Caernarvon river diversion wetlands of southeast coastal Louisiana representing the lower MRB deltaic wetlands.

Study Areas

The Caernarvon freshwater diversion is located on the Mississippi River at river mile 81.5, south of New Orleans in St. Bernard Parish, Louisiana, USA (Fig. 2.1). The diversion has been in operation since August 1991, discharging into the upper Breton Sound estuary, which contains about 1100 km² of fresh, brackish and saline marshes (Lane et al., 1999; Lane et al., 2006). Breton Sound has an open connection to the Gulf of Mexico, and is bounded by the Mississippi River levee to the west, the natural levees of Bayou La Loutre to the north, and the spoil banks of the Mississippi River Gulf Outlet to the east. Three experimental study sites were established within Breton Sound at distances near, intermediate (mid) and far from the diversion structure. The near site was co-dominated by *Panicum virgatum*, *Polygonum sp.* and *Alternanthera philoxeroides*, whereas the mid site was co-dominated by *Spartina patens* and *Schoenoplectus americanus*. The far and reference site were dominated by *Spartina patens*, *Spartina alterniflora* and *Juncus roemerianus* (Moerschbaecher, 2008). A reference site was also established to the east where it is partially isolated from the diversion discharge by Bayou Terre-Aux-Boeuf, which intercepts some of the input from the diversion. While this area is not entirely hydrologically isolated from the diversion, it is hydrologically distant from the diversion, and has been used as a reference site in other studies (Rozas et al., 2005; Piazza & La Peyre, 2007).

The Loosahatchie chute is a secondary channel located on the west bank of the Mississippi River in Crittenden County, Arkansas across from Memphis, Tennessee, USA between river miles 736.5 and 742.8 (Fig. 2.2). In the 1960s, the U.S. Army Corps of Engineers (USACE) constructed stone dikes to divert flow from the Mississippi River away from the Loosahatchie chute during periods of low flow. To restore hydrology in the Loosahatchie chute, the USACE constructed twelve notches in nine existing dikes in 2008 according to the specification of the Lower Mississippi River Conservation Committee (LMRCC). Each notch measures 7.5-60 meters wide at the top and 20-64 meters wide at the bottom with depths measuring 0.9-3.3 meters. One such notched dike was located across the northernmost section of the Loosahatchie chute, allowing flood pulsing during high river stage. Three experimental study sites were established along the western bank of the Loosahatchie chute at distances near, intermediate, and far from the notched rock dike located at the northern opening of the chute. A reference site was located north of the Loosahatchie chute, behind an intact rock dike (Figure 4.1). All sites were riparian forests dominated by black willow (*Salix nigra*) and sandbar willow (*Salix interior*), though the far site also had maple (*Acer spp.*).

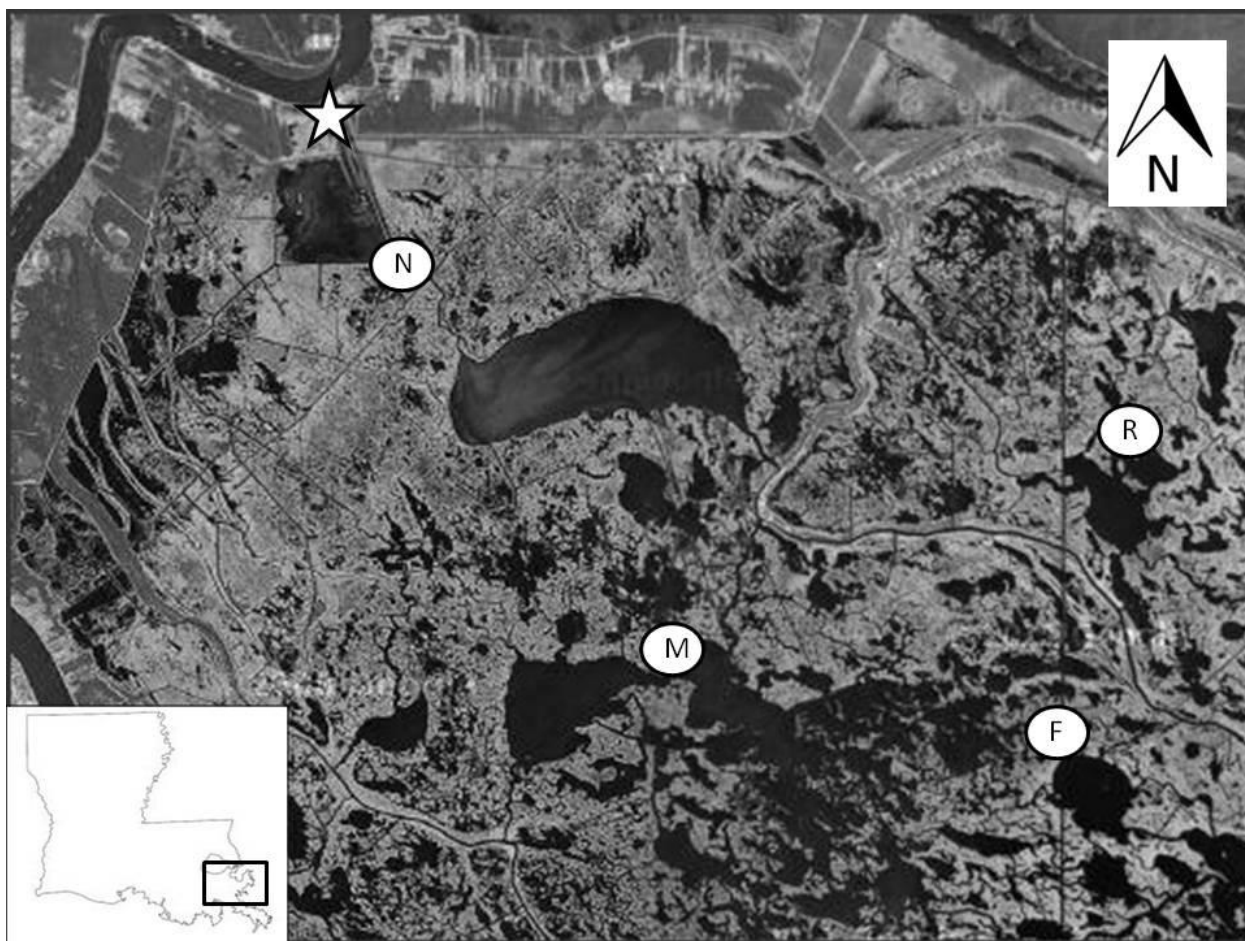


Figure 2.1: Greenhouse gas sampling sites at Caernarvon, LA. N=near site, M=mid site, F=far site and R=reference site. The Mississippi River is at the upper left, and the star represents the diversion control structure.

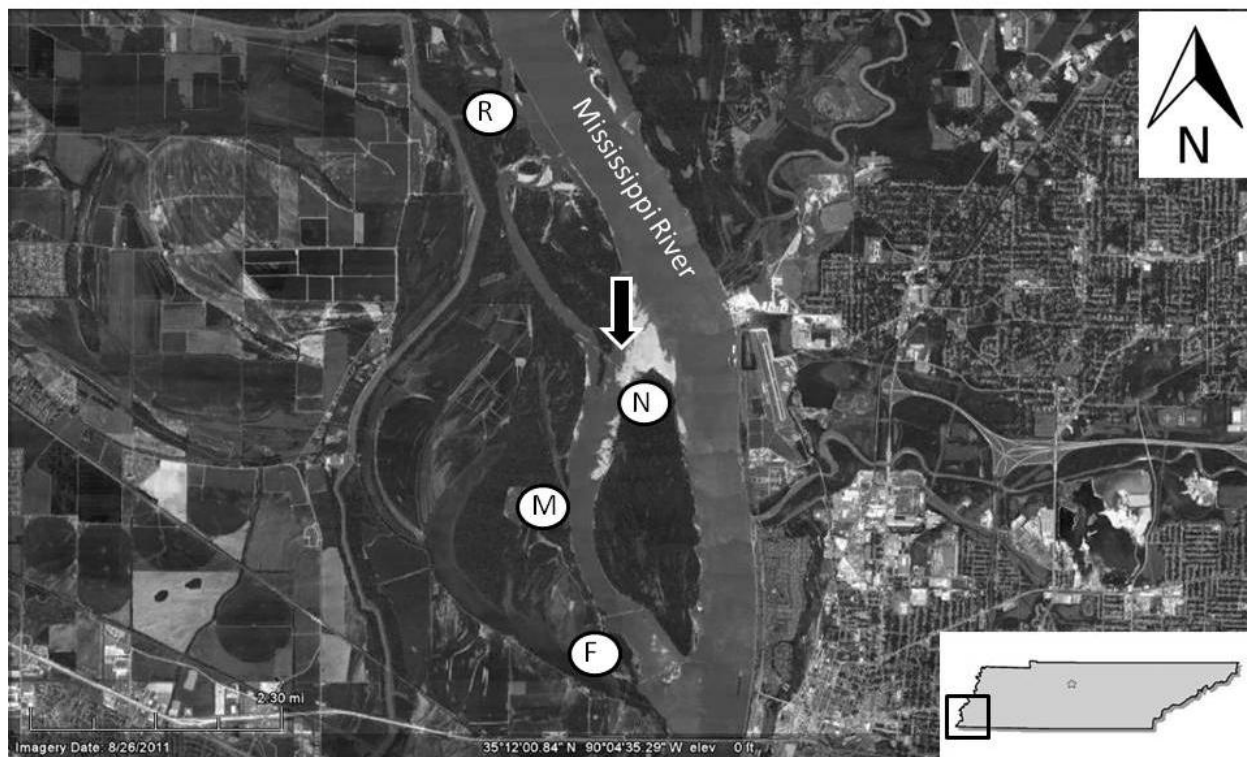


Figure 2.2: Greenhouse gas sampling sites at Memphis, TN. N=near site, M=mid site, F=far site and R=reference site, arrow=notched dike

Methods

Samples for greenhouse gas analysis were collected using Plexiglas diffusion chambers measuring 0.284 m^3 with a surface area of $.093 \text{ m}^2$ according to Faulkner et al. (1989). Each chamber was constructed with one open side, designated as the bottom with each side measuring 0.305 meters. At the top of each chamber, a hole was cut and closed with a rubber septum. Chambers were placed on the wetland surface, with the open side on the ground, allowing gases escaping the soil to collect in each chamber. The soil was more unconsolidated at the Caernarvon sites relative to the Memphis sites. To minimize the potential for out-fluxing of gases from the soil due to walking and placing the bases on the marsh surface, permanent bases for chambers were installed prior to sample collection at Caernarvon, and temporary boardwalks placed on the marsh surface were used during sample collection. Permanent bases were installed to a depth of at least a third of a meter, and the diffusion chambers were placed directly on top of the bases.

Samples were collected from the chambers using a 30-60 mL syringe, which was injected directly through the rubber septum. For each sample, 15 mL of gas inside the chamber was collected by the syringe, which was injected into a 10 mL vacutainer. Prior to sampling, vacutainers were evacuated of air using a mechanical pump or 30 mL syringe, and vacutainer caps were covered in silicone sealant to minimize leakage. Samples were collected in triplicate from each site every 30 min for 90 min after chambers were set in place. Holland et al. (1999) suggest a sampling period spanning 50 min to ensure flux captures the asymptote. A longer time period was used for this study to capture fluxes that may be small, after Hernandez and Mitsch (2006) and Altor and Mitsch (2008). Initial samples were taken a couple minutes after chambers were in place, to minimize collecting gases released due to any soil disturbance. After collection, each sample was stored out of direct sunlight until analysis. Three replicate samples were collected from each location and site during spring 2010, summer 2010 and summer 2011. Sampling during spring 2011 was not possible due to extreme flooding at Memphis. Additionally, when river stage was less than 6 m, the near site was inaccessible by boat due to the presence of a sandbar. When stage was greater than 10 m, the other sites were inaccessible by car, as roads were flooded. These limitations resulted in unbalanced sampling. Water depth, soil temperature and ambient air temperature was measured at each site during each sampling event.

Samples were analyzed for N_2O , CH_4 and CO_2 concentrations using gas chromatography (Varian 3800, Varian Inc., Palo Alto, CA) equipped with a flame ionization detector (FID) and electron capture detector (ECD). Once injected, samples were carried in a 0.5 mL sample loop and equally distributed into both columns. The injector temperature was maintained at 60°C . The FID analyzed samples for CH_4 and CO_2 , for which methanizer and column temperatures were maintained at 450°C and 250°C . The ECD analyzed samples for N_2O , for which column and detector temperatures were maintained at 60 and 300°C , respectively. The GC was calibrated for all gases at time of analysis.

Concentrations were converted from volume/volume to mass/volume concentrations using Eq. (1):

$$\text{Mass/volume concentration (mg/m}^3\text{)} = (C_v \times M \times P)/(R \times T) \quad (1)$$

where C_v is the volume/volume concentration of the gas (in ppm), M is molecular weight of the gas, P is barometric pressure (in atmospheres), T is air temperature (in degrees Kelvin) and R is the universal gas constant (0.0820575 L atm K mole) (Holland et al., 1999). For all samples, barometric pressure was assumed to be 1 atmosphere. Each flux series was graphed and checked for linearity. If R^2 values did not meet or exceed 0.80, one sample was excluded to better approximate linearity. If sample exclusion did not resolve nonlinearity (i.e., R^2 values were still below 0.80) then the flux series was excluded from analysis (Holland et al., 1999). Twelve of the 72 flux series were excluded from this analysis after failing to meet the above criteria. When $R^2 \geq 0.80$, the slope of the flux series was used to calculate gas flux using Eq. (2):

$$\text{Gas flux (mg m}^{-2} \text{ h}^{-1}\text{)} = V \times C_{\text{rate}}/A \quad (2)$$

where V is the internal volume of the air space inside the chamber (in m^3), C_{rate} is the change in gas concentration over the enclosure period, or slope of the best-fit line as calculated above (in $\text{mg m}^{-3} \text{ h}^{-1}$), and A is the area of soil covered by the chamber (in m^2) (Holland et al., 1999).

Flux rates for CH_4 and CO_2 were entered as dependent variables in a multivariate analysis of covariance (MANCOVA) with season (spring/summer), location (Caernarvon/Memphis) and site (near/mid/far/reference) as categorical independent variables and soil temperature, air temperature, and water depth as covariates. However, the data failed to meet assumptions of multivariate normality and homoscedasticity in spite of data transformations, so two separate analyses of covariance (ANCOVA) were performed. Significance for each model was determined using a Bonferroni-adjusted p-value of 0.025. After natural log transformation of fluxes and removal of two outliers for each CH_4 and CO_2 flux, the data met assumptions of normality and homogeneity, as determined by Wilks lambda values and residual plots. Analysis was performed on the transformed variables, and results are presented with back-transformations. All statistical analyses were performed using SAS 9.1 (SAS Institute Inc., Cary, NC, 2004). Nitrous oxide flux was not included in formal statistical analyses since most of the samples contained concentrations of N_2O below detection limits.

Results

A total of 58 fluxes for CH_4 and CO_2 each were used in the analysis. For CH_4 flux, 38 samples were taken in 2010 and 20 in 2011. For CO_2 flux, 39 samples were taken in 2010 and 19 in 2011. There were 18 spring and 38 summer samples, and 28 samples from Caernarvon and 30

from Memphis for each gas. There were 17 reference, 11 near, 13 mid, and 17 far site samples for each gas. Thirteen N_2O fluxes were calculated, with 6 from Caernarvon and 7 from Memphis. Methane fluxes ranged from -0.26 to $0.79 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ at Caernarvon and from -0.11 to $1.05 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ at Memphis. Carbon dioxide fluxes ranged from -0.51 to $9.37 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$ at Caernarvon and from -0.37 to $4.26 \text{ g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$ at Memphis. Nitrous oxide fluxes ranged from -0.67 to $0.66 \mu\text{g N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ at Caernarvon and from -1.13 to $2.18 \mu\text{g N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ at Memphis.

Caernarvon water depths on the marsh surface ranged from 0 to 30.5 cm . Surface water was only observed during the summer 2010 sampling period at the near and mid site, and during summer 2011 at the reference site. No sites were flooded during spring 2010, when discharge and stage (at the mouth of the diversion) were greatest (Fig. 2.3-2.4), and the far site was never flooded. Memphis water depths ranged from 0 to 22.9 cm . Samples were collected over a narrow range of river stages at Memphis (Fig. 2.5). The greatest average water depth at Memphis was at the reference site (13 cm), followed by the near (11 cm), far (9 cm) and mid (8 cm) sites. Ambient air temperatures ranged from 24.4 to 33.9° C at Caernarvon, and from 20.6 to 27.2° C at Memphis. Soil temperatures ranged from 18.9 to 28.9° C at Caernarvon, and from 11.7 to 26.7° C at Memphis.

The overall statistical model for CH_4 flux was significant ($F_{(8,49)}=3.04$, $p=0.0073$). The Memphis study area had marginally higher flux rates compared to Caernarvon ($F_{(1,49)}=4.63$, $p=0.0364$; Fig. 2.6). Methane flux did not vary by season ($F_{(1,49)}=0.01$, $p=0.9117$; Fig. 2.7) or sites ($F_{(3,49)}=1.48$, $p=0.2312$; Fig. 2.8). Methane flux did not vary with soil temperature ($F_{(1,49)}=0.480$, $p=0.4903$) or air temperature ($F_{(1,49)}=0.16$, $p=0.6865$) but decreased slightly with water depth ($F_{(1,49)}=6.78$, $p=0.0121$; Figure 2.9). However, after removal of a single influential point, the effect of water depth was non-significant, as well as the main effect of location.

The overall statistical model for CO_2 flux was significant ($F_{(8,49)}=7.45$, $p<0.0001$). However, CO_2 flux did not vary between locations ($F_{(8,49)}=0.31$, $p=0.5812$; Fig. 2.6), by season ($F_{(1,49)}=0.08$, $p=0.7739$; Fig. 2.7) or sites ($F_{(3,49)}=1.63$, $p=0.1951$; Fig. 2.8). Carbon dioxide flux decreased with water depth ($F_{(1,49)}=7.90$, $p=0.0071$; Figure 2.9), but did not vary with soil temperature ($F_{(1,49)}=1.34$, $p=0.2523$) or air temperature ($F_{(1,49)}=2.66$, $p=0.1090$).

