A multi-scale investigation of nutrient dynamics in the Lake Pontchartrain Estuary and Basin

Eric Daniel Roy
Louisiana State University and Agricultural and Mechanical College, eroy5@tigers.lsu.edu

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A MULTI-SCALE INVESTIGATION OF NUTRIENT DYNAMICS IN THE LAKE PONTCHARTRAIN ESTUARY AND 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

Eric Daniel Roy
B.S., Old Dominion University, 2006
M.S., Ohio State University, 2008
December 2013
This work is dedicated to my parents, Janie and Gary, my sister Kelly, and my wife Jenny
who provided the support, inspiration, and loving patience
that made this dissertation possible.
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TABLE OF CONTENTS

ACKNOWLEDGEMENTS .......................................................................................................................... iii

LIST OF TABLES ........................................................................................................................................ viii

LIST OF FIGURES .................................................................................................................................. x

LIST OF EQUATIONS ........................................................................................................................... xiv

ABSTRACT ........................................................................................................................................... xvi

CHAPTER 1: INTRODUCTION ............................................................................................................. 1

CHAPTER 2: NITRATE FLUX INTO THE SEDIMENTS OF A SHALLOW Oligohaline Estuary DURING LARGE FLOOD PULSES OF MISSISSIPPI RIVER WATER ................................................................................................................. 6

  2.1. Introduction ................................................................................................................................... 6

  2.2. Materials and Methods .................................................................................................................. 9

   2.2.1. Study Site ................................................................................................................................. 9

   2.2.2. Sediment Sampling and Characterization ..................................................................................10

   2.2.3. Nitrate Diffusive Flux Laboratory Incubations .........................................................................12

   2.2.4. In Situ Porewater Nitrogen and Diffusion ................................................................................14

   2.2.5. Model for Nitrate Flux to Sediments during the 2008 Bonnet Carré Spillway Event ...............15

  2.3. Results and Discussion ..................................................................................................................16

   2.3.1. Sediment Characterization ......................................................................................................16

   2.3.2. Sediment Core Nitrate Flux Experiments ...............................................................................17

   2.3.3. Porewater Nitrogen Profiles and Diffusion .............................................................................20

   2.3.4. Comparison of Methods ..........................................................................................................21

   2.3.5. Comparison of Nitrate Loss Rates with Other Systems ..........................................................22

   2.3.6. Primary Pathway of Nitrate Reduction in Lake Pontchartrain Sediments .................................23

   2.3.7. Nitrate Removal by Flux to Sediments during the 2008 Bonnet Carré Spillway Event .............24

CHAPTER 3: INTERNAL LOADING OF PHOSPHORUS FROM SEDIMENTS OF LAKE PONTCHARTRAIN (LOUISIANA, USA) WITH IMPLICATIONS FOR EUTROPHICATION .......................................................................................................................... 25

  3.1. Introduction ................................................................................................................................... 25

  3.2. Materials and Methods .................................................................................................................. 29

   3.2.1. Study Site ................................................................................................................................. 29

   3.2.2. Sediment Sampling ................................................................................................................... 30

   3.2.3. Sediment Characterization ...................................................................................................... 31

   3.2.4. Metals Analysis ......................................................................................................................... 32

   3.2.5. Chlorophyll a (chl a) and Microscopy Analyses ..................................................................... 32
3.2.6. Intact Sediment Core Experiments ..............................................................33
3.2.7. Data Analysis ...............................................................................................34
3.2.8. Model of DIP Flux from Sediments Under P-Depleted Conditions ............34

3.3. Results ........................................................................................................................35
  3.3.1. Sediment Characterization ...........................................................................35
  3.3.2. Extractable DIP and Oxygen Conditions ....................................................36
  3.3.3. Phytoplankton Biomass and Species Composition ......................................37
  3.3.4. DIP Flux across the Sediment-Water Interface during Laboratory Incubations .................................................................38
  3.3.5. DIP Flux from Sediments by Diffusion under DIP-Depletion ...................41

3.4. Discussion ...................................................................................................................42
  3.4.1. DIP Flux across the Sediment-Water Interface ...........................................42
  3.4.2. Oxygen Conditions in Lake Pontchartrain Sediments .................................43
  3.4.3. Annual Internal Phosphorus Loads from Diffusion .................................44
  3.4.4. Potential for Episodic Pulses of DIP from Lake Pontchartrain Sediments .................................................................47
  3.4.5. Potential Effects of Internal P Loading on the Lake Pontchartrain Ecosystem .................................................................47

CHAPTER 4: ESTUARINE ECOSYSTEM RESPONSE TO THREE LARGE-SCALE MISSISSIPPI RIVER FLOOD DIVERSION EVENTS .................................................................50
  4.1. Introduction .................................................................................................................50
  4.2. Materials and Methods ...............................................................................................53
    4.2.1. Study Area ......................................................................................................53
    4.2.2. Bonnet Carré Spillway Freshwater Discharges and Physical Plume Characteristics .................................................................55
    4.2.3. Lake Pontchartrain Transect Salinity and Surface Water Temperature ....55
    4.2.4. Bonnet Carré Spillway Nutrient Loading ....................................................56
    4.2.5. Lake Pontchartrain Water Quality Data for 1997 and 2008 .....................57
    4.2.6. 2011 Lake Pontchartrain Transect Water Quality ....................................58
    4.2.7. Laboratory Analyses ....................................................................................58
    4.2.8. Nitrate Plume Collapse Period .....................................................................59
    4.2.9. Weather Analysis .........................................................................................59
    4.2.10. Northern Tributary Data ..........................................................................60

4.3. Results .........................................................................................................................61
  4.3.1. Bonnet Carré Spillway Freshwater Discharges ...........................................61
  4.3.2. Size and Dispersal of the Sediment-rich Freshwater Plume .................61
  4.3.3. Lake Pontchartrain Salinity and Surface Water Temperature ...............62
  4.3.4. Bonnet Carré Spillway Nutrient Loading ....................................................65
  4.3.5. Water Quality Dynamics during the 1997 Spillway Opening .....................70
  4.3.6. Water Quality Dynamics during the 2011 Spillway Opening ....................70
  4.3.7. Comparison of Nitrate Plume Collapse .......................................................72
  4.3.8. Comparison of CyanoHAB Dynamics .........................................................72
  4.3.9. Comparison of Post-Spillway Closure Weather .........................................74
  4.3.10. Northern Tributary Discharge .................................................................74
LIST OF TABLES

Table 2.1. Select physiochemical properties of sediments in Lake Pontchartrain in field conditions and following intact core water column NO3− loss experiments using aerobic and anaerobic incubations. Data are mean values (n = 2 for field characterization cores, n = 4 for aerobic cores, n = 3 for anaerobic cores) ± 1 standard error..........................................................17

Table 2.2. Mean NO3− flux rates ± 1 standard error from the water column to sediments, as well as mass transfer coefficients, in intact sediment cores from Lake Pontchartrain under aerobic (n = 4) and anaerobic (n = 3) laboratory incubations for two high NO3− flood cycles. No significant differences were found between aerobic and anaerobic incubations for either station during both floods (p > 0.05 in all cases) ..........................................................................................................19

Table 3.1. Sediment characteristics for cores sectioned during field collection. Data are mean values (n = 3) ± 1 standard deviation..................................................................................................................35

Table 3.2. Sediment concentrations (mg kg−1) of aluminum, iron, magnesium, and calcium in characterization cores sectioned during field collection. Data are mean values (n = 3) ± 1 standard deviation ........................................................................................................................................36

Table 3.3. Mean extractable DIP values (mg kg−1) ± 1 standard deviation of Lake Pontchartrain sediments for characterization cores sectioned in the field upon collection and intact experiment cores incubated in the laboratory. Letters indicate statistically significant differences (p < 0.05) among treatments for a given station and sediment interval ..........................................................37

Table 3.4. Mean dissolved inorganic phosphorus flux rates (mg DIP-P m−2 d−1) from Lake Pontchartrain sediments to the water column by diffusion under anaerobic and aerobic laboratory incubations and maximum DIP flux rates under anaerobic conditions. Numbers and letters indicate statistically significant differences (p < 0.05) among stations and oxygen conditions, respectively. All data are mean values (n = 3) ± 1 standard deviation ..........................................40

Table 4.1. Physical characteristics, nitrate (NO3−-N) plume collapse times, and phytoplankton dynamics in Lake Pontchartrain during the Bonnet Carré Spillway inflow events in 1997, 2008, and 2011 .........................................................................................................................................62

Table 4.2. Average annual nutrient loads to Lake Pontchartrain from northern tributaries and from the Bonnet Carré Spillway in 1997, 2008, and 2011. The final two columns show 2011 spillway loads divided by 1997 and 2008 spillway loads, respectively .............................................................69

Table 4.3. Weather characteristics during the period following the closure of the Bonnet Carré Spillway in 1997, 2008, and 2011. Data is from the National Climatic Data Center (Louis Armstrong New Orleans Int’l Airport). Letters indicate significant differences at the α = 0.05 level for different time periods ...........................................................................74
Table 5.1. Equations and data sources used to calculate P flows in the analysis .........................95

Table 5.2. Anthropogenic P cycling metrics in the study region of the Upper Lake Pontchartrain Basin during 2001-2005 and 2006-2010.................................................................109
LIST OF FIGURES

Figure 1.1. Biogeochemistry across space and time. Black dots indicate specific spatiotemporal scales of investigation for the four research chapters presented. Dotted-line ovals delineate the range of cross-scale connection existing within and among chapters, illustrating the overall continuity of the dissertation. The range in scale circled for biogeochemical process goes down to the molecular level, however in reality electron transport is the basis........................................3

Figure 2.1. Terra-1 MODIS band 1 (red) reflectance data obtained during the 2008 Bonnet Carré Spillway opening (White et al. 2009) with sampling stations (white ○) superimposed (SWI = Spillway Inflow, PS = Peeper Station, LC = Lake Center). Orange tones depict sediment-laden Mississippi River water (high red band reflectance values). Blue tones depict low red band reflectance and land is colored black .............................................................................................11

Figure 2.2. Changes in mean NO3-N concentrations ± 1 standard error of the water column under aerobic (n = 4) and anaerobic (n = 3) laboratory incubations for intact sediment cores from (a) the Bonnet Carré Spillway inflow and (b) the lake center station in Lake Pontchartrain .............18

Figure 2.3. Vertical distribution of nitrate (a) and ammonium (b) concentrations in the overlying water column and sediment porewater at Station PS within the freshwater plume during the 2011 Bonnet Carré Spillway opening. The horizontal dashed line represents the sediment-water interface. Linear regression lines are shown for data at depths between -3 cm and +3 cm used to determine the concentration gradient (∆C/∆z) for Eqn. 2.3 of NO3-N concentration (C) with depth (z) .........................................................................................................................................21

Figure 3.1. Location of the three lake stations in Lake Pontchartrain used in this study: 1 - Lake Center (LC), 2 - Northwest Quadrant (NWQ), and 3 - Spillway Inflow (SWI). Figure courtesy of Dr. C. Li .........................................................................................................................................30

Figure 3.2. Changes in mean dissolved inorganic phosphorus concentration ± 1 standard error of the water column under anaerobic and aerobic laboratory incubations for intact sediment cores from the (A) lake center, (B) northwest quadrant, and (C) Bonnet Carré Spillway inflow in Lake Pontchartrain (n = 3 per O2 condition) ...........................................................................................39

Figure 3.3. Final water column mean dissolved iron concentrations ± 1 standard error for anaerobic and aerobic water columns at the lake center (LC), northwest quadrant (NWQ), and spillway inflow (SWI) stations in Lake Pontchartrain. Significant differences (p < 0.05) between anaerobic and aerobic incubations at each station are indicated by different letters. Significant differences (p < 0.05) among stations for either anaerobic or aerobic water columns are indicated by different numbers ..................................................................................................................................40
Figure 3.4. Potential regeneration of dissolved inorganic phosphorus (DIP) to the water column in Lake Pontchartrain under phosphorus-depleted conditions by diffusive flux from sediments over 60 days. The model is based on measured maximum rates of diffusive flux for the lake center (LC), northwest quadrant (NWQ), and spillway inflow (SWI) stations. In the case of LC, the maximum concentration used to determine the maximum flux rate (0.055 mg SRP-P L⁻¹) is achieved in <60 days. Uptake of regenerated DIP by phytoplankton assimilation is neglected for all cases. Circles show mean DIP concentrations measured by Bargu et al. (2011) for Lake Pontchartrain water along a fixed transect in the western portion of the estuary with salinity between 1-2 PSU on May 30, 2008 (t = 0, n = 8) and June 17, 2008 (t = 18, n = 3) ....................41

Figure 3.5. Annual dissolved inorganic phosphorus (DIP) loads to the Upper Pontchartrain Estuary for (A) normal years and two years during which the Bonnet Carré Spillway was opened: (B) 1997 and (C) 2008. Individual loads (Mg) are shown in parentheses within the legend. Load estimates are based on tributary annual mean values and 1997 spillway information provided by McCorquodale et al. (2009) except for diffusive flux from sediments (this study) and the 2008 Bonnet Carré Spillway opening (White et al. 2009).........................46

Figure 4.1. Location of the Lake Pontchartrain estuary and its northern watershed (shaded) in southeast Louisiana, USA. The location of the Bonnet Carré Spillway inflow is shown by an arrow and the estuary’s two eastern outlets are indicated by ⊗ ....................................................54

Figure 4.2. MODIS satellite imagery of Lake Pontchartrain on (a) April 29, 2008 and (b) May 17, 2011 provided by the LSU Earth Scan Laboratory and the US Naval Research Laboratory at the Stennis Space Center in Mississippi, respectively. Orange or red tones depict sediment-laden Mississippi River water (measured as red band reflectance in 2008 and beam attenuation at 547 nm in 2011). Blue tones depict estuarine water and land is colored black and green/brown in the 2008 and 2011 images, respectively. The 10 stations shown as ∆ comprise the 30-km transect used in this and past studies (White et al. 2009; Bargu et al. 2011). The 3 stations shown as ○ (CW-1, CW-4, and CW-7) were sampled by LDEQ in 1997 ........................................................56

Figure 4.3. Timing, rate, and total magnitude of Bonnet Carré Spillway discharge in 1997 (dashed), 2008 (solid), and 2011 (dotted). Data is from the US Army Corps of Engineers...........62

Figure 4.4. Area of sediment-rich freshwater plume in Lake Pontchartrain as a function of time identified using satellite imagery from the LSU Earth Scan Laboratory during the diversions in 2008 (White et al., 2009) and 2011 (this study) ............................................................................63

Figure 4.5. 1997 monthly measurements of salinity, Secchi depth (m), water temperature (°C), and NO₃-N (mg L⁻¹) during February-August made by the Louisiana DEQ at three stations on the Lake Pontchartrain Causeway (Figure 4.2, ○). The shaded region indicates the period during which the spillway was open (March 17 – April 18, 1997).................................................................64

Figure 4.6. Salinity along the 30-km 10-station study transect (Figure 4.2, ∆) during (a) the spillway opening, (b) nitrate collapse, and (c) post-nitrate collapse periods in 2008 (left panel) and 2011 (right panel). 2008 data are from White et al. (2009) and Bargu et al. (2011) ...............66
Figure 4.7. Surface water temperature along the 30-km 10-station study transect (Figure 4.2, ∆) during (a) the spillway opening, (b) nitrate collapse, and (c) post-nitrate collapse periods in 2008 (left panel) and 2011 (right panel). 2008 data are from White et al. (2009) and Bargu et al. (2011).

Figure 4.8. 2011 salinity, Secchi depth (m), dissolved inorganic phosphorus (mg DIP-P L$^{-1}$), ammonium (mg NH$_4$-N L$^{-1}$), nitrate (mg NO$_3$-N L$^{-1}$), dissolved silica (mg DSi L$^{-1}$) and chlorophyll-$a$ (µg L$^{-1}$) measurements across the 30-km 10 station transect in Lake Pontchartrain extending from the Bonnet Carré Spillway inflow (0.9 km) to the lake center (29.5 km) (Figure 4.2, ∆). The left and right panels show stations 0.9-11.1 km and 14.2-29.5 km from the spillway inflow, respectively. The shaded regions indicate the period during which the spillway was open (May 9 – June 20, 2011). Dotted lines in the NH$_4$-N plots indicate the detection limit. Chl $a$ measurements are courtesy of E. Smith and Dr. S. Bargu.

Figure 4.9. Phytoplankton group composition across the 30 km transect extending northeast from the Bonnet Carré Spillway inflow (Figure 4.2, ∆) during the period of increased Chl $a$ observed following the 2011 opening. Data courtesy of E. Smith and Dr. S. Bargu.

Figure 4.10. Freshwater input (km$^3$) from northern tributaries in an average non-diversion year, 1997, 2008, and 2011, as well as from the Bonnet Carré Spillway diversions in 1997, 2008, and 2011.

Figure 4.11. Monthly (gauged + ungauged) discharge (km$^3$) from northern tributaries (Fig. 1) into Lake Pontchartrain during April-June of 1997, 2008, and 2011.

Figure 4.12. Estuarine biogeochemical dynamics during large inflows of nitrate-rich freshwater. Diagram is based on observations in Lake Pontchartrain during the 2008 and 2011 Bonnet Carré Spillway openings. Dotted line indicates that the system can move from P-limitation to N-limitation in < 1 month during warm periods (water temperature ≥ 25°C).

Figure 5.1. The study region and Pontchartrain Basin parishes in coastal Louisiana, USA. Land and water shaded darkly in the lower left inset indicates elevation less than 0.5 m in the Pontchartrain Basin (with the exception of Lake Pontchartrain). Source: National Elevation Dataset (NED), US Geological Survey.

Figure 5.2. Five-year mean annual phosphorus flows (Mg P y$^{-1}$) in the study region of the Upper Pontchartrain Basin for 2001-2005 and 2006-2010 (in parentheses).

Figure 5.3. (a) Historic nominal price for diammonium phosphate (DAP) fertilizer (US$ per Mg P) during 1985-2010 (NASS, 2011) and purchased phosphorus fertilizer (Mg P) in the seven Louisiana parishes of the Upper Pontchartrain Basin during 2000-2010 (LDAF, 2010). (b) April Louisiana crude oil first purchase nominal price (US$ per barrel) during 1985-2010 (EIA, 2011).
Figure 5.4. Correlations between (a) total phosphorus fertilizer sold in the seven study region Louisiana parishes of the Upper Pontchartrain Basin during 2000-2010 (LDAF, 2010) and mean annual U.S. diammonium phosphate fertilizer nominal price (NASS, 2011), (b) April US crude oil first purchase nominal price (EIA 2011) and mean annual US diammonium fertilizer nominal price during 2000-2010, and (c) total phosphorus fertilizer sold in the seven parishes of the Upper Pontchartrain Basin during 2000-2010 and April Louisiana crude oil first purchase price (EIA, 2011) ..................................................................................................................................107

Figure 5.5. Total human populations living within the seven Upper Pontchartrain Basin Louisiana parishes with land inside the study region and four Lower Pontchartrain Basin Louisiana parishes (Orleans, Jefferson, St. Bernard, Plaquemines). Discontinuities in 2005 correspond to Hurricane Katrina. Source: Solid lines, US Census (2002, 2012a); Dashed lines are projections made in 2009 by the State of Louisiana (2009) ........................................................108

Figure 5.6. Temporal trends in animal and crop production, animal feed, and manure on a phosphorus (P) basis for the seven Louisiana parishes having land within the study region......110

Figure 5.7. Phosphorus (P) input (Mg P y⁻¹) for the (a) food production subsystem, (b) consumption subsystem, and (c) overall system in the study region of the Upper Lake Pontchartrain Basin during 2001-2005 and 2006-2010. Fates of P input are shown for each system and time period. Sums of each bar represent total P input. Approximate atmospheric deposition is shown by dotted lines .............................................................................................113

Figure 5.8. Future coast? Recent residential development in the Upper Pontchartrain Basin has been characterized by decentralization and is disconnected from food production. This settlement pattern presents several challenges for improving anthropogenic phosphorus cycling. Photo credit: M. Seibert ...............................................................................................................123
LIST OF EQUATIONS

Equation 2.1. \( C(t) = C(0)e^{(\sigma/k)t} \) .................................................................13

Equation 2.2. \( R = \rho C \) ....................................................................................13

Equation 2.3. \( F = D_{eff} \frac{\Delta C}{\Delta z} \) .................................................................14

Equation 2.4. \( D_{eff} = \phi^n D \) .............................................................................15

Equation 2.5. \( A(t) = (5.71 \times 10^7)t \quad (0 \leq t \leq 11, \ n = 3) \)
\( A(t) = (-1.58 \times 10^7)t + (7.70 \times 10^8) \quad (11 < t \leq 48, \ n = 3) \)
\( A(t) = 0 \quad (t = 49) \) ...............................................................................15

Equation 2.6. \( M_{red} = \sum_{i=0}^{49} A(t) \times R \times 10^{-9} \) .........................................................16

Equation 2.7. \( R = -0.015 \times C \) .............................................................................20

Equation 3.1. \( C(t) = \frac{M(t - 1) + A \times F_{max}}{A \times d \times 1000} \) .............................................34

Equation 5.1. \( P_{balance} = \sum_{i=1}^{I} \text{INFLOW} - \sum_{i=1}^{O} \text{OUTFLOW} \) ..................................103

Equation 5.2. \( PB_{region} = 0 = \left[ \sum_{i=1}^{I} \text{INPUT} + \text{ATMOSPHERE} \right] \)
\( - \left[ \sum_{i=1}^{RU} \text{PRODUCTS} + \sum_{i=1}^{L} \text{LEAKAGE} \right] + \Delta \text{STORAGE} + \Delta \text{WWT & LANDFILL} \) ...104

Equation 5.3. \( \text{Food}_P_{efficiency} = \frac{\text{Food}_{local}}{\sum_{i=1}^{I} \text{INPUT} + \text{ATMOSPHERE}} \) .............................................104
Equation 5.4. \( \text{Anthropogenic } P \text{ cycling efficiency} = \frac{\sum_{i=1}^{n} \text{PRODUCTS} + \text{Food local}}{\sum_{i=1}^{n} \text{INPUT}} \)
ABSTRACT

Humans are responsible for global-scale alteration of nitrogen (N) and phosphorus (P) biogeochemical cycles to support food production. Increases in N and P inputs into soils and waste-streams has resulted in excessive nutrient loading to surface waters, including the Mississippi River, leading to eutrophication. Here I investigated N and P dynamics occurring in the Lake Pontchartrain Estuary and Basin. I measured two biogeochemical processes using intact sediment core incubations and quantified their importance in the context of nutrient-rich Mississippi River flood diversions through the Bonnet Carré Spillway. I show that diffusion of nitrate-N into sediments accounts for a substantial magnitude of nitrate loss from the water column during diversions, but plays a relatively minor role in the transformation of the large amount of nitrate received. Diffusive flux of P from sediments is a significant source of dissolved inorganic P to the water column and may be an important contributor to summertime blooms of N-fixing harmful algae.

I present a comparative analysis of ecosystem response in Lake Pontchartrain during the three most recent Bonnet Carré Spillway openings (1997, 2008, and 2011). Nutrients in the Mississippi River diversion plume are rapidly depleted during summertime, after which sediment P loading restores N-limited conditions. Several interrelated chemical and physical parameters influence ecosystem response during diversion events and there is no simple stimulus-response relationship between N loading and harmful cyanobacterial blooms. In 2011, cyanobacteria were likely suppressed by hydraulic flushing.

Accounting for P and improving human P use efficiency are critical tasks given the finite global supply of phosphate rock. I used material flow analysis to examine anthropogenic P cycling in the Upper Pontchartrain Basin for 2001-2005 and 2006-2010. Mass balances
encompassed human-mediated P fluxes in food production and consumption subsystems across agricultural, developed, and forested landscapes. Increases in fertilizer and oil prices were correlated to drastic reductions (78%) in purchased inorganic P fertilizer. The dominant source of P input shifted from food production to the consumption subsystem between periods. Leakage to the Pontchartrain Estuary and the Mississippi River represented 18-24% of total P input, while the vast majority accumulated within soils, wastewater systems, and landfills.
CHAPTER 1: INTRODUCTION

The alteration of Earth’s ecosystems by humans through landscape transformation, hydroscape domestication, influence over biogeochemical cycles, degradation of biodiversity, and spread of nuisance species is widespread and growing (Vitousek et al., 1997a). Local environmental issues are often a manifestation of these global trends. The Lower Mississippi River and the adjacent Lake Pontchartrain Basin in southeastern coastal Louisiana, USA in many ways exemplify human domination of ecosystems. The domestication of the Lower Mississippi River using an extensive levee system was completed in the early 20th century, disconnecting the river from its floodplain. This large-scale manipulation of hydrology includes the Bonnet Carré Spillway, a flood release outlet that is periodically used to divert a significant portion of river water into the Lake Pontchartrain Estuary to protect the downstream city of New Orleans (Barry, 1997). Widespread fertilization of agricultural land in the Mississippi River Basin made possible through human alteration of global biogeochemical cycles has increased nutrient concentrations in the river, especially nitrate (NO$_3^-$) (Goolsby and Battaglin, 2001; Turner and Rabalais, 2003). Smaller tributaries in the Lake Pontchartrain Basin exhibit nutrient loading characteristics typical of surface waters around the world due to landscape alteration, fertilizer utilization, animal production systems, and human wastewater (Carpenter et al., 1998; Caraco and Cole, 1999; McCorquodale et al., 2009). Eutrophication, or the excessive production of organic matter in water bodies overenriched with nutrients, is the most widespread water quality issue in the United States and a concern locally in the Lake Pontchartrain Estuary (Nixon, 1995; Bargu et al., 2011). One expression of eutrophication documented globally and locally is the occurrence of harmful algal blooms of cyanobacteria (Turner et al., 2004; Paerl, 1988).
In several other ways, however, environmental issues in the Lower Mississippi River and the Lake Pontchartrain Basin reflect the constraints on human domination imposed by a transient deltaic landscape and the finite nature of Earth’s mineral and fossil resources. Historically, the Mississippi Delta was characterized by shifting sites of deltaic sedimentation (i.e., “delta lobes”) within the Gulf of Mexico coastal plain and significantly influenced by changing sea levels (Coleman, 1988). Approximately 2000-4000 years ago, shifting river channel patterns resulted in the abandonment of the Teche delta lobe and the formation of the St. Bernard lobe (Coleman, 1988). As this new location of deltaic sedimentation expanded out of the alluvial valley and onto the continental shelf, it formed the current south shore of Lake Pontchartrain. After subsequent shifts to the Lafourche delta lobe and the current Balize or “Bird Foot” delta, the land built by the St. Bernard lobe continued to largely enclose Lake Pontchartrain from the ocean and provide a terrestrial foundation for human development in and around New Orleans (Coleman, 1988). Currently this area is the location of significant concern over coastal land loss, projected sea level rise, and vulnerability to tropical storms (Day et al., 2007). Exerting tremendous influence on the environment requires substantial amounts of energy and mineral resources. From the perspective of biogeochemistry, humans have largely achieved this influence by utilizing fossil carbon-based fuels and at least doubling the rates of: (i) nitrogen input to the terrestrial nitrogen cycle using the Haber-Bosch process and (ii) transfer of phosphorus from mineral rock form to terrestrial and aquatic ecosystems by mining (Steinhart and Steinhart, 1974; Vitousek et al., 1997b; Bennett et al., 2001). Recent economic instability and projected future declines in the availability of both fossil carbon-based fuels and phosphate rock jeopardize the continuation of ecosystem domination and will likely influence human adaptation to global environmental change (Odum and Odum, 2001; Cordell et al., 2009; Murray and King, 2012).
In this dissertation, I describe dynamics related to nutrient biogeochemistry across a wide range of spatiotemporal scales in the Lake Pontchartrain Estuary and Basin (Figure 1.1).

![Figure 1.1. Biogeochemistry across space and time. Black dots indicate specific spatiotemporal scales of investigation for the four research chapters presented. Dotted-line ovals delineate the range of cross-scale connection existing within and among chapters, illustrating the overall continuity of the dissertation. The range in scale circled for biogeochemical process goes down to the molecular level, however in reality electron transport is the basis.](image)

Each chapter relates to a topic of ecological and societal relevance, considering drivers from the highly local (e.g., sediment characteristics) to the global (e.g., fertilizer prices and long-term supply). Research presented in Chapters 2 through 5 spans spatial scales from nanometers to $10^5$ kilometers and temporal scales from milliseconds to decades (these lower limits reflect the molecular level, however, in reality the lower limit extends to electron transport). Throughout, I elucidate explicit and implicit connection across three levels of inquiry in space-time: biogeochemical process, ecosystem, and basin. My perspective of human society being nested within ecosystems and subject to biogeochemical principles informs my approach to basin-scale
research and allows me to draw inspiration from the microbial world (although I am certainly not foolish enough to reduce it to such).

In Chapter 2, I present an examination of nitrate flux into the sediments of Lake Pontchartrain during Bonnet Carré Spillway openings using laboratory intact sediment core experiments and in situ field measurements. In Chapter 3, I present an investigation of internal phosphorus loading from sediments of Lake Pontchartrain using intact sediment core incubations and explore the implications for eutrophication. Both Chapters 2 and 3 document estuarine sediment biogeochemical processes unfolding on a molecular level that have ecosystem-level implications. For both cases, I use relatively simple mathematical models to estimate the influence of these biogeochemical processes on ecosystem dynamics, providing cross-scale connectivity that informed Chapter 4.

In Chapter 4, I present a comparative analysis of ecosystem response in Lake Pontchartrain to the three most recent Bonnet Carré Spillway openings. The analysis is built upon historical data available from 1997 and 2008, along with in situ data I collected during the 2011 diversion event and additional data provided by government agencies. My investigation is characterized by a focus on the systemic causal relationships that determine estuarine ecosystem response to nutrient-rich freshwater inflows and highlights a host of important environmental parameters. Amongst the parameters considered is freshwater discharge from northern tributaries, providing connectivity between internal estuarine ecosystem dynamics and basin-scale phenomenon.

