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Wetland Sediment Nutrient Flux in Response to Proposed Hydrologic Reconnection and Climate Warming

James T. Smit

A Thesis Submitted to the Graduate Faculty of

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Abstract

Wetland Sediment Nutrient Flux in Response to Proposed Hydrologic Reconnection and Climate Warming

By James T. Smit

Wetland restoration and creation are common practices, but wetlands restored or created on former agricultural land may act as a source of nutrients, rather than as a sink. I studied P sediment-water exchange in two flooded celery fields (west and east), which are designated for wetland restoration, in order to assess the effects that hydrologic reconnection of the area to an adjacent creek would have on P dynamics. We also examined the influence of climate change, specifically warming temperatures, by conducting the sediment-water exchange experiments at ambient and plus 2°C temperature conditions. Lab-based sediment core incubations revealed that TP release rates were significantly larger when sediment from the west pond was flooded with water from the creek (~40-60 mg m⁻² d⁻¹), simulating reconnection, than when west pond sediment was flooded with water from the same pond (\sim 6-20 mg m⁻² d⁻¹), simulating the current condition. Increasing ambient water temperatures by 2°C did not produce a consistently significant effect on P release rates from west pond sediment. Additionally, I did not observe a consistently significant effect of flooding or increased temperature on the release of N from west pond sediment. There was no consistently significant effect of flooding with creek water or increased temperature on east pond sediment N and P release, although the sediments still served as a net source of P, with release rates of ~2.2-4.73 mg TP m⁻² d⁻¹. The difference in response between the two ponds may have been due to prior dredging in the east pond, but not in the west. The results of this study showed that wetlands converted from agricultural areas can potentially

act as a significant source of P to downstream locations. Overall, the effects of warming on nutrient dynamics were much less pronounced than effects related to prior land use.

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Symbols and Abbreviations

P, phosphorus; N, nitrogen; NO₃-N, nitrate; NH₃-N, ammonia; SO₄, sulfate; Cl, chloride; TP, total phosphorus; SRP, soluble reactive phosphorus; OM, organic matter; DO, dissolved oxygen concentration; ORP, oxidation/reduction potential; SpCond, specific conductivity; chl *a*, chlorophyll a; total N, total nitrogen; Ca, calcium; Fe, iron; Mg, magnesium; Al, aluminum; AFDM, ash free dry mass.

Chapter I

Introduction

The quality of freshwater resources is one of the paramount issues facing the world today. Water quality refers not only to the biological, chemical, and physical characteristics of water, but also the condition of water relative to human needs. High quality renewable fresh water is essential for human life and societal well-being, and in addition to the fundamental provision of drinking water, fresh water supports large scale industry, irrigation, flood control, hydroelectric power, recreation, agriculture, and habitat for plant and animal life (Jackson et al., 2001; Baron et al., 2002). Yet, large scale human activities such as agriculture, fossil fuel combustion, and land development (Crutzen, 2002) have negatively impacted water quality through eutrophication (Smith, 2003), wetlands loss (Millennium Ecosystem Assessment, 2005), and climate change (Schindler, 2001).

Eutrophication, or the over enrichment of water bodies due to the input of excessive nutrients, negatively impacts the quality and usability of freshwater by stimulating harmful algal blooms, depleting hypolimnetic oxygen concentrations, and decreasing the amount of suitable area for wildlife habitat (Bennett et al., 2001). It is one of the leading stressors of water quality in the United States (US EPA, 1996), and eutrophication results in a cost of approximately 2.2 billion dollars annually when calculating financial losses related to recreational water usage, waterfront real estate, spending on recovery of threatened and endangered species, and drinking water (Dodds et al., 2009). Wetlands are typically thought to improve water quality through multiple beneficial ecosystem services (Millennium Ecosystem Assessment, 2005), and lessen the impacts of eutrophication (Verhoeven et al., 2006) by retaining nutrients such as nitrogen (N)

and phosphorus (P) in 1) plant biomass, 2) accreted organic matter, and 3) insoluble mineral compounds (Reddy and DeLaune, 2004). Despite these benefits, approximately half of the historic wetlands in the US have been lost (Mitsch and Gosselink, 2007), as well as nearly two thirds of the historic wetlands in the states surrounding the Great Lakes (Dahl, 1990). In response, numerous wetland restoration projects have been initiated, with many of these projects occurring on former agricultural land (Zedler, 2003). Despite the intent of these projects, wetlands constructed on former agricultural land can negatively impact water quality, and contribute to eutrophication due to the presence of legacy nutrients in the soil (Pant and Reddy, 2003; Steinman and Ogdahl, 2011). Furthermore, increasing temperatures due to climate change have the potential to enhance eutrophication (Townsend et al., 2012), promote blooms of cyanobacteria (Paerl and Huisman, 2008), threaten wetland sustainability (Millennium Ecosystem Assessment, 2005), and alter wetland biogeochemistry (Erwin, 2009). Changes in traditional weather patterns and hydrology due to climate change also are expected to negatively impact water quality (Mortsch and Quinn, 1996; Schindler et al., 1996)

The impacts of eutrophication, wetlands loss and restoration, and climate change not only have created separate and distinct environmental issues in regards to freshwater environments, but also issues that interact with and contribute to one another. These problems influence the ecological integrity of freshwater environments, as well as the ability of freshwater to meet the various requirements of humanity. Overall, the combined impact of these issues is a decrease in water quality (Figure 1.1). Thus, in order to understand water quality and the steps that can be taken to protect and improve it, it is important to examine the effects and interactions of wetlands loss and restoration, eutrophication, and climate change.

Wetlands loss and restoration

Wetlands provide many important ecosystem services that enhance water quality, such as contaminant removal and the retention of N, P, carbon, and sediment (Millennium Ecosystem Assessment, 2005; Verhoeven et al. 2006). Additionally, wetlands sustain biodiversity, mitigate flooding, and provide essential habitats for spawning fish and other organisms (Kusler et al., 1994). In spite of these benefits, wetlands have been dredged, drained, and filled throughout history in support of agricultural production and land development to support population growth (Gibbs, 2000). In total, approximately 53% of the wetlands in the United States were lost between the years of 1780 and 1980 (Mitsch and Gosselink, 2007), with some states, such as California and Ohio, losing approximately 90% of their historic wetland acreage (USDA, 2012). Specifically considering the eight states surrounding the Great Lakes, an average of 65% of historic wetland area has been lost since 1780 (Dahl, 1990).

In response to the vast amount of historic wetland loss and the associated loss of their beneficial ecosystem services, many wetland restoration and creation projects have been initiated. Since 1988, aquatic ecosystem regulations in the United States have been focused on achieving a goal of "no net loss" of wetland area and function (Gosselink, 2002). Governmental policies that were put in place to protect wetlands from development include Section 404 of the U.S. Clean Water Act, which protects wetland resources by requiring avoidance, minimization, and compensation of impacts to wetlands (National Research Council, 2001). Additionally, government programs such as the Wetlands Reserve Program provide financial incentives to encourage landowners to turn frequently flooded, marginal agricultural land into wetland conservation easements (USDA, 2012). These policies help to retain and restore the ecosystem

services provided by wetlands, as well as increase land value proximal to wetland areas (Kaza and BenDor, 2013).