Thirteen nitrous oxide fluxes were calculated, with 6 from Caernarvon and 7 from Memphis. In order to estimate the average flux at each location, fluxes with concentrations below detection limits were assumed to be zero. For Caernarvon, fluxes averaged $0.02 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$, and ranged between -0.67 and $0.66 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$. For Memphis, fluxes averaged $0.09 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$, and ranged between -1.13 and $2.18 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$.

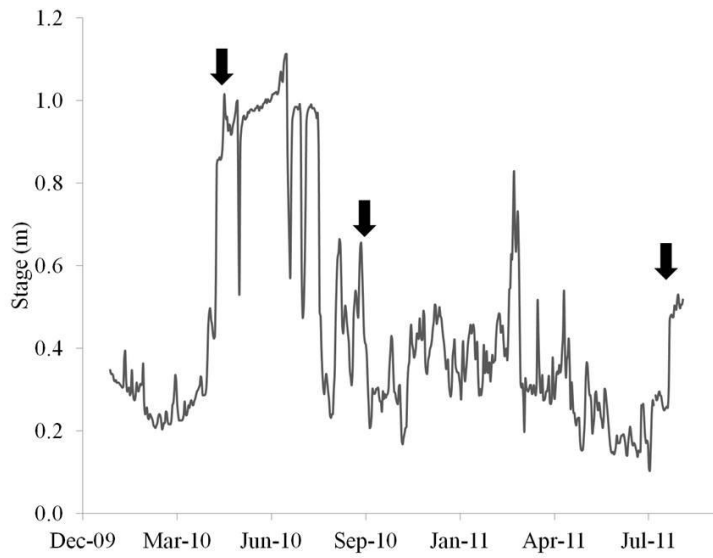


Figure 2.3: Gage stage at Caernarvon during the study period (January 2010-August 2011). Arrows indicate stage at sampling dates

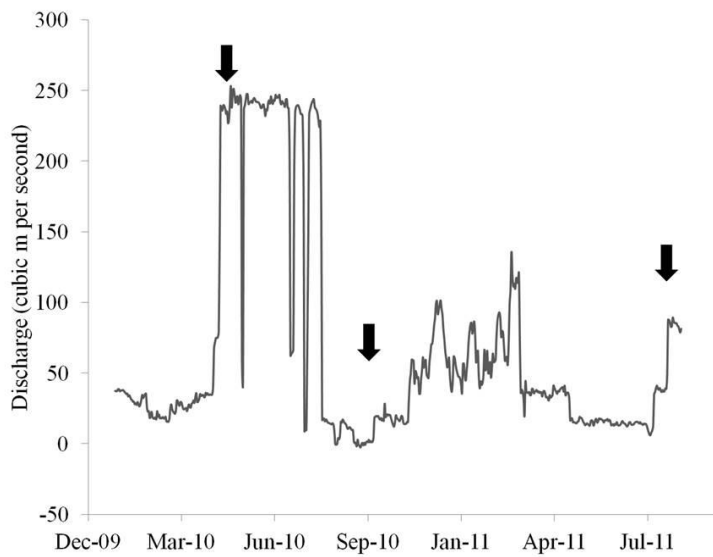


Figure 2.4: Discharge at Caernarvon during the study period (January 2010-August 2011). Arrows indicate sampling dates

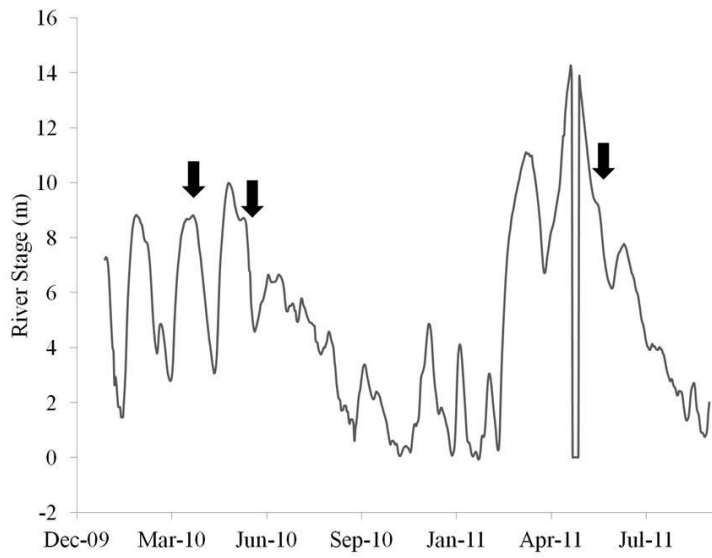


Figure 2.5: River stage at Memphis during the study period (January 2010-August 2011). Arrows indicate sampling dates

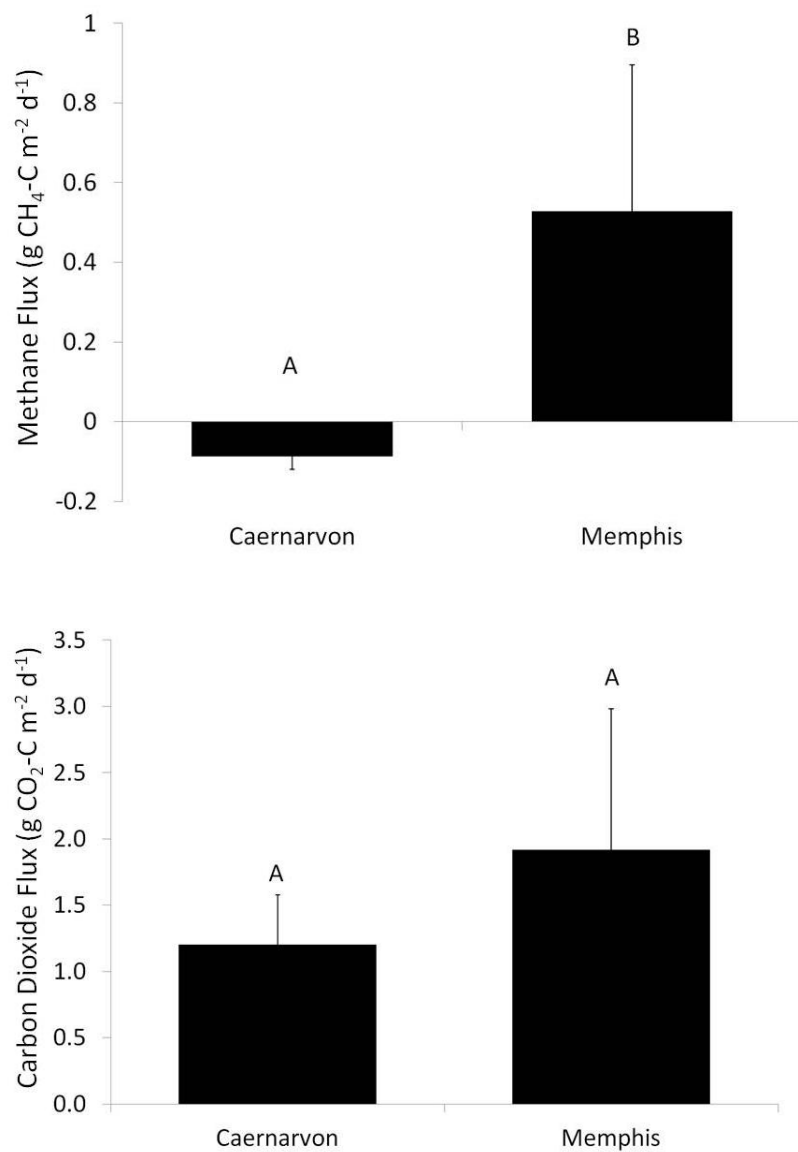


Figure 2.6: Mean CH₄ (top) and CO₂ (bottom) fluxes for a coastal wetland at Caernarvon, LA and a restored riparian wetland at Memphis, TN. Different letters indicate significant differences ($P < 0.025$), as determined by Bonferroni-adjusted multiple comparison test.

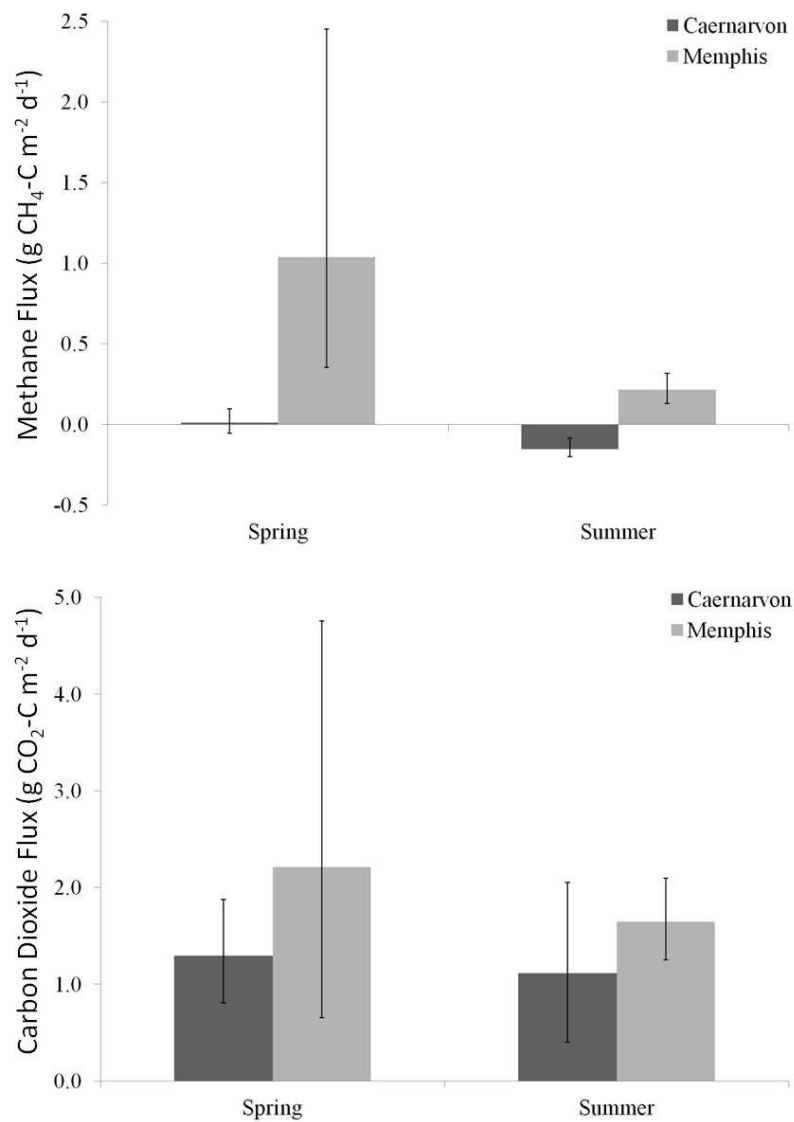


Figure 2.7: Seasonal differences of mean CH₄ (top) and CO₂ (bottom) fluxes for a coastal wetland at Caernarvon, LA and a restored riparian wetland at Memphis, TN.

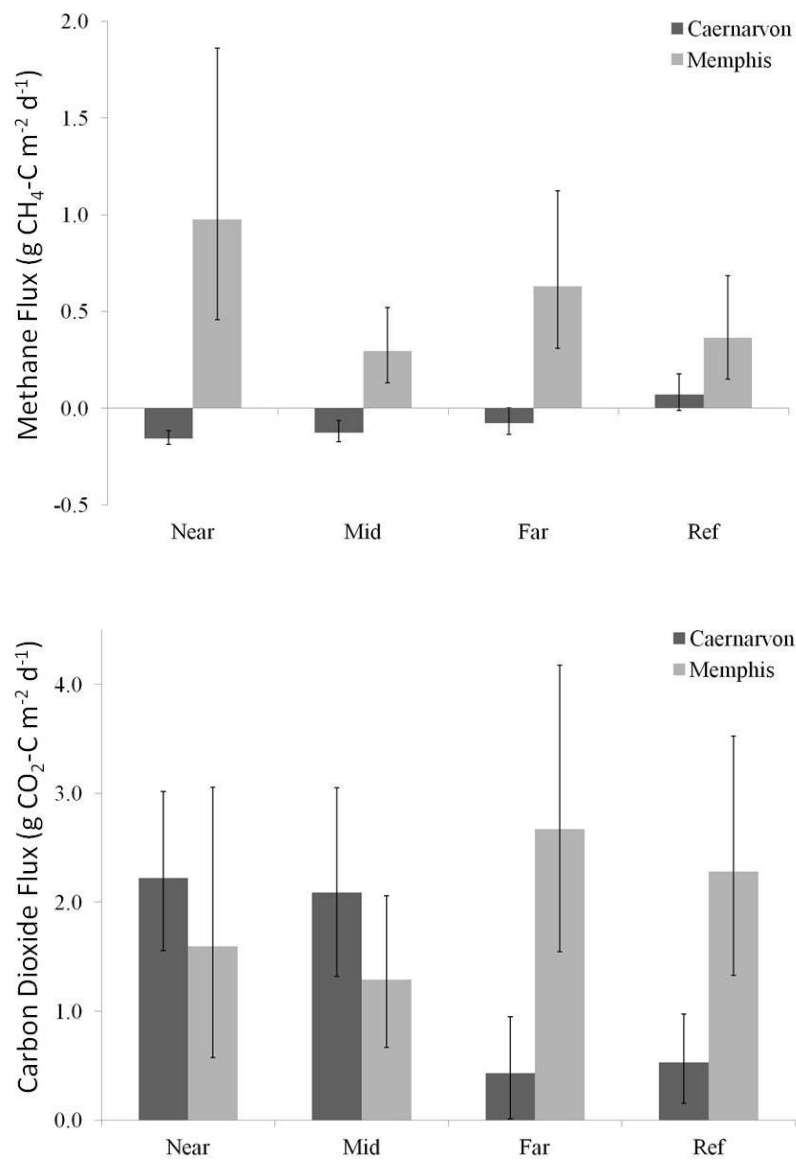


Figure 2.8: Site-specific differences in mean CH₄ (top) and CO₂ (bottom) fluxes for a coastal wetland at Caernarvon, LA and a restored riparian wetland at Memphis, TN.

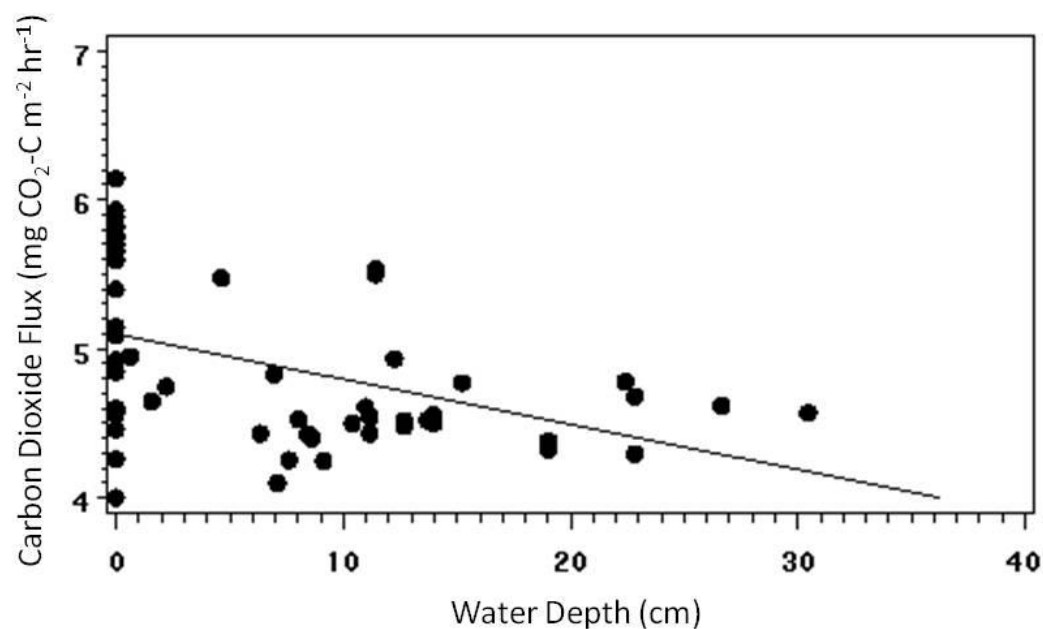
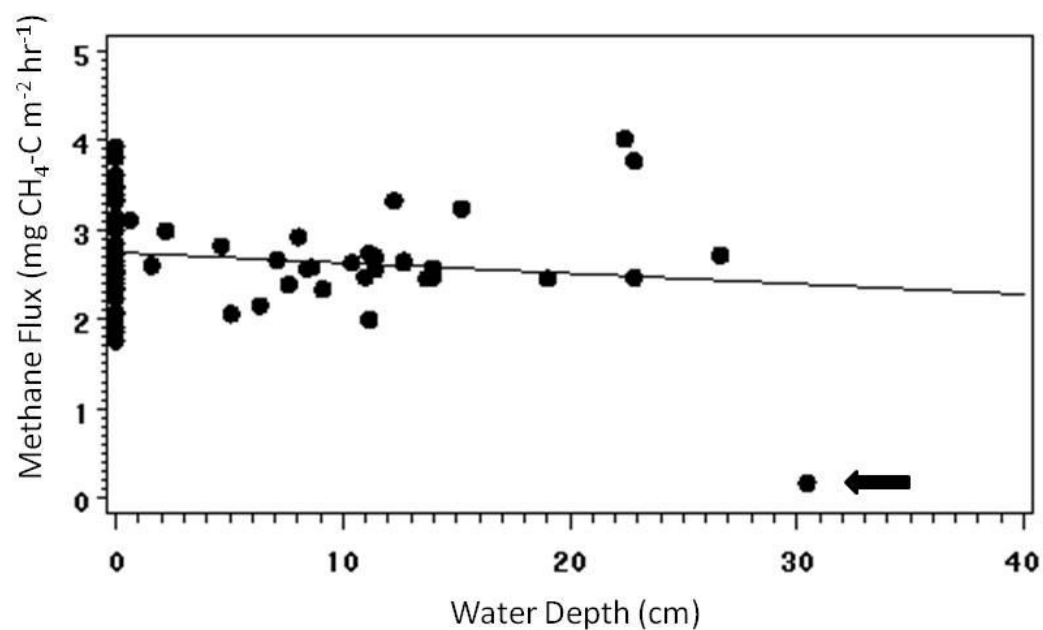
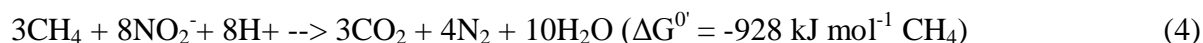
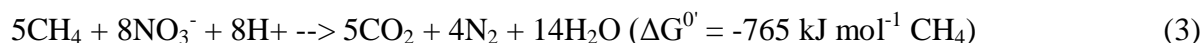


Figure 2.9: Fluxes of CH_4 and CO_2 with variations in water depth with trend lines. The arrow indicates an influential data point that, when excluded, removes the relationship between methane flux and water depth.