In Chapter 5, I use material flow analysis to examine anthropogenic phosphorus cycling in the Upper Lake Pontchartrain Basin for two 5-y time periods spanning 2001-2010 to capture the effects of fertilizer economics and population growth partially driven by the impact of
Hurricane Katrina in the lower basin in 2005. The mass balances I have constructed encompass human-mediated phosphorus flows in food production and consumption subsystems across agricultural, developed, and forested/wetland landscapes. Watershed phosphorus loading to Lake Pontchartrain is included in my analysis, connecting basin trends on the order of decades to current and future estuarine biogeochemistry and ecology. I synthesize results from the material flow analysis to: (i) provide environmental management recommendations for the present and (ii) lay foundation for a vision of successful human adaptation to multiple unfolding global environmental challenges including coastal population migration, economic instability, finite phosphate rock supply, and pervasive eutrophication. Finally, I summarize the findings presented in this dissertation in Chapter 6 and discuss the implications and applications of my research for both local environmental issues and larger scale management of biogeochemical cycles.
CHAPTER 2: NITRATE FLUX INTO THE SEDIMENTS OF A SHALLOW OLIGOHALINE ESTUARY DURING LARGE FLOOD PULSES OF MISSISSIPPI RIVER WATER

2.1. Introduction

Human alteration of the global nitrogen (N) cycle due to agriculture and other activities has approximately doubled the rate of N input into the terrestrial N cycle and has greatly increased the transfer of N through rivers to coastal ecosystems (Vitousek et al., 1997b). The result has been widespread coastal eutrophication, expressions of which can include harmful algal blooms and hypoxia (Smith and Schindler, 2009). These global trends are exemplified in the Mississippi River basin where a nearly threefold increase in the N load carried by the river has contributed to the expansion of the second largest zone of coastal hypoxia in the world on the adjacent Gulf of Mexico continental shelf (Goolsby et al., 2001; Rabalais et al., 2002a).

In addition to coastal eutrophication and hypoxia in the Gulf of Mexico, Mississippi River flooding is of significant concern in coastal Louisiana. After the Great Flood of 1927, the Bonnet Carré Spillway was constructed by the U.S. Army Corps of Engineers to protect New Orleans, LA from massive flooding (Barry, 1997). The spillway can divert approximately 17% (7.1 ML s⁻¹; 250,000 ft³ s⁻¹) of the flood level Mississippi River capacity (42.5 ML s⁻¹; 1,500,000 ft³ s⁻¹) along with significant nutrient and sediment loads through the Lake Pontchartrain estuary into the Gulf of Mexico on the eastern side of the Bird’s Foot Delta (White et al., 2009).

During a 1-mo diversion event in 2008, approximately 8 km³ of water containing approximately 10,000 Mg of NO₃-N was discharged into Lake Pontchartrain (White et al., 2009). The spillway was again opened in May 2011. Phytoplankton growth in Lake Pontchartrain is

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1 This chapter previously appeared as: Roy, E.D., White, J.R. 2012. Nitrate flux into the sediments of a shallow oligohaline estuary during large flood pulses of Mississippi River water. Journal of Environmental Quality 41:1549-1556. It is reprinted by permission of ACSESS-Alliance of Crop, Soil, and Environmental Science Societies provided by Copyright Clearance Center (see Appendix).
typically N limited, and there is concern that opening the Bonnet Carré Spillway can trigger
eutrophic conditions (Turner et al., 2002; Turner et al., 2004; Bargu et al., 2011). During
spillway openings, potential pathways of nitrate ($\text{NO}_3^-$) removal from the water column in Lake
Pontchartrain include flux into sediments, assimilation by phytoplankton, and transport to the
coastal ocean. Estimates of the magnitudes of these pathways are essential for determining the
ecological consequences of pulses of N-rich Mississippi River water into Lake Pontchartrain.

My focus in this study is $\text{NO}_3^-$ flux into the sediments of Lake Pontchartrain. Potential
major pathways of $\text{NO}_3^-$ reduction after diffusion into the sediment include respiratory
denitrification and dissimilatory $\text{NO}_3^-$ reduction to ammonia (DNRA). These reduction pathways
can alter $\text{NO}_3^-$ concentration gradients between the water column and sediment porewater.
Therefore, diffusive flux rates of $\text{NO}_3^-$ into the sediment are limited by $\text{NO}_3^-$ reduction in the
sediment. Respiratory denitrification is a microbial-mediated process whereby facultative
anaerobic bacteria in sediment utilize $\text{NO}_3^-$ or nitrite ($\text{NO}_2^-$) as the terminal electron acceptor
during the oxidation of organic carbon (microbial respiration), resulting in the production of
gaseous end products, $\text{N}_2\text{O}$ and $\text{N}_2$, which are lost to the atmosphere (Reddy and DeLaune,
2008). The rate of water column $\text{NO}_3^-$ loss by respiratory denitrification in sediments has been
shown to depend on the concentrations of $\text{NO}_3^-$ and $\text{O}_2$ in the overlying water column. The latter
determines (i) the thickness of the oxic zone in the sediment that water column $\text{NO}_3^-$ must diffuse
across to reach the denitrification zone and (ii) whether respiratory denitrification is driven by
water column $\text{NO}_3^-$ or sediment porewater $\text{NO}_3^-$ produced by nitrification (Rysgaard et al., 1994).
Critically, respiratory denitrification can reduce the amount of inorganic N available for primary
production in the water column, thereby preventing algal blooms. Previous researchers have
documented respiratory denitrification throughout coastal Louisiana (Rivera-Monroy et al.,
Dissimilatory NO\textsubscript{3}\textsuperscript{-} reduction to ammonia (DNRA) is a process mediated by obligate anaerobic bacteria where NO\textsubscript{3}\textsuperscript{-} is reduced to NH\textsubscript{4}\textsuperscript{+} by dissimilative NO\textsubscript{3}\textsuperscript{-} reductase enzymes (Reddy and DeLaune, 2008). DNRA requires high electron pressure (i.e., a high carbon to NO\textsubscript{3}{-} ratio), low redox potential, and/or high sulfate concentrations (Tiedje, 1988; Burgin and Hamilton, 2007; Reddy and DeLaune, 2008). An important difference between DNRA and respiratory denitrification is that the NH\textsubscript{4}{+} produced by DNRA in sediments can be regenerated to the water column and contribute to eutrophication as NH\textsubscript{4}{+} or as NO\textsubscript{3}{-} following nitrification (Burgin and Hamilton, 2007). There are other NO\textsubscript{3}{-} reduction pathways in sediments other than DNRA and respiratory denitrification; however, these additional pathways typically result in the conversion of NO\textsubscript{3}{-} to N\textsubscript{2} gas (Burgin and Hamilton, 2007) and therefore are grouped here with respiratory denitrification and referred to collectively as “denitrification.”

No direct experimental measurements of water column NO\textsubscript{3}{-} loss in Lake Pontchartrain by flux into sediments have been reported. Previous researchers have based indirect estimates of denitrification in Lake Pontchartrain on water column measurements and mass balance (Turner et al., 2004) or utilized measured rates from other estuaries in models of Lake Pontchartrain (McCorquodale et al., 2009). Available measurements of bottom water dissolved O\textsubscript{2} in Lake Pontchartrain indicate aerobic conditions (dissolved O\textsubscript{2} \gg 2 \text{ mg L}\textsuperscript{-1}) in spring and summer during both normal conditions and spillway diversion events (McCorquodale et al., 2002; Brammer et al., 2007; White et al., 2009). It has been hypothesized that episodic events of hypoxia may go undetected (Brammer et al., 2007).

Several experimental and in situ methods exist for estimating NO\textsubscript{3}{-} flux into aquatic sediments (Cornwell et al., 1999). Previous researchers have noted that water column NO\textsubscript{3}{-} concentration is a key parameter for determining NO\textsubscript{3}{-} flux into sediments (e.g., Mengis et al.,
1997; Birgand et al., 2007). Consequently, comparing results from studies utilizing a wide range of NO$_3^-$ concentrations is problematic, especially in coastal Louisiana given that there is a paucity of NO$_3^-$ reduction studies at NO$_3^-$ concentration levels that typically enter these systems (Rivera-Monroy et al., 2010). Additionally, reporting a single rate fails to adequately describe the diffusion process in a manner that accounts for the impacts of variable water column NO$_3^-$ concentrations, thereby limiting analyses across space and time, including modeling applications. My objective in this study was to utilize a combination of techniques to estimate the potential for water column NO$_3^-$ removal by flux into Lake Pontchartrain sediments and determine the primary pathway of NO$_3^-$ transformation in the sediments. I develop an equation for the rate of NO$_3^-$ flux into sediments as a function water column NO$_3^-$ concentration, increasing the applicability of results. Results herein are expected to aid the construction of ecosystem-level N budgets and models of Lake Pontchartrain during high-N loading disturbances from the Bonnet Carré Spillway. I also develop a simple model for determining the maximum amount of water column NO$_3^-$ loss likely accounted for by flux into sediments during the 2008 Bonnet Carré Spillway event.

2.2. Materials and Methods

2.2.1. Study Site

Lake Pontchartrain is a shallow (mean depth = 3.7 m), oligohaline estuary with a surface area of 1637 km$^2$ and a volume of approximately 6 km$^3$ located just north of New Orleans, LA (Turner et al., 2002). Freshwater containing NO$_3^-$ enters the lake via several small rivers along the northern rim, from the south contained in pumped urban runoff from the New Orleans area, and from the southwest where Mississippi River water enters as both seasonal leakage and episodic large pulses through the Bonnet Carré Spillway. The Bonnet Carré Spillway is a
managed flood-release valve utilized only when the lower Mississippi River flood stage threatens New Orleans and downstream communities (most recent openings: 1997, 2008, 2011) and capable of diverting up to approximately 17% of the flood stage of the Mississippi River into Lake Pontchartrain.

2.2.2. Sediment Sampling and Characterization
Intact sediment cores 20-30 cm in length were collected from two stations in Lake Pontchartrain: one station proximal to the Bonnet Carré Spillway inflow (0.9 km from spillway inflow) and the other in the lake center (25.9 km from spillway inflow) (Figure 2.1). Sand, silt, and clay contents, as well as sediment characteristics, were determined from 20-30 cm cores collected on March 5, 2010 by driving a 7-cm diameter piston-core sampler into the sediment. A single core from the peeper station (4.9 km from Spillway inflow) was also collected for grain size analysis. Cores were sectioned on return to the laboratory and stored at 4°C for subsequent analysis. Sediment core samples used for the NO₃⁻ diffusive flux experiment were collected on Sept. 23, 2010 and Sept. 30, 2010. At the Spillway inflow and lake center stations, 9 cores were collected in total: 2 cores for determining in situ sediment characteristics, 4 cores for aerobic laboratory incubations, and 3 cores for anaerobic laboratory incubations.

Particle size (sand, silt, and clay) was determined using Stoke’s law and a hydrometer in a 1-L graduated cylinder containing water, 40 g dry soil, and 25 mL of a 200 g L⁻¹ sodium hexametaphosphate solution (Day, 1956; Patrick, 1958). Gravimetric moisture content was determined by placing field-moist subsamples in a forced-air oven at 70°C until constant weight. Bulk density was calculated on a dry weight basis. Mass loss on ignition was measured on dried, ground subsamples by difference after combustion at 550°C for 4 h in a muffle furnace as a proxy for % organic matter content (White and Reddy, 2000).
Extractable NH$_4$-N and NO$_3$-N were determined by shaking triplicate subsamples with 25 mL of 2 M KCl at a ratio of approximately 1:40 (g dry soil:extractant) for 1 hr on a longitudinal shaker. Samples were centrifuged for 10 min at 5000 rpm and filtered through Whatman no. 42 filter paper. Extractable NH$_4$-N and NO$_3$-N were quantified colorimetrically using the SEAL AQ2 Automated Discrete Analyzer (SEAL Analytical, West Sussex, UK), as were all dissolved inorganic N measurements made in this study. Student’s $t$ tests were used to determine significant differences in sediment properties at the $\alpha = 0.05$ significance level grouping all cores by station ($n = 9$ per station). Data normality for sediment properties was determined using the Kolmogorov-Smirnov test ($\alpha = 0.01$) and log-transformed to fit a normal distribution when necessary.
2.2.3. Nitrate Diffusive Flux Laboratory Incubations

High NO$_3^-$ loading events were simulated in intact sediment cores by draining the original water column, re-flooding the cores with a 1:2 mix of filtered water collected at the Spillway inflow and deionized water (salinity = 0.68), and then spiking the water columns (volume = 0.77 L) with a NO$_3^-$ solution (KNO$_3$ and deionized water) to produce concentrations of 2 mg NO$_3$-N L$^{-1}$, the maximum observed in the Mississippi River (Lane et al., 1999). Filtered field water was mixed with deionized water in order to produce fresher flood water while retaining dissolved biological and chemical characteristics of the field water. Cores were placed in a water bath to maintain consistent temperature (~20.9 °C) and incubations were carried out in the dark for the duration of the experiment. For the aerobic incubation, room air was bubbled continuously into the water columns to maintain aerobic conditions (dissolved O$_2$ = 4.1-5.4 mg L$^{-1}$). For anaerobic incubations, O$_2$-free nitrogen gas was bubbled into the water column continuously to purge all O$_2$ (Roy et al., 2012). Anaerobic cores were sealed with rubber stoppers to prevent the entrance of O$_2$ (dissolved O$_2$ < 0.75 mg L$^{-1}$). Samples (5 mL) were collected every 1 to 2 d from the center of the water column, filtered through 0.45-µm membrane syringe filters, and analyzed for NO$_3$-N. Additional floodwater (<10 mL) was introduced approximately 2 h prior to sampling to maintain a 0.77-L water column. After 2 wk, the intact cores were emptied of floodwater, re-flooded and spiked with NO$_3^-$.$^-$ Maximum NO$_3$-N loss rates were calculated from the steepest portion of individual core NO$_3$-N loss curves including a minimum of three data points (Malecki et al., 2004). Nonparametric Wilcoxon rank sum tests were performed to determine significant differences in flux rates at the $\alpha = 0.05$ significance level.

To avoid the limitations associated with reporting a single rate and increase the applicability of study results, an equation was developed here to estimate the rate of NO$_3^-$ flux
into the sediments as a function of water column NO$_3^-$ concentration. For each of the 8 combinations of station, O$_2$ condition, and experimental flood (e.g., spillway Inflow, anaerobic incubations, flood 1), mean values of NO$_3^-$ concentration ($C$, mg NO$_3$-N m$^{-3}$) were calculated at each time interval (note: 1 mg NO$_3$-N L$^{-1}$ = 1000 mg NO$_3$-N m$^{-3}$). Using these mean values, an exponential trendline was fit to the data in the form of,

Equation 2.1: \[ C(t) = C(0)e^{(\rho/h)t} \]

where $\rho$ = mass transfer coefficient (m d$^{-1}$), $h$ = water column depth (0.2 m), and $t$ = time of incubation (d). Eqn. 1 is based on the first order nutrient retention process with respect to the time of travel in streams (Stream Solute Workshop, 1990), which is related to the mass transfer coefficient ($\rho$) by Birgand et al. (2007). Only data from the first approximately 7 d of each incubation was used to determine these trendlines due to the fact that in most cases NO$_3^-$ concentrations approached 1 mg NO$_3$-N L$^{-1}$ at $t = 7$ d, the minimum concentration to which this method should be applied according to Birgand et al. (2007). Correlation coefficients ($r^2$) for the exponential trendlines ranged from 0.96 to 1.00. The mass transfer coefficient ($\rho$) is the velocity at which a molecule moves from the water column into sediments as a result of biological demand or sorption processes (Peterson et al., 2001). The term conveniently describes the NO$_3^-$ removing affinity of sediments and associated microbial communities independent of water column NO$_3^-$ concentration (Birgand et al., 2007). Utilizing $\rho/h$ in Equation 2.1, $\rho$ was determined for each of the 8 data sets. The areal rate of change in NO$_3^-$ concentration ($R$, mg NO$_3$-N m$^{-2}$ d$^{-1}$) was then determined as a function of $\rho$ and $C$,

Equation 2.2: \[ R = \rho C \]

as in previous studies (e.g., Peterson et al., 2001).
2.2.4. In Situ Porewater Nitrogen and Diffusion

The opening of the Bonnet Carré Spillway during the 2011 Mississippi River flood provided a unique opportunity to measure *in situ* dissolved inorganic N profiles at the sediment-water interface. The NO₃⁻ and NH₄⁺ gradients across the sediment-water interface were examined at the peeper station (4.9 km from spillway inflow) shown in Figure 1 using dialysis porewater samplers (“peepers”, Urban et al., 1997) deployed in duplicate on June 4, 2011. During deployment, the peepers were within the freshwater Mississippi River plume entering the lake via the Bonnet Carré Spillway (salinity = 0.17 to 0.18). Water depth was approximately 4 m and surface water temperature ranged from 24.3 to 27.6 °C. PEEPers consisted of 50 cm x 10 cm x 2.5 cm lexan blocks that have 8 cm³ chambers machined at 1-cm vertical intervals covered with membrane filter paper (0.45 µm pore size, Pall). Prior to deployment, chambers were filled with N₂-purged deionized water, after which peepers were placed in a N₂-purged water bath over night and then sealed within the anaerobic water bath during transport to maintain anoxic conditions. PEEPers were lowered into the sediment so that roughly half of the chambers were submerged in the sediment while the top chambers were within the water column and remained in place for 9 d. Upon retrieval, samples were collected using individual syringes and stored on ice during transport to the laboratory where they were then stored at 4 °C until analysis for NO₃⁻N and NH₄-N. Surface water samples were also collected and analyzed for NO₃-N and NH₄-N.

Fickean diffusive flux of NO₃⁻ (F) across the sediment-water interface was estimated as,

\[ F = D_{\text{eff}} \frac{\Delta C}{\Delta z} \]

where \( D_{\text{eff}} \) is the effective areal sediment diffusion coefficient (cm² d⁻¹) and \( \Delta C/\Delta z \) is the concentration gradient of NO₃⁻ (Urban et al., 1997). The value used for \( \Delta C/\Delta z \) was determined based on linear regression using points along the sharp decrease in NO₃⁻ observed at the
sediment-water interface (Urban et al., 1997). Following Urban et al. (1997), $D_{eff}$ was calculated as,

Equation 2.4:  
$$D_{eff} = \phi^n D$$

where $\phi$ is the porosity, $n$ is a constant set here to equal 1 (Urban et al., 1997), and $D$ is the molecular diffusion coefficient for NO$_3^-$ in water (1.64 cm$^2$ d$^{-1}$ at 25 °C, Li and Gregory, 1974). Porosity, measured as weight loss upon drying sediments for 72 hrs at 70 °C (Urban et al., 1997), was 0.39 for the peeper station. Therefore, $D_{eff} = 0.64$ cm$^2$ d$^{-1}$.

2.2.5. Model for Nitrate Flux to Sediments during the 2008 Bonnet Carré Spillway Event

To investigate the potential water column NO$_3^-$ removal by flux into sediments during the 2008 Bonnet Carré Spillway opening (total NO$_3^-$ load ≈ 10,000 Mg, mean NO$_3^-$ concentration ≈ 1.4 mg L$^{-1}$, White et al., 2009), a model was developed based on plume surface area and the aerial NO$_3^-$ loss equation ($R$, Equation 2.2). A piecewise function was used to estimate the freshwater plume area for each day of the 2008 Bonnet Carré Spillway event and subsequent plume collapse period:

Equation 2.5:  
$$A(t) = (5.71 \times 10^{-7})t \quad (0 \leq t \leq 11, \ n = 3)$$

$$A(t) = (-1.58 \times 10^{-7})t + (7.70 \times 10^{8}) \quad (11 < t \leq 48, \ n = 3)$$

$$A(t) = 0 \quad (t = 49)$$

where $A(t) =$ plume area (m$^2$) and $t =$ day (0-49) from April 11, 2008 to May 30, 2008. Discrete data used to determine the function were obtained using satellite imagery (White et al. 2009). Results from Bargu et al. (2011) indicate that the NO$_3^-$-N associated with the freshwater plume was depleted by May 30, 2008.
The following function was utilized to determine the total mass of NO$_3$-N in the plume removed by flux into sediments during the 2008 Bonnet Carré Spillway diversion event:

Equation 2.6:  
\[
M_{\text{sed}} = \sum_{i=0}^{49} A(t) \times R \times 10^{-9}
\]

where \(M_{\text{sed}}\) = total mass of NO$_3$-N removed by flux to sediments (Mg) and \(R\) = the NO$_3^-$ loss rate (mg NO$_3$-N m$^{-2}$ d$^{-1}$) determined here using \(C = 1400\) mg NO$_3$-N m$^{-3}$ in Equation 2.2.

2.3. Results and Discussion

2.3.1. Sediment Characterization

Sediments at the Spillway inflow were predominantly composed of sand (31%) and clay (61%), while those in the lake center were composed mainly of silt (58%) and clay (34%). Peeper station sediments were within this range, made up primarily of 25% silt and 59% clay. The organic content of Lake Pontchartrain sediments ranged from approximately 3 to 9%.

Spillway inflow sediments were characterized by significantly \((p < 0.05)\) greater bulk density and significantly \((p < 0.05)\) lower organic content than those from the lake center (Table 2.1). Extractable NO$_3^-$ data confirm that water column NO$_3^-$ diffusing into the sediment was in fact reduced and did not accumulate in the porewater relative to field cores (Table 2.1). The greater extractable NH$_4^+$ values observed at all depths for experiment cores in comparison to field cores representing in situ conditions (Table 2.1) indicate that NH$_4^+$ produced by the mineralization of organic N was accumulating during the laboratory incubation. In comparison, under field conditions in Lake Pontchartrain where surface sediments are frequently resuspended by wind-waves (Flocks et al., 2009), disturbance of sediments likely limits the accumulation of porewater NH$_4^+$. The absence porewater NO$_3^-$ accumulation suggests that accumulating NH$_4^+$ was not oxidized to NO$_3^-$ or was oxidized and the resulting NO$_3^-$ immediately reduced. This lack of porewater NO$_3^-$ accumulation indicates that the sediment depth to which water column NO$_3$-N had
to diffuse to encounter anaerobic conditions that promote reduction was extremely small during the experiment regardless of the water column O2 concentration.

Table 2.1. Select physiochemical properties of sediments in Lake Pontchartrain in field conditions and following intact core water column NO3− loss experiments using aerobic and anaerobic incubations. Data are mean values (n = 2 for field characterization cores, n = 4 for aerobic cores, n = 3 for anaerobic cores) ± 1 standard error.

<table>
<thead>
<tr>
<th>Station</th>
<th>Interval</th>
<th>Treatment</th>
<th>Bulk Density (g cm−3)</th>
<th>Organic Matter (%)</th>
<th>*Extractable NO3-N (mg kg−1)</th>
<th>Extractable NH4-N (mg kg−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spillway Inflow</td>
<td>0-5</td>
<td>Field</td>
<td>0.88 ± 0.03</td>
<td>3.43 ± 0.71</td>
<td>0.79 ± 0.16</td>
<td>0.63 ± 0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aerobic</td>
<td>1.10 ± 0.04</td>
<td>2.99 ± 0.12</td>
<td>1.13 ± 0.07</td>
<td>7.34 ± 0.80</td>
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<tr>
<td></td>
<td></td>
<td>Anaerobic</td>
<td>0.98 ± 0.14</td>
<td>3.24 ± 0.45</td>
<td>0.97 ± 0.02</td>
<td>12.4 ± 2.1</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>Field</td>
<td>0.95 ± 0.18</td>
<td>4.14 ± 0.31</td>
<td>1.20 ± 0.39</td>
<td>1.06 ± 0.09</td>
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<tr>
<td></td>
<td></td>
<td>Aerobic</td>
<td>1.12 ± 0.04</td>
<td>2.81 ± 0.27</td>
<td>0.72 ± 0.01</td>
<td>17.7 ± 1.4</td>
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<td></td>
<td></td>
<td>Anaerobic</td>
<td>0.91 ± 0.13</td>
<td>5.31 ± 2.17</td>
<td>0.43 ± 0.10</td>
<td>27.7 ± 5.9</td>
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<td>10-15</td>
<td>Field</td>
<td>0.92 ± 0.04</td>
<td>2.90 ± 0.97</td>
<td>1.28 ± 0.71</td>
<td>13.8 ± 2.7</td>
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<td>Aerobic</td>
<td>1.16 ± 0.05</td>
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<td></td>
<td>Anaerobic</td>
<td>1.11 ± 0.06</td>
<td>3.47 ± 0.81</td>
<td>0.66 ± 0.12</td>
<td>25.3 ± 4.9</td>
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<tr>
<td>Lake Center</td>
<td>0-5</td>
<td>Field</td>
<td>0.30 ± 0.01</td>
<td>9.12 ± 1.35</td>
<td>1.61 ± 0.23</td>
<td>0.00 ± 0.00</td>
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<td></td>
<td></td>
<td>Aerobic</td>
<td>0.33 ± 0.02</td>
<td>7.99 ± 0.22</td>
<td>1.36 ± 0.04</td>
<td>32.2 ± 1.2</td>
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<tr>
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<td>Anaerobic</td>
<td>0.33 ± 0.02</td>
<td>7.47 ± 0.24</td>
<td>1.16 ± 0.04</td>
<td>50.1 ± 11.1</td>
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<tr>
<td></td>
<td>5-10</td>
<td>Field</td>
<td>0.46 ± 0.03</td>
<td>8.11 ± 1.22</td>
<td>2.13 ± 1.13</td>
<td>17.0 ± 2.5</td>
</tr>
<tr>
<td></td>
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<td>Aerobic</td>
<td>0.40 ± 0.02</td>
<td>7.43 ± 0.22</td>
<td>1.38 ± 0.34</td>
<td>78.8 ± 5.1</td>
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<td>Anaerobic</td>
<td>0.43 ± 0.03</td>
<td>5.94 ± 0.38</td>
<td>0.55 ± 0.16</td>
<td>76.4 ± 3.6</td>
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<td>10-15</td>
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<td>Aerobic</td>
<td>0.40 ± 0.02</td>
<td>8.49 ± 0.30</td>
<td>1.13 ± 0.06</td>
<td>94.3 ± 7.4</td>
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<td></td>
<td>Anaerobic</td>
<td>0.46 ± 0.04</td>
<td>7.68 ± 0.32</td>
<td>0.50 ± 0.05</td>
<td>94.0 ± 7.1</td>
</tr>
</tbody>
</table>

*Extractable NO3-N data reported here are intended to be interpreted relatively amongst field and experiment cores. Determining porewater concentrations based on these values is problematic due to the large dilution factor and NO3-N concentration method detection limit. In situ porewater measurements presented below provide a more accurate estimate of porewater NO3-N concentrations in Lake Pontchartrain sediments during N-rich flood pulses.

2.3.2. Sediment Core Nitrate Flux Experiments

During the first flood of the intact incubation cores from the spillway inflow and lake center stations, water column NO3− concentrations decreased from approximately 2 mg NO3-N L−1 to 0.64-1.06 mg NO3-N L−1 over approximately 13 d (Figure 2.2a). Maximum NO3− loss rates were not significantly different between O2 treatments for both stations or among stations (Table 2.2). For the second laboratory NO3− flood event, water column NO3− concentrations decreased
from approximately 2 mg NO₃-N L⁻¹ to 0.66-0.95 mg NO₃-N L⁻¹ over approximately 15 d (Figure 2.2b), and there was again no significant difference in NO₃-N flux rates between O₂ treatments for both stations or among stations (Table 2.2). Mean maximum NO₃-N flux rates ranged from -24.3 to -61.9 mg NO₃-N m⁻² d⁻¹. The lack of a significant difference in flux rates for aerobic and anaerobic incubations suggests that (i) O₂ availability in the benthic waters of Lake Pontchartrain does not limit NO₃⁻ reduction and (ii) nitrification of sediment porewater ammonium was not a significant source of NO₃⁻ (Rysgaard et al., 1994).

Figure 2.2. Changes in mean NO₃-N concentrations ± 1 standard error of the water column under aerobic (n = 4) and anaerobic (n = 3) laboratory incubations for intact sediment cores from (a) the Bonnet Carré Spillway inflow and (b) the lake center station in Lake Pontchartrain.
Table 2.2. Mean NO$_3^-$ flux rates ± 1 standard error from the water column to sediments, as well as mass transfer coefficients, in intact sediment cores from Lake Pontchartrain under aerobic ($n = 4$) and anaerobic ($n = 3$) laboratory incubations for two high NO$_3^-$ flood cycles. No significant differences were found between aerobic and anaerobic incubations for either station during both floods ($p > 0.05$ in all cases).

<table>
<thead>
<tr>
<th>Flood</th>
<th>Site</th>
<th>Aerobic Core Incubation</th>
<th>Anaerobic Core Incubation</th>
<th>In Situ Porewater Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max NO$_3$-N Flux Rate</td>
<td>Mass Transfer Coefficient $\rho$</td>
<td>Max NO$_3$-N Flux Rate</td>
<td>Mass Transfer Coefficient $\rho$</td>
</tr>
<tr>
<td></td>
<td>mg NO$_3$-N m$^{-2}$ d$^{-1}$</td>
<td>m d$^{-1}$</td>
<td>mg NO$_3$-N m$^{-2}$ d$^{-1}$</td>
<td>m d$^{-1}$</td>
</tr>
<tr>
<td>1</td>
<td>Spillway Inflow</td>
<td>-46.6 ± 4.5</td>
<td>-0.015</td>
<td>-53.0 ± 9.47</td>
</tr>
<tr>
<td></td>
<td>Lake Center</td>
<td>-61.9 ± 12.1</td>
<td>-0.023</td>
<td>-52.9 ± 14.0</td>
</tr>
<tr>
<td>2</td>
<td>Spillway Inflow</td>
<td>-26.4 ± 4.5</td>
<td>-0.009</td>
<td>-24.3 ± 7.1</td>
</tr>
<tr>
<td></td>
<td>Lake Center</td>
<td>-33.1 ± 6.0</td>
<td>-0.013</td>
<td>-35.7 ± 8.6</td>
</tr>
<tr>
<td>~</td>
<td>Peeper Station</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
</tbody>
</table>
Mass transfer coefficients ($\rho$) ranged from -0.009 to -0.023 m d$^{-1}$ (Table 2.2). Utilizing the mean value of $\rho$ determined here for all incubations (aerobic mean = anaerobic mean = 0.015 m d$^{-1}$), the rate of NO$_3^-$ diffusion into the sediment ($R$, mg NO$_3$-N m$^2$ d$^{-1}$) can be modeled as a function of water column NO$_3^-$ concentration ($C$, mg NO$_3$-N m$^{-3}$) by,

Equation 2.7: \[ R = -0.015 \times C \]

Birgand et al. (2007) suggest this methodology based on $\rho$ should be applied when a clear concentration gradient in NO$_3^-$ exists at the sediment-water interface and NO$_3$-N concentrations are $>1$ mg L$^{-1}$. Both conditions were met here.