The practice of restoring wetlands on farmland is seen as an environmentally prudent endeavor; however, issues can arise when considering the specific land use history, and water/sediment dynamics of these areas. Where wetlands are restored on soil that was farmed, it is perhaps inevitable that there will be an initial period of equilibration (Aldous et al., 2005) when the sediments act as a source of nutrients instead of as a sink (Newman and Pietro, 2001). Thus, in the short term, nutrients from past agricultural practices may be transferred to the water after re-flooding (Lindenberg and Wood, 2009). This effect is counteractive to the one of the main goals of wetland restoration and can exacerbate issues that negatively impact water quality such as eutrophication.

Eutrophication

Eutrophication is another process that negatively impacts water quality, and can be influenced by wetlands loss and restoration. Eutrophication is defined as the process by which water bodies become more productive through increased input of nutrients (Welch and Jacoby, 2004), such as N and P. This process decreases water quality by increasing algal biomass, shifting algal community composition to bloom forming species and potentially toxic cyanobacteria, depleting water column dissolved oxygen through increased microbial respiration, and decreasing fish production (Smith, 2003). Anthropogenic sources of N include agricultural runoff (Nosengo, 2003), wastewater discharge, and atmospheric deposition (Rabalais, 2002). P also is found in agricultural runoff and wastewater discharges; however, P can also be supplied to a water body through internal loading from sediments with high P concentrations (Søndergaard et al., 2003). P is typically understood to be the main nutrient driving eutrophication in freshwater environments (Schindler et al., 2008); however, N and temperature are also significant predictors of trophic state (Beaulieu et al., 2013). Overall, strategies that reduce both N and P loading into freshwater environments are thought to be the most effective when attempting control eutrophication (Conley et al., 2009).

Wetlands are one of the most effective means to reduce eutrophication, as they have the potential to retain nutrients naturally, specifically the nutrients N and P. This ecosystem service is becoming even more valuable due to the ongoing eutrophication of freshwater resources worldwide (Smith, 2003), and the focus on limiting the amount of anthropogenic N and P entering lakes and the oceans (Conley et al., 2009). The mechanisms that regulate P retention within wetlands include: sedimentation of particulate P, sorption/desorption reactions, biological uptake, and long term P storage in peat (Dunne, 2006). The mechanisms of microbial denitrification, sedimentation, and plant uptake all contribute to N retention and removal in wetland systems, with microbial denitrification contributing the most to N loss (Saunders and Kalff, 2001; Picard et al., 2005; Scott et al, 2008). Consequently, wetland preservation and restoration is often seen as a tool that can be used to facilitate the recovery of eutrophic water bodies; but, careful considerations of specific land use history should be incorporated into restoration efforts (Zedler, 2003).

Climate change

Climate change represents an additional environmental issue that is impacting water quality, as well as interacting with other water quality stressors. Since the advent of the industrial era, human activities have been adding large amounts of energy-absorbing gasses to Earth's atmosphere, and increasing the proportion of solar energy that is retained within the atmosphere (Ramanathan, 1988). This occurrence is referred to as global climate change, and it affects not only temperature, but also traditional weather patterns and the frequency of extreme weather events such as droughts and floods (IPCC, 2007). Current global model predictions based on various emission scenarios predict that climate change will cause a temperature increase between 0.3 and 4.8° C by the end of the 21st century (IPCC, 2013). In aquatic ecosystems, it is suggested that warming temperatures will result in increased stratification, more prevalent benthic hypoxia, a greater tendency for internal nutrient loading (Townsend et al., 2012), and an overall increase in freshwater eutrophication. Climate change has been recognized as a major threat to the integrity of wetland ecosystems, worldwide (Hulme, 2005).

Additional, detrimental impacts resulting from increased temperatures and extreme weather events include: altered base flows and hydrology; increased flooding; increased soil erosion and sedimentation; decreased water quantity and quality; and altered biogeochemistry (Erwin, 2009). Considering wetland biogeochemistry and nutrient retention, increased temperatures could stimulate organic P mineralization and release (Kadlec and Reddy, 2001), as well as decrease water column dissolved oxygen concentrations and stimulate P release from mineral compounds (Holdren and Armstrong, 1980). Conversely, the microbial processes that regulate N cycling and retention in wetlands may operate more efficiently due to the increased

rate of microbial reactions that would result as a consequence of increased temperatures (Kadlec and Reddy, 2001).

Conclusion

Overall, the effects of wetlands loss and restoration, eutrophication, and climate change on water quality are numerous and synergistic (Figure 1.1). Because of this, a comprehensive approach is necessary to appropriately examine the many direct and indirect impacts that these issues have on water quality, including the many complex physical, chemical, and biological interactions that occur between them. Thus, the value of research that is done with the aim of improving or maintaining water quality through the use of wetlands is enhanced by including both eutrophication and climate change, so that the most accurate conclusions and recommendations can be made.



Figure 1.1. Conceptual model displaying the various drivers, stressors, processes, ecological outcomes, and societal outcomes which together impact our definition and determination of water quality.

My work

My study was conducted on two flooded fields, now technically ponds, that were formerly used for celery farming and have been designated for wetland restoration. The ponds are located approximately 250 m NE of Bear Lake (Muskegon County, MI) (Chapter 2, Figure 2.1). Bear Lake is a shallow, eutrophic, drowned river mouth lake that is fed primarily by a small tributary, Bear Creek. The two ponds are located adjacent to Bear Creek, and are separated by an earthen berm. Bear Lake connects to Muskegon Lake, Michigan through a small navigation channel. Muskegon Lake is a larger drowned river-mouth system that connects directly to Lake Michigan through another navigation channel, and has a long history of environmental impairments that have resulted in the lake being designated as an Area of Concern (AOC) in the Great Lakes. The Muskegon Lake AOC designation also includes Bear Lake. Currently, the Muskegon Lake AOC listing includes nine Beneficial Use Impairments (BUIs), of which one is for eutrophication and undesirable algae (Steinman et al., 2008). Restoration goals for the eutrophication BUI include limiting surface total P and chlorophyll a concentrations within the AOC boundaries to 30 and $10 \mu g L^{-1}$, respectively. Various projects have been undertaken within the Muskegon Lake AOC aimed at removing the AOC listing. These projects include the redirection of direct effluent discharge from Muskegon Lake to the Muskegon County Wastewater Management System, the remediation of numerous former industrial sites with contaminated soil and groundwater, and the remediation of Ruddiman Creek, a contaminated urban tributary to Muskegon Lake (Steinman et al., 2008). Yet, significant environmental issues, such as potentially toxic cyanobacteria blooms, poor quality shoreline habitat, and mid-summer hypoxic zones, still plague the lake at this current time.