Discussion

Methane fluxes averaged $0.53 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ at the Memphis sites, a riparian wetland in the central Mississippi River Basin. This value falls within the range of fluxes for fresh water wetlands found in the literature (Table 2.1). DeLaune et al. (1983) found fluxes that averaged $0.43 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ in a coastal Louisiana fresh marsh. Alford et al. (1997) found fluxes of $0.14 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ for a forested swamp and $0.25 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ from a freshwater marsh in Louisiana. Fluxes averaged between 0.02 and $0.35 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ in two created freshwater wetlands in Ohio (Altor & Mitsch, 2008; Nahlik & Mitsch, 2010). Yu et al. (2008) found fluxes ranged from 0 to $0.54 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ along a hydrological gradient in a bottomland hardwood forest in Louisiana.

The average methane flux at Caernarvon ($-0.09 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$) indicate that it was a mild sink for methane. Methane flux is determined by the balance between methane production and consumption, reviewed by (Segers, 1998). Microbial nitrate/nitrite oxidation of methane results in end-products of carbon dioxide, dinitrogen gas and water (Eq. 3 and 4)(Raghoebarsing et al., 2006).



This would suggest that suppression of CH_4 flux via oxidation may lead to increased CO_2 flux. Methane oxidation is influenced by soil moisture content, oxygen availability, nitrate concentrations, and light availability (King, 1990b; King, 1990a; Roslev & King, 1996; Torn & Harte, 1996; Bodelier & Laanbroek, 2004). Though wetlands have rarely been found to be sinks for CH_4 , Yu et al. (2008) found a swamp-upland transition site to be a sink during warm months. High CH_4 oxidation rates have been found to eliminate as much as 94% of the methane produced in wetlands and rice paddies (Schütz et al., 1989; King, 1990b). However, the observed effect of location is dependent upon a single flux value calculated at Caernarvon. Removal of the low flux value results in no difference between locations, and increases the average flux to positive values. Also, some Caernarvon samples were taken when the marsh was not flooded. Day et al. (2009a) found that only the mid-estuary marshes stay permanently flooded, with the upper estuary marshes flooded when the diversion is operated at high discharge, and the lower estuary marshes, along with the reference marshes, are rarely flooded. In this study, the near and mid sites were not flooded when we made measurements during the spring of 2010. However, the soil was always saturated. It is therefore likely that both sites are mild sources for methane.

We found no significance between flux values and the environmental variables water depth, soil temperature and air temperature. The lone exception is the negative relationship between CO_2 flux and water depth, as has been found elsewhere (Moore & Knowles, 1989; Moore & Dalva, 1993). Methane flux is often positively correlated with flooding depth and duration (Moore & Knowles, 1989; Altor & Mitsch, 2006). During spring 2010 sampling, the sampling date with

the highest discharge and gage stage, no water was observed on the marsh soil at Caernarvon. At Caernarvon, water depth on the marsh surface is influenced by diversion discharge, precipitation and seasonal storm fronts that push Gulf waters into the estuary (Lane et al., 1999). Sampling when water depth was greatest was most often during storm frontal passages, when sampling would be dangerous. This made the timing of sampling trips at times when the marsh was flooded, yet accessible, difficult. Though the marsh was rarely flooded, saturated soils were observed at all sites at all times. Little variation in water depth existed at the Memphis sites among sampling trips at each site due to the limitations in site accessibility previously mentioned. The difference in water depths between Caernarvon and Memphis may explain the difference observed in methane flux between the two locations, but water depth was not correlated with methane flux after removal of a single data point.

Methane and carbon dioxide flux has been found to be positively correlated with temperature (Mikkela et al., 1995; MacDonald et al., 1998; Wickland et al., 2001). Our study failed to find a relationship between fluxes and temperature. It is likely that the range of temperatures observed in the field was not expansive enough to capture responses of CH₄ and CO₂ flux. The aforementioned limitations to site access occurred especially in winter and fall preventing sampling across all seasons, which would have provided more expansive ranges of environmental data.

Nitrous oxide emissions were generally non-detectable at both locations. However, when considering the detectable fluxes, the average flux at Caernarvon was lower than that from Memphis, though this is unlikely to be a significant difference. Our results are comparable to those from other studies (Table 2.2). We found higher fluxes at Memphis, a freshwater site, than Caernarvon, a site with a fresh to saltwater gradient. Smith et al. (1983) found fluxes decreased along a fresh-saline gradient in coastal Louisiana. Memphis also had greater water depths than Caernarvon. However, water depth is often negatively correlated with N₂O emissions (Regina et al., 1996; Hua et al., 1997). Assuming N₂O emissions observed in this study represent 1% of the denitrification end-products (Hernandez & Mitsch, 2006), we calculated denitrification rates for Memphis and Caernarvon to be 8.91 mg N m⁻² d⁻¹ and 1.98 mg N m⁻² d⁻¹, respectively. Lindau et al. (2009) found denitrification rates of 0.22 mg N m⁻² d⁻¹ in sediments of Davis Pond, a diversion-impacted coastal bay in Louisiana. Lindau et al. (2008) found rates of denitrification between 0.06 and 4.7 mg N m⁻² d⁻¹ in a Louisiana cypress swamp over a similar temperature range as that of this study. A study of another riparian forest in southeastern USA found denitrification rates of 4.3 mg N m⁻² d⁻¹ (Lowrance et al., 1995).

According to the results of this study, the restoration efforts had no effect on greenhouse gas emissions within the wetland complex. At Memphis, this is likely due to observed low organic matter composition (R. DeLaune, personal communication), which reduces CH₄ and N₂O emissions. Microbes utilize organic carbon as an energy source in respiration (Reddy & DeLaune, 2008). In the lower estuary at Caernarvon, CH₄ production is likely limited in the

Table 2.1: Literature values for wetland methane fluxes. All fluxes have been converted to g CH₄-C m⁻² d⁻¹.

CH ₄	Wetland Type	Source
0.04 – 0.44	Fresh	DeLaune et al. (1983)
0.75	Fresh	Crozier and DeLaune (1996)
0.15 – 0.25	Fresh	Alford et al. (1997)
0.18 – 0.35	Fresh	Altor and Mitsch (2008)
0 – 0.54	Fresh	Yu et al. (2008)
0.01 – 0.19	Fresh	Nahlik and Mitsch (2010)
0.53	Fresh	Current study
1.2	Intermediate	Crozier and DeLaune (1996)
0.91	Intermediate	Alford et al. (1997)
0.01 – 0.20	Brackish	DeLaune et al. (1983)
0.25 – 0.70	Brackish	Crozier and DeLaune (1996)
0.37	Brackish	DeLaune and Pezeshki (2003)
0.01	Salt	DeLaune et al. (1983)
0.02 – 0.30	Salt	Crozier and DeLaune (1996)
-0.09	Fresh-Salt	Current study

Table 2.2: Literature values for wetland nitrous oxide fluxes. All fluxes have been converted to $\text{mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$.

N₂O	Wetland Type	Source
0.12	Fresh	Smith et al. (1983)
0.17	Fresh	Hernandez & Mitsch (2006)
1.00	Fresh	Kadlec & Knight (2008)
-5.5-32.7	Fresh	Wang et al. (2008)
55	Fresh	Yu et al. (2008)
0.09	Fresh	Current study
0.06-0.13	Brackish	Smith et al. (1983)
0.03-0.08	Salt	Smith et al. (1983)
0.03	Salt	Smith & DeLaune (1983)
0.02	Fresh-salt	Current study

warmer parts of the year by high concentrations of sulfate in salt water (Crozier & DeLaune, 1996), which moves into the area when diversion discharge is low and is preferentially utilized as a terminal electron acceptor over inorganic carbon (Ponnamperuma, 1972). Seasonally high salinities have been observed in the lower estuary, especially when discharge is low (Lane et al., 2007). In the upper estuary, CH₄ production is likely limited by high concentrations of nitrate in river water (Jugsujinda et al., 1995), as has been observed in other studies (Lane et al., 1999; Lane et al., 2004). Nitrate may undergo denitrification in anaerobic soils, with end-products of N₂O and dinitrogen gas (N₂). We found few detectable fluxes of N₂O, indicating complete transformation of N₂O to N₂ during denitrification, which occurs when soil available carbon and water content are high (Weier et al., 1993).

Overall, this study indicates that utilizing diversions and restored secondary channels to restore wetlands and reduce nutrient loading to the Gulf will have minimal impact on wetland greenhouse gas fluxes. Current diversion management techniques appear appropriate in terms of limiting greenhouse gas production. However, further studies of varying spatial and temporal scales are needed to better understand the seasonal and annual trends of fluxes. Additional environmental factors should be investigated to better understand the underlying mechanisms regulating greenhouse gas dynamics in the Basin.

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CHAPTER 3

SPATIAL AND TEMPORAL VARIATIONS IN NUTRIENTS AND WATER QUALITY PARAMETERS IN THE DIVERSION-IMPACTED BRETON SOUND ESTUARY

Introduction

Large seasonal hypoxic zones (areas with less than 2 mg/l dissolved oxygen in coastal bottom water) began forming in the northern Gulf of Mexico on the continental shelf near the Louisiana coast in the 1960s (Osterman et al., 2009). These hypoxic zones, referred to as “dead zones”, are formed when nearshore Gulf waters stratify during the warmer part of the year due to inadequate mixing, which prevents downward oxygen diffusion from surface waters. Oxygen is reduced in bottom waters from the decomposition of organic matter formed in the upper layer during large phytoplankton blooms fueled by nutrient-rich fresh waters. Recent hypoxic zones have exceeded 20,000 km² in areal extent (Turner et al., 2008). Although the factors affecting the extent and severity of coastal hypoxia are complex (Bianchi et al., 2010), there is a clear link between Mississippi River nitrate export and coastal phytoplankton productivity (Justic et al., 1995; Rabalais et al., 1996; Rabalais et al., 2002b; Lohrenz et al., 2008).

The Mississippi River, which drains approximately 40% of the contiguous United States, annually exports an average of nearly 1×10^6 tonnes of nitrate (NO₃⁻) to the Gulf of Mexico, and concentrations have more than doubled since 1950 (Goolsby & Battaglin, 2001). Reasons for this increased nitrogen export include increased fertilizer application, more efficient drainage of agricultural fields, and expansion in corn and soybean production (Howarth et al., 2002; Donner et al., 2004; Zhang & Schilling, 2006). Additionally, extensive construction of artificial levees during the 20th century prevented seasonal flood waters from reaching Mississippi River floodplain wetlands, which serve as natural sinks for nutrients and sediments (Day et al., 2000; Mitsch et al., 2001; Day et al., 2003a).

Mississippi River deltaic wetlands were historically stabilized and enhanced by sediment input from seasonal river floods, as well as hurricanes and tides (Day et al., 2000). Wetland expansion continued until the early 20th century, when this trend was reversed resulting in a loss of 4500 km² by the end of the century (Barras et al., 2003). Sediment delivery to deltaic wetlands decreased due to levee and dam construction within the Basin (Day et al., 2000; Blum & Roberts, 2009), resulting in an 85% decrease in sediment supply during the 20th century (Syvitski et al., 2009). Subsidence, a process of soil and sediment compaction, currently exceeds 10 mm yr⁻¹ in many regions of coastal Louisiana (Tornqvist et al., 2008), outpacing delta-building processes. Additionally, canal construction has resulted in altered hydrology and has contributed to coastal wetland loss (Day et al., 2000).

River diversions have been implemented in the Mississippi River deltaic plain to slow wetland loss and promote wetland regeneration. Diversions have been shown to increase vertical accretion and marsh development (DeLaune et al., 2003; Lane et al., 2006), though evidence

suggests that diversions may make wetlands more susceptible to erosion during hurricanes (Howes et al., 2010). Diversions also have been shown to help promote riverine nutrient uptake and removal (Lane et al., 1999; 2007), and have therefore been proposed as a partial solution to coastal hypoxia (Mitsch et al., 2001; Day et al., 2003b).

The purpose of this study is to investigate the long-term temporal and spatial nutrient patterns in the Breton Sound estuary, a coastal Louisiana estuarine wetland complex that receives Mississippi River water input via the Caernarvon river diversion. Null hypotheses tested include: (1) no correlations exist between water quality parameters, (2) no seasonal or temporal variation in nutrient concentration exists, (3) nutrient removal efficiency is unrelated to loading rate, and (4) there is no seasonal variation in nutrient removal efficiency.

Study Area

The Caernarvon diversion is located on the Mississippi River at river mile 81.5, south of New Orleans, Louisiana, USA (Fig. 3.1). Operational since August 1991, the diversion discharges river water into Breton Sound, a coastal estuary containing 1100 km² of fresh, brackish, and saline marshes. Breton Sound, which has an open connection to the Gulf of Mexico to the south, is bounded by the Mississippi River levee to the west, the natural levees of Bayou La Loutre to the north, and the spoil banks of the Mississippi River Gulf Outlet to the east. Water quality sampling sites were established over several years beginning in 2000 for a number of studies (Lane et al., 2004; Lane et al., 2007; Day et al., 2009b) including unpublished data, resulting in a large database of water quality measures within the Breton Sound. Eight sites that were common to all studies were retained for inclusion in the database (Figure 1.1).

Methods

Water samples were collected nearly monthly from January 2001 to December 2010 with gaps in sampling from August 2002 to February 2003, and from September 2004 to February 2007. Samples were collected at each site from a depth of 10-20 cm in acid-washed one-liter plastic containers (APHA, 1985). Samples were kept frozen until analysis. Water quality parameters included nitrite + nitrate (NO_x), ammonium (NH₄-N), total nitrogen (TN), phosphate (PO₄-P), total phosphorus (TP), silicate (SiO₄-Si), total suspended solids (TSS), salinity and chlorophyll a (CHL). Samples analyzed for NO_x and NH₄ were filtered prior to analysis using 0.45 µm Millipore filters. Concentrations of all chemical constituents were determined from standard methods (APHA, 1985); refer to Lane et al. (1999; 2004) for more detailed discussions on sample analysis. The resulting database included 755 observations of the 9 water quality parameters. Samples were divided into seasonal groups, with spring defined as March-May samples, summer defined as June-August samples, fall defined as September-November samples and winter defined as December-February samples, after the manner of Lane et al. (1999).

Nutrient loading rate and removal efficiency was calculated for NO_x along each transect. Nitrate-nitrite was the only nutrient for which river concentration data was available throughout the study period. Loading rate was calculated using Eq. (1):

Loading rate (mg m⁻² sec⁻¹)

$$= ([C_{river}] * D) / A \quad (1)$$

where [C_{initial}] is the initial concentration of the chemical constituent when it enters the estuary (in mg/L), D is discharge (in m³ s⁻¹) and A is areal extent (m²) of the estuary, 848 km², after Hyfield et al. (2008). Loading rate was then converted to units of g m⁻² yr⁻¹. Removal efficiency was calculated adjusting for dilution due to mixing of saline Gulf water using Eq. (2):

Removal efficiency (%)

$$= \left((1 - r_{sal}) - \frac{[C]}{[C_{river}]} \right) * 100 \quad (2)$$

where r_{sal} is the percentage of saline water at the sampling station, [C] is the concentration of the chemical constituent at the sampling station, and [C_{river}] is the concentration of the chemical constituent when it enters the estuary from the diversion. Removal efficiency was calculated for each station along each transect, as well as for the entire estuary.

Correlations among the water quality parameters were determined using Pearson correlation coefficients. An initial multivariate analysis of covariance (MANCOVA) was performed with water quality parameters serving as dependent variables with season as the categorical independent variable, with year as a block and discharge and distance from diversion as covariates. However, violations of the assumptions of multivariate normality and homoscedasticity could not be resolved after outlier removal and data transformation. Instead, nine separate analyses of covariance (ANCOVA) were performed and significance for each model was determined using a Bonferroni-adjusted p-value of 0.0055 ($\alpha=0.05/9$). Normality was determined quantitatively by measuring skewness and kurtosis and qualitatively by examining frequency histograms of residuals and Q-Q plots. Homogeneity was determined by examining a scatter plot of the residuals. Concentrations of all constituents except silicate were natural log-transformed to meet assumptions of homogeneity and normality. The assumption of normality was validated for all transformed dependent variables except NH₄. Data transformation had no affect on ANOVA results, except for TSS and CHL. All variables were therefore entered into ANOVAs in their untransformed state, except for TSS and CHL. The assumption of homogeneity was violated for NO_x, NH₄ and salinity. However, parametric statistical procedures tend to be robust against violations of these assumptions, especially when sample sizes are large (Miliken & Johnson, 1984; Neter et al., 1996).