2.3.3. Porewater Nitrogen Profiles and Diffusion

Sharp negative gradients in NO$_3^-$ concentration occurred at the sediment-water interface for both peeper replicates in Lake Pontchartrain during the 2011 spillway opening (Figure 2.3a). The greatest concentrations existed 2-7 cm above the sediment surface. The mean concentration of these data points (1.16 mg NO$_3$-N L$^{-1}$) was approximately equal to the surface water NO$_3^-$ concentration of 1.13 mg NO$_3$-N L$^{-1}$, suggesting little vertical variation in NO$_3^-$ in the water column, as seen by White et al. (2009), until approximately 3 cm above the sediment surface. Below this point there was a negative gradient through the sediment until negligible concentrations of NO$_3$-N were found 3 cm below the sediment surface. Replicate concentration gradients $\Delta C/\Delta z$ between ±3 cm were 0.21 ($r^2 = 0.95$) and 0.22 ($r^2 = 0.86$). Mean Fickean diffusive flux, $F$, of NO$_3^-$ (± 1 SE) was -1.38±0.02 mg NO$_3$-N m$^{-2}$ d$^{-1}$ (Table 2.2). In contrast to the NO$_3^-$ profiles, NH$_4^+$ concentrations were negligible from 2-7 cm above the sediment surface and then increased linearly with depth at the sediment-water interface and within the sediments (Figure 2.3b).
Figure 2.3. Vertical distribution of nitrate (a) and ammonium (b) concentrations in the overlying water column and sediment porewater at Station PS within the freshwater plume during the 2011 Bonnet Carré Spillway opening. The horizontal dashed line represents the sediment-water interface. Linear regression lines are shown for data at depths between -3 cm and +3 cm used to determine the concentration gradient ($\Delta C/\Delta z$) for Eqn. 2.3 of NO$_3$-N concentration ($C$) with depth ($z$).

2.3.4. Comparison of Methods

Inserting the water column NO$_3$- concentration observed in the field during the in situ porewater measurements (1160 mg NO$_3$-N m$^{-3}$) into Equation 2.7 yields a rate of NO$_3$- flux into sediments, $R$, of -17.4 mg NO$_3$-N m$^{-2}$ d$^{-1}$, more than 10-fold greater than the rate determined based on Fickean diffusion (-1.38 mg NO$_3$-N m$^{-2}$ d$^{-1}$, Table 2.2). Previous researchers have reported similar discrepancies in results for these two methods (e.g., >10-fold difference, Mengis et al., 1997). There are limitations to both approaches including (i) the difficulty of recreating boundary layer effects (Mengis et al., 1997), (ii) uncertainty associated with the molecular diffusion coefficient $D$ in Equation 2.4, and (iii) the inadequate spatial resolution of porewater profiles needed to observe rapid mineralization processes that can occur at the sediment surface (Urban et al., 1997). NO$_3$- flux rates in Lake Pontchartrain calculated here based on peeper data likely underestimate actual flux rates due to a low diffusion coefficient and insufficient vertical
resolution, thus yielding a lower limit estimate, as concluded previously by Mengis et al. (1997) for peeper measurements of NO$_3^-$ flux into sediments.

2.3.5. Comparison of Nitrate Loss Rates with Other Systems

Rates of water column NO$_3^-$ loss in Lake Pontchartrain found here for high NO$_3^-$ loading events (-1.4 to -61.9 mg NO$_3$-N m$^{-2}$ d$^{-1}$, Table 2.2) fall within the range reported for other estuarine environments (Herbert, 1999). Gardner and White (2010) report a mean NO$_3^-$ loss rate of -137 mg NO$_3$-N m$^{-2}$ d$^{-1}$ for the Davis Pond marsh, an emergent vegetated ecosystem that receives diverted Mississippi River water, based on intact soil cores with 2 mg NO$_3$-N L$^{-1}$ floodwater. Linear regression of results from Gardner and White (2010) for several floodwater NO$_3^-$ concentrations indicates that the mass transfer coefficient, $\rho$, for Davis Pond Marsh is equal to -0.075 m d$^{-1}$. Comparison with results from this study (overall mean $\rho = -0.015$ m d$^{-1}$) illustrates that macrophyte-dominated marsh ecosystems receiving diverted Mississippi River water can potentially reduce NO$_3^-$ concentrations at a rate approximately 5 times greater than Lake Pontchartrain sediments. There are two major factors in these differences. Organic matter content in Lake Pontchartrain sediments (approximately 3-9%) is substantially lower than in the soils of Davis Pond marsh, with values of approximately 24 to 63% organic matter by weight typical of coastal LA wetlands (DeLaune and White, 2012). Therefore, carbon availability may help explain the much lower rates of NO$_3^-$ flux into Lake Pontchartrain sediments due to a reduced microbial demand for NO$_3^-$ as the terminal electron acceptor (White and Reddy, 2001).

In addition, convective flow through the plant, known as the transpiration stream, increases the flux of surface water constituents down into the wetland soil (Sorrell and Brix, 2003) which can significantly increase NO$_3^-$ loss from the water column in vegetated systems.
2.3.6. Primary Pathway of Nitrate Reduction in Lake Pontchartrain Sediments

Whether the dominant pathway of NO$_3^-$ reduction in sediments is DNRA or denitrification can be determined based on the availability of carbon, NO$_3^-$, and sulfate (Burgin and Hamilton, 2007). Previous research suggests DNRA is favored in NO$_3^-$ limited environments rich in available carbon, whereas denitrification is favored under carbon limited conditions with ample NO$_3^-$ (Tiedje, 1988). During Mississippi River diversion events, Lake Pontchartrain sediments are exposed to NO$_3$-N concentrations > 1 mg L$^{-1}$ at the sediment-water interface. Given this high availability of NO$_3^-$ combined with the low organic content of Lake Pontchartrain sediments (approximately 3-9%, Table 2.1), it is very unlikely that DNRA is the favored pathway. Furthermore, if DNRA was the dominant pathway of NO$_3^-$ reduction in the intact core experiment, the resulting NH$_4^+$ would have reentered the water column and been nitrified to NO$_3^-$ in the aerobic incubations, reducing the rate of water column NO$_3^-$ loss in comparison to anaerobic incubations where nitrification would be inhibited. The equivalent rates of NO$_3^-$ loss in aerobic and anaerobic incubations (Table 2.2) indicates that this was not occurring. Finally, during Bonnet Carré Spillway openings, the oligohaline Lake Pontchartrain estuary becomes fresh (salinity ≤ 0.18 PSU) in the region impacted by the Mississippi River plume (White et al, 2009), thereby decreasing the availability of sulfide that can promote chemolithoautotrophic DNRA, as observed in high salinity systems (e.g., An and Gardner, 2002). It is therefore concluded here that denitrification is the likely dominant pathway of NO$_3^-$ reduction in Lake Pontchartrain sediments when subjected to flood pulses of Mississippi River water. This denitrification appears to be driven primarily by water column NO$_3^-$ concentration, but may be limited by carbon availability. Given available carbon, the denitrifier population would be expected to increase and become more active after continuous exposure to high NO$_3^-$
concentrations. The absence of an increase in NO$_3^-$ flux rates from flood event 1 to flood event 2 (Table 2.2) therefore suggests potential carbon limitation of denitrification in Lake Pontchartrain sediments (White and Reddy, 1999).

2.3.7. Nitrate Removal by Flux to Sediments during the 2008 Bonnet Carré Spillway Event

Using Equation 2.7 above with $C = 1400$ mg NO$_3$-N m$^{-3}$ (the 2008 Bonnet Carré Spillway plume concentration observed by White et al. 2009), the rate of NO$_3^-$ flux to Lake Pontchartrain sediments, $R$, is equal to -21.0 mg NO$_3$-N m$^{-2}$ d$^{-1}$. Inserting this value in Equation 2.6, it is estimated that NO$_3^-$ flux to sediments accounted for approximately 3.1% (309 Mg NO$_3$-N) of water column NO$_3^-$ loss during the entire 2008 Bonnet Carré Spillway diversion event, including the period when the spillway was open and the plume-collapse after its closure (total NO$_3$-N load = 10,000 Mg). These results suggest that a significant magnitude of NO$_3^-$ is denitrified in Lake Pontchartrain sediments during Bonnet Carré Spillway openings and that denitrification is an important process in the estuary’s N cycle. However, as suggested by Turner et al. (2004) based on indirect measurements, the impact of denitrification appears to be relatively minimal during large pulses of inorganic N to Lake Pontchartrain associated with Mississippi River flood diversions due to the immense loading rate (e.g., 10,000 Mg NO$_3$-N over 1 mo in 2008). There may also be longer pathways to N removal by denitrification in the system following these large pulses, beginning with the decomposition of phytoplankton, followed by mineralization, nitrification, and denitrification processes in the sediments (White and Reddy, 2003).
3.1. Introduction

Eutrophication has been defined as “an increase in the rate of supply of organic matter to an ecosystem” (Nixon, 1995). While several factors can contribute to eutrophication, the enrichment of aquatic systems with phosphorus (P) and nitrogen (N) is the most common (Nixon, 1995; Cloern, 2001). Eutrophication can lead to harmful algal blooms of cyanobacteria (CyanoHABs), oxygen depletion, and fish kills, all of which negatively impact humans in terms of reduced environmental quality and increased management costs (Wetzel, 2001; Wilson and Carpenter, 1999). Coastal Louisiana is particularly vulnerable to eutrophication because it receives a large input of nutrients from upstream agricultural activities and wastewater inputs delivered via the Mississippi River (Rabalais et al., 2002b). Watershed nonpoint source P and N pollution has long been identified as the major cause of eutrophication in the United States (Carpenter et al., 1998). However, internal loading of P from sediments can also significantly impact the nutrient budgets of estuarine and freshwater ecosystems (Malecki et al., 2004; Reddy et al., 2007) and have important implications for management efforts aimed at alleviating eutrophication. For example, the eutrophication of some freshwater lakes has proven to be irreversible regardless of severe reductions in external P loading due to previous P accumulation in sediments and the continuing release of this P to the water column after management action has been taken (Carpenter et al., 1999).

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2 This chapter previously appeared as: Roy, E.D., Nguyen, N.T., Bargu, S., White, J.R. 2012. Internal loading of phosphorus from sediments of Lake Pontchartrain (Louisiana, USA) with implications for eutrophication. Hydrobiologia 684:69-82. It is reprinted by permission of Springer provided by Copyright Clearance Center (see Appendix).
Expressions of eutrophication, including CyanoHABs, have been documented in Lake Pontchartrain, LA, particularly in the northwest quadrant of the lake (Dortch and Achee, 1998; McCorquodale et al., 2009; Mize and Demcheck, 2009; Bargu et al., 2011). External nutrient loading to the oligohaline Lake Pontchartrain estuary is associated with nonpoint source and point source pollution in the watershed delivered by the fresher Lake Maurepas and several small rivers, urban runoff pumped from the New Orleans area, and leakage of Mississippi River water through the Bonnet Carré Spillway in the southwest corner of the lake (Penland et al., 2002; Turner et al., 2002). Freshwater diversions of nutrient-laden Mississippi River water through the Bonnet Carré Spillway when the Lower Mississippi River flood stage threatens New Orleans may cause the receiving waters in Lake Pontchartrain to become more eutrophic. For example, CyanoHABs were reported following the 1997 spillway opening (Dortch and Achee, 1998; Turner et al., 2004). On the other hand, recent observations indicate that the large nutrient influx from the 2008 spillway opening first produced a diatom bloom that stripped the water column of nutrients, after which N-fixing HAB species became dominant in the summer (Bargu et al., 2011). This pattern suggests limited direct plume influence on the summer CyanoHAB in 2008. The majority of the toxic cyanobacteria species observed in Lake Pontchartrain after the 2008 Spillway diversion event competed well at low nutrient levels relative to diatoms, most likely due to their ability to fix atmospheric N and/or store P (Thompson et al., 1994; Dignum et al., 2005; Bargu et al., 2011). It is therefore important to investigate P dynamics within the lake that may play a critical role in promoting CyanoHABs under certain environmental conditions.

One source of P to phytoplankton in Lake Pontchartrain is internal loading from sediments by both diffusion driven by concentration gradients and advection caused by wind-waves. Physical resuspension by wind-waves can dominate the upward transport of P in some
shallow lakes (Havens et al., 2007). Sediments in Lake Pontchartrain are predominantly silt and clay with several isolated areas where sand content is greater than 50% (Flocks et al., 2009). Lake Pontchartrain is a wind-dominated system and the currents associated with storm-generated waves frequently resuspend surface sediments (Flocks et al., 2009). Effects of this resuspension include increased sediment oxygen demand, increased biological oxygen demand, restricted sequestration of contaminated material that enters the lake, and potential release of sediment-bound nutrients into the water column (Malecki et al., 2004; Flocks et al., 2009).

External nutrient loading, over time, increases the concentration of nutrients in the sediment that can be released back into the overlying water column (Reddy et al., 1998). After receiving elevated external inputs of P for decades, some wetland systems including the Florida Everglades are now greatly impacted by internal P flux, a phenomenon referred to as “phosphorus legacy” (Bostic et al., 2010; Reddy et al., 2011). In other aquatic systems, external nutrient loading remains the primary factor directly influencing ecological response. Before managers can devise successful nutrient reduction strategies in any watershed, knowledge of the size and mobility of the internal P loading is required to better assess external load reduction needs. The sedimentary P cycle is characterized by burial of inorganic P, degradation of organic P, and interaction of phosphate with metal oxides in the sediment. Inorganic P in sediments is found in combination with amorphous and crystalline forms of iron, magnesium, aluminum, and calcium (Malecki-Brown et al., 2007). Depending on carbonate availability, inorganic P can also be more permanently immobilized in the form of authigenic P minerals (e.g., carbonate fluorapatite) (Ruttenberg and Berner, 1993; Rozan et al., 2002). Microbial processes mediating fluxes of P bound to metal oxides are largely dependent on environmental factors that vary with time (Thayer, 1971). Changes in sediment redox conditions caused by changes in oxygen
concentrations in the overlying water column can result in the benthic regeneration of metal oxides and associated phosphate (Sundby et al., 1986; Kemp, 1989). The release of bioavailable dissolved inorganic P (DIP) to the water column can contribute to eutrophication.

Primary production in Lake Pontchartrain is typically N-limited (Turner et al., 2004), but due to the massive amounts of inorganic N loaded to Lake Pontchartrain during Bonnet Carré Spillway openings (~10,000 t of NO₃-N in 2008, molar N:P = 58.9, White et al., 2009), the region of the estuary impacted by the Mississippi River can switch from N-limited to P-limited (Mize and Demcheck, 2009). The depletion of water column DIP in the presence of bioavailable N increases the DIP concentration gradient between the sediment porewater and water column, thereby increasing rates of diffusive flux. Initial field evidence of this process of high N loading, followed by P depletion, and eventual P regeneration is reported for the 2008 Bonnet Carré Spillway event by Bargu et al. (2011) for Lake Pontchartrain waters along a fixed transect in the western portion of the estuary with salinity between 1-2 PSU (this range was chosen to minimize dilution impacts). Following the closure of the Spillway, DIP concentrations first decreased from ~0.05 mg DIP-P L⁻¹ to <0.01 mg DIP-P L⁻¹ from May 5th to 30th, after which a rebound to ~0.04 mg DIP-P L⁻¹ was observed on June 17th. Internal loading of P from sediments is a potential source for this P regeneration.

In this chapter, I address diffusion of DIP from Lake Pontchartrain sediments as a source of P regeneration to the water column. There are several methods available to measure DIP flux across the sediment- water interface by diffusion including simple one-dimensional diagenetic models employing Fick’s first law of diffusion based upon pore water concentration gradients (Kemp, 1989) and measuring changes in water column nutrient concentrations over time from intact sediment cores (Fisher and Reddy, 2001; Malecki et al., 2004). My specific objectives here
were to: (i) determine sediment, water column, and phytoplankton characteristics at multiple locations in the estuary, (ii) determine mean and maximum rates of DIP diffusive flux from sediments using intact cores under aerobic and anaerobic incubations, (iii) use measured maximum rates of diffusive flux and a simple model to estimate the potential for water column DIP regeneration in Lake Pontchartrain under DIP-depleted conditions that have been observed following large pulses of N, and (iv) estimate the annual internal load of DIP from the sediment to the overlying water column by diffusion. Taken together, these objectives address two hypotheses: (1) diffusive flux of DIP from sediments is a significant source of DIP in the annual DIP budget for Lake Pontchartrain and (2) under DIP-depleted water column conditions following large external pulses of bioavailable N, internal DIP loading by diffusive flux can regenerate DIP to previously observed levels rapidly (<2 months). Lastly, I discuss the possible implications of internal DIP loading for the growth of potentially toxic cyanobacteria under low-nutrient conditions.

3.2. Materials and Methods

3.2.1. Study Site

Lake Pontchartrain is a shallow (mean depth = 3.7 m), estuary with a surface area of 1637 km² and a volume of approximately 6 km³ located just north of New Orleans, LA (Turner et al., 2002). External loading of DIP to Lake Pontchartrain occurs primarily through seasonal runoff via several tributaries on the northern shore and episodic high loading events in those years that the Bonnet Carré Spillway is opened to alleviate Lower Mississippi River flooding concerns. There is some evidence that tributary DIP loading is increasing due to urbanization on the estuary’s north shore. Silcio et al. (2010) report a 3.4 fold increase in the loading of DIP to Lake Maurepas since 2003 and suggest that it is linked to erosion caused by new construction,
fertilization of new lawns, and stress to existing wastewater treatment facilities. Under typical conditions, estuarine water exchanges with the saline Gulf of Mexico via three restricted outlets to the east/southeast, one of which has been permanently closed in 2010 (Turner et al., 2002). Salinity in the estuary depends on freshwater discharges and wind conditions, and ranges from 2 to 9 PSU (practical salinity units) under normal conditions (Li et al., 2008). Available measurements of bottom water dissolved oxygen in Lake Pontchartrain indicate aerobic conditions (dissolved oxygen >> 2 ppm) in spring and summer during both normal conditions and spillway diversion events (McCorquodale et al., 2002; Brammer et al., 2007; White et al., 2009). It has been suggested that episodic events of hypoxia may go undetected (Brammer et al., 2007).

3.2.2. Sediment Sampling

Three sampling locations were selected to represent different regions of Lake Pontchartrain (Figure 3.1). One of the stations was proximal to the Bonnet Carré Spillway inflow (SWI), one was in the lake center (LC), and one was in the northwest quadrant (NWQ) where CyanoHABs have been repeatedly observed. Sediments at the spillway inflow are predominantly sand and clay, while those in the lake’s center and the northwest quadrant are composed mainly of silt and clay (DeLaune et al., 2008). Intact sediment core samples were collected on June 16, 2010 by driving a 7 cm diameter piston-core sampler into the sediment. At each station, 9 cores were collected in total: 3 cores for sediment characterization, 3 cores for anaerobic laboratory incubations, and 3 cores for aerobic laboratory incubations. Sediment cores were 20-30 cm in length and no compaction occurred during either retrieval or transportation. Characterization cores were immediately sectioned at 5 cm intervals in the field and stored on ice until return to the lab where they were stored at 4 °C until analyzed.
3.2.3. Sediment Characterization

Upon return to the laboratory, samples for sediment characterization were analyzed for total P, extractable DIP, organic matter, moisture content, and bulk density. Solid-phase total P analysis involved combustion of oven-dried subsamples at 550 °C for 4 h in a muffle furnace and subsequent dissolution of the ash in 6 M HCl on a hot plate (Anderson, 1976) and concentrations were determined using a Seal Analytical AQ2 discrete analyzer (Method 365.1; USEPA, 1993). Extractable DIP (PO₄-P) was determined by shaking triplicate soil samples with 25 mL of 1 M KCl at a ratio of approximately 1:50 (g dry soil:extractant) on a longitudinal shaker for 1 h. Samples were centrifuged for 10 min and vacuum-filtered through Whatman #42 filter paper, after which the supernatant was analyzed for DIP (Method 365.1; USEPA, 1993). Organic matter content was determined as loss on ignition (LOI) using ash weight divided by sediment weight.
(White and Reddy, 1999). Moisture content was determined by placing homogenized wet sediment into a drying oven at 70 °C until constant weight. Bulk density was calculated for the sediment intervals on a dry weight basis.

3.2.4. Metals Analysis

Water column and sediment metals concentrations were measured using methods described by Malecki-Brown and White (2009). Water samples (100 mL) were filtered through a 0.45 µm membrane filters, acidified with concentrated trace metal-grade nitric acid to pH < 2 and analyzed for dissolved metals. For total metals, sediments were dried for 24 h at 105 °C and then ground. Approximately 1 g of dry ground sediment was placed in a 75 mL glass digestion tube and digested with 3 mL of concentrated trace-metal grade nitric acid at approximately 120 °C for 8 h. The digests were brought to 50 mL total volume with deionized water, shaken, and allowed to settle for approximately 6 h before centrifuging. Metal determinations for both dissolved and total metals were performed using a Varian model MPX ICP-OES courtesy of Dr. R.P. Gambrell.

3.2.5. Chlorophyll $a$ (chl $a$) and Microscopy Analyses

Chl $a$ and microscopy analyses were performed courtesy of Dr. S. Bargu. Triplicate 1 L surface water samples were collected at each sample station in clean polypropylene bottles and stored in the dark on ice for biological analyses. Upon return to the lab, chl $a$ was determined as a measure of phytoplankton biomass. Fifty mL sub-samples of surface water were filtered through 25 mm GF/F filters. Filters were then extracted for 24 h in 90% aqueous acetone at –20 °C and subsequently analyzed for chl $a$ using a Turner fluorometer (Model 10-AU) (Parsons et al., 1984). Subsamples preserved with 2% gluteraldehyde and kept in the dark at room
temperature and were analyzed for species composition of the phytoplankton community using an inverted microscope (Axiovert 135, Zeiss).

3.2.6. Intact Sediment Core Experiments

The remaining intact sediment cores underwent anaerobic (3 per station) and aerobic (3 per station) incubation. The water column for each core was drained and then re-filled with water from its respective lake station that was filtered through no. 4 Whatman (Maidstone, UK) filter paper (20-µm), resulting in a 20 cm water column. Re-flooding was done slowly by trickle to minimize sediment disruption. Salinities for stations SWI and LC were 1.78 and 1.90 PSU, respectively. For anaerobic incubations, O₂-free nitrogen gas was bubbled into the water column to purge all oxygen in the core for 24 hours initially and then 2 hours per day thereafter. Anaerobic cores were sealed with rubber stoppers to prevent the entrance of O₂. For the aerobic incubation, room air was bubbled continuously into the water columns for the duration of the experiment to maintain fully aerobic conditions. All cores were placed in a water bath to maintain temperature (25°C) and incubations were carried out in the dark. Dissolved oxygen and pH were monitored throughout the course of the experiment.

The DIP flux from sediments to the water column was quantified by measuring changes in water column DIP concentrations over time (Fisher and Reddy, 2001; Malecki et al., 2004). At designated intervals, 9 mL of water was collected from the water column using a syringe and filtered through a 0.45 membrane syringe filter. After sampling, an equal amount of filtered station water was added back to the core to maintain the water column volume. The total incubation time was 15 days with a total of 13 discrete sampling events. Water samples were characterized for DIP using a Seal Analytical AQ2 discrete analyzer (Method 365.1; USEPA, 1993).
3.2.7. Data Analysis

Mean DIP flux rates were calculated from the slope of the best-fit line from DIP concentration vs. time curves for the first 8 days of the experiment. Maximum DIP flux rates for anaerobic cores were calculated using the steepest portion of each individual DIP concentration vs. time curve including at least 3 data points. Data normality was determined using the Kolmogorov-Smirnov test ($\alpha = 0.01$). Data was log-transformed to fit a normal distribution if necessary. T-tests were performed to determine significant differences ($p < 0.05$) in sediment characteristics, water column DIP concentrations, DIP flux rates, trace metal concentrations, and solid-phase metal concentrations among sample stations and between oxygen conditions.

3.2.8. Model of DIP Flux from Sediments under P-Depleted Conditions

In order to estimate the feasible rate of water column DIP concentration increase in Lake Pontchartrain due to diffusive flux from sediments under DIP-depleted conditions, an algorithm was developed based on the maximum rates of DIP flux by diffusion determined here. The sediment surface area of DIP-regeneration ($A$) was assumed to be equal to the maximum area of the high N:P ratio Mississippi River plume in Lake Pontchartrain during the Bonnet Carré Spillway opening of 2008 as determined by satellite imagery ($6.13 \times 10^8$ m²; White et al., 2009). Water column depth ($d$) was assumed to be equal to the mean depth of Lake Pontchartrain (3.7 m; Turner et al., 2002). The water column was assumed to be well-mixed and water column DIP concentration at time $t$ ($C$, mg DIP-P L$^{-1}$) was determined as:

Equation 3.1: $C(t) = \frac{M(t - 1) + A \times F_{\text{max}}}{A \times d \times 1000}$

where $M(t - 1) =$ total mass of DIP in water volume (mg) at time $t - 1$ and $F_{\text{max}} =$ the maximum DIP flux rate by diffusion (mg DIP-P m$^{-2}$ d$^{-1}$). At $t = 0$, $M$ was set equal to zero to represent P-
depletion. This simple model was run for 60 days at a one day time-step using maximum DIP flux rates by diffusion determined here for each station.

3.3. Results

3.3.1. Sediment Characterization

Sediment characteristics measured, including total phosphorus (TP), organic matter content (LOI), moisture, and bulk density, were not significantly different between the lake center and northwest quadrant stations for both the 0-5 cm and 5-10 cm intervals (Table 3.1, \( p > 0.05 \) in all cases except moisture at 5-10 cm). In general, sediments from the spillway inflow were characterized by less TP, LOI, and moisture content, and higher bulk density in comparison to the lake center and northwest quadrant stations (\( p < 0.05 \) in all cases except total P at 5-10 cm for spillway inflow vs. lake center). Sediments from the spillway inflow are composed of sand and clay, as opposed to the fine silts and clays found at the lake center (DeLaune et al., 2008).

Table 3.1. Sediment characteristics for cores sectioned during field collection. Data are mean values (\( n = 3 \)) ± 1 standard deviation.

<table>
<thead>
<tr>
<th>Station</th>
<th>Interval</th>
<th>Total P cm</th>
<th>*LOI %</th>
<th>Moisture %</th>
<th>Bulk Density g cm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Center</td>
<td>0-5</td>
<td>510 ± 32</td>
<td>7.84 ± 1.47</td>
<td>74.2 ± 2.7</td>
<td>0.29 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>455 ± 11</td>
<td>6.16 ± 1.02</td>
<td>69.5 ± 0.8</td>
<td>0.38 ± 0.03</td>
</tr>
<tr>
<td>Northwest Quadrant</td>
<td>0-5</td>
<td>461 ± 11</td>
<td>8.79 ± 0.16</td>
<td>74.9 ± 0.8</td>
<td>0.32 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>499 ± 29</td>
<td>5.53 ± 0.3</td>
<td>61.7 ± 1.6</td>
<td>0.48 ± 0.06</td>
</tr>
<tr>
<td>Spillway Inflow</td>
<td>0-5</td>
<td>390 ± 4.3</td>
<td>3.20 ± 0.84</td>
<td>37.5 ± 1.0</td>
<td>1.05 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>414 ± 30</td>
<td>3.27 ± 0.66</td>
<td>32.4 ± 1.3</td>
<td>1.23 ± 0.05</td>
</tr>
</tbody>
</table>

*LOI = loss on ignition (organic matter content).
Sediment from the lake center and the northwest quadrant stations exhibited similar concentrations of aluminum, iron, magnesium, and calcium in the 0-5 cm sediment layer (Table 3.2). In comparison, the spillway inflow sediments had significantly \((p < 0.05)\) lower concentrations of aluminum, iron, and magnesium, corresponding to lower values of TP. The spatial differences in sediment parameters are likely due to the influence of periodic influxes of Mississippi River water and associated sediment via the Bonnet Carré Spillway.

Table 3.2. Sediment concentrations (mg kg\(^{-1}\)) of aluminum, iron, magnesium, and calcium in characterization cores sectioned during field collection. Data are mean values \((n = 3) ± 1\) standard deviation.

<table>
<thead>
<tr>
<th>Site</th>
<th>Interval</th>
<th>Al</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Center</td>
<td>0-5</td>
<td>54,864 ±</td>
<td>12,963 ±</td>
<td>3,083 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>597</td>
<td>246</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>52,942 ±</td>
<td>12,817 ±</td>
<td>6,382 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>932</td>
<td>246</td>
<td>3,251</td>
</tr>
<tr>
<td>Northwest Quadrant</td>
<td>0-5</td>
<td>52,830 ±</td>
<td>12,438 ±</td>
<td>4,111 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,322</td>
<td>174</td>
<td>546</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>42,295 ±</td>
<td>10,963 ±</td>
<td>27,614 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,979</td>
<td>869</td>
<td>20,664</td>
</tr>
<tr>
<td>Spillway Inflow</td>
<td>0-5</td>
<td>13,646 ±</td>
<td>4,447 ±</td>
<td>19,008 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>738</td>
<td>364</td>
<td>8,834</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>16,566 ±</td>
<td>6,137 ±</td>
<td>10,470 ±</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,368</td>
<td>568</td>
<td>2,629</td>
</tr>
</tbody>
</table>

3.3.2. Extractable DIP and Oxygen Conditions

During the laboratory experiment, dissolved oxygen concentrations in aerobic cores were consistently between 5.0 and 7.0 mg L\(^{-1}\). These oxygen concentrations corresponded well to field measurements of surface water on June 16, 2010 at the three sample stations (dissolved O\(_2\) = 6.8-7.3 mg L\(^{-1}\)). Dissolved oxygen measurements of the water column verified that the anaerobic cores were in fact anaerobic (mean dissolved O\(_2\) ± 1 standard error = 0.39 ± 0.04 mg L\(^{-1}\)) and was confirmed by the significant flux of manganese from the sediment under anaerobic conditions (data not shown). Sediment extractable DIP data (Table 3.3) indicate that
characterization cores sectioned in the field had similar concentrations of extractable DIP to experimental cores for which anaerobic conditions were imposed. To the contrary, experimental cores exposed to continuous aerobic water column conditions had significantly \((p < 0.05)\) lower extractable DIP concentrations, indicating that the oxygenation of the sediments during the aerobic laboratory experiment led to soluble P binding with abundant metal oxides in the sediment.

Table 3.3. Mean extractable DIP values \((\text{mg kg}^{-1}) \pm 1\) standard deviation of Lake Pontchartrain sediments for characterization cores sectioned in the field upon collection and intact experiment cores incubated in the laboratory. Letters indicate statistically significant differences \((p < 0.05)\) among treatments for a given station and sediment interval.