In regards to the eutrophication and undesirable algae BUI, Muskegon Lake has largely reached the goal of being under 30 μ g L⁻¹ TP (Steinman et al., 2008), but Bear Lake has remained above this target concentration (MDEQ, 2011). This prevents the BUI from being removed from the Muskegon Lake AOC listing. A total maximum daily load (TMDL) requirement for P was placed on Bear Lake in 2008, which involves reducing the TP concentration from a mean of 44 μ g L⁻¹ to 30 μ g L⁻¹ (MDEQ, 2008). An indirect modeling approach used in the TMDL concluded that a large proportion of the P in Bear Lake was from internal loading via the lake sediments (MDEQ, 2008). Thus, it was thought that the best way to decrease P loads in Bear Lake was to limit internal loading. More recent work performed by Grand Valley State University in 2011 and 2012 used diel oxygen measurements in two areas of the lake and sediment coring experiments to determine more accurate internal loading rates (Steinman and Ogdahl, 2013). This study concluded that external loading was the more significant source of Bear Lake P, with internal loading contributing a smaller fraction (Steinman and Ogdahl, 2013). Thus, in order to meet the TMDL for Bear Lake, greater reductions from the watershed, not the lake sediments, were warranted. Therein is the motivation for reconnecting and restoring the two former celery fields in the Bear Lake watershed. The rationale is that the two ponds, once reconnected to Bear Creek, will act as a flow through wetland and to retain nutrients in the wetland before they reach the lake. However, it is unknown how land use history, hydrologic reconnection, increasing temperatures due to climate change, as well as the interaction among these possible stressors, will affect the ability of this area to retain nutrients and the resulting water quality in Bear Lake.

My specific objectives for the study of these wetlands were to determine 1) if the sediments in question will serve as a source or sink of nutrients once the area is hydrologically reconnected

to Bear Creek, and 2) how climate warming will impact nutrient dynamics between the sediment and water column. To achieve these objectives, sediment core samples were taken from the two ponds and exposed to varying water column treatments and temperature regimes. Additionally, separate experiments were performed in July and October 2013 to investigate the impact of seasonality. It was my also my goal that my research would influence the restoration design of study area by highlighting potential issued, and providing information in regards to what the effects of reconnection and climate change may have on this specific restoration area.

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Chapter II

Wetland Sediment Nutrient Flux in Response to Proposed Hydrologic Reconnection and Climate Warming

Introduction

Wetland habitats provide many important ecosystem services, including flood control, fish and wildlife habitat, biodiversity preservation, and the retention of N and P (Millennium Ecosystem Assessment, 2005). Yet, large areas of natural wetlands in the United States have been degraded or filled due to land development in support of agricultural production and population growth (Gibbs, 2000), with several states having lost more than 90% of their historic wetland acreage (USDA, 2012). Currently, climate change-driven alterations in temperature are seen as major threats to wetlands (Ferrati et al., 2005). Increasing temperatures have the possibility to alter traditional wetland biogeochemistry (Erwin, 2009) by decreasing oxygen solubility (Kadlec and Reddy, 2001), increasing organic N and P mineralization, accelerating N transformation rates, and accelerating adsorption and precipitation rates of P (Reddy and DeLaune, 2004). Additionally, increased benthic microbial metabolism stimulated by elevated temperatures has the potential to decrease sediment oxygen concentrations, resulting in reduced sediment redox potential and P release (Holdren and Armstrong, 1980; Redshaw et al., 1990).

In response to the amount of historic wetland loss and the associated loss of beneficial ecosystem services, many wetland restoration and creation projects have been initiated. Local and national programs now promote restoration activities, and many wetland restoration projects occur on former agricultural land (Zedler, 2003; USDA, 2012). However, wetlands restored on former agricultural land have the potential to act as a source of nutrients to the overlying water

column (Pant and Reddy, 2003; Duff et al., 2009; Ardón et al., 2010; Kinsman-Costello et al., 2014), instead of as a sink. This has implications for wetland restoration in that many potential restoration areas could act as a source of nutrients, and negatively impact water quality.

I studied a former deltaic wetland in west Michigan that was converted to farmland in the early 1900s, and taken out of production in the late1990s/early 2000s. The area formerly was used for celery farming, but now is flooded and split into two separate ponds that are hydrologically isolated from one another by a road, as well as from an adjacent creek by an earthen berm (Figure 2.1). The area is now designated for wetland restoration. The proposed restoration design involves removal of the berm that separates the ponds and the creek, allowing each pond to reconnect individually to the creek and potentially act as a flow through wetland. Increased nutrient retention in this area would benefit the downstream receiving water body, Bear Lake, which is impacted by high concentrations of P. Indeed, the state of Michigan has placed Bear Lake on its 303(d) list of impaired water bodies, and proposed a TMDL that would require a reduction in water column TP concentration from a current mean of 0.044 mg L^{-1} to 0.03 mg L⁻¹ (MDEQ, 2008a). However, previous studies have shown that reflooding of drained agricultural areas can stimulate nutrient release (Pant and Reddy, 2003; Duff et al., 2009; Ardón et al., 2010; Kinsman-Costello et al., 2014), but relatively less is known about nutrient release from flooded areas in response to hydrologic reconnection.

The study's objectives were to determine 1) if the sediments in question will serve as a source or sink of nutrients once the area is hydrologically reconnected to the adjacent creek, and 2) how climate warming may affect nutrient exchange between the sediment and water column. I hypothesized that reconnection would increase the flux of N and P from the sediment to the water column, at least in the short term, given the concentration gradient that would be generated

between the relatively low-nutrient creek water and the relatively high nutrient pond sediment. I also hypothesized that elevated temperatures would increase the flux of P to the water column and decrease the flux of reactive N, because higher temperatures would stimulate benthic microbial metabolism, resulting in decreased sediment oxygen concentrations, and thereby create reducing conditions in the sediment favorable for P release and denitrification.

Materials and methods

Study area

The Bear Lake Wetland Restoration Area is located in western Michigan (Muskegon County), approximately 250 m NE of Bear Lake, which is a drowned river mouth lake whose main tributary is Bear Creek (Figure 2.1). The area consists of two shallowly flooded fields, hereafter referred to as ponds, which were formerly used for celery farming. The two ponds are designated east and west based on their position relative to Witham Drive, which runs north-south and separates the two ponds from one another. The surface areas of the east and west ponds are 12 and 22 acres, respectively. Bear Creek flows adjacent to the two ponds on their north side, and the three hydrologic areas have been separated by an earthen berm since the wetlands were converted to agriculture in the early 1900s. Although the earthen berm and Witham Drive separate surface water flow between the areas, there is still potential for subsurface flow, which has not been investigated to date. The east and west ponds were kept in celery production until 1995 and 2002, respectively (G. Mund, personal communication, 2012). Shortly after farming activities in the area ceased, water pumps used to keep the ponds from

flooding were shut off (G. Mund, personal communication, 2012). Since that time, both ponds have remained inundated to varying extents.

Portions of the east unit were dredged to mine muck and peat between the years of 1995 and 2002 to a depth of 3 to 15 feet, and clay/sand fill was added in certain areas to facilitate dredging operations (G. Mund, personal communication, 2012). The west unit was never dredged, and the sediments impacted by agriculture were present at the time of this study.



Figure 2.1. Bear Lake Wetland Restoration Area sampling locations in Muskegon, MI. Filled circles indicate the sampling locations within each pond. Bear Creek flow is from east to west. Inset: location of the Bear Lake Wetland Restoration Area within the Laurentian Great Lakes Region. Experimental design

Sediment cores taken from the east and west ponds were flooded with either Bear Creek water to represent hydrologic reconnection, or with water from the pond in which they were collected to simulate the current condition. To simulate the effects of climate warming, cores were incubated at either the average ambient water temperature at the time of sediment core collection (ambient condition) or at 2°C higher than the measured ambient temperature, using two separate growth chambers (details below). In the Great Lakes region, annual air temperatures are predicted to increase by 1.4 ± 0.6 °C in the near future and from 3 ± 1 °C to 5 ± 1.2 °C by the end of the century depending on different emissions scenarios (Hayhoe et al., 2010). I assume that this projected increase will be similar to average water temperatures in small, shallow water bodies, such as my study area, that do not have a large and deep reservoir of cool water. Hence, my increased temperature regime represents a realistic scenario of water warming in the near future, and a conservative estimate of predicted warming by the end of the century.