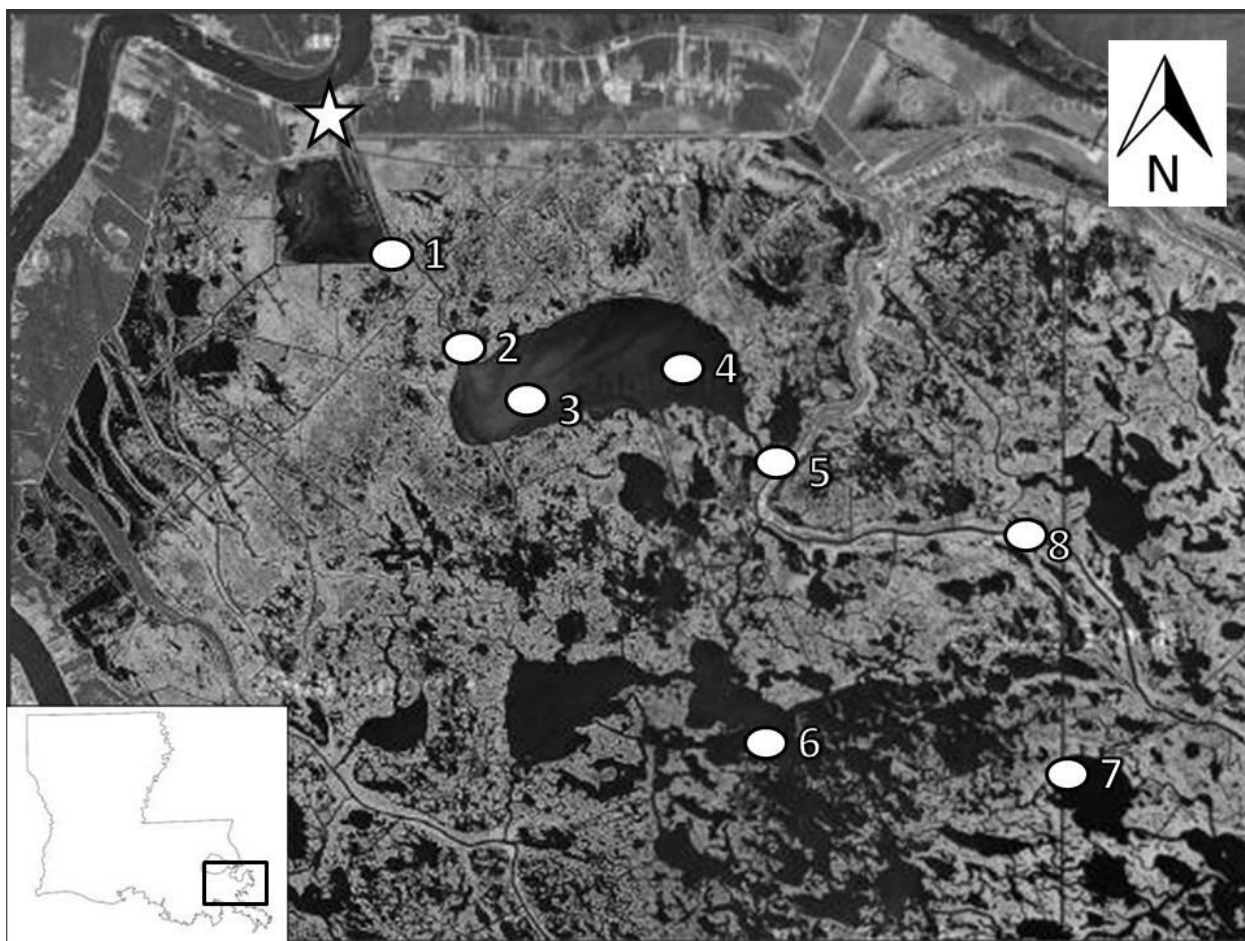


Figure 3.1: Water quality sampling sites in Breton Sound, LA. The star indicates the location of the Caernarvon River diversion control structure.

Removal efficiencies for the entire estuary were entered into ANCOVAs with season as the categorical independent variable and loading rate as the covariate. Removal efficiencies were transformed to meet assumptions of normality and homogeneity, but transformations did not change the results of the model. Therefore, analysis results on untransformed data are reported. All statistical analyses were performed using SAS 9.1 (SAS Institute Inc., Cary, NC, 2004).

Results

A total of 749 samples were included in the analysis. Nitrate and TN were strongly correlated with one another ($\rho=0.8349$; Table 3.1) and TP was moderately correlated with PO_4 ($\rho=0.5758$). Silicate was moderately correlated with NO_x ($\rho=0.5402$) and TN ($\rho=0.5211$). Seasonal sample sizes ranged from 145 during the fall and 253 during the spring. Discharge ranged from 0 to 253 $\text{m}^3 \text{s}^{-1}$, with an average of $66.91 (\pm 2.75) \text{m}^3 \text{s}^{-1}$ on sampling dates (Fig. 3.2). Discharge averaged $89 \pm 4.6 \text{m}^3 \text{s}^{-1}$ in the spring, $79 (\pm 5.3) \text{m}^3 \text{s}^{-1}$ in the winter, $53 (\pm 5.4) \text{m}^3 \text{s}^{-1}$ in the summer and $30 (\pm 6.8) \text{m}^3 \text{s}^{-1}$ in the fall.

Nitrate-nitrite concentrations ranged from 0 to 3.28 mg/L. After significance was determined for the covariates distance ($F_{(1,655)}=360.60$, $p<0.0001$) and discharge ($F_{(1,655)}=108.33$, $p<0.0001$), NO_x varied significantly between seasons ($F_{(3,655)}=28.72$, $p<0.0001$) with concentrations highest in winter and lowest in the summer and fall (Fig. 3.3). Nitrate concentrations increased in response to increasing discharge (Fig. 3.6) and decreased with increasing distance from the diversion (Fig. 3.4). The salinity mixing diagram indicates the estuary is a strong sink for NO_x (Fig. 3.8).

Ammonium concentrations ranged from 0 to 0.71 mg/L and did not vary among seasons ($F_{(3,654)}=0.64$, $p<0.5877$) or with distance ($F_{(1,654)}=5.98$, unprotected $p=0.0148$). Ammonium concentrations increased slightly with increasing discharge ($F_{(1,654)}=8.24$, $p=0.0042$; Fig. 3.6). The salinity mixing diagram indicates the estuary is generally a source for NH_4 (Fig. 3.8).

Phosphate concentrations ranged from 0 to 0.19 mg/L and varied among seasons ($F_{(3,658)}=26.34$, $p<0.0001$), with concentrations greatest in the fall and lowest in the spring (Fig. 3.3). Phosphate concentrations decreased with increasing distance ($F_{(1,658)}=116.01$, $p<0.0001$; Fig. 3.4), but did not vary with discharge ($F_{(1,658)}=1.18$, $p=0.2778$). The salinity mixing diagram indicates the estuary is generally a source of PO_4 in fall and summer and a sink in winter and spring (Fig. 3.8).

Total nitrogen concentrations ranged from 0.21 to 4.23 mg/L and varied among season ($F_{(3,585)}=21.58$, $p<0.0001$), with concentrations highest in the winter and lowest in the fall (Fig. 3.3). Concentrations increased with increasing discharge ($F_{(1,585)}=20.49$, $p<0.0001$; Fig. 3.6) and decreased with increasing distance from the diversion ($F_{(1,585)}=301.61$, $p<0.0001$; Fig. 3.4). The salinity mixing diagram indicates the estuary is generally a sink for TN (Fig. 3.8).

Table 3.1: Pearson correlation coefficients for the water parameters analyzed in this study. Blank cells represent correlations not significant at $\alpha = 0.05$; bold values represent moderate to strong correlations.

	NO _x	NH ₄	TN	PO ₄	TP	Silicate	TSS	Salinity	Chl <i>a</i>
NO _x									
NH ₄	0.1018								
TN	0.8349	0.0852							
PO ₄	0.3188		0.3353						
TP	0.1603		0.2644	0.5758					
Silicate	0.5402		0.5211	0.4804	0.3651				
TSS	0.3578	0.0979	0.2950		0.1362	0.1606			
Salinity	-0.3853	-0.0880	-0.3103	-0.2371	-0.2768	-0.2555			
Chl <i>a</i>	-0.4487		-0.2818	-0.1862	0.1518	-0.1948	-0.1341	0.1138	

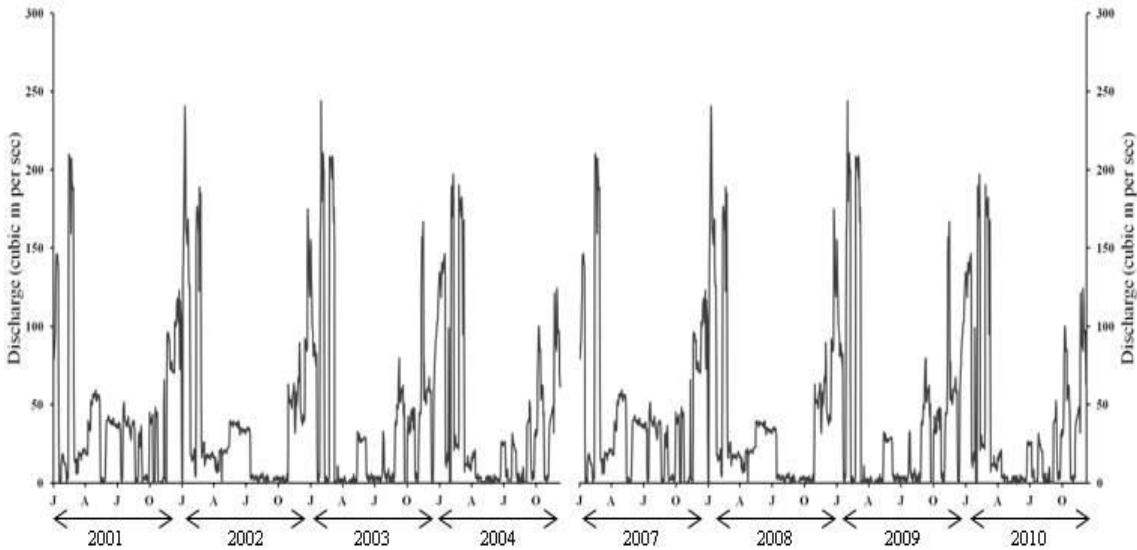


Figure 3.2: Instantaneous daily discharge at the Caernarvon river diversion during the study period.

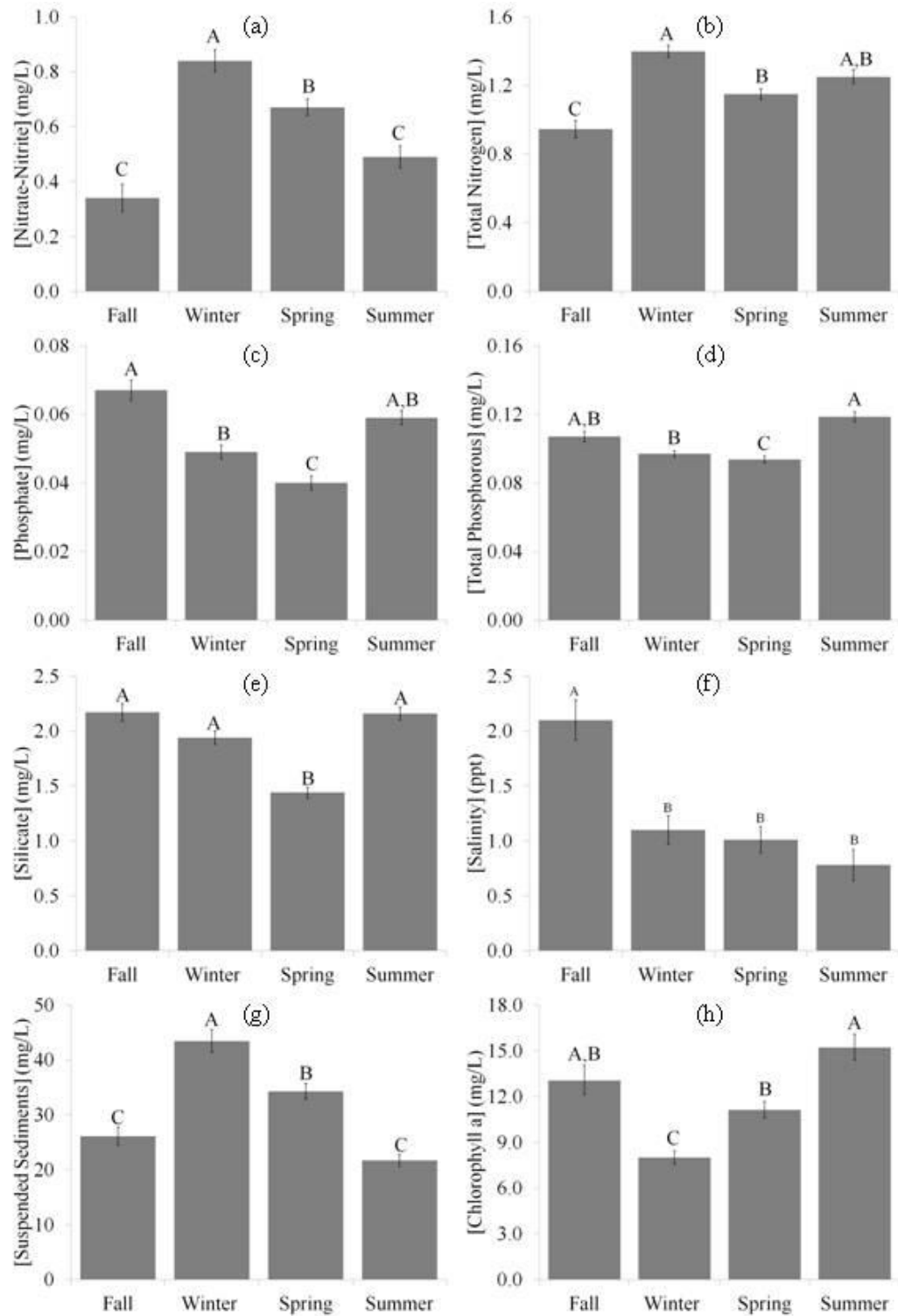


Figure 3.3: Seasonal variation in mean concentrations (± 1 s.e.) of water quality parameters. Different letters indicate significant differences ($P < 0.0055$), as determined by Bonferroni-adjusted multiple comparison test.

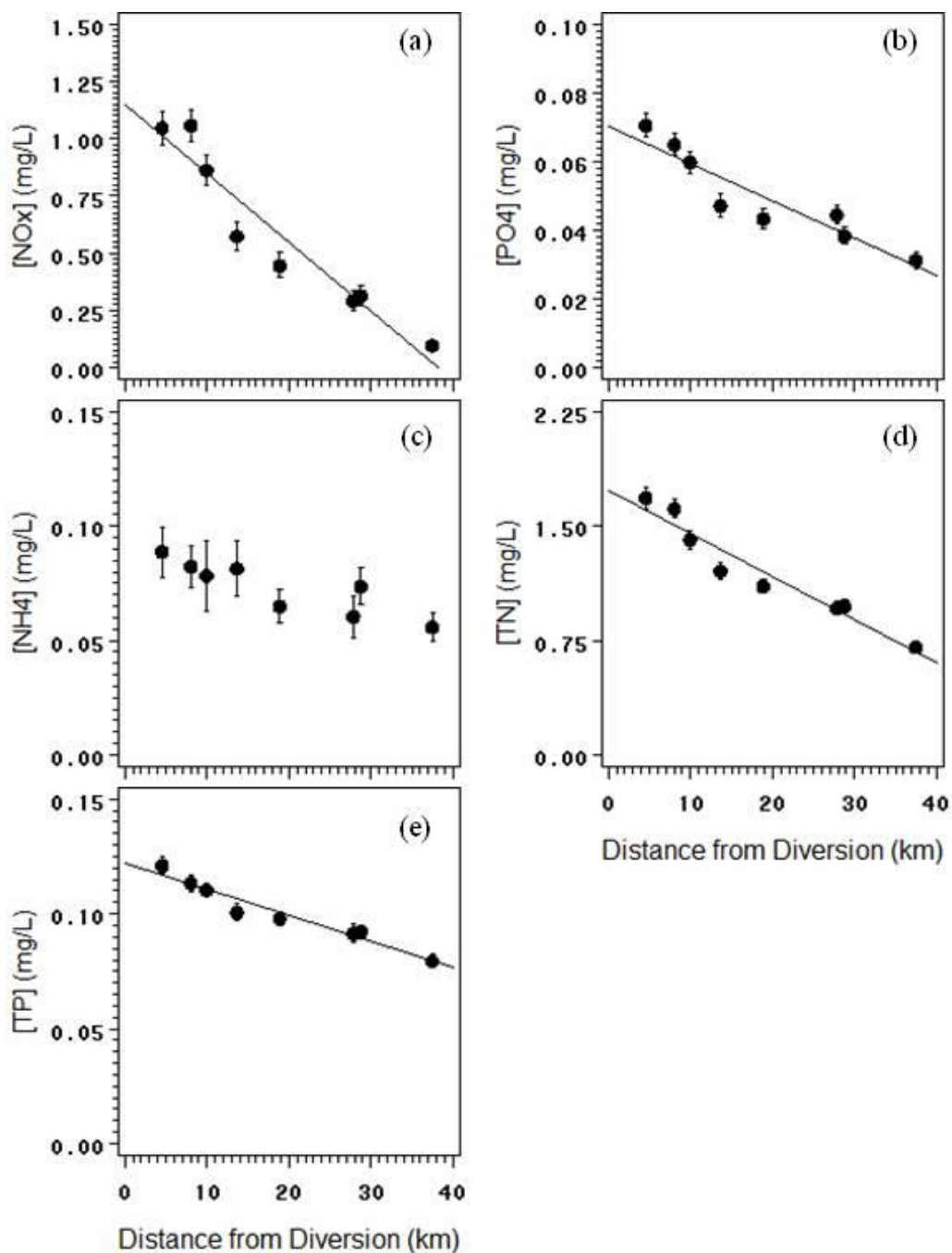


Figure 3.4: Relationship between N- and P-containing water quality parameters and distance from the diversion. Parameters include (a) nitrate-nitrite, (b) phosphate, (c) ammonium, (d) total nitrogen, and (e) total phosphorus. Data points represent mean concentrations (± 1 s.e.) of each water quality parameter. Trend lines indicate statistical significance with the covariate distance.