<table>
<thead>
<tr>
<th>Station</th>
<th>Interval</th>
<th>Field Characterization</th>
<th>Anaerobic Lab Experiment</th>
<th>Aerobic Lab Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Center</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0-5</td>
<td>0.96 ± 0.37(^a)</td>
<td>0.80 ± 0.24(^a)</td>
<td>0.05 ± 0.08(^b)</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.96 ± 0.25(^a)</td>
<td>1.08 ± 0.15(^a)</td>
<td>0.52 ± 0.07(^b)</td>
</tr>
<tr>
<td>Northwest Quadrant</td>
<td>0-5</td>
<td>0.73 ± 0.29(^a)</td>
<td>0.82 ± 0.34(^a)</td>
<td>0.05 ± 0.08(^b)</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.76 ± 0.11(^a)</td>
<td>0.58 ± 0.07(^a)</td>
<td>0.11 ± 0.16(^b)</td>
</tr>
<tr>
<td>Spillway Inflow</td>
<td>0-5</td>
<td>0.45 ± 0.11(^a)</td>
<td>0.35 ± 0.02(^a)</td>
<td>0.07 ± 0.03(^b)</td>
</tr>
<tr>
<td></td>
<td>5-10</td>
<td>0.33 ± 0.09(^a)</td>
<td>0.25 ± 0.02(^a)</td>
<td>0.00 ± 0.00(^b)</td>
</tr>
</tbody>
</table>

3.3.3. Phytoplankton Biomass and Species Composition

In general, lake phytoplankton biomass and diversity were low at the time of sampling in June 2010. The chl \(a\) concentrations \((\pm 1\) standard error) in the lake center and the northwest quadrant stations were similar, averaging 3.59 ± 0.38 \(\mu\text{g L}^{-1}\) \((n = 6)\), while the concentration of chl \(a\) was significantly lower at 2.14 ± 0.08 \(\mu\text{g L}^{-1}\) \((n = 3)\) for the spillway inflow station \((p < 0.05)\). The phytoplankton community at the lake center station was composed of the diatom *Skeletonema* and potentially toxin-producing cyanobacteria *Anabaena* and *Microcystis*. The potentially toxic *Anabaena* was more abundant than the other two groups at the northwest quadrant station which is consistent with findings from previous samplings (Turner et al., 1999;
S. Bargu, unpublished data). The spillway inflow station contained potentially toxic *Microcystis* at lower presence.

### 3.3.4. DIP Flux across the Sediment-Water Interface during Laboratory Incubations

DIP concentrations at the onset of the flux experiment corresponded to those occurring in the field during sampling. Mean initial DIP concentrations were 0.03, 0.03, and 0.04 mg DIP-P L\(^{-1}\) for the lake center, NW quadrant, and spillway inflow stations, respectively (Figure 3.2). Based on observations shown in Figure 3.2, calculated mean rates of DIP flux across the sediment-water interface (averaged for each station) ranged from 0.30 to 1.06 mg DIP-P m\(^{-2}\) d\(^{-1}\) (Table 3.4). There were no significant differences between stations for mean DIP fluxes during either the aerobic or anaerobic incubations. Anaerobic mean DIP flux rates were significantly (**p** < 0.05) higher than the aerobic mean flux rates for the lake center and spillway inflow stations, as well as for the overall mean rate. Anaerobic and aerobic mean DIP flux rates for the northwest quadrant station were not significantly different. Calculated maximum rates of DIP flux by diffusion (averaged for each station) for anaerobic incubations ranged from 2.89 to 4.21 mg DIP-P m\(^{-2}\) d\(^{-1}\) with no significant differences among stations (Table 3.4). Maximum flux rates for aerobic incubations (averaged for each station) ranged from 1.82 to 3.16 mg DIP-P m\(^{-2}\) d\(^{-1}\), with the overall mean significantly (**p** < 0.05) less than for anaerobic incubations. However, on a station basis, the trend of significantly greater maximum flux rates for anaerobic incubations was significant only at the spillway inflow.

No significant (**p** < 0.05) difference in final water column dissolved Fe was observed between anaerobic and aerobic incubations at the spillway inflow station, despite significantly greater DIP flux rates in anaerobic cores (Figure 3.3).
Figure 3.2. Changes in mean dissolved inorganic phosphorus concentration ± 1 standard error of the water column under anaerobic and aerobic laboratory incubations for intact sediment cores from the (A) lake center, (B) northwest quadrant, and (C) Bonnet Carré Spillway inflow in Lake Pontchartrain (n = 3 per O₂ condition).
Table 3.4. Mean dissolved inorganic phosphorus flux rates (mg DIP-P m\(^{-2}\) d\(^{-1}\)) from Lake Pontchartrain sediments to the water column by diffusion under anaerobic and aerobic laboratory incubations and maximum DIP flux rates under anaerobic conditions. Numbers and letters indicate statistically significant differences (\(p < 0.05\)) among stations and oxygen conditions, respectively. All data are mean values (\(n = 3\)) ± 1 standard deviation.

<table>
<thead>
<tr>
<th>Station</th>
<th>Mean DIP Flux by Diffusion</th>
<th>Max DIP Flux by Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anaerobic mg DIP-P m(^{-2}) d(^{-1})</td>
<td>Anaerobic mg DIP-P m(^{-2}) d(^{-1})</td>
</tr>
<tr>
<td>Lake Center</td>
<td>(1.084 \pm 0.39^a)</td>
<td>(1.421 \pm 1.19^a)</td>
</tr>
<tr>
<td>Northwest Quadrant</td>
<td>(1.069 \pm 0.20^a)</td>
<td>(1.289 \pm 1.44^a)</td>
</tr>
<tr>
<td>Spillway Inflow</td>
<td>(1.106 \pm 0.15^a)</td>
<td>(1.386 \pm 0.58^a)</td>
</tr>
<tr>
<td>Overall Mean</td>
<td>(0.87 \pm 0.19^a)</td>
<td>(3.66 \pm 0.68^a)</td>
</tr>
</tbody>
</table>

Figure 3.3. Final water column mean dissolved iron concentrations ± 1 standard error for anaerobic and aerobic water columns at the lake center (LC), northwest quadrant (NWQ), and spillway inflow (SWI) stations in Lake Pontchartrain. Significant differences (\(p < 0.05\)) between anaerobic and aerobic incubations at each station are indicated by different letters. Significant differences (\(p < 0.05\)) among stations for either anaerobic or aerobic water columns are indicated by different numbers.
For sediment from the lake center, final water column dissolved Fe was significantly \((p < 0.05)\) greater during anaerobic incubations. However, in this case no significant difference was observed for DIP flux rate between anoxic and oxic cores. No correlation between the fluxes of Fe and DIP across the sediment-water interface was observed.

3.3.5. DIP Flux from Sediments by Diffusion under DIP-Depletion

Using Equation 3.1 and calculated maximum rates of DIP flux by diffusion in anaerobic incubations (Table 3.4), water column DIP regeneration following DIP-depletion is shown for each station in Figure 3.4.

Figure 3.4. Potential regeneration of dissolved inorganic phosphorus (DIP) to the water column in Lake Pontchartrain under phosphorus-depleted conditions by diffusive flux from sediments over 60 days. The model is based on measured maximum rates of diffusive flux for the lake center (LC), northwest quadrant (NWQ), and spillway inflow (SWI) stations. In the case of LC, the maximum concentration used to determine the maximum flux rate (0.055 mg SRP-P L\(^{-1}\)) is achieved in <60 days. Uptake of regenerated DIP by phytoplankton assimilation is neglected for all cases. Circles show mean DIP concentrations measured by Bargu et al. (2011) for Lake Pontchartrain water along a fixed transect in the western portion of the estuary with salinity between 1-2 PSU on May 30, 2008 \((t = 0, n = 8)\) and June 17, 2008 \((t = 18, n = 3)\).
These results indicate that an internal pulse of DIP following DIP-depletion could increase water column concentrations from below detection to the levels loaded via the Mississippi River (approximately 0.05 mg DIP-P L\(^{-1}\)) in less than 60 days. The magnitude of this episodic internal DIP load will depend on the areal extent of DIP-depletion in Lake Pontchartrain influenced by the Bonnet Carré Spillway plume. For example, if the sediment surface area exposed to a DIP-depleted water column is equal to the maximum N-rich freshwater plume area in 2008 (613 km\(^2\)), the internal load by diffusion could amount to 106-142 Mg DIP-P over 60 days in the plume region.

3.4. Discussion

3.4.1. DIP Flux across the Sediment-Water Interface

Release of P from sediments under anoxic conditions in aquatic systems is attributed to iron reduction due to lower redox conditions in the sediment (Mortimer, 1941). Phosphorus that is removed from the water column by binding with ferric iron (Fe\(^{3+}\)) in the sediment under oxic conditions can be subsequently liberated from the sediments under anoxic conditions as Fe\(^{3+}\) is reduced to soluble ferrous iron (Fe\(^{2+}\)). The P is then released into the water column by diffusion driven by concentration gradients in sediment porewater and the water column (Upchurch et al., 1974; Shaffer, 1986). Field water column DIP concentrations reported here (0.03-0.04 mg DIP-P L\(^{-1}\)) fall within the range observed by White et al. (2009) and Bargu et al. (2011) in Lake Pontchartrain during the spring and summer of 2008 for both more typical estuarine water and freshwater loaded via the Bonnet Carré Spillway (0.00-0.07 mg DIP-P L\(^{-1}\)). The impacts of water column DIP concentration on DIP diffusive flux from sediments are discussed in detail below.

In freshwater lakes, increases in water column dissolved iron concentrations are typically observed concurrently with the release of DIP from sediments (e.g., Moore and Reddy, 1994)
and the molar ratio between dissolved Fe and dissolved PO₄ (i.e., the Fe/P release ratio) under anoxic conditions is typically \( \geq 2 \) (Mortimer, 1941; Gunners and Blomqvist, 1997). To the contrary, the Fe/P ratio is much lower in estuarine and marine systems (\( \leq 1 \)), presumably due to the greater supply of sulfide, which binds a larger fraction of soluble Fe as iron sulfides than in freshwater environments (Capone and Kiene, 1988; Morse et al., 1987; Gunners and Blomqvist, 1997). The Fe/P release ratios ranged from 0.1-0.9 for Lake Pontchartrain sediments, falling within the range of ratios reported by Gunners and Blomqvist (1997) for estuarine and marine systems. The lack of correlation between water soluble Fe and P observed here was likely due to the binding of iron by sulfides. For Fe/P release ratios less than approximately 2, there is insufficient iron to bind all dissolved phosphate and therefore the scavenging of P by precipitating ferric iron in an oligohaline system like Lake Pontchartrain is likely less effective than in freshwater systems (Gunners and Blomqvist, 1997). This may increase the bioavailability of P in the estuary.

3.4.2. Oxygen Conditions in Lake Pontchartrain Sediments

My results in this study indicate that the magnitude of the internal DIP load in Lake Pontchartrain is dependent in some areas upon whether surface sediments are primarily aerobic or anaerobic (Table 3.4). Available data indicate that the water column in Lake Pontchartrain is generally aerobic (McCorquodale et al., 2002; Brammer et al., 2007; White et al., 2009, this study) with the potential for undetected episodic occurrences of hypoxia (Brammer et al., 2007). Turner et al. (2004) assume implicitly that surface sediments in Lake Pontchartrain are aerobic due to an aerobic overlying water column, limiting anaerobic sedimentary biogeochemical processes. However, results from this study indicate that both control cores sectioned in the field and cores subjected to anaerobic conditions had significantly greater concentrations of
extractable DIP at both the 0-5 cm and 5-10 cm layers in comparison to the aerobic cores (Table 3.3). The lower concentrations of DIP in the aerobic cores were likely a result of the binding of soluble P in the sediments to metal oxides caused by the introduction of oxygen into the sediments by vigorously bubbling room air. These results therefore suggest that sediments in Lake Pontchartrain were anaerobic in the field during the time of collection, despite the aerobic water column. It appears that even under an oxygenated water column subjected to repeated wind mixing, the fine-grained sediments in Lake Pontchartrain largely limit the diffusion of oxygen. This finding has implications for nutrient cycling at the sediment-water interface, including the rate of DIP flux from sediments by diffusion.

3.4.3. Annual Internal Phosphorus Loads from Diffusion

I calculated the annual internal load of DIP to Lake Pontchartrain using the overall mean DIP flux rates (Table 3.4). A shortcoming of the annual internal load calculation, as with all such studies, is that the lake-wide load estimate is based on limited stations, three in this case, sampled at one point in time and may not capture the full range of spatio-temporal heterogeneity for DIP flux in Lake Pontchartrain. The calculated annual mean internal load of DIP to Lake Pontchartrain from sediments ranged from 227 Mg P y⁻¹ under 100% aerobic conditions to 517 Mg P y⁻¹ under the assumption that the bulk of the surface sediments are anaerobic 100% of the time. My data suggest that the latter is more likely the case and that is the rate used to calculate the annual DIP load below. This calculation assumes that sediment porewater DIP is continuously regenerated, thereby maintaining the concentration gradient to support flux of DIP into the water column. Available evidence from anaerobic incubations supports this assumption over short time-scales (Table 3.3). The contribution of the internal total P load may be even more significant than reported here given that the loads calculated in this study consists only of the
DIP fraction of the internal P load. The total internal P load to Lake Pontchartrain contains dissolved inorganic P (DIP), particulate P, as well as dissolved organic P.

McCorquodale et al. (2009) provide a phosphorus budget for the lake in terms of total P and suggest that the ratio of DIP:TP is approximately 0.5 during “normal open water conditions” and approximately 0.2 in the plume of the Bonnet Carré Spillway. The DIP:TP fraction is likely dynamic in reality and further research is needed to verify this assumption. In order to gauge the relative contribution of the annual internal DIP load from sediments, TP loads under normal conditions (mean annual values) and spillway plume conditions presented by McCorquodale et al. (2009) were multiplied by 0.5 and 0.2, respectively, and used to construct an annual DIP budget for the Upper Pontchartrain Estuary (Figure 3.5).

Despite the uncertainty of the DIP:TP fraction, it is apparent that internal flux of DIP from the sediments to the water column by diffusion (517 Mg DIP-P y⁻¹) is a significant source of bioavailable P to the Lake Pontchartrain ecosystem (30-33% of total loading in spillway years, 44% in non-spillway years), potentially greater than or equal to the total annual DIP load delivered by tributaries to Lakes Maurepas and Pontchartrain (annual mean = 444 Mg DIP-P y⁻¹). Additionally, wind-induced sediment resuspension could significantly increase the transport of sediment P to the water column. In Florida’s Lake Okeechobee, a system with a similar surface area to mean depth ratio to that of Lake Pontchartrain, wind-induced sediment resuspension has been estimated to transport 6-18 times more P to the water column than flux via diffusion (Moore and Reddy, 1994). However, sediment resuspension may be a source, sink, or have no net impact on water column DIP that may limit primary production and harmful algal blooms depending on sediment geochemistry (Havens et al., 2007). Further research is needed to determine the impact of sediment resuspension by wind on P cycling in Lake Pontchartrain.
Figure 3.5. Annual dissolved inorganic phosphorus (DIP) loads to the Upper Pontchartrain Estuary for (A) normal years and two years during which the Bonnet Carré Spillway was opened: (B) 1997 and (C) 2008. Individual loads (Mg) are shown in parentheses within the legend. Load estimates are based on tributary annual mean values and 1997 spillway information provided by McCorquodale et al. (2009) except for diffusive flux from sediments (this study) and the 2008 Bonnet Carré Spillway opening (White et al. 2009).

During the Bonnet Carré Spillway diversion events in 1997 and 2008, the DIP budget of the lake was dramatically altered increasing the total annual DIP load by 400-526 Mg, an increase of 34-45% (Figure 3.5). The episodic loading of nutrients via the spillway over a relatively brief period of time has received attention in the context of eutrophication and harmful algal blooms in Lake Pontchartrain (Turner et al., 2004; Bargu et al., 2011). My results indicate that the slower release of DIP from sediments by diffusive flux over the course of an entire year may provide as much DIP to Lake Pontchartrain as these relatively short-term (month long) diversion events.
3.4.4. Potential for Episodic Pulses of DIP from Lake Pontchartrain Sediments

My results in this chapter illustrate that internal loading of DIP by diffusion may not always act as a slow P feedback in cases when DIP becomes depleted. During the laboratory incubations, DIP concentrations increased in a logarithmic fashion (Figure 3.2), having maximum rates of DIP flux at lower water column DIP concentrations that were much greater than the mean rates used to construct the lake-wide annual DIP budget (Table 3.4). Based on these maximum flux rates for anaerobic incubations and a simple model of DIP regeneration from the sediments to the water column in Lake Pontchartrain under DIP-depleted conditions, it appears that a large internal pulse of DIP following the initial external N pulse is feasible (Figure 3.4). Without additional external loading of N, such an internal DIP pulse could result in a return to N-limited conditions over a relatively short period of time. Also plotted on Figure 4 are two points showing water column concentrations of DIP in Lake Pontchartrain waters with salinity between 1-2 PSU on May 30, 2008 (t = 0) and June 17, 2008 (t = 18) based on data from Bargu et al. (2011). This observed increase in DIP concentration occurred at a greater rate than that based on maximum rates of DIP diffusive flux from sediments measured here. This increased rate of DIP regeneration is possibly due to advective flux of P from sediments. Further field work is needed to verify DIP regeneration from sediments and determine the relative importance of both diffusion and advection processes.

3.4.5. Potential Effects of Internal P Loading on the Lake Pontchartrain Ecosystem

Chl a concentrations measured for this study (2.14-3.81 µg L⁻¹) courtesy of Dr. S. Bargu were at the low end of the range observed by Bargu et al. (2011) in Lake Pontchartrain during the spring and summer of 2008 for both more typical estuarine water and freshwater loaded via the Bonnet Carré Spillway (2.76-54.65 µg L⁻¹). Potentially toxic cyanobacteria species were
observed at all stations in this study. Previous research in Lake Pontchartrain indicates that toxic cyanobacteria are most abundant when water temperature is high, waters are calm, and nutrient concentrations are low (Bargu et al., 2011). Under summertime low-nutrient conditions, cyanobacteria can out-compete diatoms due to efficient nutrient uptake related to their surface area, N-fixation and P-storage capabilities, and reduced grazing pressure enabled by toxicity (Thompson et al., 1994; Dignum et al., 2005). However, cyanobacteria biomass under these conditions will ultimately remain low due to nutrient limitation unless an additional source of nutrients becomes available. By late July of 2008 following the collapse of nutrients loaded via the Bonnet Carré Spillway, N-fixing cyanobacteria dominated the phytoplankton community while dissolved inorganic nitrogen remained below detection (Bargu et al. 2011). Under these conditions, internal loading of P from sediments may play a critical role in stimulating growth of toxic cyanobacteria and possibly even bloom formation, especially species that are capable of N-fixation. To better understand algal bloom formation in the lake, increased monitoring of nutrient biogeochemistry and phytoplankton parameters is needed during both normal years and those during which the spillway is opened. Harmful algal blooms are patchy and therefore this scenario may differ across space depending on local environmental conditions and sediment biogeochemistry.

My results from this chapter have significant implications for the management of eutrophication in Lake Pontchartrain, including blooms of toxic cyanobacteria. Continual internal loading of DIP from sediments may limit the effectiveness of modest reductions in external P loading from the watershed designed to mitigate eutrophication, as well as increase the sensitivity of the lake to any increases in external nutrient loading (Reed-Andersen et al., 2000). The latter is of particular concern in the Upper Pontchartrain Estuary where significant
human population growth has occurred in the watershed following migration out of New Orleans after Hurricane Katrina in 2005, potentially increasing external loading of DIP (Silcio et al., 2010). Such an increase in external DIP loading coupled with the internal DIP loading reported here may exacerbate eutrophication and harmful algal blooms in portions of the estuary. Clearly, any plan to reduce eutrophication requires taking into account internal loading of P from sediments when determining restoration strategies.
CHAPTER 4: ESTUARINE ECOSYSTEM RESPONSE TO THREE LARGE-SCALE MISSISSIPPI RIVER FLOOD DIVERSION EVENTS

4.1. Introduction

Two prominent environmental effects by humans over the last century have been (1) the alteration of global biogeochemical cycles leading to widespread impairment of surface waters by nitrogen (N) and phosphorus (P) (Nixon, 1995; Vitousek et al., 1997b; Bennett et al., 2001) and (2) the significant manipulation of hydrology in many large river basins (Dynesius and Nilsson, 1994). Nutrient loads to surface waters around the world have increased due to human alteration of the landscape and the expansion of fertilizer utilization in agriculture (Carpenter et al., 1998; Caraco and Cole, 1999; Goolsby and Battaglin, 2001). Additionally, dam construction, freshwater withdrawals, irrigation, and inter-basin diversions now moderately or strongly affect nearly 80% of freshwater discharged by large rivers in the northern temperate zone (Dynesius and Nilsson, 1994). In his review of coastal eutrophication, Cloern (2001) called for recognition of the engineered nature of many coastal physical systems and increased exploration of the interaction between nutrient enrichment and hydrologic manipulation. While many studies of eutrophication assume the perspective that “nutrient enrichment is an isolated signal,” there has been an increased recognition since the end of the 20th century that coastal systems are influenced by multiple, interacting stressors, including hydrologic manipulation (Cloern, 2001).

The Lower Mississippi River has been altered significantly in terms of both nutrient chemistry and hydrology since the early 20th century. The large increase in fertilizer application to agricultural lands in the Mississippi River basin after World War II increased nutrient concentrations in the river, especially nitrate (NO$_3^-$) (Goolsby and Battaglin, 2001; Turner and

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Rabalais, 2003). Flood control levees constructed in the early 20th century disconnected the Mississippi River from its floodplain (Barry, 1997) and today the lower river is a highly engineered system comprised of diversions designed for flood protection (White et al., 2009) and salinity management (Lane et al., 2004; Gardner and White, 2010). There are further plans to use river diversions designed for sediment delivery as a coastal restoration tool (State of Louisiana, 2012).

Following the Great Flood of 1927, the Bonnet Carré Spillway was constructed in 1931 to serve as a flood release outlet for the Lower Mississippi River to protect the downstream city of New Orleans from catastrophic flooding (Barry, 1997). During operation, the spillway diverts Mississippi River flood waters rich in nutrients into the oligohaline Lake Pontchartrain estuary. Since construction, the spillway has been opened ten times, most recently from May 9 to June 20, 2011 in response to the extreme flood stage of the Lower Mississippi River. The timing and duration of spillway openings both vary, resulting in differences in freshwater discharge, nutrient loading, and other environmental parameters that may influence estuarine ecosystem response.

Collectively, Bonnet Carré Spillway openings constitute a case study of the effects of large, episodic inflows of nutrient-rich freshwater on estuarine nutrient and phytoplankton dynamics. Openings can discharge volumes greater than the entire volume of the Lake Pontchartrain estuary over a short time period (approximately 1 mo.) and dramatically alter the annual nutrient budget (Turner et al., 2002; McCorquodale et al., 2009). Phytoplankton production in Lake Pontchartrain is typically limited by N (McCorquodale et al., 2009). The addition of N-laden Mississippi River water to an N-limited system has raised concerns over harmful cyanobacterial blooms (CyanoHABs) following diversion events (Turner et al., 2004). CyanoHABs can be composed of cyanobacteria species that are capable of atmospheric N₂
fixation (e.g., *Anabaena* spp.) or non-N-fixing species (e.g., *Microcystis* spp.) and tend to occur in systems with calm conditions, low flushing rates, high surface water temperatures (usually >25°C), and low molar DIN:DIP ratios (<15) (Paerl, 1988; Paerl and Huisman, 2008). However, non-N-fixing potentially toxic cyanobacteria (*Microcystis* spp.) can rapidly take advantage of conditions where N:P ratios are high (Paerl, 1988; Smith, 1990; Paerl and Millie, 1996). Upper salinity limits for *Anabaena* spp. have been reported as high as 15 (Moisander et al., 2002), while *Microcystis* spp. tend to occur in fresher waters with salinity < 2 (Lehtimaki et al., 1997) and can tolerate salinities as high as 10 in some cases (Tonk et al., 2007).

Recent research has highlighted the interactions between hydrologic inflows and bloom dynamics of harmful algae, one negative consequence of eutrophication (Roelke and Pierce, 2011; Bargu et al., 2011). Inflows to coastal ecosystems can stimulate primary and secondary production and change community composition by altering salinity, delivering N and P, and connecting habitats (Cloern, 2001; Miller et al., 2008; Roelke and Pierce, 2011). However, the influence of inflows on harmful algal blooms is complex (Roelke and Pierce, 2011). While nutrient loading has been shown to initiate and exacerbate harmful algal blooms in many cases (Paerl et al. 2011), the creation of fluctuating, turbulent environments by associated hydrologic inflows can limit formation of single-species blooms or terminate blooms present prior to the inflow event (Moustaka-Gouni et al., 2006; Roelke et al., 2010; Mitrovic et al., 2011). Turbulence has been shown to inhibit photosynthesis, N₂-fixation, and growth of the potentially harmful cyanobacteria *Anabaena* spp., as well as cause disaggregation, cell and filament damage, and rapid die-offs (Paerl, 1996; Paerl et al., 2001).

Ecosystem response to Bonnet Carré Spillway inflow events has been variable. It is critical to understand different factors that may influence CyanoHAB formation following these
events in Lake Pontchartrain due to the potential for cyanobacteria to have deleterious effects on fisheries and human health (Paerl, 1988). My objectives in this study were to: (1) characterize the timing, magnitude, and nutrient composition of Mississippi River discharge from the Bonnet Carré Spillway in 1997, 2008, and 2011, (2) describe the physical characteristics of the freshwater plume in 2011 as compared to 1997 and 2008, (3) compare water quality and biological observations from 2011 to previous observations in 1997 and 2008, and (4) investigate environmental parameters that may influence CyanoHAB formation following spillway events including weather conditions and discharge from tributaries on Lake Pontchartrain’s northern shore. I approach the question of what effect these inflow events have on CyanoHABs in Lake Pontchartrain from a systems perspective in an attempt to move beyond an oversimplified stimulus-response model (i.e., nitrogen loading causes CyanoHABs) towards a greater understanding of the multiple stressors that interact to determine estuarine ecosystem response.

4.2. Materials and Methods

4.2.1. Study Area

Lake Pontchartrain (Figure 4.1) is a shallow (mean depth = 3.7 m), oligohaline estuary located in coastal Louisiana with a surface area of 1637 km² and a volume of approximately 6 km³ (Turner et al., 2002). Freshwater enters the estuary from several tributaries along the northern shore, New Orleans urban runoff, and the Bonnet Carré Spillway in the southwest corner as both small seasonal leakage and episodic large pulses when opened. Lake Pontchartrain water exchanges with the Gulf of Mexico via two outlets located to the east and the estimated residence time with tidal flushing included is approximately 60 days (Swenson, 1980).

Salinity in the estuary typically ranges from 2-9 (Li et al., 2008). During spring Mississippi River floods, the Bonnet Carré Spillway can deliver up to 17% (7.1 ML s⁻¹ or
250,000 ft³ s⁻¹) of the flood level Mississippi River capacity (42.5 ML s⁻¹ or 1,500,000 ft³ s⁻¹) to Lake Pontchartrain and drastically alter both the freshwater and nutrient budgets of the estuary (Turner et al., 2002; White et al., 2009).

Figure 4.1. Location of the Lake Pontchartrain estuary and its northern watershed (shaded) in southeast Louisiana, USA. The location of the Bonnet Carré Spillway inflow is shown by an arrow and the estuary’s two eastern outlets are indicated by ⊗.

Very limited historical CyanoHAB information is available for Lake Pontchartrain outside of the three years addressed in this study. There has been no documentation of major CyanoHABs following past official Bonnet Carré Spillway openings in 1973, 1975, 1979, and 1983 or during years between and after these openings (Porrier and King, 1998). Porrier and King (1998) observed a small surface accumulation of Anabaena sp. near the northern shore in June 1993, large surface accumulations of Anabaena sp. in late June 1994, and a major bloom of Anabaena sp. from late June through mid-July in 1995. Some introduction of Mississippi River
water occurred via the spillway from late April to late May in 1994 (0.64 km³; Lane et al., 2001) and for several days in 1995 due to vandalism. No analyses are available that investigate factors leading to these previous CyanoHAB observations.

4.2.2. Bonnet Carré Spillway Freshwater Discharges and Physical Plume Characteristics

Daily discharge data for the Bonnet Carré Spillway in 1997 is from Perret et al. (1997), while discharge data for the 2008 and 2011 openings were provided by the US Army Corps of Engineers. MODIS satellite imagery available from the Louisiana State University Earth Scan Laboratory was utilized to determine the areal extent of the sediment-rich freshwater plume in Lake Pontchartrain in 2008 (White et al., 2009) and 2011 (this study). Similar satellite imagery was not available for the 1997 event, although plume dispersal information was available from Waters et al. (2009) and Chao et al. (2012). Useful satellite imagery was available for six nonconsecutive days in May prior to and during the 2011 Bonnet Carré Spillway opening. Excessive cloud cover or glare restricted additional imagery in May and June of 2011. Pixel-counting using ImageJ software available from the United States National Institutes of Health (http://rsb.info.nih.gov/ij/) was used to estimate areal coverage of the sediment-laden freshwater plume originating from the spillway for available images. Pixel-based area was converted to km² based on the percent of Lake Pontchartrain’s total surface area (1637 km²) covered by sediment-rich river water.

4.2.3. Lake Pontchartrain Transect Salinity and Surface Water Temperature

Monthly salinity and water temperature data from the 1997 event were obtained from the Louisiana Department of Environmental Quality (LDEQ) for 3 stations (CW-1, CW-4, CW-7) on the Lake Pontchartrain Causeway, which spans the north-south axis of the estuary (Figure 4.2, ○). A 30-km 10-station transect extending northeast from the Bonnet Carré Spillway inflow to
the center of Lake Pontchartrain was used in studies of the 2008 diversion event (White et al., 2009; Bargu et al., 2011) and again here for the 2011 field study (Figure 4.2, Δ).

Figure 4.2. MODIS satellite imagery of Lake Pontchartrain on (a) April 29, 2008 and (b) May 17, 2011 provided by the LSU Earth Scan Laboratory and the US Naval Research Laboratory at the Stennis Space Center, respectively. Orange or red tones depict sediment-laden Mississippi River water (measured as red band reflectance in 2008 and beam attenuation at 547 nm in 2011). Blue tones depict estuarine water and land is colored black or green/brown. The 10 stations shown as Δ comprise the 30-km transect used in this and past studies (White et al. 2009; Bargu et al. 2011). The 3 stations shown as ○ (CW-1, CW-4, and CW-7) were sampled by LDEQ in 1997.

Sampling in 2011 occurred on May 8\textsuperscript{th} pre-spillway opening, on four dates while the spillway was opened, and on seven dates post-spillway closure between June 21\textsuperscript{st} and August 10\textsuperscript{th}. During each sampling, salinity (using the Practical Salinity Scale) and water temperature were measured \textit{in situ} 10 cm below the surface using a handheld YSI (Model 556). Salinity and surface water temperature were analyzed for periods during the spillway opening, during the depletion of nitrate following spillway closure, and post-nitrate collapse as determined by Bargu et al. (2011) for 2008 and methods outlined below for 2011.