In total, I used two levels of water source (Bear Creek and ambient pond) and two levels of temperature (ambient and plus 2°C), resulting in four treatment combinations for each pond. Each treatment combination was replicated six times, with the four cores from each sampling location being treated as one block.

Field sampling and procedure

Two separate experiments were performed in July and October of 2013 to determine if nutrient exchange differed between the two seasons. Slightly different incubation periods,

sampling days, and temperature regimes were used in the two experiments (Table 2.1). Four sediment cores and one additional sample for sediment analysis were collected at each of six sampling sites in both the east and west ponds (Figure 2.1), resulting in a total of 48 sediment cores and 12 sediment samples collected per experiment. Sampling sites within the two ponds were selected through a modified random selection process where each pond was gridded and divided into six equal sections, and one location was selected randomly from each section. Areas within 10m of the edge of the ponds were excluded to avoid possible edge effects.

Table 2.1. Experimental parameters for experiments conducted in July and October.

Date	Ambient Temperature (°C)	+2 Temperature (°C)	Incubation Length (Days)	Sampling Dates
July	23	25	25	Initial, 1, 5, 10, 15, 20, 25
October	17	19	24	Initial, 3, 6, 12, 18, 24

Sediment cores were obtained using a modified piston coring apparatus (Fisher et al. 1992; Steinman et al., 2004). The modified piston corer was constructed of a 0.6-m long, ~7-cm inner diameter, 7.6-cm outer diameter polycarbonate tube that was marked in 1-cm increments. A polyvinyl chloride assembly coupled with a 3.81-cm in-line sump pump check valve was used to drive cores into the sediment, and provide suction within the tube when the core was retrieved. The modified corer was positioned vertically at the sediment water interface, and core tubes were carefully driven into the sediment to minimize disruption of the sediment surface, to a depth of at least 15 cm. After this, the bottom of the core tube was sealed with a rubber stopper and duct
tape, and the top with a plastic cap. The resulting sediment core consisted of at least 15 cm depth of sediment and an overlying water column of 45 cm. Upright sediment cores were transported to the lab within 6 hours after collection for each experiment. An additional 5-cm deep sediment core sample was collected at each site using the modified coring apparatus (Steinman et al., 2009). After collection, the 5 cm deep sample was extruded from the core tube, and stored in a plastic bag for additional analysis.

Water column readings of temperature, dissolved oxygen concentration (DO), pH, specific conductivity (SpCond), and chlorophyll *a* (chl *a*) concentration, were taken using a YSI 6600 sonde (YSI Incorporated, Yellow Springs, OH) positioned just below the water surface at each of the six sampling sites within each pond. Additionally, water to be used for subsequent laboratory experiments was collected separately from central areas in the east and west ponds, and one location in Bear Creek, and stored in acid washed 10-L carboys. All water samples, sediment cores, and sediment samples were placed on ice shortly after collection, and stored this way until transported to the lab, usually within 6 hr.

Laboratory procedure

In the laboratory, sediment cores were adjusted to a consistent sediment depth of 15 cm by removing sediment from the bottom of the core, and the overlying water column was carefully removed to within 5 cm of the sediment surface by using a siphon apparatus. Concurrently, carboys of water from the west pond, east pond, and Bear Creek to be used for core tube re-flooding were filtered (1-µm filter; Graver Technologies, Glasgow, DE) using a peristaltic pump (Pall Corporation, Timonium, MD). Readings of temperature, DO, SpCond, chl

a concentration, and pH were taken on the filtered water using a YSI 6600 sonde before being added to the core tubes. Also, separate 1-L samples of 1- μ m filtered water from the east pond, west pond, and Bear Creek were taken and analyzed for conductivity and hardness according to standard laboratory methods (APHA, 1998), as well as for total phosphorus (TP), soluble reactive phosphorus (SRP), nitrate (NO₃-N), ammonia (NH₃-N), sulfate (SO₄), and chloride (Cl) concentration (details below). Sediment core tubes were then flooded to a water column depth of 25 cm with corresponding 1- μ m filtered east pond, west pond, or Bear Creek water depending on the specific water source treatment. After flooding, remaining water from the east pond, west pond, and Bear Creek was filtered through a 0.2- μ m filter (Graver Technologies, Glasgow, DE) using the peristaltic pump, stored in acid-washed carboys in a refrigerator, and used to refill core tubes after each sampling during the experiment.

Sediment cores were then placed in one of two darkened environmental growth chambers (Revco Scientific, Asheville, NC; Powers Scientific Inc, Pipersville, PA) depending on the specific temperature treatment required for each sediment core. Temperature accuracy within the environmental chambers was validated by using an additional incubation thermometer in each incubator. Air was gently bubbled into the cores using aquarium pumps to maintain water column oxygen concentrations at 75–100% equilibrium with atmospheric oxygen throughout the incubation period. This followed my expectation that the overlying water column in these shallow wetland areas would remain relatively well mixed and oxygenated (Reddy and DeLaune, 2004). During the incubation period, water samples were taken at the midpoint in the water column through a sampling port inserted in the plastic cap on the top of the core tube. For each core tube, three separate water column subsamples were taken per sampling day. These included a 60-ml unfiltered sample for TP analysis, a 20-ml 0.45-µm filtered sample for SRP, NO₃-N, Cl,

and SO₄ analysis, and an additional 20-ml unfiltered sample for NH₃-N analysis. Filters (0.45- μ m ThermoFisher Nylon Syringe Filter, ThermoFisher Scientific, Waltham, MA) were acid washed prior to use. In total, 100 ml of water were removed from the water column of the core tubes per sampling. NH₃-N, NO₃-N, SRP, SO₄, and Cl samples were immediately frozen after collection, and TP samples were stored at 4°C. To maintain a constant water column depth, core tubes were refilled after sampling with 100 ml of 0.2- μ m filtered water that was collected at the time of coring from the two ponds and creek. Additionally, a YSI Pro-DO sonde was used to record dissolved oxygen concentration at the midpoint of the water column and near the water/sediment interface on each sampling day.