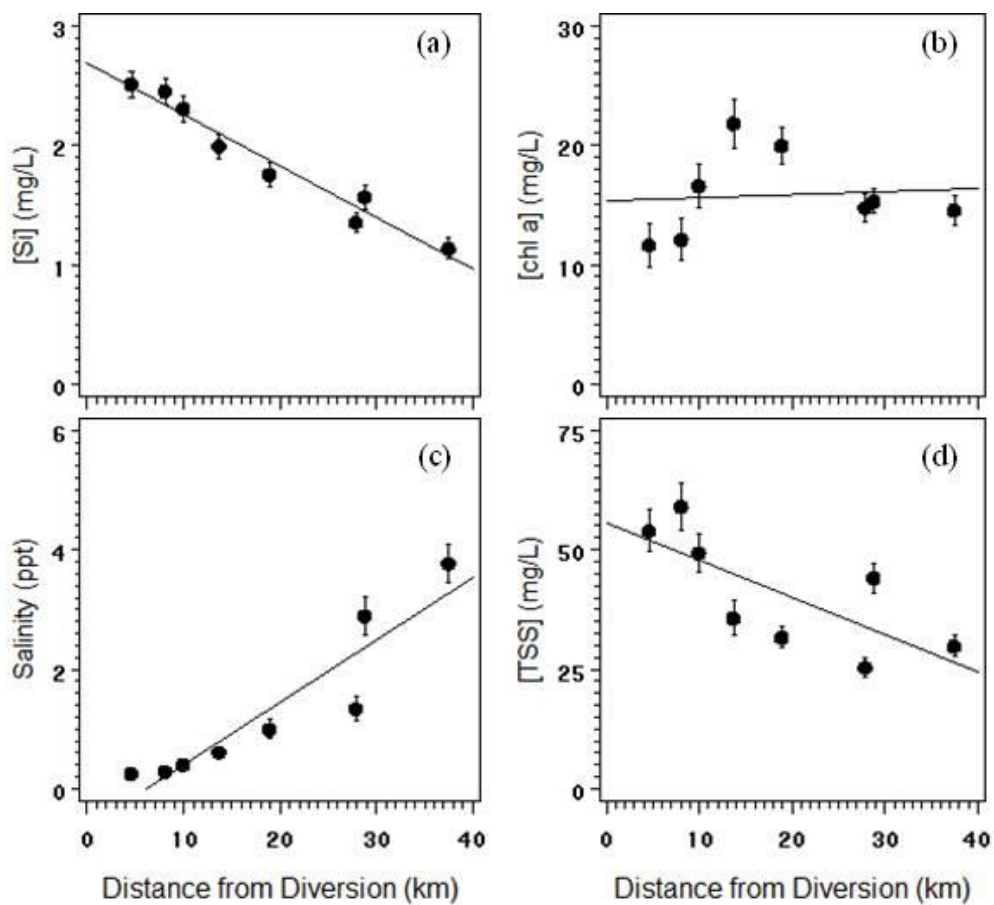


Figure 3.5: Relationship between (a) SiO_4 , (b) CHL *a*, (c) salinity and (d) TSS and distance from the diversion. Data points represent mean concentrations (± 1 s.e.) of each water quality parameter. Trend lines indicate statistical significance with the covariate distance.

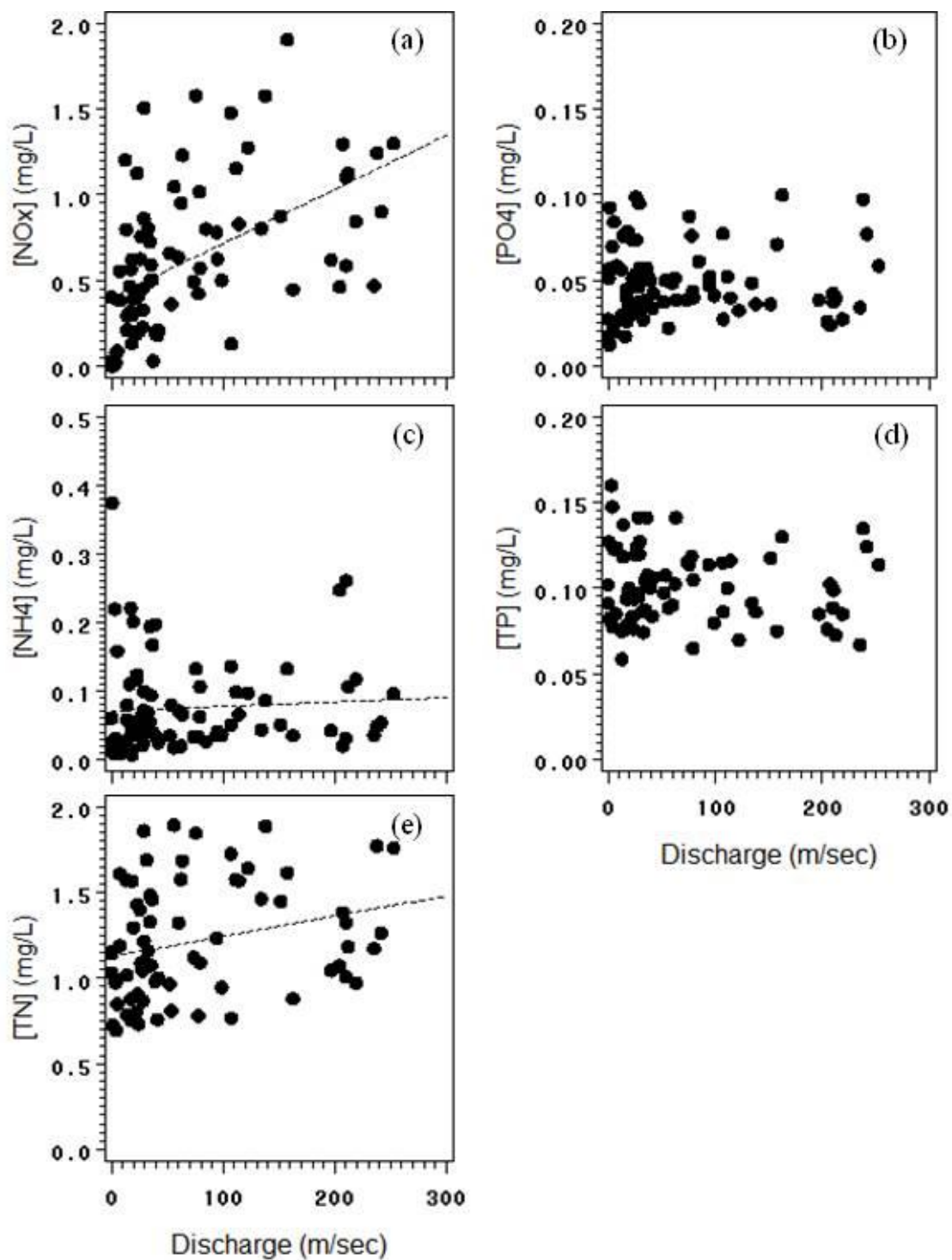


Figure 3.6: Concentrations of NO_x, PO₄, NH₄, TP and TN in relation to discharge. Trend lines indicate statistical significance with the covariate discharge.

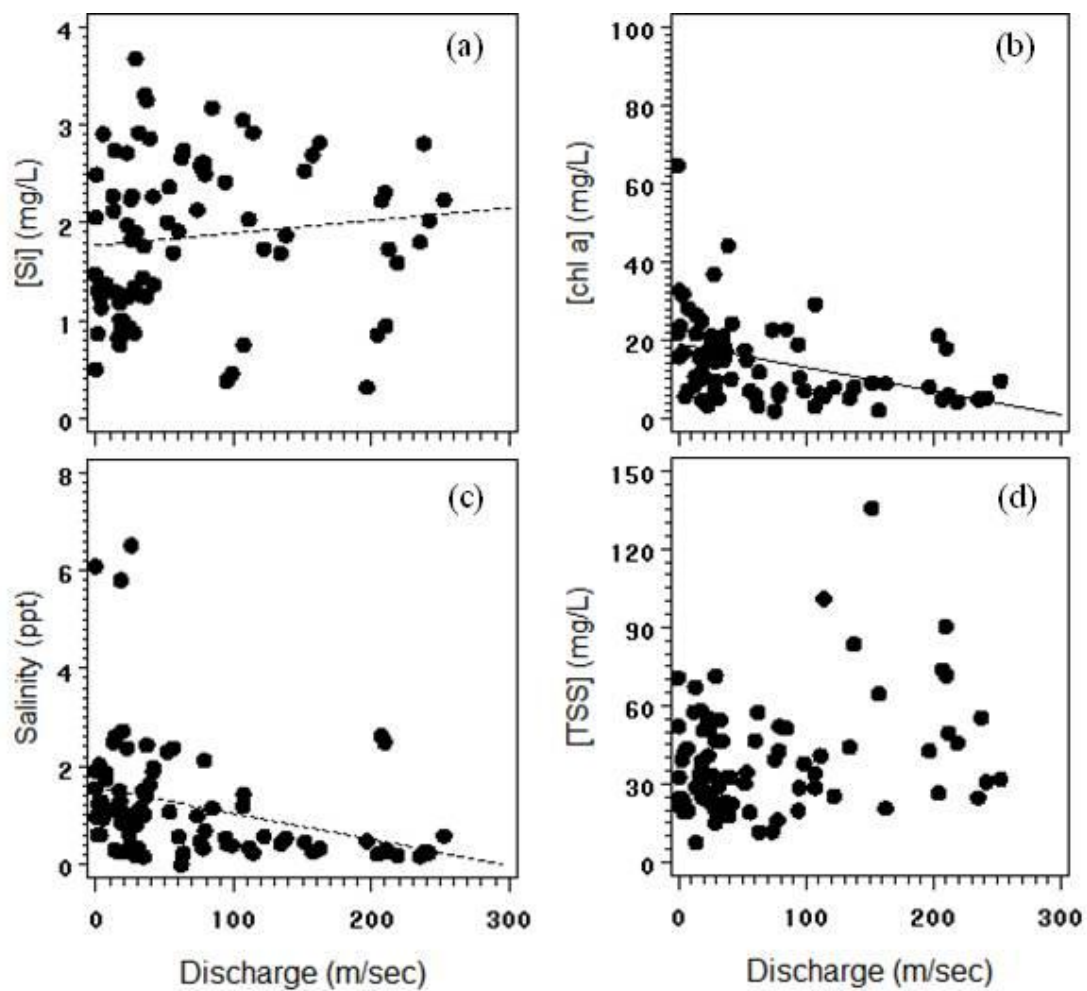


Figure 3.7: Concentrations of (a) SiO_4 , (b) CHL a, (c) salinity and (d) TSS in relation to distance. Trend lines indicate statistical significance with the covariate discharge.

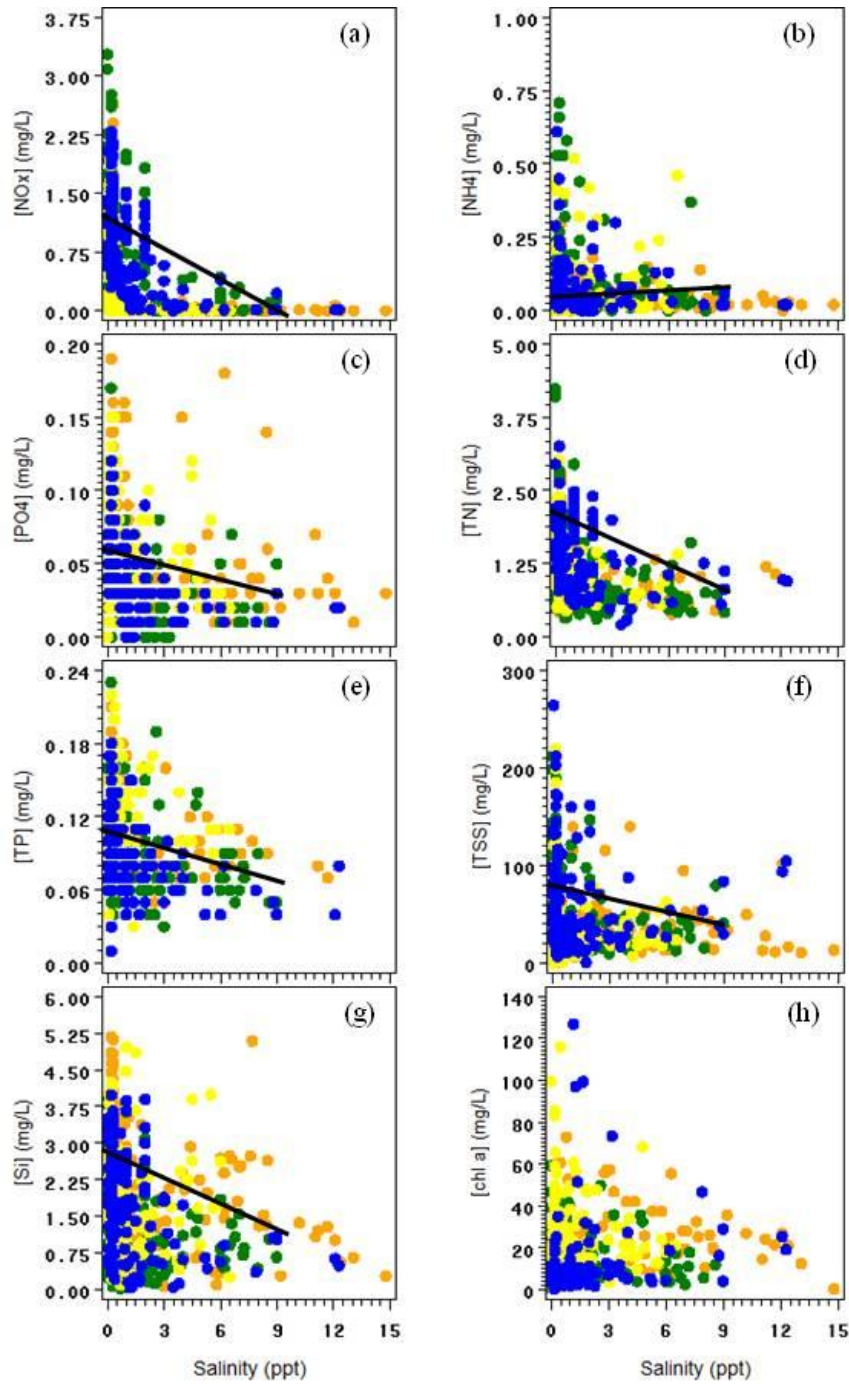


Figure 3.8: Salinity mixing diagrams of with circles representing individual data points and solid lines representing the conservative mixing line with respect to the river and the lower estuary. Water quality parameters include (a) NO_x , (b) NH_4 , (c) PO_4 , (d) TN, (e) TP, (f) TSS, (g) SiO_4 , and (h) CHL *a*. Orange = fall, green = spring, yellow = summer, blue = winter.

Total phosphorus concentrations ranged from 0.01 to 0.23 and varied among seasons ($F_{(3,585)}=20.89$, $p<0.0001$), with concentrations highest in the summer and fall and lowest in the winter and spring (Fig. 3.3). Concentrations decreased with distance ($F_{(1,585)}=111.64$, $p<0.0001$; Fig. 3.4), though TP did not vary with discharge ($F_{(1,585)}=0.32$, $p=0.5930$). The salinity mixing diagram indicates that the estuary is a sink for TP in the winter and spring and a source in summer and fall (Fig. 3.8).

Silicate concentrations ranged from 0.03 and 5.18 and varied among seasons ($F_{(3,659)}=35.66$, $p<0.0001$), with concentrations highest in the fall, summer and winter and lowest in the spring (Fig. 3.3). Silicate concentrations increased with discharge ($F_{(1,659)}=28.20$, $p<0.0001$; Fig. 3.7) and decreased with increasing distance ($F_{(1,659)}=261.91$, $p<0.0001$; Fig. 3.5). The salinity mixing diagram indicates that the estuary is generally a sink for SiO_4 in the winter and spring and a source in the fall (Fig. 3.8).

Total suspended sediment concentrations ranged from 1 to 264 mg/L and varied among seasons ($F_{(3,659)}=37.52$, $p<0.0001$), with concentrations highest in winter and lowest in summer (Fig. 3.3). Concentrations of TSS generally decreased with increasing distance ($F_{(1,659)}=59.75$, $p<0.0001$), though TSS concentrations at 30 km are as high as concentrations within 10 km (Fig. 3.5). TSS concentrations did not vary with discharge ($F_{(1,659)}=3.95$, $p=0.0474$; Fig. 3.7). The salinity mixing diagram indicates that the estuary is generally a sink for TSS but can be a source at higher salinities (Fig. 3.8).

Chlorophyll a concentrations ranged from 0.40 to 126.98 mg/L and varied seasonally ($F_{(3,649)}=24.42$, $p<0.0001$), with concentrations greatest in the summer and fall and lowest in the winter (Fig. 3.3). Concentrations generally increased with increasing distance from the diversion ($F_{(1,659)}=22.98$, $p<0.0001$) with maximum concentrations at a distance of 20 km (Fig. 3.5). Concentrations generally decreased with increasing discharge ($F_{(1,659)}=94.16$, $p<0.0001$; Fig. 3.7). The salinity mixing diagram shows the estuary is a source for chlorophyll, especially during the summer and fall (Fig. 3.8).

Salinity ranged from 0 to 14.8 PSU and varied among seasons ($F_{(3,659)}=12.62$, $p<0.0001$), with salinity greatest in the fall (Fig. 3.3). Salinity decreased with increasing discharge ($F_{(1,659)}=27.21$, $p<0.0001$; Fig. 3.7) and increased with increasing distance from the diversion ($F_{(1,659)}=275.35$, $p<0.0001$; Fig. 3.5).

Loading rate of NO_x averaged $3.49 \text{ g N m}^{-2} \text{ yr}^{-1}$ during the study period. Mixing adjusted removal efficiency averaged 86% and varied among seasons ($F_{(3,73)}=15.29$, $p<0.0001$), with lower efficiencies during the winter relative to all other seasons (Table 3.2). Removal efficiency decreased with increasing loading rate ($F_{(1,73)}=8.37$, $p=0.0050$), though the relationship is most dramatic during the spring and winter seasons (Fig. 3.9). Removal efficiency increased with increasing distance from the diversion structure (Table 3.3).