4.2.4. Bonnet Carré Spillway Nutrient Loading

Total NO\textsubscript{x}, NH\textsubscript{4}\textsuperscript{+}, DIN, and DSi loads in 2008 were calculated based on total event discharge and inflow concentrations measured by White et al. (2009) using identical methods to those employed here. Water samples (250 mL) were collected 10 cm below the surface from the
station nearest the spillway inflow (Figure 2) on 4 dates in 2011 (May 18\textsuperscript{th}, May 28\textsuperscript{th}, June 4\textsuperscript{th}, June 16\textsuperscript{th}) using acid-washed polyethylene bottles, placed on ice, and returned to the laboratory immediately for processing. Discrete nutrient measurements (methods detailed below) were then used to estimate daily concentrations for the duration of the 2011 event based on linear interpolation. Daily concentrations were then multiplied by the corresponding daily discharge and summed over the event to calculate 2011 nutrient loads for NO\textsubscript{x}-N, NH\textsubscript{4}-N, DIP, and DSi.

Spillway inflow concentrations of NO\textsubscript{x} (1.28 mg N L\textsuperscript{-1}), DIP (0.05 mg P L\textsuperscript{-1}), and DSi (2.91 mg Si L\textsuperscript{-1}) for 1997 were estimated based on mean values ($n = 4$) of concentrations measured by the USGS in the Mississippi River at Baton Rouge (USGS Station 07374000) during the period the spillway was open. Mean concentrations at the spillway inflow in Lake Pontchartrain measured by White et al. (2009) and in this study corresponded well to mean concentrations in the Mississippi River at Baton Rouge measured by the USGS during the 2008 and 2011 inflow periods (within ±10% for NO\textsubscript{x}-N and DSi, ±20% for DIP). Therefore, loads in 1997 based on USGS measurements for NO\textsubscript{x}-N, DIP, and DSi are comparable to those reported here for 2008 and 2011. NH\textsubscript{4}\textsuperscript{+} concentrations in the Mississippi River at Baton Rouge measured by the USGS were near or below their 1997/2008 detection limit of 0.02 mg N L\textsuperscript{-1} during the diversion periods for all three years. However, 2008 and 2011 measurements made by White et al. (2009) and in this study, respectively, both indicate that mean concentrations of NH\textsubscript{4}\textsuperscript{+} at the spillway inflow in Lake Pontchartrain were 0.03 mg N L\textsuperscript{-1}. Therefore, it is assumed that the 1997 NH\textsubscript{4}\textsuperscript{+} concentration equaled 0.03 mg N L\textsuperscript{-1} as well to improve comparison.

4.2.5. Lake Pontchartrain Water Quality Data for 1997 and 2008

Secchi depth and NO\textsubscript{x}-N measurements taken monthly from 3 stations located on the Lake Pontchartrain Causeway before, during, and after the 1997 Bonnet Carré Spillway opening
were available from LDEQ (Figure 4.2, ○). Chlorophyll data for 1997 was available from Turner et al. (2004). White et al. (2009) and Bargu et al. (2011) documented water quality data in Lake Pontchartrain during and after the 2008 Bonnet Carré Spillway event for the same 10-station transect used here for 2011 (Figure 4.2, Δ), providing a more robust comparison.

4.2.6. 2011 Lake Pontchartrain Transect Water Quality

Water clarity was measured along the 30-km 10-station transect in 2011 (Figure 4.2, Δ) using a Secchi disk (Wetzel, 2001). Water samples (250 mL) were collected 10 cm below the surface for NOx, NH4+, DIP, and DSi analyses using acid-washed polyethylene bottles, placed on ice, and returned to the laboratory immediately for processing. Additional water samples were collected by E. Smith and Dr. S. Bargu 10 cm below the surface at each station for microscopic analyses and Chl a measurements as the measure of phytoplankton biomass.

4.2.7. Laboratory Analyses

Upon return to the laboratory, 30 mL of each water sample was vacuum-filtered through 0.45 μm membrane filters and analyzed for NOx-N (Method 353.2, USEPA 1993), NH4-N (Method 350.1, USEPA 1993) and DIP (Method 365.1, USEPA 1993) on a Seal Analytical (Mequon, Wisconsin) AQ2+ discrete analyzer using standard colorimetric methods. DSi was measured on filtered subsamples using an autoanalyzer courtesy of T. Blanchard (Method 4500-SiO2).

Chl a concentrations were determined as the indicator of phytoplankton biomass courtesy of E. Smith and Dr. S. Bargu. Subsamples were filtered onto 25 mm GF/F filters and filters were placed in 15 mL centrifuge tubes, covered with aluminum foil and kept frozen until analysis (< 2 wks). Filters were then extracted for 24 h in 90% aqueous acetone at –20 °C and fluorescence was measured before and after acidification with hydrochloric acid using a Turner fluorometer.
A gridded Sedgwick-Rafter slide (Wildco) was used to examine two 1 mL replicates of water from each lugol’s preserved archive sample on an Axio Observer - A1 inverted microscope (Zeiss). The samples were allowed to settle for 30-45 min before examination began. Groups of phytoplankton that were counted by E. Smith for the community composition were cyanobacteria, chlorophytes, centric diatoms, pennate diatoms, flagellates, and dinoflagellates. At least 20-1 mm² grids were counted for each sample.

4.2.8. Nitrate Plume Collapse Period

The NOx-N plume collapse time is defined here as the number of days between the closure of the spillway and the collapse of NOx-N concentrations to ≤ 0.1 mg L⁻¹ within the region of the estuary affected by the diversion. Estimates for the NOx-N plume collapse time during the 2008 and 1997/2011 events are based on data reported by Bargu et al. (2011) and in this study, respectively.

4.2.9. Weather Analysis

Hourly data for wind speed and air temperature from the nearby New Orleans International Airport (US National Climatic Data Center, WBAN 12916) were used to calculate daily means and characterize weather conditions during the 30 days following spillway closures in 1997, 2008, and 2011. Data from 31-60 days post-spillway closure were also analyzed for 1997 due to the large CyanoHAB in Lake Pontchartrain observed in 1997 approximately 2 months after the spillway closure (Turner et al., 2004). Missing data in the hourly dataset for wind speed and air temperature were filled by linear interpolation. Daily mean weather data was log transformed to fit a normal distribution and analyzed using one-way ANOVAs to determine whether or not any significant differences existed among the 30 day time periods at the α = 0.05
level. Specific differences among daily mean weather parameters during 30 day time periods were then tested for significance at the $\alpha = 0.05$ level using Tukey’s HSD test.

4.2.10. Northern Tributary Data

Monthly tributary discharge data were obtained for five northern tributaries from the USGS for 1997, 2008, and 2011 and corrected to represent the entire watershed. Special attention is paid to the April-June periods each year due to the estuary’s mean 60-d residence time, the months of earliest and latest spillway closures, and previous observations of CyanoHABs in June post-spillway closure. Monthly tributary discharge data was obtained for the Amite River near Denham Springs (USGS Station 7378500), the Tangipahoa River at Robert (USGS Station 7375500), the Tchefuncte River near Folsom (USGS Station 7375000), the Tickfaw River at Holden (USGS Station 7376000), and the Natalbany River at Baptist (USGS Station 7376500). The total Upper Lake Pontchartrain watershed area (12476 km$^2$) was determined from the areas reported by Seaber et al. (1987) for the five hydrologic cataloging units that comprise the basin: 08070202 (Amite, 4895 km$^2$), 08070203 (Tickfaw, 1888 km$^2$), 08070204 (Lake Maurepas, 1862 km$^2$), 08070205 (Tangipahoa, 1979 km$^2$), and 08090201 (Liberty Bayou-Tchefuncte, 1834 km$^2$). Available discharge data represented 49% of the total Upper Lake Pontchartrain watershed. Discharge values for the gauged drainage area were corrected to represent the entire watershed based on the relationship between average annual daily discharge per unit area and drainage area for the Pontchartrain watershed (Roblin, 2008). Mean annual discharge from northern tributaries in the Pontchartrain basin is 6.1 km$^3$ based on the average long-term daily flow for the watershed (0.0156 m$^3$ s$^{-1}$ km$^{-2}$; Roblin, 2008) and the 12,476 km$^2$ watershed area. Mean nutrient loads from northern tributaries have been estimated to
be 1367 Mg NO₃-N y⁻¹, 1002 Mg NH₄-N y⁻¹, and 444 Mg DIP y⁻¹ (McCorquodale et al., 2009; Roy et al., 2012).

4.3. Results

4.3.1. Bonnet Carré Spillway Freshwater Discharges

The three spillway events analyzed were all characterized by the discharge of a volume of Mississippi River water greater than the total volume of Lake Pontchartrain. The 2011 opening had the largest total discharge (21.9 km³) and occurred later than the events in 1997 (11.7 km³) and 2008 (7.5 km³) (Figure 4.3). Discharges in 1997, 2008, and 2011 were equal to 176%, 113%, and 330% of Lake Pontchartrain’s volume, respectively (Table 4.1).

4.3.2. Size and Dispersal of the Sediment-rich Freshwater Plume

The greater discharge in 2011 resulted in a near-linear increase in the sediment-rich freshwater plume area to a maximum of approximately 1200 km² 14 days post-opening in comparison to the 616 km² plume observed by White et al. (2009) in 2008 (Figure 4.4). The maximum turbid freshwater plume areas in 2008 and 2011 were equal to 38% and 73% of the total surface area of Lake Pontchartrain, respectively. Previous research indicates that the sediment-rich freshwater plume extended over a majority of the estuary in 1997 (Waters et al., 2009; Chao et al., 2012) as in 2011. The leading plume edge initially traveled along the southern edge of Lake Pontchartrain in 1997 (Waters et al., 2009; Chao et al., 2012), 2008 (White et al., 2009), and 2011 (Figure 4.2). Sediment-rich water was observed exiting Lake Pontchartrain via both of its eastern outlets in satellite imagery on May 23, 2011, indicating that the leading edge of the turbid freshwater plume traveled across the estuary in ≤ 14 days in 2011.
4.3.3. Lake Pontchartrain Salinity and Surface Water Temperature

Salinity at the 3 stations on the Lake Pontchartrain Causeway monitored by LDEQ in 1997 (Figure 4.2, ○) ranged from 4.9-6.0 on February 17th and decreased to 3.8-4.4 on March 10th one week prior to the 1997 spillway opening (Figure 4.5).
Measurements taken on April 14, 1997 while the spillway was open indicate that stations CW-4 and CW-7 in the central and southern portions of the causeway, respectively, were inundated with Mississippi River water. Salinity near the northern shore (CW-1) the same day was 1.7. Following spillway closure in 1997, salinity gradually increased at CW-4 and CW-7 over the next several months and was 1.4-1.8 on August 11th. Salinity at CW-1 initially declined on May 12th following spillway closure and remained below 0.8 through August 11th. Water temperature at these three stations in 1997 ranged from 17.3-18.5°C on March 10th prior to the spillway opening and decreased to ~16°C at CW-4 and CW-7 on April 14th during the spillway event (Figure 4.5). Following spillway closure in 1997 water temperature gradually increased to 21.8-22.7°C on May 12th and was >26°C in June.
Figure 4.5. 1997 monthly measurements of salinity, Secchi depth (m), water temperature (°C), and NO$_x$-N (mg L$^{-1}$) during February-August made by the Louisiana DEQ at three stations on the Lake Pontchartrain Causeway (Figure 4.2, ○). The shaded region indicates the period during which the spillway was open (March 17 – April 18, 1997).

Salinity (Figure 4.6) and surface water temperature (Figure 4.7) dynamics in 2008 are described in detail in White et al. (2009) and Bargu et al. (2011). In 2011, salinity in Lake Pontchartrain across the sample transect (Figure 4.2, △) ranged from 2.6-4.9 on May 8th prior to
the 2011 spillway opening (Figure 4.8). Lower salinities at stations closest to the spillway indicated leakage of Mississippi River water through the spillway prior to its opening. Salinity on May 18, 2011 during the spillway opening was ≤ 0.15 at all stations except the two furthest from the inflow (0.79-2.72) (Figure 4.6). Fluctuations in salinity occurred at the three stations furthest from the inflow through June 16, 2011. Surface water temperature was > 20.0 °C at all stations on May 18, 2011 and increased to > 28.2 °C at all stations by June 16, 2011 (Figure 4.7).

Following spillway closure on June 20th, salinity averaged (± 1 standard deviation) 0.34 ± 0.30 across the transect on June 21st and remained below 1.2 at all stations through July 11th during the nitrate collapse period with evidence of slow dilution by estuarine water (Figure 4.6). Surface water temperatures were > 29.0 °C at all stations during the nitrate collapse period in 2011 (Figure 4.7). On August 10, 2011 salinity remained ≤ 1.2 at all stations, indicating a much slower rate of salinity increase following spillway closure than observed in 2008 by Bargu et al. (2011) (Figure 4.6). Post-nitrate collapse surface water temperatures in 2011 were > 28.7 °C at all stations (Figure 4.7).

4.3.4. Bonnet Carré Spillway Nutrient Loading

Spillway nutrient loading to Lake Pontchartrain during the three events was correlated to discharge (Table 4.2). In all three events, the DIN pool in spillway influx was consistently dominated by NO₃⁻ with total NOₓ-N loads of 14949, 9714, and 25395 Mg in 1997, 2008, and 2011, respectively. In general nutrient loads were 1.7-2.0 times greater in 2011 than in 1997 and 2.6-3.6 times greater in 2011 than in 2008.
Figure 4.6. Salinity along the 30-km 10-station study transect (Figure 4.2, Δ) during (a) the spillway opening, (b) nitrate collapse, and (c) post-nitrate collapse periods in 2008 (left panel) and 2011 (right panel). 2008 data are from White et al. (2009) and Bargu et al. (2011).
Figure 4.7. Surface water temperature along the 30-km 10-station study transect (Figure 4.2, Δ) during (a) the spillway opening, (b) nitrate collapse, and (c) post-nitrate collapse periods in 2008 (left panel) and 2011 (right panel). 2008 data are from White et al. (2009) and Bargu et al. (2011).
Figure 4.8. 2011 salinity, Secchi depth (m), dissolved inorganic phosphorus (mg DIP-P L$^{-1}$), ammonium (mg NH$_4$-N L$^{-1}$), nitrate (mg NO$_3$-N L$^{-1}$), dissolved silica (mg DSi L$^{-1}$) and chlorophyll-$a$ (µg L$^{-1}$) across the 30-km 10 station transect in Lake Pontchartrain extending from the Bonnet Carré Spillway inflow (0.9 km) to the lake center (29.5 km) (Figure 4.2, Δ). The left and right panels show stations 0.9-11.1 km and 14.2-29.5 km from the spillway inflow, respectively. Shaded regions indicate the period during which the spillway was open (May 9 – June 20, 2011). Dotted lines in the NH$_4$-N plots indicate the detection limit. Chl $a$ measurements are courtesy of E. Smith and Dr. S. Bargu.
For all events the DIN:DIP molar ratio of spillway inflow waters (≥ 50:1) was well above the Redfield ratio of 16:1, indicating potential for P limitation of primary production. The DSi:DIN molar ratio of spillway influx was near or greater than 1:1 for all events. Spillway loads of DIN and DIP were equal to 4-11 and 0.8-2.5 times, respectively, loads from northern tributaries in an average non-diversion year (McCorquodale et al., 2009; Roy et al., 2012) (Table 4.2).

Table 4.2. Average annual nutrient loads to Lake Pontchartrain from northern tributaries and from the Bonnet Carré Spillway in 1997, 2008, and 2011. The final two columns show 2011 spillway loads divided by 1997 and 2008 spillway loads, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Northern Tributaries</th>
<th>Bonnet Carré Spillway</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NO₃⁻ + NO₂⁻ (Mg NOₓ⁻N)</strong></td>
<td>1,367&lt;sup&gt;a&lt;/sup&gt;</td>
<td>14,949&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>NH₄-N (Mg N)</strong></td>
<td>1,002&lt;sup&gt;a&lt;/sup&gt;</td>
<td>350&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>DIN (Mg N)</strong></td>
<td>2,369&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15,299</td>
</tr>
<tr>
<td><strong>DIP (Mg P)</strong></td>
<td>444&lt;sup&gt;b&lt;/sup&gt;</td>
<td>584&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>DSi (Mg Si)</strong></td>
<td>-</td>
<td>33,985&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>McCorquodale et al. (2009). <sup>b</sup>Roy et al. (2012). <sup>c</sup>Based on measurements made by the USGS in the Mississippi River at Baton Rouge. <sup>d</sup>NH₄-N inflow concentration assumed to be equal to 2008 and 2011. <sup>e</sup>Based on values reported in White et al. (2009).
4.3.5. Water Quality Dynamics during the 1997 Spillway Opening

Secchi depth ranged from 0.6-1.7 m on March 10, 1997 (Figure 4.5). Following the opening of the spillway, Secchi depth on April 14th decreased to 0.2 m at CW-4 and CW-7 and to 0.9 m at CW-1. Minimum Secchi depth at CW-1 was observed on May 12th (0.6 m) followed by a gradual increase to 1.8 m in August. Gradual increases in water clarity were observed at CW-4 and CW-7 following spillway closure with Secchi depth equal to 0.7-1.3 m in June. Nitrate concentrations on April 14th during the 1997 spillway opening were 1.2-1.3 mg NO\textsubscript{x}-N L\textsuperscript{-1} at CW-4 and CW-7 and 0.4 mg NO\textsubscript{x}-N L\textsuperscript{-1} at CW-1 near the northern shore (Figure 4.5). Nitrate then decreased at CW-4 and CW-7 with time following spillway closure and was < 0.1 mg NO\textsubscript{x}-N L\textsuperscript{-1} in July.

4.3.6. Water Quality Dynamics during the 2011 Spillway Opening

Mean Secchi depth (± 1 standard deviation) in Lake Pontchartrain was 0.9 ± 0.2 m on May 8, 2011 prior to the 2011 spillway opening and decreased to 0.3 ± 0.1 m during the spillway opening (Figure 4.8). Following spillway closure on June 20, 2011, Secchi depth increased to as high as 3.4 m in July under NO\textsubscript{3}\textsuperscript{-} depleted conditions and remained > 0.76 m at all stations through August with several measurements > 2 m.

Nitrate concentrations on May 18, 2011 in the Mississippi River plume ranged from 1.04-1.27 mg NO\textsubscript{x}-N L\textsuperscript{-1} (Figure 4.8). Over the course of the spillway opening in 2011, NO\textsubscript{3}\textsuperscript{-} concentrations remained ≥ 1 mg NO\textsubscript{x}-N L\textsuperscript{-1} at stations with salinity ≤ 0.2 except on June 16th when concentrations began to decline. Nitrate concentrations decreased rapidly following spillway closure and by July 11th, NO\textsubscript{x}-N concentrations were below detection (detection limit = 0.016 mg L\textsuperscript{-1}) at the majority of stations (Figure 4.8), indicating a NO\textsubscript{3}\textsuperscript{-} plume collapse time of 21 days (Table 4.1). Nitrate concentrations largely remained below 0.04 mg NO\textsubscript{x}-N L\textsuperscript{-1} at all
stations through August. NH₄-N concentrations were often below detection (< 0.022 mg L⁻¹) and never increased above 0.07 mg L⁻¹ throughout the spillway opening and post-closure period (Figure 4.8).

The mean measured DIP-P concentration was 0.054 mg L⁻¹ in spillway inflow waters. Water column DIP concentrations decreased rapidly in Lake Pontchartrain between June 4th and June 30th with depletion occurring earlier with increased distance from the spillway due partially to dilution (Figure 4.8). Following DIP depletion across the entire transect during and after spillway closure, concentrations rebounded at all sites and by July 27th were greater than the concentration of loaded Mississippi River water at all stations.

Water column DSi concentrations were near or above 3 mg L⁻¹ within the Mississippi River plume during the opening, before rapidly decreasing below 0.5 mg L⁻¹ between June 30th and July 11th (Figure 4.8). DSi concentrations remained low before increasing rapidly between July 27th and August 10th to > 2 mg L⁻¹.

On May 8, 2011, Chl a values were relatively low (mean ± 1 standard deviation = 3.6 ± 1.1 µg L⁻¹) and then increased during the spillway opening at stations further from the spillway inflow (up to 35 µg L⁻¹) (Figure 4.8). Results indicate that low light availability (measured as Secchi disk depth) corresponded to low phytoplankton biomass (measured as Chl a) within the sediment-rich Mississippi River plume near the spillway inflow despite available nutrients. Immediately following spillway closure, the Chl a concentration reached a maximum of 45.1 µg L⁻¹ on June 21st at 4.9 km from the spillway inflow. Chlorophyll peaks corresponded to depletion of NO₃⁻ and DIP of Mississippi River origin (Figure 4.8). Chlorophytes were the dominant phytoplankton group at the time and location of maximum Chl a and accounted for a spatial average of 52-76% of the phytoplankton group composition during the period of greatest Chl a
(June 16th, 21st, and 25th) (Figure 4.9). Cyanobacteria accounted for a spatial average of 7-22% of the group composition during this period. Phytoplankton biomass declined after June 25th and by July 11th Chl a concentrations were < 8.6 µg L⁻¹ at all sites. No substantial increases in biomass were observed from this time through the final sampling on August 10th (Figure 4.8).

4.3.7. Comparison of Nitrate Plume Collapse

The observed times for NOx plume collapse following spillway closure were identical in 2008 and 2011 at 21 days despite the differences in overall discharge volume and total NOx load (Table 4.1). In both cases NOx depletion corresponded to increases in phytoplankton biomass with little dilution by higher salinity estuarine water (salinity ≤ 2 and ≤ 1 in 2008 and 2011, respectively, during NOx collapse). A substantially longer time for NOx collapse in 1997 was determined from the LDEQ data. NOx-N was not ≤ 0.1 mg L⁻¹ until July 14th (87 days following closure) at any of the three stations monitored. Comparison of the 1997 result with 2008 and 2011 is compromised by the fact that NOx measurements were made at different temporal resolution by different laboratories using different sample locations (all 1997 measurements > 20 km from spillway inflow). Aspatial mean NOx results from 7 stations on the Lake Pontchartrain Causeway reported by Turner et al. (2004) indicate a similar NOx-N depletion time for 1997 to the one determined here using LDEQ data.

4.3.8. Comparison of CyanoHAB Dynamics

Dominance of the phytoplankton community by CyanoHAB species was observed in 1997 (June 10th, Turner et al., 2004) and 2008 (May 21st, Bargu et al., 2011) following spillway closure, but not in 2011 (Figure 4.9).
Figure 4.9. Phytoplankton group composition across the 30 km transect extending northeast from the Bonnet Carré Spillway inflow (Figure 4.2, △) during the period of increased Chl $a$ observed following the 2011 opening. Data courtesy of E. Smith and Dr. S. Bargu.

Maximum Chl $a$ concentrations were 855 (surface water scum), 58, and 45 µg L$^{-1}$ for 1997, 2008, and 2011, respectively. The 1997 CyanoHAB occurred nearly 2 months after the spillway was closed, while the 2008 CyanoHAB occurred within 2 weeks of closure (Table 4.1).
4.3.9. Comparison of Post-Spillway Closure Weather

The three Bonnet Carré Spillway events analyzed here had closures in April (1997), May (2008), and June (2011) (Figure 4.3). The 30 day time period following closure in 2011 was characterized by significantly higher daily mean air temperature than periods analyzed in 1997 and 2008 at the $\alpha = 0.05$ level (Table 4.3). The 30 days following spillway closure in 1997 were significantly colder than the other periods at $\alpha = 0.05$ and relatively windy, while days 31-60 in 1997 were more comparable to weather observations for the 30 days following spillway closure in 2008. The mean of daily mean wind speeds during the 30 days following closure in 2011 was the lowest of all periods analyzed, although 2011 wind speeds were not significantly different than days 31-60 in 1997 (Table 4.3).

Table 4.3. Weather characteristics during the period following the closure of the Bonnet Carré Spillway in 1997, 2008, and 2011. Data is from the National Climatic Data Center (Louis Armstrong New Orleans Int’l Airport). Letters indicate significant differences at the $\alpha = 0.05$ level for different time periods.

<table>
<thead>
<tr>
<th>Year</th>
<th>1997</th>
<th>1997</th>
<th>2008</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Days After Spillway Closure</td>
<td>1 - 30</td>
<td>31 - 60</td>
<td>1 - 30</td>
<td>1 - 30</td>
</tr>
<tr>
<td>Daily Mean Wind Speed (m s$^{-1}$)</td>
<td>4.0 ± 1.4$^a$</td>
<td>3.2 ± 0.8$^{b,c}$</td>
<td>3.6 ± 1.1$^{a,b}$</td>
<td>2.9 ± 1.1$^c$</td>
</tr>
<tr>
<td>Daily Mean Air Temp. (°C)</td>
<td>21.3 ± 2.2$^a$</td>
<td>25.3 ± 1.7$^b$</td>
<td>26.0 ± 2.2$^b$</td>
<td>28.9 ± 1.2$^c$</td>
</tr>
</tbody>
</table>

4.3.10. Northern Tributary Discharge

Total annual discharge from northern tributaries was 9.4, 6.0, and 3.7 km$^3$ in 1997, 2008, and 2011 (Figure 4.10). The ratios of spillway discharge to total annual northern tributary discharge in 1997, 2008, and 2011 were 1.2, 1.3, and 5.9, respectively. Total April-June northern tributary discharge was equal to 3.5, 1.2, and 0.4 km$^3$ for 1997, 2008, and 2011, respectively.
(Figure 4.11). Discharge in 1997 for April-June was 3.0 and 8.2 times greater than total
discharges over the same period in 2008 and 2011, respectively. Approximately 54% of
discharge from northern tributaries over this time period in 1997 occurred in April (1.9 km$^3$).
Discharges from tributaries for April and April-June of 1997 were equal to 16% and 30% of total
spillway discharge that year, respectively. The ratios of spillway discharge to April-June
tributary discharge in 1997, 2008, and 2011 were 3.4, 6.4, and 51.6, respectively. Notable in
2008 was the highest May discharge (0.8 km$^3$) of the three years despite dry conditions in April.

4.4. Discussion

4.4.1. Physical and Salinity Factors Affecting CyanoHAB Formation during Inflows

Freshwater inflow during Bonnet Carré Spillway events can approximately equal (1997,
2008) or greatly exceed (2011) annual input from northern tributaries (Figure 4.10). The
immense rate of freshwater discharge through the spillway during diversions (up to nearly 9000
m$^3$ s$^{-1}$ in 2011, Figure 4.3) results in a relatively rapid expansion of a freshwater plume that can
affect a significant portion of Lake Pontchartrain (Figures 4.4 and 4.6).
Figure 4.11. Monthly (gauged + ungauged) discharge (km³) from northern tributaries (Figure 4.1) into Lake Pontchartrain during April-June of 1997, 2008, and 2011.

The plume is characterized horizontally by a narrow (< 10 km) edge of mixed fresh and estuarine water (Figure 4.6) and is vertically well mixed (White et al., 2009). Essentially, the plume behaves as a river flowing through the shallow estuary during the inflow event. The tendency for plume waters to travel along the southern rim of the estuary is driven by the Coriolis effect, but can also be affected by wind (White et al., 2009). The leading plume edge moves rapidly through the estuary to its eastern outflows. We observed turbid plume waters exiting Lake Pontchartrain ≤ 14 days following the spillway opening in 2011. Sediment-rich water was observed exiting the estuary on April 29, 2008, 18 days following the spillway opening that year (White et al., 2009). Finally, McCorquodale et al. (1998) estimated that the shortest travel time of plume waters to outlets during the 1997 event was 6 days. These observations indicate that the minimum plume travel time from the spillway to Lake Pontchartrain’s eastern outlets during diversions can be 3-10 times shorter than the estuary’s mean residence time of 60 days during non-diversion periods (Swenson, 1980).
Plume waters near the spillway during the opening are characterized by high suspended sediments (White et al., 2009) and low Secchi depth (Figure 4.8). Additionally, the high discharge rate creates a turbulent, horizontally dynamic, and vertically well-mixed environment in the region near the spillway. Phytoplankton biomass (represented here as Chl \( a \)) in this region of the freshwater plume is therefore limited by light availability and flushing rate despite readily available nutrients (Figure 4.8).

Phytoplankton compete for loaded nutrients as light limitation is alleviated and physical disturbance decreases, either in regions more distant from the spillway during the opening or following spillway closure (Figure 4.8). Continued freshwater inflow causes continued horizontal displacement of water in regions further from the spillway despite less turbulent and turbid conditions, resulting in outflow to the coastal ocean (Figure 4.2). Previous research has shown that cyanobacteria exhibit greater relative biomass when flushing is minimal (i.e., less horizontal displacement of the water column) (Paerl, 2006). Therefore, the river-like nature of the flowing freshwater plume during spillway events likely provides a competitive advantage for diatoms and chlorophytes.

Temperature and wind are two physical factors that may also influence phytoplankton community composition during the period of nutrient assimilation and peak phytoplankton biomass. Cyanobacteria generally exhibit greater growth rates at high surface water temperatures (> 25°C) than diatoms, although chlorophytes also achieve maximum growth rates at > 25°C (Paerl et al., 2011). Diverted Mississippi River water that is cooler than resident estuarine water quickly warms in the estuary as air temperatures increase (Figures 4.5 and 4.7). Not surprisingly, diversion timing affects temperature dynamics. The earlier diversion period in 1997 resulted in surface water temperatures < 18°C during the initiation of the nitrate collapse period (Figure 5).
in comparison to 24-28°C and 28-32°C during nitrate collapses in 2008 and 2011, respectively (Figure 4.7). While surface water temperatures immediately following the earlier spillway closure in 1997 were not as favorable for rapid cyanobacterial growth as identical periods in 2008 and 2011, temperature was > 26°C by June (Figure 4.5) when a large-scale CyanoHAB was observed by Turner et al. (2004).

Lake Pontchartrain is an exposed, wind-dominated estuary and wind-induced turbulence and turbidity can limit cyanobacterial success in estuaries due to disruption of vertical stratification and surface bloom formation (Paerl, 2006). However, my results show that the 30-day mean of the daily mean wind speeds following spillway closure in 2011 was lower than those of the same periods in 1997 and 2008 when CyanoHABs were observed (Table 3). This suggests that wind-wave action was not the dominant factor responsible for the absence of cyanobacterial dominance in 2011 (Table 4.3).