TP, SRP, and NH₃-N concentrations were analyzed on a Bran+Luebbe Autoanalyzer (SEAL Analytical, Mequon, Wisconsin; APHA, 1998). NO₃-N, SO₄, and Cl concentrations were analyzed by ion chromatography on a Dionex ICS-2100 (APHA, 1998). The additional sediment samples collected from each sampling location in both ponds were analyzed for percent moisture, percent organic matter, total N, metals (Ca, Fe, Mg, Al) and ash free dry mass (AFDM). Metals analysis was performed according to EPA method 6010B using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (U.S. EPA, 1994). Sediment NO₃-N as N, NO₂-N as N, and total Kjeldahl nitrogen were analyzed using EPA methods 300.0 Rev. 2.1 and 351.2 Rev. 2.0 (U.S. EPA, 1993). Total sediment N was then calculated as a sum of these analyses. AFDM analysis was performed by combusting a pre-weighed subsample of sediment at 550°C for 1 h. Percent organic matter content was measured as loss due to combustion. Sediment TP was analyzed as described previously, using a subsample of ashed material. Sediment Fe:P ratios were determined by weight using dry weight TP and Fe concentrations. Analysis

Maximum apparent nutrient release rate calculations were based on the methodology used in Steinman et al. (2004). In brief, the maximum rate of increase of water column TP, SRP, NO₃-N, and NH₃-N was determined using the following equation:

$$N_{flux} = (C_t - C_0) * V / A$$

where, N_{flux} is the rate of TP, SRP, NO₃-N, or NH₃-N release in mg m⁻²d⁻¹; C_t is the concentration of TP, SRP, NO₃-N or NH₃-N at time t; C_0 is the TP, SRP, or NH₃-N concentration of the initial refill water (Pant and Reddy, 2003); V is the volume of the overlying water column; and A is the planar surface area of the sediment. In the case of NO₃-N, C_0 was the concentration of NO₃-N on the sampling day where I began to see a trend of increasing concentration. Flux calculations were based on the linear portions of the water column nutrient concentration curves measured through time in order to capture the maximum apparent release rate, however, C_0 and C_t could not be consecutive dates in order to avoid potential short term bias. Additionally, a calculation was performed to determine the maximum nutrient concentration increase in the water column of each sediment core, regardless of the day on which it was reached during the incubation period. To calculate this value, I subtracted the initial (C_0) concentration of each nutrient from the maximum concentration (C_{max}) of each nutrient measured in the water column of each sediment core during the incubation period.

Two-way repeated measures analysis of variance (ANOVA), with two levels of water source treatment (Bear Creek vs. west or east pond water) and two levels of temperature (ambient vs. plus 2°C) as factors, and time as the repeated measure, was used to test for differences in nutrient concentrations in the water column of sediment cores over the incubation period. Maximum apparent nutrient release rates and maximum nutrient concentration increases were tested using blocked two-way ANOVAs with water source treatment and temperature treatment as the main effects, and sampling site as the blocking factor. In all ANOVAs, the two ponds were treated and analyzed separately. When necessary, data were transformed (ln, square root, reciprocal, power) to meet the assumptions of ANOVA. Normality was tested using the Shapiro-Wilk goodness of fit test, and equality of variance was tested using Bartlett's test. When data did not meet the assumptions of ANOVA and transformation was ineffective, core water column data were analyzed using ANOVA and the results noted as exploratory.

Sediment and water column characteristics were compared between the east and west ponds using t-tests. Sediment and water column characteristics expressed as percentages were arcsine-square root-transformed prior to analysis. Additionally, sediment and water column data that were not normally distributed or had unequal variance were transformed (ln, square root, reciprocal, power) prior to analysis. Data that still failed to meet normality and equal variance assumptions after transformation were analyzed using a Mann-Whitney Rank Sum test. All statistical analyses were conducted using R software (R Core Team, 2013).

Results

Water column and sediment analysis

Water column conditions varied between the two ponds at the time of sampling, despite their close spatial proximity (Table 2.2). The water column in the two ponds had significantly different mean values of DO and SpCond in both July and October. SpCond was significantly higher in the west pond, while DO was significantly higher in the east pond (Table 2.2).

Additionally, mean chl *a* was significantly higher in the east pond in July, while mean pH was significantly higher in the east pond in October but not July (Table 2.2).

Sediment characteristics also varied between the two ponds (Table 2.3), which is presumably related, at least in part, to the prior dredging of the east pond. Mean sediment TP and OM were typically higher in west pond compared to east pond (Table 2.3). Conversely, mean values of Al, Fe, Ca, and Mg were typically higher in the sediments of the east than west pond (Table 2.3). Mean sediment total N values were not significantly different between the two ponds. Mean Fe:P ratios in the sediment by weight were significantly higher in the east pond compared to the west pond (Table 2.3).

Table 2.2. Summary of mean (\pm SE, n=6) YSI readings of temperature, dissolved oxygen (DO), pH, specific conductivity (SpCond), and chlorophyll *a* (Chl *a*), measured in the field in July and October in the west and east ponds at the time of core collection. P-values represent the results of comparisons between west and east ponds using a t-test (t) or Mann-Whitney Rank Sum Test (r). Significant differences are in bold.

		West	East		
		mean	mean	test	p-value
July	$DO (mg L^{-1})$	3.34 ±0.61	8.78 ±0.59	t	<0.001
	SpCond (μ S cm ⁻¹)	639 ± 6.54	595 ± 1.86	t	<0.001
	Chl a (µg L ⁻¹)	8.25 ±1.31	19.13 ±1.34	r	0.003
	pH	8.31 ±0.24	8.80 ± 0.08	t	0.135
	Temperature	23.40 ±0.30	23.31 ±0.08	r	0.864
October	$DO (mg L^{-1})$	5.78 ± 1.16	9.70 ±0.29	r	0.026
	SpCond (µS cm ⁻¹)	802 ±2.73	584 ±2.95	t	<0.001
	Chl a (µg L ⁻¹)	12.87 ±2.47	11.27 ±0.43	r	0.575
	pH	8.28 ± 0.17	9.39 ±0.05	r	0.005
	Temperature	17.79 ±0.22	18.55 ±0.15	r	0.132

Table 2.3. Summary of mean (±SE, n=6) sediment Ca, Al, Fe, Mg, organic matter (OM), total N, total P measured in July and October in the west and east ponds. P-values represent the results of comparisons between west and east ponds using a t-test (t) or Mann-Whitney Rank Sum Test (r). Significant differences are in bold.

		West	East		
		mean	mean	test	p-value
July	Total P (mg kg ⁻¹)	3476 ± 1088	958 ± 309	t	0.045
	OM (%)	33 ±7	18 ±5	t	0.138
	Al (mg kg ⁻¹)	635 ±118	1463 ±129	t	<0.001
	$Ca (mg kg^{-1})$	2250 ± 200	8517 ±2317	t	<0.001
	$Fe (mg kg^{-1})$	1232 ± 160	$2200 \pm \! 158$	t	0.003
	Mg (mg kg ⁻¹)	252 ±38	2108 ±691	t	<0.001
	Total N (% by dry weight)	0.59 ±0.21	0.43 ±0.12	t	0.537
	Fe:P (by weight)	0.69 ± 0.22	7.66 ± 4.09	t	0.041
October	Total P (mg kg ⁻¹)	4028 ±907	960 ±457	t	0.034
	OM (%)	40 ±5	13 ±6	r	0.006
	Al (mg kg ⁻¹)	2067 ±409	1300 ±346	t	0.332
	$Fe (mg kg^{-1})$	2517 ±253	$2417\pm\!500$	t	0.875
	Ca (mg kg ⁻¹)	5550 ±447	10867 ±4351	t	0.823
	Mg (mg kg ⁻¹)	442 ±41	3355 ±1773	t	<0.001
	Total N (% by dry weight)	0.83 ±0.15	0.49 ± 0.24	r	0.521
<u>.</u>	Fe:P (by weight)	0.83 ± 0.18	10.44 ± 3.91	t	0.029

Change in nutrient concentration during incubation

Prior to sediment core reflooding, 1-µm filtered water from the west pond had TP and SRP concentrations that were more than an order of magnitude higher than TP and SRP concentrations in water from the east pond and Bear Creek (Table 2.4). Concentrations of NO₃-N were highest in Bear Creek water (Table 2.4). NH₃-N concentrations were below detection across the three sampling areas (Table 2.4). Filtered water from Bear Creek had the lowest pH while water from the east pond had the highest (Table 2.4). Phosphorus concentrations were greater during July than October, but were still quite high regardless of season, especially in the west pond (Table 2.4). Alkalinity, hardness, and SpCond values were variable in the three areas in experiments conducted in July and October (Table 2.4).