Table 3.2: Nitrate loading rate ($\text{g NO}_x\text{-N m}^{-2} \text{ yr}^{-1}$) and removal efficiency (%), adjusted for salinity mixing, in the Breton Sound estuary with seasonal averages. N = number of transects for which loading and removal were calculated. Overall loading rate and removal efficiency are averaged across all seasons. Different superscripted letters indicate Bonferroni-adjusted differences among seasonal means.

	Overall	Season			
		Spring	Summer	Fall	Winter
Loading Rate	3.49	4.93	2.29	1.10	3.50
Adj. Rem. Eff.	86	87 ^a	98 ^a	92 ^a	74 ^b
N	78	30	16	10	22

Table 3.3: Nitrate removal efficiency (%) at varying distances from the diversion structure adjusted for salinity mixing in the Breton Sound estuary.

Distance (km)	4.6	8.1	10	13.7	18.9	27.9	28.8	37.5
Dilution adj. RE	22	23	34	54	60	71	78	79

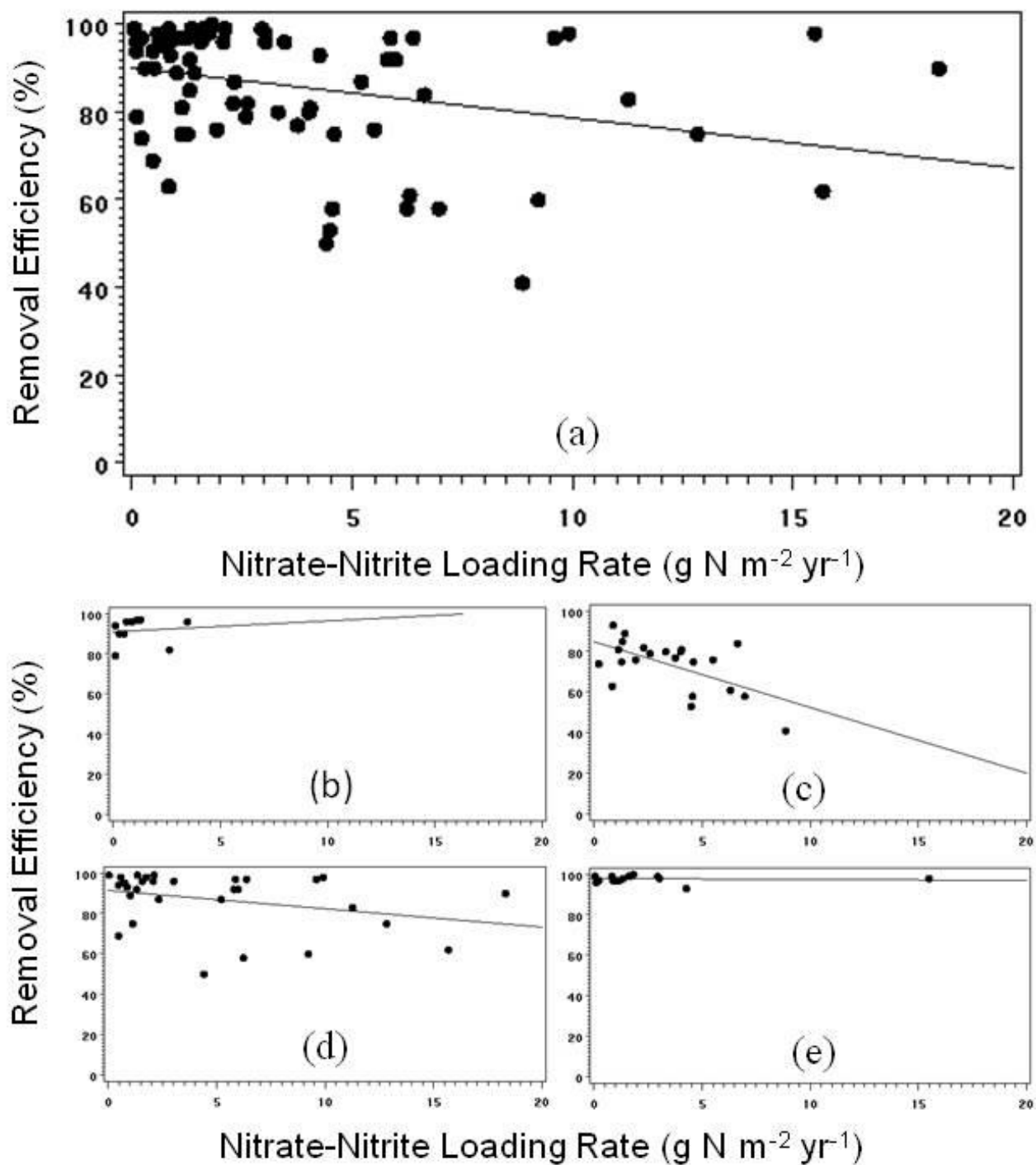


Figure 3.9: The relationship between loading rate and removal efficiency of NO_x in the Breton Sound (a) across all seasons and for (b) fall, (c) winter, (d) spring and (e) summer.

Discussion

The seasonal patterns of NO_x , NH_4 , TN, TP and TSS concentrations were generally similar to those found by Lane et al. (1999), a study that spanned the three years before and three years after initial operation of the diversion. The results of this study indicate that NO_x is rapidly removed from the estuary. Concentrations were greatest near the diversion, which contributes 67-83% of the NO_x input into the estuary (Hyfield et al., 2008). Once in the estuary, NO_x was non-conservatively removed, indicating the estuary is a sink for NO_x as well as TN. Total nitrogen was highly correlated with NO_x , as TN is about equally composed of NO_x and organic nitrogen (Lane et al., 1999). Lane et al. (1999) also found the estuary was a sink for NO_x and TN, but over a smaller time scale. Mitsch et al. (2005) found nitrate reductions in created riverine wetlands between 21 and 52%. Nitrate reduction pathways in the Breton Sound include denitrification, dilution with Gulf water, burial, and microbial and macrophyte uptake (Day et al., 2003a). Denitrification results in the end-products nitrous oxide (N_2O) and dinitrogen gas (N_2). Nitrous oxide flux averaged $0.0008 \text{ mg N}_2\text{O-N m}^{-2} \text{ hr}^{-1}$ during the spring and summer (Chapter 2). Estimated N_2 fluxes ranged from 0.02 to $0.08 \text{ mg N}_2\text{-N m}^{-2} \text{ hr}^{-1}$, based on $\text{N}_2:\text{N}_2\text{O}$ ratios of 22:1 (Schlesinger, 1997) and 100:1 (Hernandez & Mitsch, 2006), respectively. Spring and summer NO_x loading at Caernarvon averaged $0.46 \text{ mg NO}_x\text{-N m}^{-2} \text{ hr}^{-1}$, indicating that denitrification is a minor removal process in Breton Sound. However, Hyfield et al. (2008) concluded that denitrification is a major removal process in the Sound annually. More research is needed to quantify the fate of NO_3 in the Sound. Higher NO_x concentrations were associated with higher discharges, likely due to the negative relationship between removal efficiency and loading rate (Lane et al., 2003; Mitsch et al., 2005). Removal efficiency also varied seasonally, with the least removal occurring in the winter. Perez et al. (2011) found NO_x and TN concentrations were negatively correlated with temperature. Denitrification rates are inhibited at cold temperatures (Nowicki, 1994; Day et al., 2003a; Silvennoinen et al., 2008), limiting a major nitrate removal pathway for the estuary (Delaune & Jugsujinda, 2003; VanZomerem, 2011) during the winter.

The results indicate the estuary is a source for NH_4 , comparable to the results of Lane et al. (1999). Hyfield et al. (2008) found that atmospheric deposition represented the largest input source of NH_4 (57-62%) to the estuary, with the diversion serving as a secondary source (12-31%). Although a minor source, we found that the operation of the diversion did affect NH_4 concentrations. Ammonium concentrations increased with increasing salinity, as has been found in Fourleague Bay, LA (Perez et al., 2011). This may be due to limited sediment adsorption capacity with increases in salinity (Rysgaard et al., 1999). Gardner et al. (1991) found residence time of NH_4 in sediments decreased in response to increased salinity, due to the binding of dissolved ions in saltwater to clay and sediment particles. This prevented the adsorption of NH_4 , reducing its residence time in the sediment. Ammonium also is released through organic matter decomposition (mineralization).

The estuary acted as both a sink and a source for PO_4 and TP, depending upon the season. At times, dilution with high salinity Gulf waters was primarily responsible for decreasing concentrations away from the diversion structure. However, the results of this study indicate that TP reductions were greatest within the first 10 km, in accordance with the results of Lane et al. (2004). Concentrations were greatest in the summer and fall, and lowest in the spring. The diversion serves as the dominant source of phosphorus, accounting for as much as 60% of TP input (Hyfield et al., 2008). Phosphate is adsorbed onto clay particles under high concentrations, and desorbed under low concentrations (Reddy & DeLaune, 2008). Removal occurs due to burial and nutritive uptake, and may be regenerated through decomposition and sediment resuspension.

The primary source of silicate in estuaries is the weathering of terrestrial sediments and clays delivered by riverine input (Tréguer et al., 1995). The results of this study indicate silicate is reduced in the winter and spring. This coincides with peak diatom populations in the region (Dortch et al., 2001). One of the removal pathways of silicate is uptake by diatoms, which assimilate the nutrient into their tests. Adsorption and subsequent burial represents the lone permanent removal pathway for silicate (Day, 1989). The estuary was generally a source for silicate in the summer and fall probably representing dissolution of tests.

Chlorophyll *a* concentrations were greatest in the fall and summer, in the mid estuary and when discharge was low, conditions in which TSS concentrations were lowest. Lane et al. (2007) found similar patterns of chlorophyll concentrations and TSS for flow-through data in the estuary. The same seasonal patterns have been observed for phytoplankton in other estuaries (Rudek et al., 1991; Lewitus et al., 1998). These results support their proposed mechanism for this pattern; that is that high discharge during the spring and winter results in increased turbidity, resulting in light limitation that limits aquatic productivity. In contrast, turbidity decreases in the estuary during summer and fall when the diversion is operated at low discharge. However, sediments are often resuspended in the lower estuary due to storm activity.

The results of this study indicate that the diversion wetlands are effectively removing nutrient inputs to the Gulf, especially in the case of nitrate. To reduce the effects of hypoxia in the Gulf, our results indicate the diversion could be managed to maximize nitrate removal by operating at low or pulsing discharge, especially in the winter. This would increase residence time, thereby increasing nitrate removal (DeLaune et al., 2005). However, decreasing discharge also may result in rapid settling of sediments out of the water column in the upper estuary, limiting the range of marsh building through mineral sediment input. Further studies are needed to determine the seasonally optimum discharge for both nitrate removal and suspended sediment distribution.

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CHAPTER 4

NUTRIENT LOADING RATES AND REMOVAL EFFICIENCY IN RIPARIAN WETLANDS UNDER RESTORED HYDROLOGY

Introduction

Among the world's largest wetland systems, the Mississippi River Basin (MRB) wetlands have been described as among the most anthropogenically disturbed (Shaffer & Day, 2007; Keddy et al., 2009). Water quality in the basin has worsened, with nitrate concentrations doubling to an average of 1.45 g N L^{-1} since 1950, and export to the Gulf has doubled to about one million tonnes per year (Goolsby & Battaglin, 2001). Changes in agricultural practices are largely responsible for increased nutrient loads in the river: increased rates of fertilizer application, an expansion in soybean and corn production, and increased surface water runoff due to more efficient drainage systems (Howarth et al., 2002; Donner, 2003; Donner et al., 2004; Zhang & Schilling, 2006). An extensive system of artificial levees was constructed along the lower Mississippi River during the 20th century, preventing seasonal inundation of the floodplain. This has isolated the river from its floodplain wetlands, which historically served as nitrogen sinks (Day et al., 2000; Mitsch et al., 2001; Day et al., 2003b).

Increased nitrogen loading to the Gulf of Mexico has resulted in increased extent and severity of seasonal hypoxic zones. These areas of coastal bottom waters with dissolved oxygen concentrations of less than 2 mg/L form when high nutrient concentrations fuel phytoplankton blooms. Oxygen is consumed during decomposition of the resulting organic matter. Stratification during the summer prevents downward diffusion of oxygen from surface waters, resulting in poorly oxygenated bottom waters. The areal extent of the hypoxic zones varies, but can reach as much as 20,000 km² (Turner et al., 2008). Factors affecting the severity and extent of the dead zone are varied (Bianchi et al., 2010), but nitrate export is a main contributor to phytoplankton productivity (Justic et al., 1995; Rabalais et al., 2002a; Lohrenz et al., 2008).

The MRB has also experienced large-scale alluvial wetland loss (Shaffer & Day, 2007). Clear-cutting of bottomland hardwood forests for timber and development of agricultural land began in the 19th century (Turner & Rabalais, 2003). During the 20th century, an estimated 30 million ha of wetlands were drained (Mitsch et al., 2001), primarily for agricultural development (Hefner & Brown, 1984; Wilen & Frayer, 1990). Additional factors contributing to wetland loss include levee and dam construction (Day et al., 2003b; Blum & Roberts, 2009), which have isolated floodplain wetlands from historical nutrient and sediment loads.

Restoration efforts are needed that simultaneously address water quality and wetland loss issues. River diversions and restored hydrologic regimes offer the potential for water quality amelioration and wetland expansion (Mitsch & Day, 2006; Day et al., 2009b). Several diversions are currently in operation in the deltaic wetlands of the MRB. One diversion in

particular, Caernarvon, has demonstrated the ability to improve water quality, with high nutrient removal efficiencies (Lane et al., 1999; Lane et al., 2006).

Removal efficiency (RE) is the percent reduction of a nutrient (e.g., nitrogen, phosphorus) from the water column, which occurs as the nutrient is retained in the wetland or released to the atmosphere (Blahnik & Day, 2000). Removal efficiency is inversely related to loading rate (Richardson & Nichols, 1985; Hunter et al., 2009), which is the amount of a nutrient supplied to a given area of wetland over a specified time (Blahnik & Day, 2000). Loading rate increases with increasing nutrient concentration and decreases with increasing wetland areal extent. To improve water quality within the MRB, restoration efforts that deliver high RE are needed.

The purpose of this study is to determine if restoring hydrologic regimes in the central MRB can offer high removal of nutrients, especially nitrogen. Specifically, the goals of this study are (1) to determine spatial patterns of nutrient concentrations in a secondary channel under restored pulsing hydrology, (2) to calculate nutrient loading rates and removal efficiencies for the channel and surrounding wetlands and (3) to compare those removal efficiencies to those at Caernarvon and other wetlands within the MRB.

Study Sites

The Loosahatchie Chute is a secondary channel located on the west bank of the Mississippi River in Crittenden county, Arkansas, USA across from Memphis, Tennessee between river miles 736.5 and 742.8 (Fig 4.1). The surrounding wetlands are riparian *Salix nigra* and *Salix interior* forests. In the 1960s, the U.S. Army Corps of Engineers (USACE) constructed stone dikes measuring between 100 and 600 meters in length to divert flow from the Mississippi River away from the Loosahatchie Bar secondary shipping channel during periods of low flow. To restore hydrology in the Loosahatchie chute, twelve USACE –designed notches were constructed in nine existing dikes in 2008 according to the specification of the Lower Mississippi River Conservation Committee. Each notch measures between 7.5 and 65 meters wide with depths measuring 0.9-3.3 meters. These notches allow riverine water to flow into the Loosahatchie chute during periods of high flow. This effort was funded by the US Fish and Wildlife Service Fish Passage Program, Audubon Society and non-governmental conservation organizations to restore flow to habitats of two federally listed species (pallid sturgeon and least tern), as well as other wildlife.

The Caernarvon freshwater diversion is located on the Mississippi River at river mile 81.5, south of New Orleans in St. Bernard Parish, Louisiana, USA. The control structure is a five-box culvert with vertical lift gates for managed flow. The diversion has been in operation since August 1991. Since discharge began, the control structure has discharged into the Breton Sound estuary, which contains 1100 km² of fresh, brackish and saline marshes. Breton Sound has an open connection to the Gulf of Mexico, and is bounded by natural and artificial levees and spoil banks. Wetlands within the Breton Sound were originally formed as part of the Plaquemines-St.

Bernard delta lobes (Roberts, 1997). More detailed descriptions of this area can be found in Day et al. (2009b) and Lane et al (1999; 2007).

Methods

Five transects were established along the length of the Loosahatchie chute for the purpose of water quality sampling (Fig. 4.1). Each transect originated at the center of the channel and terminated at the western shore. Samples were taken from three stations along each transect: the center of the channel, the shoreline and an intermediate station. At each sampling location, dissolved oxygen (DO), water depth, and flow velocity and direction were measured. DO was measured using a YSI DO meter and water depth was measured using a depth sounder. Stream flow velocity was measured using a flow meter. Once flow velocity was obtained, flow direction was determined by aligning a compass with the flow meter in the direction of the maximum flow. Three separate transects were carried out in March and June 2010 and June 2011. River stage at time of sampling was between 5 and 9 m above reference datum (Fig. 4.2). Flooding of the riparian wetland generally occurred when river stage exceeded 4 m. The amount of wetlands under inundation varies with river stage, but the chute was inaccessible during low or high river stage. When stage was less than 5 m, the emergence of a sandbar prohibited access to the chute. When stage was greater than 9 m, the river was often unsafe for navigation due to large floating debris.