Following spillway closure, mixing of estuarine water with the freshwater plume occurs at a pace and areal extent depending on the magnitude of the diversion (Figure 4.6). Salinity in Lake Pontchartrain is typically low enough (< 10) to not limit N-fixing *Anabaena* spp. or certain non-N-fixing *Microcystis* spp. In 1997 (Figure 4.5) and 2011 (Figure 4.6), salinity remained below 2 at all stations through August, indicating that salinity likely did not limit *Microcystis* spp. Salinity increased above 2 following nitrate collapse in 2008 (Bargu et al., 2011; Figure 4.6), however at this time growth of *Microcystis* spp. was likely restricted by lack of available DIN.
4.4.2. Bioavailable Nutrient Dynamics during Inflows

My results illustrate a sequence of estuarine nutrient dynamics in response to large inflows of Mississippi River water (Figure 4.12). Findings in 2008 (Bargu et al., 2011) and 2011 (this study) indicate that NO$_3^-$ concentrations can decrease rapidly to below detection in approximately three weeks following spillway closure when water temperature $\geq 25^\circ$C (Table 4.2). Only a small percentage of incoming NO$_3^-$ is removed via denitrification in sediments (e.g., 3% in 2008) due to the immense NO$_3^-$ loading rate during spillway openings (Roy and White 2012). Submerged aquatic vegetation (SAV) in Lake Pontchartrain exists primarily on the northeastern shore of the estuary with only small isolated patches existing on the southeastern shore (Cho and Poirrier, 2005). SAV likely plays an insignificant role in nutrient uptake during spillway events due to its relatively small areal extent, the high loading rate of nutrients, and the tendency for plume waters to travel along the southern portion of the estuary. Therefore, the vast majority of loaded NO$_3^-$ is either assimilated by phytoplankton or transported to the coastal ocean. The combination in 2011 of rapid NO$_3^-$ decline and slow influx of higher salinity dilution water to the transect region (Figure 4.8) suggests that phytoplankton assimilation could possibly account for the majority of DIN-depletion that year. Further research is needed to make mass balance estimates of nitrate assimilated versus loaded to the coastal ocean. Nitrate remained the dominant form of DIN throughout the study period in 2011. Oscillations in NH$_4$-N at low concentrations (Figure 4.8) were likely a result of mineralization processes, phytoplankton assimilation, and release from sediments due to concentration gradients (Wawrik et al., 2004; Roy and White 2012).
Figure 4.12. Estuarine biogeochemical dynamics during large inflows of nitrate-rich freshwater. Diagram is based on observations in Lake Pontchartrain during the 2008 and 2011 Bonnet Carré Spillway openings. Dotted line indicates that the system can move from P-limitation to N-limitation in < 1 month during warm periods (water temp. ≥ 25°C).

Phosphorus bioavailability in Lake Pontchartrain during and after spillway events likely plays an important role in phytoplankton community response. The high DIN:DIP molar ratio of inflowing freshwater (≥ 50, Table 4.2) leads to potential P-limitation during the nitrate collapse period (Mize and Demcheck, 2009). Once loaded DIP is rapidly assimilated during this period, further primary production relies on internal sources of DIP including mineralization and internal loading from sediments. These P-limited conditions put N-fixing cyanobacteria (*Anabaena* spp.) at a competitive disadvantage (Paerl, 1988). Following the depletion of both water column DIP and DIN in 2011, the rapid rebound in DIP concentrations observed (Figure 4.8) could only occur by internal loading from sediments because northern tributaries were in drought conditions (Figure 4.11) and there was no significant external source of DIP. Roy et al. (2012) show that
internal P loading from Lake Pontchartrain sediments occurs regardless of bottom water oxygen availability and estimate that internal DIP loading by diffusion alone has the potential to regenerate water column DIP concentrations from below detection to the Mississippi River concentration during the 2011 event (0.05 mg P L$^{-1}$) in < 60 days. My field observations (Figure 4.8) suggest that this internal pulse of P from sediments can return the system to pre-inflow N-limitation conditions even faster (< 1 month following spillway closure), perhaps due to additional advective flux. High Secchi disk transparency and low chlorophyll $a$ measurements following July 11, 2011 (Figure 4.8) indicate that primary productivity was limited by N at this time. The dynamic interaction between high external N loading during inflows and subsequent internal P loading and return to N-limitation observed here (Figure 4.12) has rarely been documented in estuaries (Cook et al., 2010). Diverted Mississippi River water can also be a source of sediment-bound P in addition to DIP (Zhang et al., 2012). Further research is needed to determine whether there is a legacy effect of spillway openings on the potentially bioavailable phosphorus pool in Lake Pontchartrain sediments.

Si bioavailability is also a factor that can determine phytoplankton community response to inflows by influencing diatom success (Turner, 2002). The DSi:DIN molar ratio in Mississippi River water is near or above 1:1 during diversion periods (Table 4.2), indicating nutrient conditions favorable for diatom growth (Redfield et al., 1963; Officer and Ryther, 1980; Lane et al., 2001). Following nitrate collapse in 2011, DSi concentrations plummeted, potentially indicating diatom uptake, before rebounding a few weeks later (Figure 4.8). The observed rebound was likely due to the dissolution of diatom silica and internal loading from sediments (Conley et al., 1988).
4.4.3. Phytoplankton Community Dynamics during and after Inflows

The Lake Pontchartrain environment is physically and chemically dynamic during and after spillway events, leading to equally dynamic biological responses. The spatiotemporal dynamics of cyanobacteria in 2008 illustrate a sequence of interrelated nutrient depletion and species appearance (Bargu et al., 2011). At stations directly influenced by the spillway plume, *Microcystis* spp. was the first cyanobacterium observed as NO$_3^-$ depletion progressed (centric diatoms and chlorophytes were dominant), while *Anabaena* spp. was initially observed at low abundance in waters outside of the spillway plume influence where nutrient concentrations were low. Following depletion of spillway-loaded NO$_3^-$, there was a shift to cyanobacterial dominance by N-fixing *Anabaena* spp. It is likely that P release from sediments contributed to this bloom of N-fixers (Roy et al., 2012), as observed in other systems including the Baltic Sea (Vahtera et al., 2007). In contrast, cyanobacteria never achieved dominance following the 2011 closure (Figure 4.9).

The ecosystem dynamics in Lake Pontchartrain following freshwater inflow events that we have described (Figure 4.12) coupled with observations in 2008 lead to two questions about phytoplankton response in 2011. First, why wasn’t there a bloom of *Microcystis* spp. immediately following the closure of the spillway when both DIN and DIP were readily available? Second, why wasn’t there a bloom of N-fixing *Anabaena* spp. after spillway DIN was depleted, sediments provided an internal source of P, and N-limited conditions were restored?

There are two factors that may help answer the first question: water column physical disturbance and the form of DIN present. Surface water temperatures of 30°C likely enabled maximum growth rates for both chlorophytes and cyanobacteria upon spillway closure in 2011 (Paerl et al., 2011). The dominance of chlorophytes during the period of maximum
phytoplankton biomass in 2011 (Figure 4.9), the absence of *Microcystis* spp. dominance in 2008, and previous observations of chlorophytes and diatoms outcompeting cyanobacteria during high inflow events in temperate estuaries (Paerl, 2006) all suggest that physical disturbance of the water column during spillway events may give chlorophytes or diatoms the competitive edge during the nutrient collapse period as light increases and horizontal displacement (i.e., flushing) continues. Whether diatoms or chlorophytes dominate is likely a function of temperature and therefore diversion timing, with higher temperatures similar to those observed in 2011 favoring chlorophytes. Another possible factor is the dominance of the DIN pool by NO\textsubscript{3}. Blomqvist et al. (1994) suggest that high NO\textsubscript{3} concentrations favor eukaryotic phytoplankton, while non-N-fixing cyanobacteria (*Microcystis* spp.) are more competitive at low NO\textsubscript{3} concentrations with sufficient NH\textsubscript{4}. Observations by Jacoby et al. (2000) support this notion.

I hypothesize that the greater freshwater discharge, greater plume areal extent, and later diversion timing in 2011 compared to 2008 (Figures 4.3 and 4.4) all played important roles in limiting the success of N-fixing *Anabaena* spp. during the late summer period of N-limitation in 2011. The 2011 diversion occurred during the time period when CyanoHABs were observed in both 1997 and 2008 (Table 4.1). Hydraulic alteration to increase turbulence and flushing has been found to prevent or terminate *Anabaena* spp. blooms in river systems (Mitrovic et al., 2011). The spillway diversion may have achieved the same function on a massive scale in Lake Pontchartrain in 2011, eliminating the *Anabaena* spp. seed population necessary for bloom formation. This is supported by the high water velocity (> 2 m s\textsuperscript{-1}) at locations proximal to the spillway in Lake Pontchartrain, consistent with the large volume of discharge.
4.4.4. The 1997 CyanoHAB and Potential Watershed Factors

The large CyanoHAB consisting of *Anabaena* spp. and *Microcystis* spp. in 1997 documented by Turner et al. (2004) stands out as the most dramatic ecosystem response in Lake Pontchartrain following a recent spillway inflow event. The most unique characteristics of the 1997 event in comparison to 2008 and 2011 were: (i) the earlier timing of the diversion event (Figure 4.3), (ii) the substantially longer NO$_x$ depletion time (Table 4.2, Figure 4.5), and (iii) the substantially greater discharge from northern tributaries for April-June that year (Figure 4.11). The large difference (66 days) in NO$_x$ depletion time in 1997 compared to 2008 and 2011 was likely influenced by the earlier diversion timing that year (Figure 4.3), along with significantly colder air temperatures, relatively windy conditions (Table 4.3), colder water temperatures (Figure 4.5), and low water clarity (< 0.7 m) (Figure 4.5) following spillway closure.

I hypothesize that discharge from northern tributaries may also influence ecosystem response to spillway events and CyanoHAB formation in Lake Pontchartrain. Nearly one third the amount of water loaded by the spillway in 1997 was discharged from northern tributaries during April-June that year. Modeling results have suggested a tendency for algal blooms in Lake Pontchartrain to be initiated in the northwest quadrant of the estuary during spillway events despite higher DIN concentrations in the southwest near the spillway (McCorquodale et al., 2009). The lower mean DIN concentration in tributaries (approximately 0.34 mg N L$^{-1}$, McCorquodale et al., 2009) does not necessarily preclude CyanoHAB formation in portions of the estuary influenced by these rivers and may favor N-fixing *Anabaena* spp. given available P in tributaries and internal P loading from estuarine sediments. Northern regions of Lake Pontchartrain can remain mostly isolated from the spillway plume during openings (Figure 4.2) and then later be influenced by spillway-derived water via mixing post-closure (Bargu et al.,...
Therefore, discharge from northern tributaries can remain the dominant source of nutrients and biology for portions of the estuary during spillway events depending on plume hydrodynamics.

The Mississippi River plume affected a majority of Lake Pontchartrain in both 1997 (Waters et al., 2009; Chao et al., 2012) and 2011 (Figure 4.4). However, there was substantially less freshwater loaded by tributaries to northern portions of the estuary in 2011 in comparison to 1997 (Figure 4.10). Given the translocation of resident cyanobacteria from the majority of the estuary during the immense 2011 diversion event, the lack of northern tributary influence potentially further decreased the probability of rapid cyanobacterial development in the northern estuary that could expand southward. The earlier diversion timing in 1997 and subsequent longer time period of nutrient availability provided more time (approximately 2 mo.) for high freshwater input from tributaries in April-June to influence the estuary prior to the June CyanoHAB. The greater portion of the northern half of the estuary that was unaffected by spillway waters during the diversion in 2008 (Figure 4.4) likely enabled the formation of a seed population in that region. This is likely because *Anabaena* spp. were first observed outside of the spillway plume’s influence in 2008 and gained dominance only after some mixing of spillway water and estuarine water had occurred (Bargu et al., 2011). Further research is needed to develop an understanding of how northern tributaries can influence CyanoHABs in Lake Pontchartrain during both diversion and non-diversion years.

4.5. Conclusions

The variability in Lake Pontchartrain ecosystem response to Bonnet Carré Spillway openings suggests that there is not a simple stimulus-response relationship between N loading and estuarine CyanoHAB formation during large freshwater inflows. Nutrient loading during
spillway openings consistently produces relatively high chlorophyll levels, however CyanoHAB formation is not guaranteed. A complex set of parameters including N loading, timing, diversion magnitude, plume hydrodynamics, nutrient molar ratios, internal P loading, weather, and northern tributary discharge can all play a role in ecosystem response. My work provides a framework for understanding the relationships among large inflows of nitrate-rich freshwater to estuaries, internal nutrient dynamics, and factors determining cyanobacteria success (Figure 4.12). Physical disturbance of the water column associated with plume hydrodynamics and NO$_3^-$ dominance of the DIN pool likely favor nonharmful eukaryotic phytoplankton species over non-N-fixing cyanobacteria during spillway openings and immediately following spillway closure. My results suggest that the magnitude and timing of hydraulic flushing in 2011 may have been responsible for the paucity of N-fixing cyanobacteria observed.
5.1. Introduction

From a biogeochemistry perspective, heterotrophic life on Earth involves a pursuit of carbon for linkage with other major elements including nitrogen (N) and phosphorus (P) to maintain structure, energetics, and function (Reddy and DeLaune, 2008). Humans have been perhaps the most successful of Earth’s heterotrophs at exploiting and affecting global biogeochemical cycles (Smil, 2000; Bennett et al., 2001). Current food production systems largely depend on the availability of affordable fossil fuels and inorganic fertilizers containing N and P to stimulate primary production and feed a global population trending towards 9 billion (Tilman et al., 2001). One result of this global influence on nutrient cycling has been pervasive eutrophication, or the excessive production of organic matter in water bodies overenriched with N and P (Nixon, 1995).

Recent research has brought attention to the paradox of P: this widespread aquatic contaminant is also a finite mineral resource essential to future human survival for which there is no substitute (Elser, 2012). Industrial inorganic phosphate fertilizer production requires high-quality phosphate rock formed over geologic time scales (Crosby and Baily, 2012). Therefore, even though P is obviously not disappearing, the rate of its global, largely one-way dispersal from concentrated rock to diffuse concentrations in aquatic systems is troubling from a resource management perspective. Cordell et al. (2009) ignited debate on future P availability by suggesting that a peak in global phosphate rock production could occur within decades. An unplanned descent from “peak phosphorus” would have serious implications for global food security. Recently, the reliability of their Hubbert curve analysis has been challenged (Vaccari and Strigul, 2011; Scholz and Wellmer, 2013), longer timelines of resource depletion have been
suggested (Van Vuuren et al., 2010), and it has been emphasized that future P availability will be
driven by dynamic interactions between supply and demand (Scholz and Wellmer, 2013).
However, the debate over the timeline of phosphate rock depletion should not overshadow the
more immediate situation of poor resource management (McGill, 2012). Both those concerned
about P availability in coming decades and those unconvinced of a near-term P crisis promote
improving the efficiency of human P use to achieve sustainable P management and reduce
environmental degradation (Childers et al., 2011; Scholz and Wellmer, 2013).

Moving towards more sustainable P management requires an understanding of
anthropogenic P fluxes at multiple spatial and temporal scales. A number of recent studies have
used Material Flow Analysis (MFA), a technique based on the principle of mass balance (Baker,
2009), to foster greater understanding of how P travels through human-dominated landscapes. P
budgets have been constructed and analyzed for multiple scales (Cordell et al., 2012) including
farm (Öborn et al., 2005), household (Fissore et al., 2011), town/city (Neset et al., 2008; Metson
et al., 2012b), watershed (Schussler et al., 2007), regional (Senthilkumar et al., 2012a), national
(Senthilkumar et al., 2012b; Cooper and Carliell-Marquet, 2013), and global levels (Cordell et
al., 2011). Nutrient budgets often provide a static analysis considering stocks and flows averaged
over one time interval (Metson et al., 2012c). Increasingly, studies are being conducted that
examine measured or predicted changes in P dynamics over time scales including decades
(Metson et al., 2012c; Ma et al. 2013) and centuries (Neset et al., 2010). These studies better
capture the underlying biophysical, economic, and cultural mechanisms that influence
anthropogenic P cycling.

In this paper, I present the first study to my knowledge that focuses on dynamic
anthropogenic P cycling in a coastal region over a decade. The study region is a 7-parish portion
of the Upper Pontchartrain Basin in coastal Louisiana, USA. I have specifically aimed to capture the short-term influence of economic instability (i.e., the 2008 fertilizer price spike) and human population growth on P dynamics to better understand drivers of change. Fertilizer cost is a key parameter influencing demand for P. In 2008 as the financial crisis of 2007-2008 grew into the Great Recession, rapid increases in sulfur, phosphate rock, and ammonia prices drove the prices of inorganic phosphate fertilizers to historic highs (Huang, 2009). Fertilizer prices are influenced by a complex array of supply and demand factors including energy costs, raw material costs (e.g., phosphate rock), currency value, the strength of export fertilizer associations, the increasing concentration of fertilizer industries, global population, economic growth, dietary preferences, and foreign trade policies (e.g., China imposed an increased export tariff on phosphate in 2008) (Huang, 2009; Metson et al., 2012a). The 2008 spike in P fertilizer prices offers an opportunity to assess economic influences on human-mediated P fluxes.

Human population centers result in the concentration and intensification of biogeochemical cycles in urban and agricultural portions of the landscape (Fissore et al., 2011). Coastal zones less than 10 m above sea level cover 2% of Earth’s land area, but contain 10% of the total global population and 13% of the global urban population. Many of these coastal zones are at risk to future environmental hazards including mean sea level rise and tropical storms (McGranahan et al., 2007). The Mississippi Delta in coastal Louisiana provides an example of a coastal human population facing environmental hazards associated with high rates of land loss and mean sea level rise, large amounts of land less than 0.5 m above sea level, and the impacts of tropical storms like Hurricane Katrina (Thieler and Hammar-Klose, 2000; DeLaune and White, 2012; State of Louisiana, 2012; Figure 5.1). The Pontchartrain Basin lies within this landscape.
and is home to over 40% of Louisiana residents, making it an ideal setting to examine changes in anthropogenic P cycling in a dynamic coastal zone.

Figure 5.1. The study region and Pontchartrain Basin parishes in coastal Louisiana, USA. Land and water shaded darkly in the lower left inset indicates elevation less than 0.5 m in the Pontchartrain Basin (with the exception of Lake Pontchartrain). Source: National Elevation Dataset (NED), US Geological Survey.

My primary objectives in this study were to: (1) Identify trends in P fertilizer economics and investigate the correlation of fertilizer purchases in the study region with prices; (2) Identify trends in human population in the Pontchartrain basin, including the impact of Hurricane Katrina in 2005; (3) Construct budgets representing human-mediated P fluxes in the study region of the Upper Pontchartrain Basin for two time intervals (2001-2005 and 2006-2010); (4) Identify major drivers of change in P fluxes between the two periods; (5) Assess dynamics in anthropogenic P cycling between periods; and (6) Identify opportunities for moving towards more sustainable P management in coastal basins.
5.2. Materials and Methods

5.2.1. Study Region

The Upper Pontchartrain Basin encompasses portions of southeastern Louisiana and southwestern Mississippi in the US, covering a total area of 12,476 km² (Roy et al., 2013). Here, we focus on a 9320 km² region within the watershed that includes land in five hydrologic cataloging units of the Upper Pontchartrain Basin (Amite – 08070202, Tickfaw – 08070203, Lake Maurepas – 08070204, Tangipahoa – 08070205, and Liberty Bayou-Tchefuncte – 08090201) and seven Louisiana parishes (Ascension, East Baton Rouge, East Feliciana, Livingston, St. Helena, St. Tammany, and Tangipahoa) (Figure 5.1). The study region includes portions of the Baton Rouge Metropolitan Area; the region along the northern coast of Lake Pontchartrain known locally as the North Shore including the cities of Hammond, Covington, Mandeville, and Slidell; and rural upland areas extending northwards to the Mississippi border. Wetlands cover approximately 33% of the region, with 18-20%, 11-13% 17-18%, and 11-13% of land cover accounted for by forested, shrub/scrub, agricultural (pasture + cropland), and urban/developed land, respectively (Homer et al., 2007; Fry et al., 2011).

Runoff in the study region eventually enters the Lake Pontchartrain Estuary, a shallow (mean depth = 3.7 m), oligohaline estuary with a surface area of 1637 km² (Turner et al., 2002; Figure 5.1). Water column P availability in Lake Pontchartrain can influence eutrophication dynamics including harmful blooms of cyanobacteria (Roy et al., 2013). Tributaries entering and draining the study region are the primary source of external P loading to Lake Pontchartrain during most years (McCorquodale et al., 2009). Sediments in Lake Pontchartrain contain a legacy of past external P loading and provide a significant internal source of P to the water.
column (Roy et al., 2012), as is the case in other coastal systems including the Baltic Sea (Vahtera et al., 2007).

5.2.2. System Design

The conceptual design of P flows in the study region was divided into agricultural, forested/wetland, and urban/developed landscapes (Figure 5.2). Anthropogenic P cycling in the study region was assessed based on two subsystems comprising the total system: the food production subsystem and the consumption subsystem. These two subsystem compartments are linked by the local production and consumption of food. P flows included were system inputs, internal flows, flows available for recycling or use, and leakage (Figure 5.2). P inputs to the system were atmospheric deposition, food imported for human or animal consumption, imported fertilizer, and imported chemicals. P flows available for recycling or use included biosolids from wastewater treatment operations, composted yard trimmings, harvested timber, recoverable manure, and the agricultural by-products of sugarcane bagasse. Leakage reflected the discharge of P from the system to the Mississippi River or the Lake Pontchartrain Estuary either directly or via watershed tributaries. Finally, significant quantities of P could be retained within the study region and stored primarily in soils, especially in agricultural lands (Sattari et al., 2012).

Phosphoric acid production for food and technical applications occurs within the study region at a Potash Corporation facility in Geismer, LA in Ascension Parish. Total P inflow to the facility was estimated as the sum of P production (Potash Corporation, 2013) and P discharged to the Mississippi River (LDEQ, 2013a). It is assumed that phosphoric acid produced is exported from the study region. Therefore, these P flows are presented separately from the other study region flows in the results and are not included in anthropogenic P cycling efficiency
calculations. P flows to and from additional industrial facilities that discharge wastewater to the
Mississippi River were not included in this analysis.

5.2.3. Data Sources and Quantification Methods

US cost of fertilizer P for 1985-2010 is based on data for diammonium phosphate (DAP, 18-46-0) (NASS, 2011). Pre-2001 data is presented to establish historical context. US and
Louisiana crude oil prices are used to investigate the relationship between fertilizer and energy
prices (EIA, 2011).

Data sources concerning the quantity of material flow and P concentrations used to
calculate all P flows are presented in Table 5.1 along with quantification methods. All P flows
were determined using site-specific information for the study region or data available in existing
literature. Reconciling parish-level data with watershed boundaries was accomplished using
spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA). GIRAS hydrologic units defined
by the US Geological Survey were used to delineate watershed boundaries (Steeves and Nebert,
1994). US Census Bureau data (ESRI, 2013) was used to estimate the ratio of persons and
households in each parish located within the study region. Non-farm and farm fertilizer inputs,
timber harvest, and agricultural production data were corrected to represent the study region
using NLCD land use layers for 2001 (Homer et al., 2007) and 2006 (Fry et al., 2011). P flows
were assumed to be proportional to the ratio of urban, forested, pasture, or commercial crop land
use in each parish located within the study region boundaries (i.e., within the Pontchartrain basin,
Figure 5.1). The proportion of pasture located within the study region was used to adjust farm
animal production values. All aquaculture and fisheries production, which was significantly
lesser in magnitude of P harvest than agriculture and forestry, was assumed to occur within the
study region.
Figure 5.2. Five-year mean annual phosphorus flows (Mg P y⁻¹) in the study region of the Upper Pontchartrain Basin for 2001-2005 and 2006-2010 (in parentheses).
Table 5.1. Equations and data sources used to calculate P flows in the analysis.\(^a\)

<table>
<thead>
<tr>
<th>Name</th>
<th>Equations</th>
<th>Parameters, Material Quantities, Pc, &amp; Quantification Methods(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human population*</td>
<td>= Σ(Parish population estimate)</td>
<td>Population estimates (1)</td>
</tr>
<tr>
<td>Total fertilizer input*</td>
<td>= Σ(Fertilizer sales by parish destination)</td>
<td>Fertilizer sales (2)</td>
</tr>
<tr>
<td>Fertilizer to urban lands*</td>
<td>= Total pine forest area x % forests corporately owned x % industrial forests fertilized x Fertilization rate</td>
<td>Parish-level nonfarm fertilizer use estimates for 2001-2006 (3); 2007-2010 values estimated based on % nonfarm of total fertilizer sales in 2001-2006 and total fertilizer input; Estimates further adjusted for fertilizer mass balance</td>
</tr>
<tr>
<td>Fertilizer to industrial forests (01-05)*</td>
<td>= Total pine forest area x % forests corporately owned x % industrial forests fertilized x Fertilization rate</td>
<td>Only industrial pine forests fertilized (4); Total pine forest area (5); % forests corporately owned (6); % industrial forests fertilized: 3.7% (7); Fertilization rate: 2.8 g P m(^{-2}) (7)</td>
</tr>
<tr>
<td></td>
<td>= Total pine forest area x % of forest newly planted x Fertilization rate</td>
<td>Fertilization largely declined (4); Newly planted pine seedlings continued to be fertilized (8); Total pine forest area (5); % forests corporately owned (6); Newly planted: 0.62% (7); Fertilization rate: 2.8 g P m(^{-2}) (7)</td>
</tr>
<tr>
<td></td>
<td>= Unit of timber produced x Fresh wt. per unit x % dry wt. x Pc</td>
<td>Unit of timber produced (9); Fresh wt. per unit (10); % dry wt. (11-13); Pc (14)</td>
</tr>
<tr>
<td>P in harvested timber*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total fertilizer to agricultural lands*</td>
<td>= Total fertilizer input - Fertilizer to urban lands - Fertilizer to forests</td>
<td>In cases where estimated agricultural and urban fertilizer exceeded total purchased fertilizer, estimates were adjusted downward for hay/pasture and urban</td>
</tr>
<tr>
<td>Imported poultry litter for fertilizer</td>
<td></td>
<td>Area of pasture in study region receiving imported poultry litter from Mississippi as fertilizer = 20,000 acres in 2001-2006; 15,000 acres in 2007; 10,000 acres in 2008-2010 (15); Application rate = 2 tons poultry litter per acre per year (15); Pc = 10.9 kg P ton(^{-1}) (16)</td>
</tr>
</tbody>
</table>

*Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).

\(^a\)Pc refers to the concentration of P in material

\(^b\)Sources are indicated by numbers as follows: 1, US Census Bureau (2012a); 2, LDAF (2012); 3, Gronberg and Spahr (2012); 4, J. Cheston Stevens, Jr., Louisiana State University Agricultural Center, personal communication; 5, USDA Forest Service (2013); 6, Nelson et al. (2010) GIS layer; 7, Fox et al. (2007); 8, Brian R. Chandler, Louisiana State University Agricultural Center, personal communication; 9, LSU AgCenter (2013a); 10, Cunningham and Barry 2010; 11, Langholtz et al. (2007); 12, Newbold et al. (2001); 13, Galik et al. (2009); 14, Antikainen et al. (2004); 15, J. Cheston Stevens, Jr., Louisiana State University Agricultural Center, personal communication; 16, Gaskin et al. (2010)
Table 5.1 continued. Equations and data sources used to calculate P flows in the analysis.\textsuperscript{a}

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<tr>
<th>Name</th>
<th>Equations</th>
<th>Parameters, Material Quantities, Pc, &amp; Quantification Methods\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed &amp; crop production*</td>
<td>= Crop harvest quantity x Pc</td>
<td>Quantities of crops harvested (9); Pc (17)</td>
</tr>
<tr>
<td>Sugarcane bagasse*</td>
<td>= Sugarcane produced x Bagasse production per unit sugarcane x Pc</td>
<td>Bagasse = 162.5 kg per Mg sugarcane (18); Pc = 110 mg P kg(^{-1}) (19)</td>
</tr>
<tr>
<td>Animal production*</td>
<td>= Number of animals for meat x mean live wt. per animal x Pc + Milk production x Pc + Egg production x Pc</td>
<td>Number of animals, milk, and eggs (9); Cattle live wt. (9); Cow-calf pairs live wt.: 350.2 kg (20); Dairy cows, heifers, and calves live wt.: 635 kg, 272 kg, 227 kg (21); Egg wt.: 0.86 kg per dozen (22); Hens live wt.: 3.98 kg (23); Broilers live wt.: 2.27 kg (24); Hog and feeder pig live wt.: 64.9 kg and 32.5 kg (20); Cattle/dairy: 0.7% of live wt. (25); Milk: 0.091% of wt. (26); Poultry: 0.2% of live wt. (27); Eggs: 0.14% (27); Hogs: 1% of live wt. (28)</td>
</tr>
<tr>
<td>Horse wt.*</td>
<td>= Number of horses x mean live wt. per animal</td>
<td>Number of horses (9); Horse live wt. assumed to be 453.6 kg per horse</td>
</tr>
<tr>
<td>Total animal manure excretion*</td>
<td>= Number of animals x mean total P excretion rate for animal</td>
<td>P excretion rates (29-30); Unrecovered cattle &amp; horse manure diverted to pasture; All other unrecovered manure diverted to landscape; Broiler age assumed to be 7 wks; Rates for all other animals based on 1 y</td>
</tr>
<tr>
<td>Recoverable animal manure*</td>
<td>= Number of animals x mean recoverable P excretion rate</td>
<td>Recoverable P excretion rates (29)</td>
</tr>
</tbody>
</table>

\*Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).