TP concentration in the water column of west pond cores was significantly influenced by water source in July, as the *increase* in concentration was much greater when cores were reflooded with Bear Creek water compared to west pond water (Figure 2.2; Table 2.5). In July, TP concentrations increased from initial concentrations of ~0.1 to ~1.6-2.3 mg L⁻¹ after flooding with Bear Creek water, compared to TP increases from ~1.9 to ~2.4-2.6 mg L⁻¹ after flooding with west pond water (Figure 2.2). Similarly, in October, TP concentrations increased from ~0.1 to ~1-1.4 mg L⁻¹ after flooding with Bear Creek water, compared to TP increases from ~1.9 to ~2.4-2.6 mg L⁻¹ after flooding with west pond water (Figure 2.2). Similarly, in October, TP concentrations increased from ~0.1 to ~1-1.4 mg L⁻¹ after flooding with Bear Creek water, compared to TP increases from ~0.8 to ~1-1.4 after flooding with west pond water (Figure 2.2). Temperature had no significant effect on water column TP concentrations in either experiment (Table 2.5). In general, TP concentrations were greater in July than in October (Figure 2.2). Water column SRP in west pond sediment cores followed a similar pattern, at lower absolute concentrations, to that of TP for all treatments, with cores treated with Bear Creek water exhibiting a significantly greater increase in SRP concentration than west pond water in July, but not October (Figure 2.2, Table

2.5). Water column NH₃-N concentrations were similar in all treatments and in both seasons, with a rapid increase after inundation, a peak between days 10-15, followed by a decline (Figure 2.2); neither water source nor temperature treatment had a significant effect on NH₃-N concentration (Table 2.5). Concurrently, across all treatments and in both seasons, NO₃-N concentrations remained near initial concentrations until between days 10-15, after which they increased in concentration until the final sampling day (Figure 2.2). Water column NO₃-N concentrations were significantly influenced by water source treatment in July (Table 2.5) in that concentrations were typically higher during the beginning of the incubation period in cores reflooded with Bear Creek water than west pond water (Figure 2.2). In contrast to the P patterns, absolute NO₃-N concentrations were generally higher in October than in July (Figure 2.2).

TP concentrations in the water column of east pond cores over the incubation time were not significantly influenced by water source (Figure 2.3, Table 2.5) and in general, concentrations of TP were similar in all treatments and in both seasons (Figure 2.3). Temperature also had no significant effect on water column TP concentrations over the incubation time (Table 2.5). Water column SRP concentrations in east pond sediment cores followed a similar pattern, at lower absolute concentrations, to that of TP (Figure 2.3), and were not significantly influenced by water source or temperature (Table 2.5). Overall, P concentrations were approximately an order of magnitude lower in the east pond than west pond incubations, regardless of water source or temperature treatment (Figure 2.2, 2.3). Water column NH₃-N and NO₃-N concentration patterns of east pond sediment cores were similar to those of the west pond (Figure 2.2, 2.3). In general, water column NH₃-N concentration patterns were consistent across all treatments and in both seasons, with a rapid rise in concentration following inundation, a peak between days 10-15, followed by a decline to levels near initial concentrations (Figure 2.3). There was no significant effect of temperature on NH₃-N water column concentrations over the incubation time; however, water source did significantly influence water column NH₃-N concentration in October (Table 2.5). Again, across all treatments and in both seasons, NO₃-N concentrations remained near initial concentrations until between day 10 and 15, when they increased in concentration until the final sampling day (Figure 2.3). Water column NO₃-N concentrations were significantly influenced by water source treatment in July (Table 2.5), with concentrations typically higher in cores reflooded with Bear Creek water than with east pond water (Figure 2.3).

		West	East	Bear Creek
July	TP (mg L^{-1})	1.86	0.04	0.01
	SRP (mg L^{-1})	1.05	0.01	0.01
	NO_3 -N (mg L ⁻¹)	< 0.01	0.01	0.06
	$NH_3-N (mg L^{-1})$	<0.2	<0.2	<0.2
	рН	7.87	8.74	7.67
	Alkalinity (mg L ⁻¹)	88	106	100
	Hardness (mg L ⁻¹)	144	144	124
	SpCond (µS cm ⁻¹)	643	595	384
October	TP (mg L^{-1})	0.85	0.03	0.01
	SRP (mg L^{-1})	0.63	0.01	< 0.01
	NO_3 -N (mg L ⁻¹)	0.02	< 0.01	0.48
	NH_3 -N (mg L ⁻¹)	<0.2	< 0.2	<0.2
	pН	8.63	9.25	7.82
	Alkalinity (mg L ⁻¹)	166	80	114
	Hardness (mg L ⁻¹)	200	132	144
	SpCond (μ S cm ⁻¹)	777	337	432

Table 2.4. Water quality constituents measured in the initial re-flood water in the lab before being added to the sediment cores. Variables were measured once per location per date.



Figure 2.2. Mean (\pm 1SE, n=6) TP, SRP, NH₃-N, and NO₃-N concentrations measured in the surface water of the west pond sediment cores for the four treatment combinations (temperature: water source) over the incubation period. Amb/West, ambient temperature west pond water; +2/west, +2°C temperature west pond water; Amb/BC, ambient temperature Bear Creek water; +2/BC, +2°C temperature Bear Creek water.



Figure 2.3. Mean (± 1 SE, n=6) TP, SRP, NH₃-N, and NO₃-N concentrations measured in the surface water of the east pond sediment cores for the four treatment combinations (temperature: water source) over the incubation period. Amb/East, ambient temperature east pond water; +2/East, +2°C temperature east pond water; Amb/BC, ambient temperature Bear Creek water; +2/BC, +2°C temperature Bear Creek water.

Table 2.5. Two-way repeated measures ANOVA (a), results on concentration of TP, SRP, NH₃-N, and NO₃-N measured over time in the surface water in experimental sediment cores in July and October experiments. Asterisk (*) indicates the results of exploratory ANOVA analyses. Significant effects are in bold.