Water samples were collected at each site from a depth of 10-20 cm in acid-washed one-liter plastic containers (Greenberg et al., 1985). Samples were preserved in cold storage prior to analysis. Water quality parameters included nitrite + nitrate (NO_x), ammonium (NH_4), total nitrogen (TN), phosphate (PO_4), total phosphorus (TP), silicon (SiO_4) and chlorophyll a (CHLA). Samples analyzed for NO_x and NH_4 were filtered prior to analysis using 0.45 μm Millipore filters. The following parameters were determined by the following methods: NO_x by the automated cadmium reduction method, NH_4 by the automated phenate method, PO_4 by the automated ascorbic acid reduction method, and SiO_4 by the automated molybdate reagent/oxalic acid method, all with an Alpkem© autoanalyzer (Greenberg et al., 1985). TN and TP was determined by the persulphate oxidation method (Valderrama, 1981), and CHLA was determined using a modified version of the Strickland and Parsons (1977) technique. Pigment extract was obtained using a 40:60 solution of dimethyl sulfoxide (DMSO):90% acetone (Burnison, 1980) and measured with a Turner Designs model 10-AU fluorometer.

Dissolved oxygen, CHLA and the 6 nutrient concentrations were analyzed as dependent variables in a multivariate analysis of variance (MANOVA) with season (spring/summer), transect (1-5) and station (stream/mid/bank) as categorical independent variables. Assumptions of multivariate normality and homoscedasticity could not be met, even with transformations and outlier removal. Instead, nine separate analyses of covariance (ANCOVA) were performed and significance for each model was determined using a Bonferroni-adjusted p-value of 0.0055 ($\alpha=0.05/9$). All variables met assumptions of univariate normality and homogeneity of variance

except NH_4 , which was log transformed. Transformation did not affect the results, so the untransformed variable was used. All statistical analyses were performed with SAS 9.1 (SAS Institute Inc., Cary, NC, 2004).

Loading rates and removal efficiencies were calculated for each nutrient for each of the three sampling trips. Loading rate was calculated using Eq. (1):

Loading rate ($\text{mg m}^{-2} \text{ sec}^{-1}$)

$$= ([N_{in}] * D) / A \quad (1)$$

where $[N_{in}]$ is the initial concentration of the nutrient when it enters the chute (in mg/L), D is discharge (in m s^{-1}) and A is areal extent (m^2) of the chute and the surrounding flooded wetland. Loading rate was then converted to units of $\text{g m}^{-2} \text{ d}^{-1}$. Discharge was calculated by multiplying the average cross-sectional area of the chute where the transects are located by the average flow in the chute. Removal efficiency was calculated using Eq. (2):

Removal efficiency (%)

$$= \left(\frac{[N_{in}] - [N_{out}]}{[N_{in}]} \right) * 100 \quad (2)$$

where $[N_{out}]$ is the concentration of the nutrient at the end of the chute, and $[N_{in}]$ is the concentration of the nutrient when it enters the chute from the river. Loading rate and removal efficiency of nitrate was also calculated for Caernarvon, a coastal Louisiana estuary receiving diverted Mississippi River water. Removal efficiency at Caernarvon was adjusted for dilution with saline Gulf waters. Loading rates and removal efficiencies were calculated seasonally, for the upper and lower estuary, and for high and low discharge.

Results

Forty-five water quality samples were collected over the three sampling trips, with 30 during the summer and 15 during the spring. Spring sample temperatures averaged 8.7°C , whereas summer samples averaged 25.2°C . Spring water flow rates averaged 1.0 m sec^{-1} , and summer flow rates averaged 1.3 m sec^{-1} . Water depth averaged 7.9 m in the spring and 5.6 m in the summer. Concentrations of nitrate ranged from 1.98 to 2.62 mg L^{-1} , from 0.02 to 0.13 mg L^{-1} for NH_4 , from 1.86 to 2.84 mg L^{-1} for TN, from 0.01 to 0.15 mg L^{-1} for PO_4 , from 0.01 to 5.07 mg L^{-1} for SiO_4 , from 0.73 to $4.73 \mu\text{g L}^{-1}$ for CHLA, from 4.97 to 6.67 mg L^{-1} for DO, and from 71 to 346 mg L^{-1} for TSS.

The statistical model for NO_x was significant ($F_{7,36}=20.06$, $p<0.0001$), with summer concentrations greater than spring ($F_{1,36}=124.23$, $p<0.0001$; Fig. 4.3). There was no significant effect on NO_x with respect to transect ($F_{4,36}=2.84$, unprotected $p=0.0384$) or station ($F_{2,36}=0.23$, $p=0.7978$). The statistical model for NH_4 was not significant ($F_{7,37}=1.38$, $p=0.2434$). The statistical model for PO_4 also was not significant ($F_{7,37}=1.81$, $p=0.1146$). The statistical model

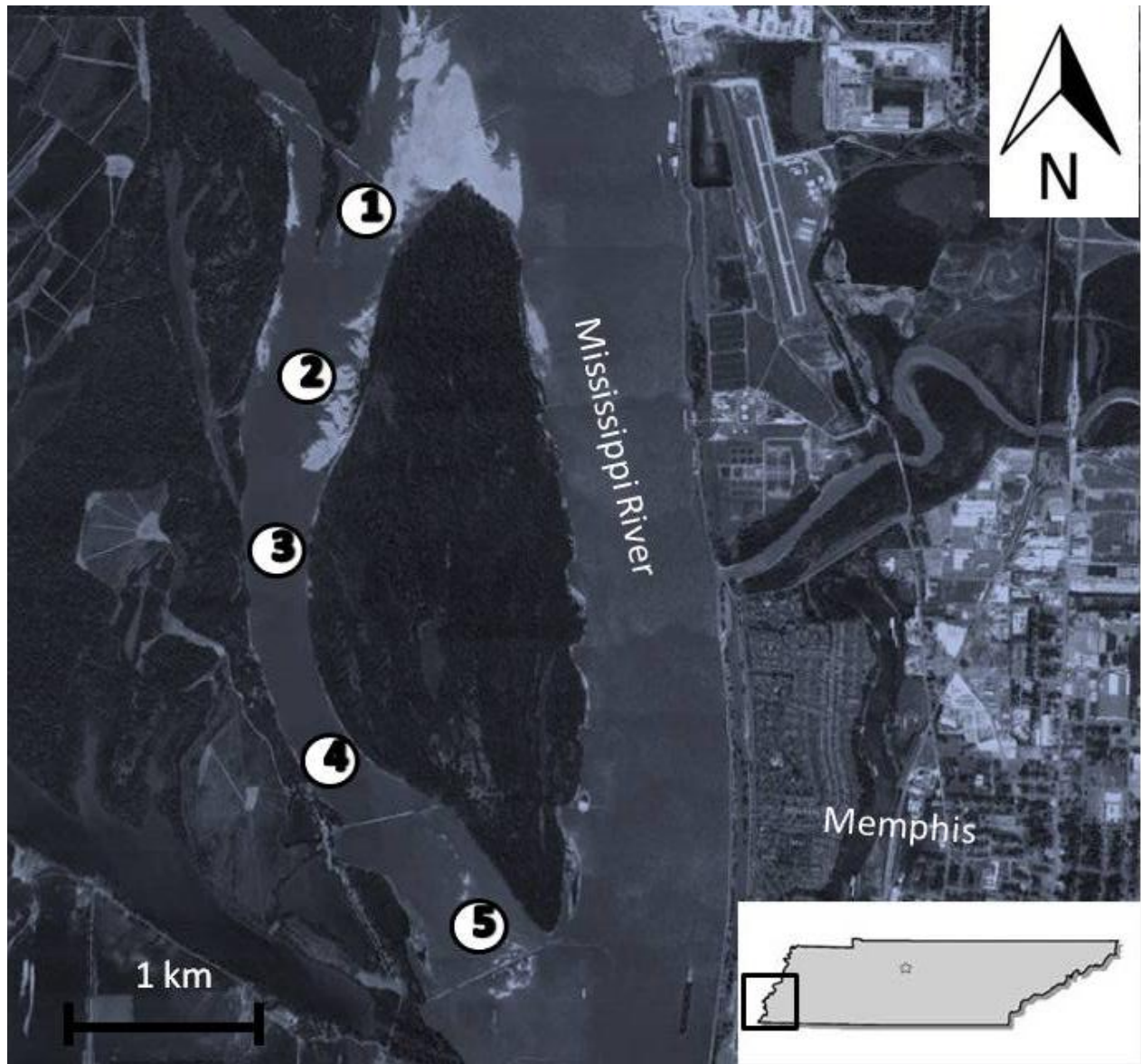


Figure 4.1: Water sampling transects at Loosahatchie Chute, a secondary channel on the Mississippi River near Memphis, TN. Numbered circles indicate the location of each water quality transect, which originate in the center of the channel and terminate on the western bank. The light colored lines crossing the channel are rock jetties constructed to limit flow in the chute during low flow. These were notched to increase flow in the chute.

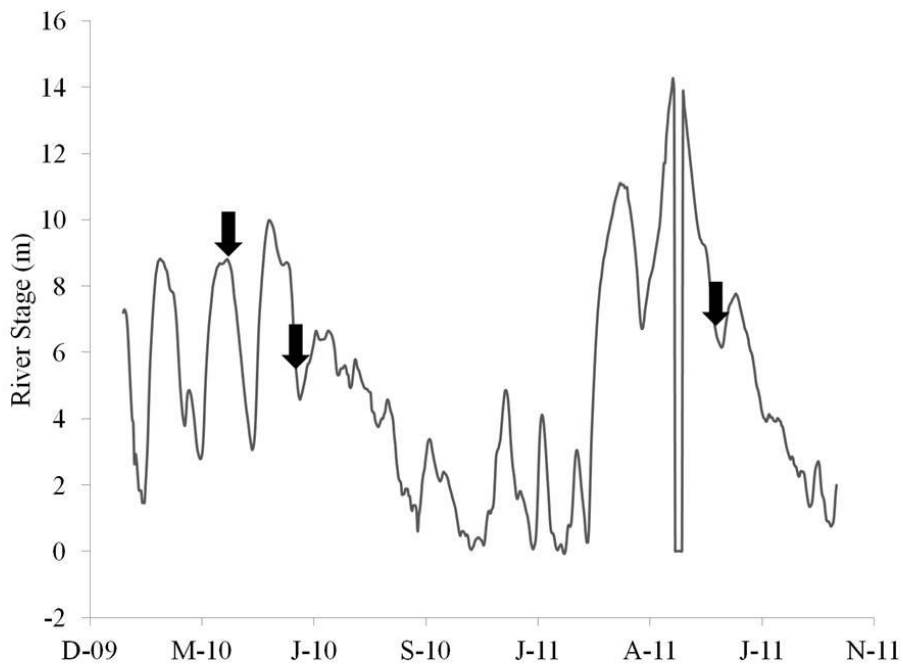


Figure 4.2: Mississippi River stage at Memphis, TN from December 2009 to November 2011. Arrows indicate stage at time of water quality sampling dates. River gage is located approximately 3 km south of sampling sites. Flooding of the riparian wetland generally occurred at 4 m. Sampling was not possible at very high or low water levels because of site inaccessibility.

for TN was significant ($F_{7,37}=43.74$, $p<0.0001$), with summer concentrations greater than spring ($F_{1,37}=294.28$, $p<0.0001$; Fig. 4.3). There was no significant effect on TN with respect to transect ($F_{4,36}=2.52$, $p=0.0578$) or station ($F_{2,36}=2.37$, $p=0.1084$). The statistical model for TP was significant ($F_{7,37}=5.09$, $p=0.0004$), with summer concentrations greater than spring ($F_{1,37}=31.87$, $p<0.0001$; Fig. 4.3). The statistical model for SiO_4 was also not significant ($F_{7,37}=1.71$, $p=0.1377$). The statistical model for DO was significant ($F_{7,18}=67.34$, $p<0.0001$), with summer measurements greater than spring ($F_{1,18}=453.49$, $p<0.0001$; Fig. 4.3). There was no significant effect on DO with respect to transect ($F_{4,22}=2.83$, $p=0.0556$) or station ($F_{2,22}=3.70$, $p=0.0450$). The statistical model for CHLA was not significant ($F_{7,22}=2.01$, $p=0.0995$). The statistical model for TSS was significant ($F_{7,37}=10.22$, $p<0.0001$), with spring concentrations greater than summer ($F_{1,37}=69.06$, $p<0.0001$; Fig. 4.3). There was no significant effect on TSS with respect to transect ($F_{4,37}=0.04$, $p=0.9971$) or station ($F_{2,37}=1.17$, $p=0.3204$).

Nitrate loading rates at Memphis ranged from 0.44 to 0.56 $\text{g m}^{-2} \text{d}^{-1}$, from 0.004 to 0.02 for NH_4 , from 0.45 to 0.64 for TN, from 0.005 to 0.02 for PO_4 , from 0.01 to 0.02 for TP, from 0.25 to 0.84 for SiO_4 , and from 19 to 62 for TSS (Table 4.1). Removal efficiencies ranged from -1% to 16% for NO_x , from -9% to 38% for NH_4 , from -3% to 15% for TN, from -96% to 2% for PO_4 , from -2% to 26% for TP, from -21% to -60% for SiO_4 , and from 0 to 4% for TSS (Table 4.1). Nitrate loading rates from Caernarvon ranged from 0 to 0.05 $\text{g m}^{-2} \text{d}^{-1}$, and removal efficiency ranged from 41% to 100%. Loading rates were highest in the spring and winter, in the upper estuary and during high discharge, and coincided with the lowest removal efficiencies (Table 4.2-4.4).

Discussion

Summer NO_x and TN concentrations were greater than spring concentrations. Nitrate concentrations comprised 97% of TN concentrations observed in this study, indicating low organic nitrogen concentrations. Peak NO_x concentrations in central MRB streams often occur during the summer (Mitsch et al., 2005), coinciding with warmer temperatures and greater DO concentrations, both of which are correlated with nitrification rates (Strauss et al., 2004), and after the first heavy precipitation events following fertilizer application on agricultural lands (Vanni et al., 2001; Turner & Rabalais, 2004). Nitrification, the microbial oxidation of ammonia to nitrite and nitrate, can be a significant source of NO_x in water bodies within the central MRB (Strauss et al., 2004). Peak NH_4 concentrations occur during the winter, and the lowest concentrations occur during the summer, when warm temperatures fuel high rates of nitrification (Antweiler et al., 1996). Temperature in the summer was almost 20° C warmer than in the spring, supporting nitrification as a major source of NO_x . Phosphate concentrations did not vary by season, though TP concentrations were greater in the summer relative to the spring. The primary removal mechanism of phosphorus from the water column is adsorption to sediment. Suspended sediment concentrations were greater in the spring, coinciding with greater discharge and river stage.

Nutrient removal efficiencies at Memphis were generally low. Removal efficiency is negatively related to loading rate (Richardson & Nichols, 1985; Hunter et al., 2009). Loading rates of nitrate were high and removal efficiencies were low at Memphis, especially relative to other studies performed within the MRB (Phipps & Crumpton, 1994; Lane et al., 2002; Fink & Mitsch, 2004; Mitsch et al., 2005)(Figure 4.4). Removal efficiency is maximized when concentrations are low or the areal extent of wetlands is large (Blahnik & Day, 2000). Potential denitrification rates (estimated in Chapter 2) were relatively high ($8.91 \text{ mg N m}^{-2} \text{ d}^{-1}$) within the wetlands. However, in this study, only a narrow band of riparian forest served as the receiving wetland, limiting the opportunity for removal through denitrification within the riparian wetlands. Site access was limited to a narrow range of river stage due hydrological conditions on the river. It is possible that sampling during high river stage would have yielded higher removal efficiencies due to the increased areal extent of the receiving wetland. But temperature is low during high stage and this would reduce the removal efficiency.

Water quality in the MRB has worsened in the past decade, primarily due to agricultural practices (Mitsch & Day, 2006). Approximately, 70% of the nitrogen and phosphorus exported to the Gulf of Mexico is from agricultural sources (Alexander et al., 2007), due to increased fertilizer application, corn and soybean expansion, and increased surface water runoff (Howarth et al., 2002; Donner, 2003; Donner et al., 2004; Zhang & Schilling, 2006). Restoring hydrologic cycles to riparian wetlands has been proposed as a means of reducing nutrient loading to the Gulf and improving water quality in the MRB generally (Mitsch et al., 2001). The results of this study indicate that the areal extent of the receiving wetlands should be taken into consideration when planning projects with the goal of water quality improvement. Reopening closed channels will have little effect on nutrient concentrations if the flow is restricted to the channel and small areas of adjacent wetlands.