\textsuperscript{a}Pc refers to the concentration of P in material

\textsuperscript{b}Sources are indicated by numbers as follows: 9, LSU AgCenter (2013a); 17, NRCS (2013); 18, Kim and Day (2011); 19, Jamil et al. (2004); 20, NASS (2012); 21, Schussler et al. (2007); 22, USDA (1995); 23, LSU AgCenter (2013b); 24, NASS (2002); 25, Tilden (1995); 26, USDA (1998); 27, NRC (1982); 28, Powers and Van Horn (2001); 29, Kellogg et al. (2000); 30, Tao and Manci (2008)

\textsuperscript{c}Short-term spikes (~100x increase) in cull hen production observed in St. Helena Parish in 2006-2007 are uncommon and likely resulted from stock replacement and updated animal welfare guidelines requiring producers to reduce stocking density (Teresia Lavergne, Louisiana State University Agricultural Center, personal communication). These cull hen production spikes were omitted from the analysis. 2006 and 2007 St. Helena parish cull hens were estimated using interpolation with 2005 and 2008 data.
Table 5.1 continued. Equations and data sources used to calculate P flows in the analysis.a

<table>
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<tr>
<th>Name</th>
<th>Equations</th>
<th>Parameters, Material Quantities, Pc, &amp; Quantification Methodsb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Animal feed required*</td>
<td>$\text{P in animal manure} + \text{P in animal products}$</td>
<td>Eqn. (21); Assumptions: Cattle and horse feed assumed to be obtained from pasture, poultry and hogs fed with feed grains. Dairy: 32% of P from pasture, 68% of P from feed grains (17, 31-32)</td>
</tr>
<tr>
<td>Imported animal feed grains</td>
<td>$\text{Animal feed grains required - Feed production}$</td>
<td>Production quantities (9); Crawfish meat wt. = 15% of fresh wt. (33); Other fish dry wt. = 20% of fresh wt. (34); Alligator wt. per unit length: 25 kg per 1.83 m (35); Alligator meat wt. = 39.5% of fresh wt. (35), Alligator dry wt. = 20% of fresh wt. (36); Crawfish: 0.239% of meat fresh wt. (37); Catfish: 0.231% of fresh wt. (37); Other fish: 0.62% of dry wt. (34); Alligator meat assumed to have P content of poultry meat: 0.82% of dry wt. (27)</td>
</tr>
<tr>
<td>Aquaculture production</td>
<td>$\text{Fresh wt. meat produced} \times % \text{dry wt. (if needed)} \times \text{Pc}$</td>
<td>Assume 50% of feed P is converted to harvested biomass. Estimate is likely conservative. E.g., 37.1% for catfish (38)</td>
</tr>
<tr>
<td>Aquaculture feed</td>
<td>$\text{Aquaculture production P} \times % \text{of feed P converted}$</td>
<td>Harvest (9); Crawfish, alligator, &amp; fish - see aquaculture; Shrimp meat wt. assumed to be 50% of catch fresh wt.; Crab meat wt. assumed to be 14% of catch fresh wt.; Shrimp Pc: 0.239% of meat fresh wt. (37); Crab Pc: 0.152% of meat fresh wt. (37)</td>
</tr>
<tr>
<td>Fisheries</td>
<td>$\text{Harvest quantity} \times \text{Pc}$</td>
<td>Assume all locally produced food is consumed locally.</td>
</tr>
<tr>
<td>Local food production</td>
<td>$\text{Crop production} + \text{Animal production} + \text{Aquaculture production} + \text{Fisheries}$</td>
<td>Assume all P consumed by humans is excreted (39); P requirement = P excretion = 2.825 g P capita$^{-1}$ d$^{-1}$ (40)</td>
</tr>
<tr>
<td>Human food P requirements</td>
<td>$\text{Human population} \times \text{Per capita P requirement}$</td>
<td>% of food wasted during retail, foodservice, consumption stages = 27% (41)</td>
</tr>
<tr>
<td>Wasted food</td>
<td>$% \text{wasted} \times \text{Total human food}$</td>
<td></td>
</tr>
</tbody>
</table>

*Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).

Pc refers to the concentration of P in material

Sources are indicated by numbers as follows: 9, LSU AgCenter (2013a); 21, Schussler et al. (2007); 27, NRC (1982); 31, Leonardi et al. (2011); 32, McCormick et al. (2001); 33, Romaire et al. (2005); 34, Boynton et al. (1995); 35, Masser (1993); 36, Leak et al. (2003); 37, Sidwell et al. (1977); 38, Brown et al. (2012); 39, Baker (2011); 40, Crites and Tchobanoglous (1998); 41, Kantor et al. (1997)
Table 5.1 continued. Equations and data sources used to calculate P flows in the analysis.\(^a\)

<table>
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<tr>
<th>Name</th>
<th>Equations</th>
<th>Parameters, Material Quantities, Pc, &amp; Quantification Methods(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total human food</td>
<td>= Human food P requirements + Wasted human food</td>
<td># of permits in study region = 14 (42); Population served by major WWTPs = 470,084 in 2001-2005 and 500,070 in 2006-2010 (42)</td>
</tr>
<tr>
<td>Imported human food</td>
<td>= Total human food - Local food production</td>
<td># of permits per flow class: $&lt; 100,000 \text{ gal d}^{-1} = 338$, $&lt; 50,000 \text{ gal d}^{-1} = 42$, $&lt; 25,000 \text{ gal d}^{-1} = 482$, $&lt; 5,000 \text{ gal d}^{-1} = 1347$ (42); Assume flow per system = upper limit of flow class; Flow class total flow = # of permits per flow class x flow per system; Eqn. used to estimate serviced populations for each flow class derived from major WWTP data: WWTP inflow = 0.0001564 x Serviced Population ($r^2 = 0.978, n = 17$); Population served by minor WWTS in study region = 314,791</td>
</tr>
<tr>
<td>Human P to major WWTPs*</td>
<td>= Population served by major WWTPs x Per capita P requirement</td>
<td># of permits per flow class: $&lt; 100,000 \text{ gal d}^{-1} = 338$, $&lt; 50,000 \text{ gal d}^{-1} = 42$, $&lt; 25,000 \text{ gal d}^{-1} = 482$, $&lt; 5,000 \text{ gal d}^{-1} = 1347$ (42); Assume flow per system = upper limit of flow class; Flow class total flow = # of permits per flow class x flow per system; Eqn. used to estimate serviced populations for each flow class derived from major WWTP data: WWTP inflow = 0.0001564 x Serviced Population ($r^2 = 0.978, n = 17$); Population served by minor WWTS in study region = 314,791</td>
</tr>
<tr>
<td>Human P to minor WWTS in 2006-2010 (permitted)*</td>
<td>= Population served by minor WWTS x Ratio of persons within parishes located in study region x Per capita P requirement</td>
<td># of permits per flow class: $&lt; 100,000 \text{ gal d}^{-1} = 338$, $&lt; 50,000 \text{ gal d}^{-1} = 42$, $&lt; 25,000 \text{ gal d}^{-1} = 482$, $&lt; 5,000 \text{ gal d}^{-1} = 1347$ (42); Assume flow per system = upper limit of flow class; Flow class total flow = # of permits per flow class x flow per system; Eqn. used to estimate serviced populations for each flow class derived from major WWTP data: WWTP inflow = 0.0001564 x Serviced Population ($r^2 = 0.978, n = 17$); Population served by minor WWTS in study region = 314,791</td>
</tr>
<tr>
<td>Human P to minor WWTS in 2006-2010 (unaccounted for/septic)*</td>
<td>= Study area population not accounted for by major WWTPs or minor WWTS x Per capita P requirement</td>
<td># of permits per flow class: $&lt; 100,000 \text{ gal d}^{-1} = 338$, $&lt; 50,000 \text{ gal d}^{-1} = 42$, $&lt; 25,000 \text{ gal d}^{-1} = 482$, $&lt; 5,000 \text{ gal d}^{-1} = 1347$ (42); Assume flow per system = upper limit of flow class; Flow class total flow = # of permits per flow class x flow per system; Eqn. used to estimate serviced populations for each flow class derived from major WWTP data: WWTP inflow = 0.0001564 x Serviced Population ($r^2 = 0.978, n = 17$); Population served by minor WWTS in study region = 314,791</td>
</tr>
<tr>
<td>Human P to minor WWTS in 2001-2005 (unaccounted for/septic)</td>
<td>= Human P to unaccounted for/septic in 2006-2010</td>
<td>Assume unaccounted for/septic population the same for 2001-2005 and 2006-2010 (121,225 persons), New residents served by major WWTPs or permitted minor WWTS</td>
</tr>
<tr>
<td>Human P to minor WWTS in 2001-2005 (permitted)</td>
<td>= Population served by minor WWTS in study region x Per capita P requirement</td>
<td>Population in 2001-2005 estimated as: Total study region population - Population served by major WWTPs - Unaccounted for/septic population = 249,817 persons</td>
</tr>
</tbody>
</table>

*Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).

\(^a\)Pc refers to the concentration of P in material

\(^b\)Sources are indicated by numbers as follows: 42, LDEQ (2013a)

98
Table 5.1 continued. Equations and data sources used to calculate P flows in the analysis.<sup>a</sup>

<table>
<thead>
<tr>
<th>Name</th>
<th>Equations</th>
<th>Parameters, Material Quantities, Pc, &amp; Quantification Methods&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total imported chemicals</td>
<td>= Human population x Per capita chemical use</td>
<td>Denitrifices: 0.012 kg P capita&lt;sup&gt;-1&lt;/sup&gt; y&lt;sup&gt;-1&lt;/sup&gt;, Dishwasher detergents: 0.125 kg P capita&lt;sup&gt;-1&lt;/sup&gt; y&lt;sup&gt;-1&lt;/sup&gt; (39); Diverted to major WWTPs and minor WWTS based on serviced populations</td>
</tr>
<tr>
<td></td>
<td>= (Human population served by major WWTPs + Human population served by permitted minor WWTS) x Per capita ground up food waste x % of population w/ garbage disposal</td>
<td>Per capita ground up food waste = 0.3 g P capita&lt;sup&gt;-1&lt;/sup&gt; d&lt;sup&gt;-1&lt;/sup&gt; (40); Assume 25% of wasted food diverted to garbage disposal for those served by major WWTPs and permitted minor WWTS; All food waste from unaccounted for/septic population diverted to landfill</td>
</tr>
<tr>
<td>Wasted food to major WWTPs and permitted minor WWTS</td>
<td>= Total effluent flow of permitted minor WWTS in study region x Pc</td>
<td>Effluent flows provided in permits (42); Effluent location determines whether discharged P enters Mississippi River or Lake Pontchartrain watershed; Pc in effluents reported in permits = 2.5-9.2 mg TP L&lt;sup&gt;-1&lt;/sup&gt;; Mean value of 4.13 mg TP L&lt;sup&gt;-1&lt;/sup&gt; assumed for 3 WWTPs not reporting Pc; Mean estimated P removal = 32%</td>
</tr>
<tr>
<td>Major WWTPs effluent</td>
<td>= Σ(WWTP effluent flow x Pc)</td>
<td>Pc in effluents assumed to by 5 mg TP L&lt;sup&gt;-1&lt;/sup&gt; (43); Mean estimated P removal = 9.6%</td>
</tr>
<tr>
<td>Permitted minor WWTS effluent</td>
<td>= Total effluent flow of permitted minor WWTS in study region x Pc</td>
<td></td>
</tr>
<tr>
<td>Unaccounted for/septic effluent</td>
<td>= P in unaccounted for septic influent</td>
<td>Assume no treatment of P</td>
</tr>
<tr>
<td>Removed P in major WWTPs &amp; permitted minor WWTS</td>
<td>= P in wastewater influent - P in wastewater effluent</td>
<td></td>
</tr>
</tbody>
</table>

*Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).

<sup>a</sup>Pc refers to the concentration of P in material

<sup>b</sup>Sources are indicated by numbers as follows: 39, Baker (2011); 40, Crites and Tchobanoglous (1998); 42, LDEQ (2013a); 43, Kadlec and Knight (1996)
Table 5.1 continued. Equations and data sources used to calculate P flows in the analysis.a

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<tr>
<th>Name</th>
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<th>Parameters, Material Quantities, Pc, &amp; Quantification Methodsb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harvested biosolids</td>
<td>( = ) Dry wt. of biosolids removed ( \times ) Pc ( \times ) Removal frequency factor ( \times ) % land applied</td>
<td>Wt. of biosolids removed data available for 2006-2010 from permits for 6 major WWTPs (42); 2 major WWTPs produce no biosolids, Biosolids for remaining estimated using eqn. derived from data: Biosolids production = ((89.533 \times ) WWTP influent in MGD) + 502.16 ((r^2 = 0.855)); 2001-2005 biosolids estimated based on serviced populations and influent compared to 2006-2010; Biosolids destination available in permits (42) used to estimate % land applied; Removal frequency factor assumed to be 0.5 because biosolids are typically not removed annually; Pc = 2.8% of dry wt. (44)</td>
</tr>
<tr>
<td>Removed P to landfill</td>
<td>( = ) Dry wt. of biosolids removed ( \times ) Pc ( \times ) Removal frequency factor ( \times ) % landfilled</td>
<td>Biosolids destination available in permits (42) used to estimate % landfilled, Removal frequency factor assumed to be 0.5 because biosolids are not removed annually from most systems; Pc = 2.8% of dry wt. (44)</td>
</tr>
<tr>
<td>WWT storage</td>
<td>( = ) Removed P – Harvested biosolids – Removed P to landfill</td>
<td></td>
</tr>
<tr>
<td>Dog population*</td>
<td>( = ) % LA households with dogs ( \times ) Study region households ( \times ) Mean dogs per household</td>
<td>% LA households with dogs = 43.4% in 2001 and 39.6% in 2006 (45); Mean dogs per household = Louisiana dog population / Louisiana households; Louisiana dog population (45); Households (46)</td>
</tr>
<tr>
<td>Total wt. of dog food per day</td>
<td>( = ) Mean dog wturence of dogs ( \times ) (Mean dog wt ( \times ) Caloric content of dog food) ( \times ) Dog population</td>
<td>Metabolic requirement of dogs = 110 kcal kg(^{-1}) d(^{-1}) (47); Mean dog wt. = 20 kg (48), Caloric content of dog food = 3.33 kcal g(^{-1}) (47)</td>
</tr>
<tr>
<td>Dog food P</td>
<td>( = ) % P in dog food ( \times ) Total wt. of dog food</td>
<td>Pc dog food = 0.8% (47)</td>
</tr>
</tbody>
</table>

*Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).
aPc refers to the concentration of P in material
bSources are indicated by numbers as follows: 40, Crites and Tchobanoglous (1998); 42, LDEQ (2013a); 43, Kadlec and Knight (1996); 44, Linderholm et al. (2012); 45, AVMA (2007); 46, US Census Bureau (2002) and US Census Bureau (2012b); 47, Fissore et al. (2011)
Table 5.1 continued. Equations and data sources used to calculate P flows in the analysis.\(^a\)

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</thead>
<tbody>
<tr>
<td>Dog P to landfill</td>
<td>(\text{Dog food P} \times % \text{dog P in feces} \times % \text{dog feces picked up})</td>
<td>(% \text{dog P expelled as feces} = 73.5%) 49; (% \text{dog feces picked up by owners} = 60%) 50</td>
</tr>
<tr>
<td>Dog P to urban landscape</td>
<td>(\text{Dog P excretion} - \text{Dog P to landfill})</td>
<td>(% \text{LA households with cats} = 26.1%) 2001 and 23.3% 2006 45; Mean cats per household = Louisiana cat population / Louisiana households; Louisiana cat population 45; Households 46</td>
</tr>
<tr>
<td>Cat population*</td>
<td>(\text{Study region households} \times \text{Mean cats per household})</td>
<td>(% \text{LA households with cats} = 26.1%) 2001 and 23.3% 2006 45; Mean cats per household = Louisiana cat population / Louisiana households; Louisiana cat population 45; Households 46</td>
</tr>
<tr>
<td>Total wt. of cat food per day</td>
<td>(\text{Eqn. (47)}; \text{Mean cat wt.} = 3.8 \text{ kg}) 48</td>
<td></td>
</tr>
<tr>
<td>Cat food P</td>
<td>(% \text{P in cat food} \times \text{Total wt. of cat food})</td>
<td>(\text{Pc cat food} = 0.8%) 47</td>
</tr>
<tr>
<td>Cat P excretion</td>
<td>(\text{Cat food P})</td>
<td>Equation (47); Assume all cat P diverted to landfill 47</td>
</tr>
<tr>
<td>Yard trimmings</td>
<td>(\text{Wt. of solid waste generated per capita} \times \text{Study region population} \times % \text{of solid waste that is yard trimmings and wood}) (\times \text{Pc})</td>
<td>Wt. of solid waste = 1 Mg capita(^{-1}) y(^{-1}) 51; % of solid waste that is yard trimmings and wood = 18.4% 52; Assume yard waste = 50% wood and 50% grass; Wood % moisture = 50% 47; Yard trimmings from EBR Parish are collected and transported to Natural Resources Recovery, LLC for composting 53; Similar procedures could not be confirmed for the other 6 parishes, therefore assume diversion to landfills; Pc by dry mass wood = 0.01335% 14; Pc grass = 0.2% 17</td>
</tr>
<tr>
<td>Atmospheric deposition*</td>
<td>(\text{Annual atm deposition rate} \times \text{Study region area} \times \text{Proportion of study region made up by respective landscape})</td>
<td>Atm deposition rate: 73 kg P km(^{-2}) y(^{-1}) 54</td>
</tr>
<tr>
<td>Leakage to Mississippi River</td>
<td>(\text{P discharged from major WWTPs to Mississippi River})</td>
<td>Effluent destination determined from permits 42</td>
</tr>
</tbody>
</table>

\(^a\)Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).

\(^b\)Pc refers to the concentration of P in material

Sources are indicated by numbers as follows: 14, Antikainen et al. (2004); 17, NRCS (2013); 42, LDEQ (2013a); 45, AVMA (2007); 46, US Census Bureau (2002) and US Census Bureau (2012b); 47, Fissore et al. (2011); 48, Baker et al. (2001); 49, Wood et al. (2004); 50, Swann (1999); 51, St. Tammany Parish Government (2008); 52, USEPA (2007); 53, Krystal Perkins, East Baton Rouge Parish Department of Public Works, personal communication; 54, Wang (2003)
Table 5.1 continued. Equations and data sources used to calculate P flows in the analysis.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Name</th>
<th>Equations</th>
<th>Parameters, Material Quantities, Pc, &amp; Quantification Methods\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leakage to Lakes Pontchartrain &amp; Maurepas</td>
<td>( = \text{Study region area} \times \text{Areal P loading rate} )</td>
<td>Methodology &amp; assumption of Pc independent of discharge (55); Areal P loading rate for each time period determined using discharge data for 8 sites in watershed (56) &amp; nearest available water quality data (57); Loading rate = 0.1715 kg TP d(^{-1}) km(^{-2}) in ‘01-’05 ((r^2 = 0.96)) &amp; 0.1248 kg TP d(^{-1}) km(^{-2}) in ‘06-’10 ((r^2 = 0.99))</td>
</tr>
</tbody>
</table>

\*Flows adjusted from parish scale to study region using spatial data sets in ArcMap 10.1 (ESRI, Redlands, CA, USA).  
\textsuperscript{a}Pc refers to the concentration of P in material  
\textsuperscript{b}Sources are indicated by numbers as follows: 55, McCorquodale et al. (2009); 56, USGS (2013); 57, LDEQ (2013b)
Material flow analysis (MFA), also referred to as substance flow analysis, was used to quantify all P flows. This quantitative technique for tracking the movement of elements or pollutants through ecosystems and societies is based on the principle of mass balance (Baker, 2009). Average P flows were quantified for two 5-y time periods (2001-2005, 2006-2010) to identify short-term changes in anthropogenic P cycling influenced by P fertilizer economics and human population change. Seventeen external (input and leakage) and thirty-five internal P flows were identified and quantified (Figure 5.2). A detailed description of each flow is provided in Table 5.1. Annual P balances were calculated for the agricultural, urban/developed, and forested/wetland landscapes. Mass balance equations were employed for each compartment and landscape in the MFA:

Equation 5.1:  \[ P_{\text{balance}} = 0 = \left( \sum_{i=1}^{I} \text{INFLOW} - \sum_{i=1}^{O} \text{OUTFLOW} \right) \]

where \( P_{\text{balance}} \) = P balance for the compartment or landscape (Mg P \( y^{-1} \)), \( \text{INFLOW} \) = P inflows (Mg P \( y^{-1} \)), \( \text{OUTFLOW} \) = P outflows (Mg P \( y^{-1} \)), \( I \) = number of inflows, and \( O \) = number of outflows. Residual P accumulation was possible in all three landscapes, as well as in wastewater removed P and landfill compartments.

Residual P in each landscape was factored into the overall change in storage in the study region’s watershed landscape. Specific sources of leakage to Lakes Pontchartrain and Maurepas (e.g., urban versus agricultural sources) were not entirely differentiated, although estimated flows discharged from major wastewater systems do directly enter surface waters. The annual P balance for the study region was calculated as:
Equation 5.2. \( PB_{\text{region}} = 0 = \left[ \sum_{i=1}^{I} INPUT + ATMOSPHERE \right] \)

\[ - \left[ \sum_{i=1}^{RU} PRODUCTS + \sum_{i=1}^{L} LEAKAGE \right] + \Delta STORAGE + \Delta WWT \& LANDFILL \]

where \( PB_{\text{region}} = \) study region P balance (Mg P y\(^{-1}\)), \( INPUT = \) deliberate P inputs to study region (Mg P y\(^{-1}\)), \( ATMOSPHERE = \) atmospheric deposition of P (Mg P y\(^{-1}\)), \( PRODUCTS = \) P flows available for recycling or use (Mg P y\(^{-1}\)), \( LEAKAGE = \) P losses to water bodies (Mg P y\(^{-1}\)), \( \Delta STORAGE = \) overall change in storage in the study region’s watershed landscape excluding wastewater removed P and landfills (“watershed retention,” Mg P y\(^{-1}\)), \( \Delta WWT \& LANDFILL = \) change in storage in wastewater treatment systems and landfills, \( I = \) number of inputs, \( RU = \) number of recycling and use flows, and \( L = \) number of leakage flows.

Human-mediated P flows were assessed for the food production and consumption subsystems, along with the overall system encompassing both subsystems. In all three cases, total P input (Mg P y\(^{-1}\)) was equal to the sum of P products (recycling and use), P leakage, P watershed retention, and P retention in landfills and wastewater systems.

The efficiency of the food production subsystem was calculated as:

Equation 5.3: \( \frac{\text{Food}_{\text{local}}}{\sum_{i=1}^{I} (INPUT + ATMOSPHERE)} \)

where \( \text{Food}_{\text{local}} = \) food produced in local agriculture (Mg y\(^{-1}\)), \( INPUT = \) deliberate P inputs to agricultural landscape (Mg P y\(^{-1}\)), \( ATMOSPHERE = \) atmospheric deposition of P in agricultural landscape (Mg P y\(^{-1}\)), and \( I = \) number of inputs.

The overall anthropogenic P cycling efficiency of the system was calculated based on human-mediated P flows as:
Equation 5.4:  \[ \text{Anthropogenic } P \text{ cycling efficiency} = \frac{\sum_{i=1}^{R} (PRODUCTS) + Food\_local}{\sum_{i=1}^{I} INPUT} \]

where \(PRODUCTS = P\) flows available for recycling or use (Mg P \(y^{-1}\)), \(Food\_local = food\) produced in local agriculture (Mg \(y^{-1}\)), \(INPUT = deliberate P inputs\) to study region (Mg P \(y^{-1}\)), \(I = number of inputs\), and \(RU = number of recycling and use flows\). Critically, this calculation does not take into consideration the total \(P\) embodied in \(P\) units entering the study system. Embodied \(P\) is the total number of \(P\) units that were needed during the creation of one unit of \(P\) in a product. For example, MacDonald et al. (2012) show that only 8% of total \(P\) input (fertilizer and feed supplements) entering the US agricultural system in 2007 was eventually consumed by humans in food. Further, the \(P\) embodied in imported human food depends on food type (e.g., meat contains a greater amount of embodied \(P\) than vegetables) (Metson et al., 2012c). These issues were not directly considered here and analysis is limited to the study region’s system boundaries.

5.3. Results

5.3.1. Phosphorus Inorganic Fertilizer Economics

The trend in the nominal price of diammonium phosphate (DAP) fertilizer indicates that the cost of \(P\) fertilizer in the US fluctuated between US$215 per Mg P and US$324 per Mg P during 1985-2002. Following 2002, DAP prices began to increase gradually at first and then rapidly between 2006 and 2008 to 3.5 times the 1985-2002 mean (Figure 5.3a). Louisiana crude oil nominal prices similarly experienced a rapid increase in the 2000s peaking in 2008 (Figure 5.3b). Total purchased \(P\) fertilizer in the seven Louisiana parishes having land within the study region ranged between 385 Mg P \(y^{-1}\) (2009) and 4080 Mg P \(y^{-1}\) (2002) (Figure 5.3a). Annual fertilizer sales to the seven parishes were strongly correlated to the price of DAP fertilizer.
Figure 5.4a, $r^2 = 0.87$) and Louisiana crude oil (Figure 5.4c, $r^2 = 0.73$). A negative linear correlation between DAP fertilizer price and purchased P fertilizer was observed for DAP prices between US$250 and US$350 per Mg (slope = -29.0 Mg P fertilizer purchased per US$ increase in DAP price, $r^2 = 0.83, n = 6$).

A substantially more gradual decline in purchased P fertilizer occurred at DAP prices greater than US$350 per Mg (slope = -1.11 Mg P fertilizer purchased per US$ increase in DAP price, $r^2 = 0.56, n = 5$). DAP fertilizer prices and US crude oil prices were positively correlated during 2000-2010 ($r^2 = 0.72$, Figure 5.4b). Mean purchased P fertilizer ± 1 standard deviation in the seven parishes was 2770 ± 1093 Mg P y$^{-1}$ during 2001-2005. A drastic decrease in purchased
fertilizer to $644 \pm 322 \text{ Mg P y}^{-1}$ was observed for 2006-2010. This data was adjusted to spatially represent the study region.

Figure 5.4. Correlations between (a) total phosphorus fertilizer sold in the seven study region Louisiana parishes of the Upper Pontchartrain Basin during 2000-2010 (LDAF, 2010) and mean annual U.S. diammonium phosphate fertilizer nominal price (NASS, 2011), (b) April US crude oil first purchase nominal price (EIA, 2011) and mean annual US diammonium fertilizer nominal price during 2000-2010, and (c) total phosphorus fertilizer sold in the 7 parishes of the Upper Pontchartrain Basin during 2000-2010 and April Louisiana crude oil first purchase price (EIA, 2011).
Overall, 2512 and 541 Mg P y$^{-1}$ were imported into the study region as inorganic fertilizer on average in 2001-2005 and 2006-2010, respectively, indicating a 78% decrease in input between periods.

5.3.2. Human Population Change

Human population in the seven Louisiana parishes of the Upper Pontchartrain Basin having land within the study region (Ascension, East Baton Rouge, East Feliciana, Livingston, St. Helena, St. Tammany, Tangipahoa) increased by 149,483 persons (16.3%) between 2001 and 2010. Nearly one third (31%) of the total population growth occurring during this period took place between 2005 and 2006 following Hurricane Katrina and the significant decline in population in the Lower Pontchartrain Basin including the city of New Orleans that resulted (Figure 5.5), indicating a translocation of people to the upper basin (Myers et al., 2008; Hori et al., 2009).

Figure 5.5. Total human populations living within the seven Upper Pontchartrain Basin Louisiana parishes with land inside the study region (Ascension, East Baton Rouge, East Feliciana, Livingston, St. Helena, St. Tammany, Tangipahoa) and four Lower Pontchartrain Basin Louisiana parishes (Orleans, Jefferson, St. Bernard, Plaquemines). Discontinuities in 2005 correspond to Hurricane Katrina. Source: Solid lines, US Census (2002, 2012a); Dashed lines are projections made in 2009 by the State of Louisiana (2009).
Approximately 89 and 90% of the population living in the seven upper Pontchartrain Basin parishes lived within the Pontchartrain watershed in 2000 and 2010, respectively. The spatially corrected, 5-y mean population estimates for the study region used in the MFAs were 841,126 and 936,086 persons for 2001-2005 and 2006-2010, respectively (Table 5.2).

Table 5.2. Anthropogenic P cycling metrics in the study region of the Upper Lake Pontchartrain Basin during 2001-2005 and 2006-2010.

<table>
<thead>
<tr>
<th></th>
<th>2001-2005</th>
<th>2006-2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food production subsystem total input (Mg P y(^{-1}))</td>
<td>3436</td>
<td>1240</td>
</tr>
<tr>
<td>Total local food production (Mg P y(^{-1}))</td>
<td>335</td>
<td>268</td>
</tr>
<tr>
<td>Food production efficiency (%)</td>
<td>9.7</td>
<td>21.6</td>
</tr>
<tr>
<td>Study region human population</td>
<td>841,126</td>
<td>936,086</td>
</tr>
<tr>
<td>Human food P available from local production (%)</td>
<td>28.2</td>
<td>20.2</td>
</tr>
<tr>
<td>Consumption subsystem total input (Mg P y(^{-1}))</td>
<td>1790</td>
<td>1806</td>
</tr>
<tr>
<td>Total study region input (Mg P y(^{-1}))</td>
<td>5453</td>
<td>3263</td>
</tr>
<tr>
<td>Anthropogenic P cycling efficiency (%)</td>
<td>21.5</td>
<td>31.9</td>
</tr>
</tbody>
</table>

5.3.3. Phosphorus Flows and Balances

Five-year mean P flows for the study region for the periods of 2001-2005 and 2006-2010 are presented in Figure 5.2.

Overall, the food production subsystem received total P inputs of 3436 and 1240 Mg P y\(^{-1}\) in 2001-2005 and 2006-2010, respectively (Table 5.2). The largest inputs to food production were imported fertilizer, imported poultry litter, and feed (Figure 5.2). Atmospheric deposition accounted for 3.5% and 9.3% of total P input in 2001-2005 and 2006-2010, respectively. Trends in agricultural production, feed, and manure in the seven parishes having land within the study region influencing subsystem P cycling are presented in Figure 5.6. Particularly noteworthy is the linear decline in milk production between 2001 and 2010 (Figure 5.6a), which contributed to decreased feed requirements (Figure 5.6d) and manure production (Figure 5.6e). Hay and sugarcane accounted for the majority of P harvested in crops (Figure 5.6f). Total food production equaled 335 Mg P y\(^{-1}\) in 2001-2005 and 268 Mg P y\(^{-1}\) in 2006-2010. The large decrease in P
inputs and continued food production during 2006-2010 resulted in a nearly 2-fold increase in food production P efficiency (Table 5.2).

However, the amount of human food P required in the consumption subsystem available through local production decreased from 28.2% to 20.2% between periods due to human population growth and a reduced magnitude of locally available food P, necessitating increased imports from outside of the system (Figure 5.2, Table 5.2). A total of 444 Mg P y\(^{-1}\) was available for

Figure 5.6. Temporal trends in animal and crop production, animal feed, and manure on a phosphorus (P) basis for the seven Louisiana parishes having land within the study region.
recycling in the form of manure and sugarcane bagasse from the food production system in 2001-2005, accounting for 12.9% of subsystem input. P available for recycling increased to 25.5% of subsystem input in 2006-2010 (Figure 5.7a). In 2001-2005, the fate of the majority of P input (77.4%, 2659 Mg P y\(^{-1}\)) was leakage and watershed retention, indicating substantial residual P on the agricultural landscape and potential for water quality implications. P leakage and watershed retention from the agricultural landscape decreased in 2006-2010 to 52.9% of input, or 656 Mg P y\(^{-1}\) (Figure 5.7a).