				TP		SRP		NH ₃ -N		N	D ₃ -N
Sediment Source	Date	Factor	DF	F	p-value	F	p-value	F	p-value	F	p-value
West Pond	July	Temperature	1	2.41	0.136	0.20	0.659	0.57	0.459	1.46*	0.242*
		Water Source	1	17.33	<0.01	30.92	<0.001	0.00	0.949	36.74*	<0.001*
		Temperature x Water Source	1	0.80	0.382	0.39	0.541	0.01	0.921	0.19*	0.673*
	October	Temperature	1	0.00*	0.946*	0.00*	0.843*	0.30*	0.593*	0.05*	0.816*
		Water Source	1	2.20*	0.154*	1.70*	0.207*	1.84*	0.190*	1.18*	0.290*
		Temperature x Water Source	1	1.87*	0.186*	0.40*	0.556*	1.91*	0.181*	3.42*	0.079*
East Pond	July	Temperature	1	0.04	0.838	0.11	0.748	0.08	0.785	2.97*	0.101*
	-	Water Source	1	0.98	0.333	0.00	0.961	0.79	0.383	26.50*	<0.001*
		Temperature x Water Source	1	0.00	0.963	0.28	0.600	0.07	0.799	0.20*	0.661*
	October	Temperature	1	0.00*	0.948*	0.09*	0.765*	0.11	0.746	0.12*	0.728*
		Water Source	1	1.51*	0.233*	0.23*	0.637*	5.28	0.032	0.78*	0.386*
		Temperature x Water Source	1	0.620*	0.440*	1.05*	0.319*	0.17	0.685	0.00*	0.950*

Maximum apparent nutrient release rate

Mean maximum apparent TP release rates from the sediment to the water column of west pond cores ranged from ~15 to ~50 mg m⁻² d⁻¹ in July and ~6 to ~60 mg m⁻² d⁻¹ in October (Figure 2.4, Table 2.6) and were significantly influenced by water source in both seasons (Table 2.7). Mean maximum apparent SRP release rate trends were similar to those of TP, with release rates exceeding TP release in some instances (Figure 2.4). SRP release rates were significantly influenced by water source treatment only in October (Table 2.7). Overall, the largest TP and SRP release rates were observed in sediment cores where west pond sediment was flooded with Bear Creek water, regardless of temperature (Figure 2.4, Table 2.6). NH₃-N release rates were generally larger in October, but relatively constant in all treatment combinations, and not significantly influenced by water source treatment or temperature (Table 2.6, 2.7). In general, NO₃-N release rates were constant in all treatment combinations, with a slight increase in release rates in October (Table 2.6). NO₃-N release rates were not significantly influenced by water source or temperature (Table 2.7).

Mean maximum apparent TP release rates from the sediment to the water column of east pond sediment cores ranged from ~2 to ~3 mg m⁻²d⁻¹ in July, and ~2 to ~4 mg m⁻²d⁻¹ in October (Figure 2.4, Table 2.6), and were not significantly influenced by water source or temperature (Table 2.7). Mean maximum apparent SRP release rates trends were similar to those of TP (Figure 2.4), and were not significantly influenced by water source or temperature; however, the interaction between temperature and water source did have a significant impact on SRP release in October (Table 2.7). Overall, east pond sediment TP and SRP release rates were approximately an order of magnitude smaller than release rates measured in the west pond (Figure 2.4, Table 2.6). NH₃-N release rates were relatively constant across all treatment combinations, but were slightly higher in July than in October (Table 2.6). NO₃-N release rates were relatively constant across all treatment combinations and in both seasons (Table 2.6). Neither NH₃-N nor NO₃-N release rates were significantly influenced by temperature or water source (Table 2.7).



Figure 2.4. Mean (± 1 SE, n=6) maximum apparent TP (total phosphorus) (A) and SRP (soluble reactive phosphorus) (B) release rates from west and east field sediment to the water column, and maximum TP (C) and SRP (D) increases in west and east field sediment core water columns. Results represent the four treatment (temperature: water source) combinations simulating hydrologic reconnection and climate warming from both the July and October experiment in the west and east field. A= ambient temperature; $+2=+2^{\circ}C$ temperature; NR= no reconnection water treatment, R= reconnection water treatment. Reconnection indicates Bear Creek water source treatment for the west and east field; no reconnection indicates west field water source treatment for water field sediment, and east field water source treatment for east field sediment.

Sediment Source	Date	Treatment Combination	TP	SRP	NH ₃ -N	NO ₃ -N		
			$mg m^{-2} L^{-1}$					
West Pond	July	Ambient: West Pond Water	15.66 ±5.77	36.32 ±7.80	42.34 ±10.09	20.47 ± 10.57		
	5	+2°C: West Pond Water	19.62 ± 5.87	29.38 ± 6.45	45.99 ±7.13	16.03 ± 17.89		
		Ambient: Bear Creek Water	39.07 ± 7.63	37.29 ±5.97	50.60 ±9.16	34.20 ± 1.13		
		+2°C: Bear Creek Water	49.90 ± 7.16	61.87 ± 13.71	49.98 ±9.53	15.40 ± 10.41		
	October	Ambient: West Pond Water	5.73 ±4.48	10.38 ± 3.20	48.85 ± 3.84	25.00 ± 4.11		
		+2°C: West Pond Water	14.42 ± 8.03	18.71 ± 8.78	58.59 ± 10.14	31.65 ±6.04		
		Ambient: Bear Creek Water	59.35 ± 10.35	37.46 ± 9.69	66.57 ± 18.49	28.27 ± 3.66		
		+2°C: Bear Creek Water	42.01 ± 10.20	34.83 ±8.14	58.94 ± 13.45	26.02 ± 8.64		
East Pond	July	Ambient: East Pond Water	2.41 ±0.65	1.64 ±0.39	71.49 ± 18.60	36.47 ±15.52		
	•	+2°C: East Pond Water	2.77 ± 0.80	1.51 ±0.29	63.25 ± 14.21	33.15 ±14.76		
		Ambient: Bear Creek Water	2.86 ± 0.43	1.67 ± 0.28	66.19 ±18.63	28.43 ± 14.28		
		+2°C: Bear Creek Water	3.11 ±0.60	1.88 ± 0.40	59.56 ± 14.69	21.13 ± 10.07		
	October	Ambient: East Pond Water	2.76 ± 0.94	0.64 ± 0.57	50.25 ± 23.14	31.46 ± 10.45		
		+2°C: East Pond Water	2.27 ± 0.38	0.14 ± 0.17	47.05 ± 20.51	43.66 ± 14.65		
		Ambient: Bear Creek Water	4.73 ±2.39	0.23 ± 0.11	55.34 ± 22.89	38.78 ± 12.34		
		+2°C: Bear Creek Water	2.53 ± 0.35	0.47 ± 0.25	51.10 ± 21.30	36.65 ± 14.90		

for west and east pond sediment cores under the various treatment combinations (temperature: water source).

Table 2.6. Comparison of the mean (±1 SE, n=6) maximum apparent release rates of TP, SRP, NH₃-N, and NO₃-N in July and October

				TP		SRP		NH ₃ -N		NO	D ₃ -N
Sediment Source	Date	Factor	DF	F	p-value	F	p-value	F	p-value	F	p-value
West Pond	July	Temperature	1	0.91	0.355	0.84	0.373	0.05	0.831	0.95	0.346
		Water Source	1	12.01	<0.01	3.03	0.102	0.77	0.395	0.20	0.658
		Temperature x Water Source	1	0.19	0.664	2.69	0.122	0.09	0.763	0.03	0.866
	October	Temperature	1	0.23	0.638	0.14	0.717	0.15	0.709	0.11	0.747
		Water Source	1	20.63	<0.001	7.83	<0.05	0.05	0.826	0.03	0.862
		Temperature x Water Source	1	2.08	0.170	0.50	0.489	0.01	0.959	0.44	0.516
East Pond	July	Temperature	1	0.32	0.583	0.03	0.868	1.13	0.305	0.13	0.726
		Water Source	1	0.55	0.472	0.67	0.427	0.41	0.531	0.50	0.491
		Temperature x Water Source	1	0.01	0.925	0.45	0.513	0.01	0.910	0.01	0.915
	October	Temperature	1	0.49	0.496	0.74	0.403	1.40	0.256	0.61	0.448
		Water Source	1	1.04	0.324	3.12	0.098	2.11	0.167	0.001	0.981
		Temperature x Water Source	1	0.03	0.860	5.05	0.040	0.03	0.870	1.23	0.285

Table 2.7. Blocked two way ANOVA results for TP, SRP, NH₃-N, and NO₃-N maximum apparent release rates depending on water

source and temperature treatments. Significant effects are in bold.