Nitrate loading rate at Memphis was high and removal was low relative to Caernarvon (Fig. 4.4). The receiving wetland at Memphis is small in comparison to that at Caernarvon, and nitrate concentrations are generally lower at Caernarvon (Lane et al., 1999). At Caernarvon, the loading rate and removal differs seasonally, spatially and with discharge (Fig. 4.5). Removal at Caernarvon is lowest in winter, when discharge is high and temperatures are low. The upper estuary has higher loading and lower removal efficiency, due to input from the Mississippi River. Removal was lower when discharge was higher, reflecting the increased loading (Blahnik & Day, 2000). When the daily loading rates we calculated are extrapolated to annual loads and compared with other studies in the MRB (Fig. 4.4 and 4.5), the Memphis and Caernarvon sites represent the two extremes of the loading-removal continuum in the Basin. Some of these changes are likely due to the vast differences in scale at which these projects operate. Diverted Mississippi River water travelled 39 km at Caernarvon versus 5.6 km at Memphis. Nitrate removal efficiency calculated for the first 5 km at Caernarvon was approximately 23%, much lower than what was found for Caernarvon as a whole. However, this is still high relative to the removal efficiencies found at Memphis, which ranged from -1% to 7%. Management

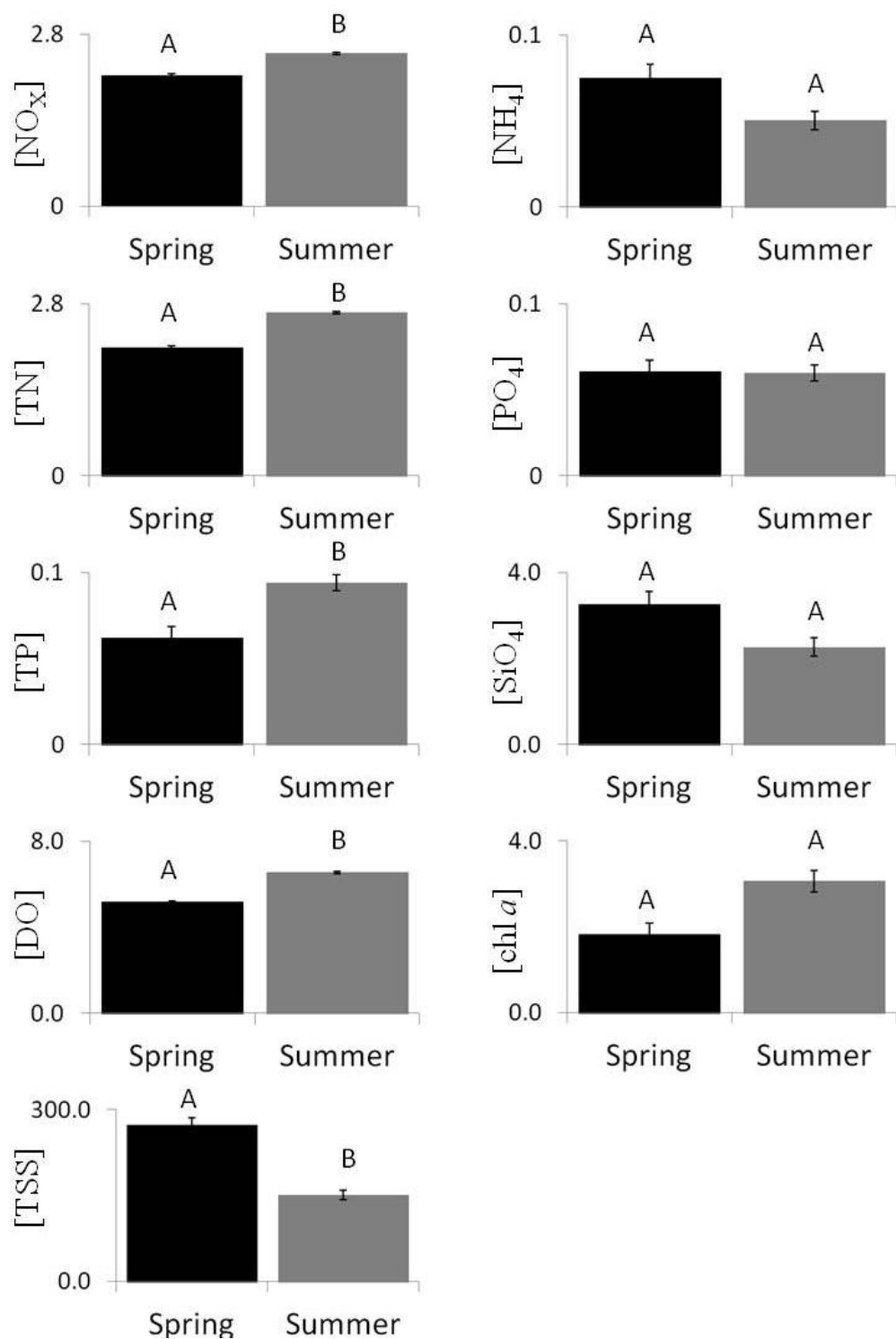


Figure 4.3: Mean seasonal concentrations of NO_x, NH₄, TN, PO₄, TP, SiO₄, DO and chl *a*. All concentrations are in mg/L, except chl *a*, which is in µg/L. Different letters indicate significant differences ($p < 0.0055$), as determined by Bonferroni-adjusted multiple comparison test.

Table 4.1: Loading rate ($\text{g m}^{-2} \text{d}^{-1}$) and removal efficiency (%) of nutrients sampled at the Loosahatchie chute. Negative removal efficiencies indicate increases in concentrations downstream within the chute.

	Spring 2010	Summer 2010	Summer 2011
NO _x			
Loading Rate	0.45	0.44	0.56
Removal Efficiency	-1	5	7
NH ₄			
Loading Rate	0.02	0.01	0.004
Removal Efficiency	17	38	-449
TN			
Loading Rate	0.45	0.46	0.64
Removal Efficiency	-3	15	3
PO ₄			
Loading Rate	0.02	0.005	0.02
Removal Efficiency	2	-96	-5
TP			
Loading Rate	0.01	0.02	0.02
Removal Efficiency	9	26	-2
SiO ₄			
Loading Rate	0.59	0.25	-
Removal Efficiency	-21	-60	-
TSS			
Loading Rate	62	19	40
Removal Efficiency	4	3	0

Table 4.2: Seasonal mean loading rate ($\text{g m}^{-2} \text{d}^{-1}$) and removal efficiency (%) of nitrate sampled at the Caernarvon river diversion in coastal Louisiana (from Chapter 3).

	Fall	Winter	Spring	Summer
Loading Rate	0.003	0.010	0.014	0.006
RE	92	74	87	98

Table 4.3: Mean loading rate ($\text{g m}^{-2} \text{d}^{-1}$) and removal efficiency (%) of nitrate in upper and lower Caernarvon river diversion wetlands in coastal Louisiana.

	Upper	Lower
Loading Rate	0.021	0.009
RE	67	74

Table 4.4: Mean loading rate ($\text{g m}^{-2} \text{d}^{-1}$) and removal efficiency (%) of nitrate during high and low discharge at the Caernarvon river diversion in coastal Louisiana.

	High Discharge	Low Discharge
Loading Rate	0.028	0.001
RE	80	90

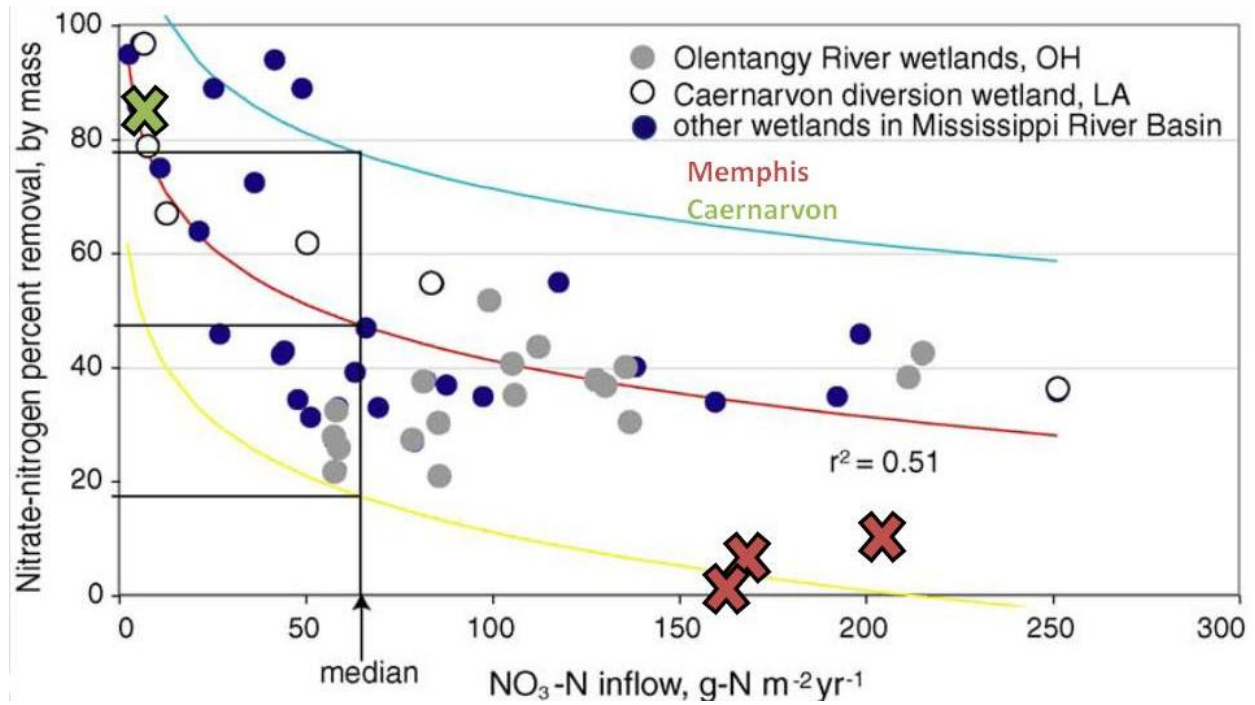


Figure 4.4: Nitrate loading rate and removal efficiency at two locations in the Mississippi River Basin: a secondary channel near Memphis, TN and the Caernarvon river diversion at Breton Sound, LA. The Caernarvon average represents an 8-year average, whereas the Memphis data points are calculated from three discrete water quality sampling trips. The data from this study are plotted along with data from earlier studies (modified from Mitsch et al. (2005) with permission).

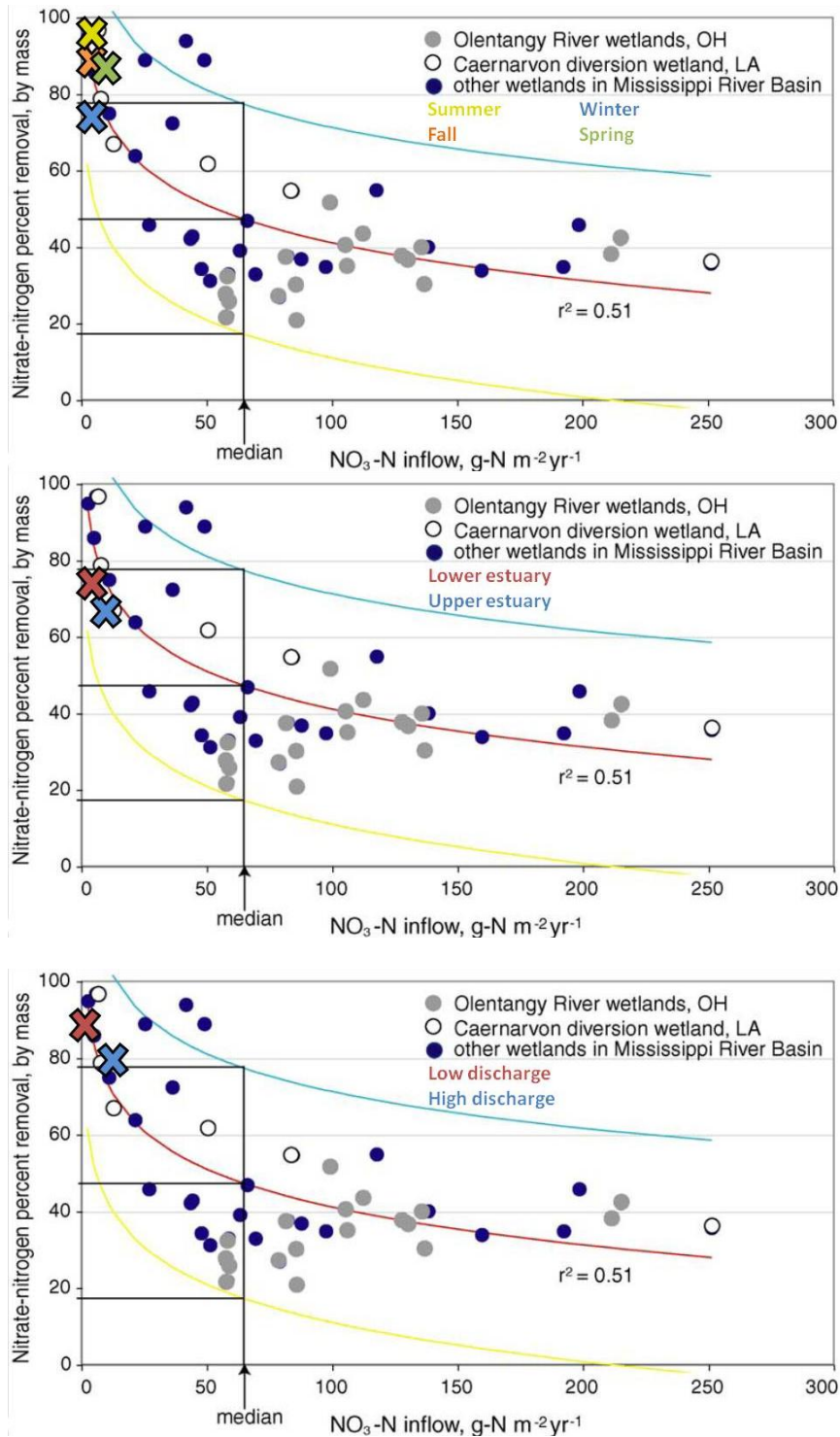


Figure 4.5: Variations in nitrate loading rate – removal relationship in response to A. seasons, B. the upper and lower estuary, and C. discharge rates at Caernarvon, LA. The data from this study are plotted along with data from earlier studies (modified from Mitsch et al. (2005) with permission).

practices must include considerations of wetland area size, loading rates, and seasonal patterns in planning and managing projects aimed at ameliorating water quality within the Mississippi River Basin.

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CHAPTER 5

SUMMARY AND CONCLUSIONS

Objectives

The purpose of this study was to determine the effects of reintroduction of riverine water to riparian wetlands and marshes, via river diversions or restored hydrology, on greenhouse gas production and nutrient dynamics. Two study sites were utilized: a riparian forested wetland in the central Mississippi River Basin near Memphis, TN under restored flood pulsing, and a river diversion estuarine wetland complex at Caernarvon, LA. Null hypotheses included:

- 1) No difference exists in emissions of methane and nitrous oxide between Memphis and Caernarvon, between sites impacted by river waters and those non-impacted, or between spring and summer.
- 2) Nutrient concentrations at Caernarvon do not vary seasonally or temporally. There is no seasonal variation in nitrate removal at Caernarvon, and removal is uncorrelated with loading rate.
- 3) Nutrient concentrations at Memphis do not vary seasonally or temporally.

Greenhouse Gas Fluxes

Methane flux averaged $0.53 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$ at Loosahatchie chute, a riparian wetland under restored hydrology located within the central Mississippi River Basin near Memphis, TN. Methane flux at Caernarvon, a river diversion-impacted estuarine wetland complex in coastal Louisiana averaged $-0.09 \text{ g CH}_4\text{-C m}^{-2} \text{ d}^{-1}$, indicating that it may be a mild sink for methane. Removal of a single influential data point results in a slightly positive flux that may not be significantly different from zero. In any case, fluxes were low at both locations and fluxes at experimental sites did not differ from reference sites located outside the impact areas. Fluxes were independent of variations in soil and ambient air temperatures. Generally, fluxes also were independent of water depth on the wetland surface, though the aforementioned influential data point resulted in a negative relationship with depth. Nitrous oxide fluxes were generally non-detectable, but fluxes averaged $0.02 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ at Caernarvon and $0.09 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ at Memphis, both low fluxes compared to values observed in the literature. At Caernarvon, low greenhouse gas fluxes and denitrification estimates may be a result of nitrate-rich water not entering the marsh during flux measurements. Future studies are needed that obtain flux measurements when the marsh is flooded with diverted riverine water. Nitrate concentrations also should be calculated at the site of flux measurements, both in the water column and the soil, to determine correlations with greenhouse gas fluxes. These results indicate that attempts to ameliorate river water quality using diversions and restored hydrologic regimes will have little impact on greenhouse gas emissions within the Mississippi River Basin. The null hypothesis of no difference in methane emission between Memphis and Caernarvon is rejected, as fluxes were

higher at Memphis. However, we fail to reject the dual null hypotheses that fluxes do not vary in response to riverine input, or between spring and summer.

Nutrient Concentrations and Removal Efficiency

Analysis of nutrient concentrations at Caernarvon indicated that the estuary was a sink for nitrate, total nitrogen and chlorophyll *a*, and a source for ammonium. The estuary was a seasonal source for phosphate and total phosphorus in the fall and summer, and a sink in winter and spring. The estuary also behaved seasonally with silicate, serving as a sink in the winter and spring and a source in the fall. The estuary also was a sink for suspended solids, though it can serve as a source in the lower estuary when sediments are redistributed due to storm passages.

All water quality parameters generally decreased with increasing distance from the diversion, except chlorophyll and salinity, which increased, and ammonium, which was unaffected. All parameters also increased with increasing discharge, except for salinity and chlorophyll, which decreased, and phosphate, total phosphorus and suspended sediments, which were unaffected. We reject the null hypothesis regarding nutrients at Caernarvon, concluding that several nutrients do respond seasonally and spatially.

At Memphis, water quality did not vary spatially, either laterally across the width of the channel, or longitudinally down the length of the channel. Parameters differed temporally, with higher concentrations of nitrate, total nitrogen, total phosphorus, and dissolved oxygen in the summer. Concentrations of ammonium, phosphate, silicate and chlorophyll *a* did not differ between summer and spring, the only seasons for which sampling occurred. We fail to reject the null hypothesis that nutrients do not differ spatially at Memphis, but reject the null hypothesis that nutrients do not differ seasonally, concluding that nitrate, total nitrogen, total phosphorus, and dissolved oxygen did respond seasonally.

At Caernarvon, nitrate is removed at a high rate from the estuary, with an average of 86% removal efficiency. Removal efficiency varied seasonally, with efficiency highest in the summer (98%) and lowest in the winter (74%). Removal was inversely related to loading rate. We therefore reject the null hypotheses that no seasonal variation in nitrate removal exists at Caernarvon, and removal is uncorrelated with loading rate. At Memphis, high loading rates, due to limited areal extent of receiving wetlands, resulted in low rates of removal efficiency of nitrate, total nitrogen and total phosphorus. Some nutrients, such as phosphate and silicate, increased when diverted through the channel. While the coastal Louisiana site served as a strong sink for nitrate, the freshwater Memphis site did not. The two sites studied in this work represent both extremes of loading rate-uptake dynamics in the Mississippi River, in part due to the differences in spatial scale. The Memphis site experiences some of the highest loading and lowest removal of nitrate in the Basin, whereas Caernarvon experiences some of the lowest loading and highest removal. This underlies the importance of considering loading rate in the design and implementation of projects aimed at reducing nutrient loads downstream.

This study indicates that using diversions and restored hydrological regimes to reduce nutrient loading to the Gulf of Mexico, in an effort to limit the extent and severity of seasonal hypoxic zones, will have little impact on greenhouse gas emissions in receiving wetlands. However, in order to maximize nutrient removal in the Mississippi River Basin, riverine waters diverted to secondary channels must reach riparian wetlands.

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