The 11.3% increase in the study region human population between time periods resulted in a 0.9% increase in total P input in the consumption subsystem from 1790 Mg P y\(^{-1}\) in 2001-2005 to 1806 Mg P y\(^{-1}\) in 2006-2010 (Table 5.2). The largest inputs to the consumption subsystem were imported human food, locally produced human food, and imported pet food (Figure 5.2). Atmospheric deposition accounted for approximately 5% of total P input during both periods. The predominant fate of P in the subsystem during both periods was leakage and watershed retention (54-58%) with a substantial amount also stored in landfills (606-663 Mg P y\(^{-1}\)) and wastewater treatment systems (45-52 Mg P y\(^{-1}\)) (Figure 5.7b). Land-applied biosolids and composted yard trimmings accounted for 108-112 Mg P y\(^{-1}\) available for recycling (6% of total input) (Figure 5.7b).

Atmospheric deposition (472 Mg P y\(^{-1}\)) dominated P inputs to the forested/wetland landscape in the study region during both periods. Estimated fertilizer P input to forests decreased from 89 Mg P y\(^{-1}\) in 2001-2005 to 15 Mg P y\(^{-1}\) in 2006-2010 while harvested timber output equaled 140 and 132 Mg P y\(^{-1}\) in each period, respectively. The forested/wetland landscape contributed of 355-421 Mg P y\(^{-1}\) to watershed retention and leakage.
Approximately 315-321 and 75-93 Mg P y\(^{-1}\) were loaded from major wastewater treatment systems to the Mississippi River and the hydroscape (surface waters + wetlands) of the Upper Lake Pontchartrain Basin, respectively (Figure 5.2). Additional potential sources of tributary P discharge in the study region are locally permitted minor wastewater systems, leakage from septic systems, and runoff from urban, agricultural and forested landscapes. Areal P loading rates in the study region to Lakes Pontchartrain and Maurepas were calculated to be 0.1715 kg P d\(^{-1}\) km\(^{-2}\) in 2001-2005 and 0.1248 kg P d\(^{-1}\) km\(^{-2}\) in 2006-2010 based on available in-stream measurements of discharge and P concentration for 8 sites (USGS, 2013; LDEQ, 2013b). The previously reported long-term average areal P loading rate for the Upper Pontchartrain Basin is 0.15 kg P d\(^{-1}\) km\(^{-2}\) (McCorquodale et al., 2009). Deviations from this mean rate are a result of both variation in discharge (i.e., 2006-2010 was drier than 2001-2005) and variation in measured P concentration (i.e., mean P concentrations in some tributaries were lower in 2006-2010). Annual mean P loads to Lakes Pontchartrain and Maurepas from the study region via tributaries were estimated to be 583 and 425 Mg P y\(^{-1}\) for 2001-2005 and 2006-2010, respectively.

5.3.4. Overall Anthropogenic Phosphorus Cycling

Overall, the study region received a total P input of 5453 Mg P y\(^{-1}\) in 2001-2005 and 3263 Mg P y\(^{-1}\) in 2006-2010, indicating a 40% decline. Anthropogenic P cycling efficiency based on human-mediated P flows increased between the two time periods from 21.5% in 2001-2005 to 31.9% in 2006-2010 (Table 5.2). Leakage accounted for 17-23% of total P input, substantial P was stored in landfills and wastewater treatment systems, and the predominant fate of overall P inputs during both study periods was retention within the watershed landscape (Figure 5.7c).
Figure 5.7. Phosphorus (P) input (Mg P y⁻¹) for the (a) food production subsystem, (b) consumption subsystem, and (c) overall system in the study region of the Upper Lake Pontchartrain Basin during 2001-2005 and 2006-2010. Fates of P input are shown for each system and time period. Sums of each bar represent total P input. Approximate atmospheric deposition is shown by dotted lines.
P products available for recycling and use equaled 692 and 560 Mg P y\(^{-1}\) in 2001-2005 and 2006-2010, respectively (14-18\% of total input), indicating that increases in anthropogenic P cycling efficiency were driven by decreases in external system inputs and not internal recycling (Figure 5.7c).

5.3.5. Industrial Phosphorus Flows

The Potash Corporation facility in Geismer, LA produces 63,265 Mg P y\(^{-1}\) of phosphoric acid for food and technical applications that is assumed to be exported from the study region and is therefore not included in Figure 5.2. Total P inflow to the facility was estimated to be 65,872 Mg P y\(^{-1}\) based on documented discharge of 2,607 Mg P y\(^{-1}\) to the Mississippi River, indicating a P efficiency of 96\%. Other industrial P flows for facilities located along the Mississippi River were not included in this analysis.

5.4. Discussion

5.4.1. Uncertainty and Limitations

Uncertainty is a concern for MFA studies that use a wide range of data sources, especially at the spatial scale analyzed in this study. My P mass balances, as in previous studies, are based on a combination of literature data, site-specific data, and local knowledge. I have made an effort to be explicit about all data sources, assumptions, and calculations in Table 1 with the goal of allowing replication. Uncertainty in the mass balances limiting my analysis emanates from a lack of documentation about food composting by individuals, potential for food waste to be greater than estimated (Senthilkumar et al., 2012b), limited measurements of P concentration in study region tributaries (McCorquodale et al., 2009), a large number (2209) of minor wastewater treatment systems in the study parishes without P information included in permits, additional industrial facilities located on the Mississippi River, and reconciling parish level data.
to the spatial boundaries of the study region. My model does not estimate the total residual P pool in soils, only the annual change in storage. Nor does it include construction materials (Metson et al. 2012b). Furthermore, it is uncertain how much of my estimates for the “available for recycling” pools are actually recycled. Despite these limitations, I believe this analysis presents a relatively comprehensive view of major human-mediated P fluxes in the Upper Pontchartrain Basin and that my results can be used to better understand drivers of change in anthropogenic P cycling in coastal regions and the implications for water quality.

5.4.2. Drivers of Change and Water Quality Implications

My results for the Upper Lake Pontchartrain Basin provide evidence that fertilizer economics can have a profound impact on P fertilizer consumption and anthropogenic P cycling at a regional/basin spatial scale in the coastal zone (Figures 5.4, 5.5a, and 5.7). Historically, P has been a low-cost commodity. Scholz and Wellmer (2013) estimate that each person consumes approximately US $6 worth of phosphate rock annually. Phosphate fertilizers can be expected to be overused by farmers given low prices in order to avoid the risk of unacceptable increases in variance of profits generated from yields (Pearce and Koundouri, 2003). It is not surprising that P application has exceeded P uptake by crops throughout many parts of the world under these conditions (MacDonald et al., 2011; Sattari et al., 2012), as exemplified in my 2001-2005 P balance (Figure 5.7a). The resulting residual P on agricultural lands contributes to significant non-point source pollution of coastal ecosystems (Nixon, 1995). Future price increases in fertilizer P could be driven intentionally by policy to mitigate eutrophication and encourage efficient P use and recycling (i.e., fertilizer taxation) or occur as a result of global economic factors (e.g., phosphate rock supply, global fertilizer demand, energy prices).
Policies in the US aimed at mitigating non-point source nutrient pollution from agriculture have historically relied on a “pay the polluter” approach where financial and technical assistance to farmers is intended to encourage voluntary adoption of pollution reduction strategies (Shortle et al., 2012). This approach has not succeeded in generating desired outcomes in many cases and incorporating elements of a “polluter pays principle” into agricultural water quality policy has been advocated (Shortle et al., 2012). Input taxation directed at pollution generating practices is one “polluter pays” economic approach to reducing downstream environmental impacts and promoting efficient use and recycling (Reijnders, 2003). Taxation of fertilizer inputs to agriculture has been practiced in different forms in multiple European countries in recent decades (Söderholm and Christiernsson, 2008). There are several challenges inherent to such strategies, including the fact that regulators generally have insufficient information concerning the marginal reduction cost function (i.e., the P reduction achieved as a function of investment in P management) (Söderholm and Christiernsson, 2008).

My results (Figure 5.4a) illustrate that increasing P fertilizer prices between US $250 and $350 per Mg DAP can dramatically reduce P fertilizer use. The cost of phosphate fertilizer was the primary reason that food producers in the region applied less P (J. Cheston Stevens, Jr., Louisiana State University Agricultural Center, personal communication). However, uncertainty remains due to additional socioeconomic factors. First, energy prices may be a confounding factor in the relationship between P fertilizer price and consumption observed here, influencing both fertilizer prices and farm budgets (Figures 5.4b and 5.4c). Second, the substantially more gradual consumption declines at price increases above US $350 per Mg DAP during 2007-2010 may have been influenced by perceived minimal fertilizer requirements by farmers and economic policy. P dynamics documented here also capture how inorganic fertilizer prices can influence
the utilization of locally available organic P sources. During 2000-2006, poultry producers north of the study region across the Mississippi border offered poultry litter in exchange for cleaning it out of broiler houses. This poultry litter was applied as fertilizer to approximately 20,000 acres of pasture in the study region during this period. Broiler producers began charging US$20-25 per ton for poultry litter when the price of inorganic fertilizer spiked. This immediately reduced the acreage in the study region receiving poultry litter by approximately 50% (J. Cheston Stevens, Jr., Louisiana State University Agricultural Center, personal communication). Further studies are needed that investigate the influence of the 2008 fertilizer price spike and additional socioeconomic factors (e.g., energy prices, federal farm policy, farmer perceptions) on inorganic fertilizer consumption and organic fertilizer usage in coastal basins (Broussard et al. 2012).

Another challenge of fertilizer taxation is that cost-effectiveness is often reduced by a focus on the consumption or sales of fertilizers rather than environmental impacts (Söderholm and Christiernsson, 2008). MFA provides an accounting method for P in agricultural landscapes that can distinguish necessary P from excess P (Schussler et al., 2007). Accounting methodologies shown here coupled with the increasingly easy access of nutrient content information (e.g., NRCS, 2013) and lessons learned from past taxation schemes based on nutrient accounting (e.g., the Netherlands during 1998-2006 where high administration costs due to the need to regulate animal manure hindered cost-effectiveness; Söderholm and Christiernsson, 2008) could provide a way forward for a P taxation scheme targeted at surplus P as a management lever to better balance P inputs and outputs in food production systems.

It is also possible that P fertilizer prices will exhibit the instability observed in 2006-2010 again in the future due to global economic factors. A report from the Economic Research Service of the US Department of Agriculture concludes that fossil energy prices could be the dominant
driver of fertilizer prices in the future given projected increases in global fertilizer demand (Huang, 2009). Fertilizers contain significant embodied energy on a global scale and agricultural systems have thus relied on “feeding fossil fuels to soil” to support a burgeoning global population since the Industrial Revolution (Ramirez and Worrel, 2006). Therefore, factors affecting energy availability (Murray and King, 2012) could greatly limit future access to inorganic P fertilizer in coastal regions with repercussions for local food production and anthropogenic P cycling.

Another important driver of change in the study region is the linear decline in milk produced by dairy operations (Figure 5.6a) and the resulting impact on feed and manure quantities (Figures 5.6d and 5.6e). Louisiana is home to mostly small-scale dairy producers, which have been declining for decades nationwide in the US. The number of US dairy operations containing milk cows sharply decreased by 88% between 1970 and 2006, while average herd size increased from 19 cows per farm in 1970 to 120 cows in 2006, indicating expansion of larger dairy farms that are more profitable due to lower production costs (MacDonald et al., 2007). Locally, the small-scale dairy industry in Louisiana has recently suffered from the expiration of the 2008 Farm Bill and the US Department of Agriculture’s Milk Income Loss Contract Program (MILC) as input costs remained high for feed, fuel, and fertilizer (LSU AgCenter, 2012). My results suggest that political and economic drivers influencing small-scale dairy farms can significantly alter P fluxes in coastal basins without large-scale facilities, leading to decreased P input, feed requirements, and manure availability.

The 2005-2006 population changes in the Pontchartrain Basin following Hurricane Katrina marked a historic transition in population distribution, with a majority of residents living in the upper basin for the first time in modern history (Figure 5.5). The influx of new residents
into the study region resulted in increased P input in the consumption subsystem slightly, with more P directed to landfills and wastewater system storage within the urban/developed landscape (Figure 5.7b). The estimated decrease in nonfarm fertilizer use in my model (Table 5.1.) helped offset increased food P requirements for the human population (Figure 5.2). These results, coupled with the decline in P input to the food production subsystem (Figure 5.7a), document a shift in the dominant origin of P input into the study area from food production to that associated with the resident human population. Environmental managers in the region should increasingly focus on P in wastewater systems in light of this shift.

The majority of population growth in the upper basin during 2001-2010 has occurred in the more suburban, exurban, and rural parishes with lower population densities of Ascension (142 persons km⁻²), Livingston (76 persons km⁻²), St. Tammany (107 persons km⁻²), and Tangipahoa (59 persons km⁻²) compared to the more urban East Baton Rouge Parish (373 persons km⁻²) in the upper basin and Orleans (783 persons km⁻²) and Jefferson (565 persons km⁻²) parishes in the lower basin (US Census, 2012b). The decentralized nature of growth (i.e., “sprawl”; Jaeger et al., 2010) has important implications for anthropogenic P cycling (Figure 5.8). A greater magnitude and percentage of human food needed to be imported from outside of the study area in 2006-2010 to feed new residents (Figure 5.2, Table 5.2), eventually ending up in wastewater systems. Less than one third (31.6%) of the new residents in the study region during 2006-2010 were served by major wastewater treatment plants (Table 5.1). The seven Upper Lake Pontchartrain Basin parishes having land in the study region contained 2226 permitted wastewater outflows during 2006-2010 with only 17 being major sanitary systems with flows greater than 100,000 gal d⁻¹ (14 located within the study region) (LDEQ, 2013a). Many newly constructed suburban communities in the region contain their own package treatment
system. Further, an estimated 121,225 persons were not accounted for by permitted systems and most likely rely on septic systems for waste handling. A decentralized human population with decentralized wastewater treatment leads to a lack of the P concentration on the landscape observed in larger cities (e.g., in large centralized wastewater treatment plants; Baker, 2011). This greatly complicates P management and recycling given current land use patterns characterized by a separation between food production and human habitation.

Significant attention in the P recycling literature has been paid to P recovery methods suited for large-scale wastewater treatment plants including harvesting of biosolids and energy-intensive P precipitation with struvite (MgNH₄PO₄·6H₂O) (Rittmann et al., 2011; Linderholm et al., 2012). At the other end of the spectrum, low-tech methods for P recovery including urine diversion and biodegradable bags for recovering human waste are being discussed and employed in developing countries (Elser and Bennett, 2011). None of these approaches are likely to have widespread applicability in coastal regions in developed nations characterized by sprawl and decentralized wastewater treatment like the Upper Pontchartrain Basin.

The State of Louisiana (2009) projects that growth in the Upper Pontchartrain Basin parishes will become exponential between 2015 and 2030, making the inland shift in the population center of the basin permanent for the foreseeable future (Figure 5.5). This will increase P input into the consumption subsystem unless enhanced internal recycling occurs or per capita P use declines. My observations capture a complex dynamic concerning future coastal habitation, environmental hazards, and anthropogenic P fluxes. When concentrated coastal urban human populations (e.g., New Orleans) are driven to migrate due to vulnerability to environmental hazards such as hurricanes and sea-level rise (Thieler and Hammar-Klose, 2000; Adger, 2006; Hori et al. 2009), the result may be a shift in population to inland portions of
coastal watersheds. This population migration alone has important implications for nutrient management and water quality. If settlement progresses in a way where sprawl is the dominant development pattern, as has been the case in the Upper Pontchartrain Basin, P will be difficult to manage and recycle in a future where increased P efficiency may become essential (Figure 5.8).

5.4.3. Opportunities for Improvement

My results indicate a substantial increase in anthropogenic cycling P efficiency in the study region of the Upper Lake Pontchartrain basin during 2001-2010 due entirely to decreased agricultural inputs (Table 5.2). Whether this increased efficiency continues into the future remains to be seen. The relatively small magnitude of the recycling and use pool coupled with the large amounts of P that continue to be retained within the watershed landscape and loaded to surface waters indicates substantial room for improvement (Figure 5.7). General strategies for enhancing recovery and recycling of P in agriculture and human communities have been discussed extensively elsewhere (Cordell et al., 2011; Childers et al., 2011; Rittmann et al., 2011) and are only summarized here. Critical components include improving the efficiency of P removal in wastewater treatment, recycling human waste P, eliminating fertilizer inputs to lawns, reduction and composting of food and yard waste, encouraging a plant-based diet, eliminating unnecessary P use in household chemicals, recycling animal manure, and moving towards a balance between P inputs and outputs in food production. Progress achieved outside of the study region could be used to guide local management. The UK offers some good examples (Cooper and Carliell-Marquet, 2013). Only 27% of agricultural P input in the UK comes from inorganic fertilizers, while food crop production P efficiency is > 80%. Furthermore, 41% of P in human wastewater is recycled and government initiatives, including municipal composting, have been enacted that decrease P flows to landfills.
Residual soil P is also a critical consideration. My results show that the annual net increase in storage of the residual P pool in agricultural lands of the Upper Pontchartrain Basin study region was substantial during 2001-2005 (Figures 5.7a). This residual P can contribute to food production P needs during periods of depressed external P inputs. For example, P inputs to agricultural soils have declined since the 1980s in many European countries, while P uptake in harvests continued to increase, possibly due to continued supply of plant-available P from the residual soil pool (Sattari et al., 2012). “Legacy P” also has significant implications for both ecosystem management and restoration (Reddy et al., 2011). Fostering a greater understanding of the magnitude and mobility of the residual soil P pool in coastal food production zones should be part of comprehensive P management.

Despite the efforts mentioned above, the UK remains dependent on imported P (Cooper and Carliell-Marquet, 2013) and the current decentralized nature of human habitation and food production in the Upper Pontchartrain Basin may limit the transferability of strategies used in Western Europe to improve P efficiency. Relatively vast physical distances between P sources and opportunities for using recycled P in food production mean that energy economics largely determine the feasibility of P recycling. For example, utilizing dairy manure for fertilization is greatly limited by transportation fuel costs. Longer distances between dairy and farmland in Louisiana have favored the use of commercial inorganic fertilizers containing a greater concentration of P by mass (Paudel et al., 2009). These limitations may become more pronounced given predictions of future constraints on energy affordability (Murray and King, 2012). An opportunity exists in coastal basins where population centers shift inland to integrate nutrient management into development and create synergies between human habitation and food
production to maximize nutrient recycling and increase the proportion of locally produced food, effectively closing the human P cycle.

Figure 5.8. Future coast? Recent residential development in the Upper Pontchartrain Basin has been characterized by decentralization and is disconnected from food production. This settlement pattern presents several challenges for improving anthropogenic phosphorus cycling. *Photo credit:* M. Seibert.

Doing so would require consideration of local ecological, economic, and cultural constraints using an interdisciplinary approach spanning ecology, agronomy, land use planning, design, engineering, and policy. To miss this historic opportunity would be disappointing given the decades-long effort to combat coastal eutrophication in the US and elsewhere, and may leave these new settlements and local agriculture vulnerable due to dependence on high-cost imports (i.e., food, feed, fertilizer) in the future.
5.5. Conclusions

The results of my MFA demonstrate that significant changes in anthropogenic P cycling have occurred between 2001-2005 and 2006-2010 in the Upper Pontchartrain Basin. Principle drivers of these changes were fertilizer economics, declining dairy production, and human population growth. The single largest change between periods was a 78% reduction in purchased inorganic P fertilizer correlated to the fertilizer and crude oil price spikes of 2008. The relationship between P fertilizer prices and P fertilizer consumption I observed, along with the MFA methods used, offer guidance for fertilizer taxation schemes aimed at reducing excess P use, however additional economic factors need to be considered and similar studies are needed in other coastal basins to build upon my findings. Reduced P inputs to the food production subsystem and increased P inputs to the human consumption subsystem have resulted in a shift in the dominant origin of human-mediated P flux into the study area, indicating that local environmental managers should give increased attention to wastewater systems. Population increase is expected to continue in the upper basin, making permanent the historic movement in population majority from the lower basin including the city of New Orleans to lands north of Lake Pontchartrain that occurred following Hurricane Katrina in 2005. The sprawl associated with this population growth presents significant challenges for P management and P recycling. Further development could instead focus on creating synergies between local agriculture and human habitation to promote energy efficient nutrient recycling and thereby decrease the need for expensive imports during times of economic uncertainty.
CHAPTER 6: CONCLUSIONS

The overarching objective of the research I have presented in this dissertation was to increase scientific understanding of nitrogen and phosphorus biogeochemistry in the Lake Pontchartrain Estuary and Basin across a range of spatiotemporal scales. My results can be used to inform local environmental managers, particularly in the context of large-scale river diversions into open water coastal environments, eutrophication in Lake Pontchartrain, and nutrient management in the Upper Lake Pontchartrain basin. Findings I have presented also have relevance beyond coastal Louisiana and address global concerns about nutrient management and pervasive eutrophication.

In Chapters 2 and 3, I investigated two biogeochemical processes in Lake Pontchartrain that occur at the sediment-water interface: (i) nitrate flux from the water column into the sediments driven by microbial-mediated nitrate reduction occurring in the sediment and (ii) diffusive flux of dissolved inorganic phosphorus (DIP) from the sediments to the water column that is dependent on sediment biogeochemistry and concentration gradients at the sediment-water interface. In Chapter 2, I found that the mean rates of nitrate flux into the sediments of Lake Pontchartrain based on mass transfer in intact cores collected in 2010 and in situ porewater measurements in 2011 were $-17.4$ and $-1.4$ mg NO$_3$–N m$^{-2}$ d$^{-1}$, respectively, for water column nitrate concentrations observed in the field in 2011. During the laboratory incubations, there was no significant difference in nitrate flux between aerobic and anaerobic treatments. I estimate that nitrate flux into sediments accounted for up to 3.1% (309 Mg NO$_3$–N) of water column nitrate loss during the 2008 Bonnet Carré Spillway event. Sediment characteristics, field measurements, and results from the laboratory experiment suggest that denitrification is the primary pathway for nitrate reduction. Even though there is significant nitrate reduction occurring in Lake
Pontchartrain sediments during Mississippi River diversion events, this pathway of nitrate loss from the water column plays a relatively minor role in the transformation of the very large amount of nitrate received during Bonnet Carré Spillway openings.

My results from Chapter 3 indicated that, on average, diffusive flux of DIP from sediments (517 Mg DIP-P y⁻¹) likely contributes approximately 30-44% of the annual total dissolved inorganic phosphorus load to the Lake Pontchartrain Estuary water column. Furthermore, internal DIP loading by diffusion has the potential to regenerate water column DIP in DIP-depleted waters to concentrations observed in the Mississippi River (0.05 mg DIP-P L⁻¹) in less than 60 days. These findings suggest that a sequence of events is feasible where external pulses of nitrogen-rich water produce phosphorus-limited conditions, followed by an internal pulse of DIP from sediments to restore nitrogen-limited conditions. This internal DIP load may be an important contributor in promoting blooms of nitrogen-fixing harmful algae in Lake Pontchartrain under summertime low-nutrient conditions.

My comparative analysis of the previous three Bonnet Carré Spillway openings presented in Chapter 4 yielded several important findings that increase the scientific understanding of hydrologic manipulation, nutrient loading, and estuarine ecosystem response. The 2011 opening occurred later in the season than the previous two lower discharge events (1997 and 2008) and was characterized by dissolved inorganic nitrogen loads 1.7 and 2.6 times greater than the 1997 and 2008 events, respectively. Rapid depletion of riverine nitrate (21 days) occurred post-spillway closure in 2011 with no associated harmful bloom of cyanobacteria and was followed by an internal pulse of DIP from sediments to restore nitrogen limitation, confirming the important role of internal DIP loading suggested by my findings in Chapter 3. My results suggest that water column nitrate can be substantially reduced in the diversion plume within Lake Pontchartrain sediments during Mississippi River diversion events, this pathway of nitrate loss from the water column plays a relatively minor role in the transformation of the very large amount of nitrate received during Bonnet Carré Spillway openings.

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Pontchartrain prior to reaching the coastal ocean, largely via phytoplankton assimilation. This is important in the context of efforts to reduce nitrate loads to the coastal Gulf of Mexico to alleviate eutrophication and related hypoxia (Rabalais et al. 2002a and 2002b). Further work is needed to estimate nutrient mass balances in Lake Pontchartrain during Bonnet Carré Spillway openings. My analysis of recent spillway openings indicated that there is not a simple stimulus-response relationship between nitrogen loading and the formation of harmful cyanobacterial blooms. Several important parameters including external nitrogen loading, timing, magnitude, plume hydrodynamics, nutrient molar ratios, internal phosphorus loading, weather, and northern tributary discharge interact to determine ecosystem response. My results suggest that the turbulent, fluctuating environment and nutrient composition during diversions does not favor harmful algal blooms of cyanobacteria and that the immense size and timing of the 2011 diversion may have resulted in near complete post-diversion cyanobacterial bloom suppression by hydraulic flushing. Continued monitoring of Lake Pontchartrain is needed during both Bonnet Carré Spillway openings and times during which northern tributaries are the dominant source of freshwater and nutrients to foster a greater understanding of factors promoting harmful blooms of cyanobacteria.

My findings in Chapters 3 and 4 indicated that phosphorus dynamics in the Lake Pontchartrain Estuary have important implications for eutrophication during both diversion and non-diversion years. While legacy phosphorus in Lake Pontchartrain sediments may originate to some degree from phosphorus entering the estuary via the Bonnet Carré Spillway during diversion events, tributaries draining the Upper Lake Pontchartrain Basin are the primary source of phosphorus to the ecosystem during most years (McCorquodale et al., 2009). The analysis of anthropogenic phosphorus cycling in the Upper Lake Pontchartrain Basin I presented in Chapter
5 was a novel approach to investigating human-mediated phosphorus flows in a coastal basin. I found that significant changes in anthropogenic P cycling have occurred between 2001-2005 and 2006-2010 in the Upper Pontchartrain Basin, including a 40% decline in P input to the overall system. Increases in fertilizer and oil prices were correlated to drastic reductions in locally purchased inorganic phosphorus fertilizer between 2001-2005 and 2006-2010 (78% decline between periods). A continual decline in dairy production altered phosphorus fluxes in the basin, leading to decreases in feed requirements and manure availability. The dominant origin of phosphorus input into the study region shifted from the food production subsystem in 2001-2005 to the human consumption subsystem in 2006-2010, indicating that local environmental managers should pay increased attention to current and future wastewater systems. The influx of new residents has been characterized by decentralized settlement that limits phosphorus recycling. Overall anthropogenic phosphorus cycling efficiency increased from 23% to 34% due largely to reduced fertilizer inputs. Leakage to the Pontchartrain Estuary and the Mississippi River represented 18-24% of total system phosphorus input, while the vast majority of phosphorus accumulated within soils, wastewater systems, and landfills.

My results from Chapter 5 offer guidance for potential fertilizer taxation schemes aimed at reducing excess phosphorus use in the Upper Lake Pontchartrain Basin, balancing phosphorus inputs and outputs in food production systems, and moving towards sustainable phosphorus management. The State of Louisiana projects that human population will continue to increase in the upper basin, making permanent the shift in population majority from the lower basin that occurred following Hurricane Katrina, and inevitably resulting in greater import of phosphorus for human consumption. A historic opportunity exists to encourage future coastal development characterized by synergies between local agriculture and human habitation to promote energy
efficient nutrient recycling. The effect would be a decreased reliance on expensive imports and uncertain future global phosphate rock supplies, along with the mitigation of current and future eutrophication.

Collectively, the results I have presented in this dissertation constitute a multi-scale approach to understanding nutrient biogeochemistry in estuarine systems and coastal basins. At every scale, context is established by processes with longer time-frames extending over a greater area. Furthermore, the mechanisms that drive processes at each scale derive from a set of processes with shorter turnover times occurring at smaller spatial extents (Carpenter and Turner, 2001). The range of spatiotemporal scales I have covered, extending from biogeochemical processes at the sediment-water interface to basin-scale changes in anthropogenic phosphorus cycling, is broad yet (of course) incomplete. Processes occurring at both larger and smaller scales than those I have discussed are important, have been studied by others, and should be investigated further in the future to continue to increase understanding of coastal environments occupied and influenced by humans in the Lake Pontchartrain Basin and elsewhere.

The term “cultural eutrophication” has been used to describe excessive organic matter production resulting from nutrient enrichment through human activity (Smith and Schindler, 2009). I believe this term correctly links the ecological effect to its cultural and socioeconomic origin and inspires the multi-scale, interdisciplinary approach I have taken in this dissertation. Mitigating persistent eutrophication both locally and globally will require an understanding of not only the biogeochemical processes occurring in aquatic systems, but also the way in which nutrients flow through human society and how these flows are shaped by a myriad of factors. It will be a significant challenge to feed 9 billion people globally under current agricultural practices without greatly expanding eutrophication world-wide (Tilman et al., 2001). In Chapter
5, I very purposefully referred to phosphorus loading to surface waters as “leakage.”

Eutrophication is a symptom of inefficiency and waste. Currently, this inefficiency can be afforded in the United States and other industrialized nations. Future constraints on the availability of fossil fuels and phosphate rock may alter this reality (Elser, 2012; Murray and King, 2012).

We can turn to the plankton world for an analogy. Zooplankton copepods will engage in “sloppy feeding” during a phytoplankton bloom when their prey is abundant and characterized by relatively large cells, losing significant amounts of potential food to their surroundings as dissolved material and limiting the transfer of energy to higher trophic levels. In contrast, during oligotrophic periods when small cells of phytoplankton dominate the prey composition, the efficiency of copepod feeding and energy transfer greatly increases (Møller, 2005). Forging a “prosperous way down” from an era of abundant carbon-based energy and phosphate rock to a future where carbon-based fuels and concentrated mineral P are more limited will be an essential, difficult undertaking at local and global scales (Odum and Odum, 2001). Continued widespread eutrophication rooted in the unidirectional flow of nutrient resources to environmental sinks will not be a viable option on the path towards a culture of energy-efficient biogeochemical prosperity and greater ecological consciousness.
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145


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Eric Daniel Roy was born to Janie and Gary Roy in Norfolk, Virginia in 1984 and spent his childhood in Virginia Beach near the mouth of the Chesapeake Bay. He earned a Bachelor of Science degree in Mechanical Engineering from Old Dominion University in 2006 with a minor in Philosophy, graduating summa cum laude. A keen interest in material and energy flows and a love for the outdoors led him to pursue the intersection of engineering and ecology. In 2008, he earned a Master of Science degree in Food, Agricultural and Biological Engineering from The Ohio State University, where he continued to work through 2009 as a Research Scientist on the Lake Erie Biocomplexity Project. His research during this period focused on developing coupled human-environment models to investigate interactions among invasive species, phosphorus fluxes, and watershed management. Following his interest in nutrient cycling, he began his doctorate in the Department of Oceanography and Coastal Sciences at Louisiana State University in 2010.