Maximum concentration increase

Mean maximum concentration increases of TP in west pond cores ranged from ~ 0.7 to ~2.6 mg L^{-1} in July, and ~0.2 to ~1.9 mg L^{-1} in October (Figure 2.4, Table 2.8), and were significantly influenced by water source in both seasons, but not by temperature (Table 2.9). Additionally, the water column increase of TP in July was significantly influenced by the interaction between water source and temperature (Table 2.9). Water column increases of SRP were significantly influenced by water source in both seasons (Table 2.9), and were at times larger than the maximum increase in TP concentration (Figure 2.4, Table 2.9). Overall, the largest increase in TP and SRP concentrations occurred in cores flooded with Bear Creek water (Figure 2.4, Table 2.8). Water column NH₃-N increases were similar across all treatment combinations (Table 2.8) and were not significantly influenced by water source or temperature (Table 2.9); however, concentration gains tended to be slightly higher in July than October (Table 2.8). NO₃-N concentration increases were significantly influenced by water source in July and October (Table 2.8) as gains tended to be larger in cores flooded with Bear Creek water in July, and conversely were larger in cores flooded with west pond water in October (Table 2.9). Temperature did not significantly influence the increase of NO₃-N (Table 2.9).

Mean maximum concentration increases of TP in east pond cores were smaller than those of the west pond (Figure 2.4, Table 2.8), and did not vary considerably across treatments or between seasons. Increases in SRP were similar across treatments and in both seasons. Overall, increases in TP and SRP in east pond cores were not significantly influenced by water source or temperature (Table 2.9). Water column concentration gains of NH₃-N did not vary greatly across treatments and were slightly larger in July than in October (Table 2.8), but were not significantly influenced by water source or temperature (Table 2.9). NO₃-N increases were similar across

treatments and in both seasons (Table 2.8), and were not significantly influenced by water source or temperature (Table 2.9).

Sediment Source	Date	Treatment Combination	TP	SRP	NH ₃ -N	NO ₃ -N
				mg	g L ⁻¹ ———	
West Pond	July	Ambient: West Pond Water	0.73 ±0.16	0.88 ±0.11	2.54 ±0.51	1.03 ±0.39
		+2°C: West Pond Water	1.07 ± 0.17	1.05 ± 0.18	3.01 ±0.66	0.62 ± 0.31
		Ambient: Bear Creek Water	1.79 ±0.36	1.35 ± 0.22	2.72 ± 0.58	1.55 ± 0.08
		+2°C: Bear Creek Water	2.63 ± 0.53	1.52 ± 0.22	2.77 ± 0.79	1.19 ±0.38
	October	Ambient: West Pond Water	0.19 ± 0.08	0.26 ± 0.06	1.15 ± 0.11	2.16 ±0.13
		+2°C: West Pond Water	0.59 ± 0.24	0.59 ± 0.21	1.80 ± 0.4	2.12 ± 0.17
		Ambient: Bear Creek Water	1.90 ± 0.27	1.37 ± 0.34	2.55 ± 0.87	1.17 ± 0.20
		+2°C: Bear Creek Water	1.02 ± 0.23	0.86 ± 0.18	1.90 ± 0.73	1.77 ±0.33
East Pond	Julv	Ambient: East Pond Water	0.12 ± 0.02	0.07 ± 0.02	2.86 ± 0.68	2.21 ±0.68
	J	+2°C: East Pond Water	0.14 ± 0.03	0.07 ± 0.01	2.60 ± 0.56	1.55 ± 0.50
		Ambient: Bear Creek Water	0.14 ± 0.01	0.08 ± 0.01	2.61 ± 0.67	2.38 ± 0.63
		+2°C: Bear Creek Water	0.14 ± 0.01	0.08 ± 0.02	2.32 ± 0.59	1.69 ±0.53
	October	Ambient: East Pond Water	0.07 ± 0.02	0.03 ± 0.01	2.14 ± 0.86	2.14 ±0.56
		+2°C: East Pond Water	0.08 ± 0.02	0.03 ± 0.01	1.99 ± 0.67	2.68 ± 0.82
		Ambient: Bear Creek Water	0.12 ± 0.05	0.03 ± 0.01	1.47 ± 0.58	2.06 ± 0.52
		+2°C: Bear Creek Water	0.07 ± 0.01	0.05 ± 0.02	1.28 ± 0.45	2.13 ± 0.67

Table 2.8. Comparison of the mean (±1 SE, n=6) maximum concentration increases of TP, SRP, NH₃-N, and NO₃-N in July and

October for west and east pond sediment cores under the various treatment combinations.

				TP		S	SRP		NH ₃ -N		D ₃ -N
Sediment Source	Date	Factor	DF	F	p-value	F	p-value	F	p-value	F	p-value
West Pond	July	Temperature	1	2.47	0.137	0.77	0.395	0.20	0.658	3.13	0.097
		Water Source	1	10.76	<0.01	5.68	<0.05	0.01	0.955	7.76	<0.05
		Temperature x Water Source	1	0.01	0.931	0.00	0.992	0.14	0.713	0.004	0.952
	October	Temperature	1	0.98	0.337	0.01	0.979	0.01	0.956	1.89	0.189
		Water Source	1	19.56	<0.01	12.93	<0.01	0.49	0.494	10.65	<0.01
		Temperature x Water Source	1	7.03	<0.05	3.31	0.089	4.26	0.057	2.38	0.144
East Pond	July	Temperature	1	0.46	0.508	0.05	0.819	1.56	0.231	1.67	0.216
		Water Source	1	0.43	0.524	0.63	0.439	1.44	0.249	0.08	0.777
		Temperature x Water Source	1	0.46	0.508	0.10	0.755	0.01	0.944	0.001	0.977
	October	Temperature	1	0.11	0.750	0.79	0.390	0.25	0.627	1.58	0.229
		Water Source	1	1.31	0.271	1.94	0.185	3.92	0.066	1.78	0.202
		Temperature x Water Source	1	0.66	0.430	1.30	0.272	0.01	0.956	0.96	0.344

Table 2.9. Blocked two way ANOVA results for TP, SRP, NH₃-N, NO₃-N and maximum concentration increases depending on water source and temperature treatments. Significant effects are in bold.

Discussion

Previous studies have shown that drained agricultural soils can release nutrients upon reflooding (Pant and Reddy, 2003; Duff et al., 2009; Ardón et al., 2010; Kinsman-Costello et al., 2014), but fewer studies have investigated nutrient dynamics in flooded agricultural soils in response to hydrologic reconnection as part of a wetland restoration. Here I show, based on laboratory experiments, that hydrologic reconnection of a creek and flooded agricultural area can result in nutrient release, and thus have negative impacts on downstream water quality. My results also indicate the degree to which nutrients serve as a source are influenced by land use history (Sharpley et al. 2013). Overall, the core water column nutrient concentrations, maximum apparent nutrient release rates, and maximum nutrient concentration increases from the July and October experiments clearly show that reconnecting the west pond to Bear Creek has the potential to significantly increase the flux of P from the sediment to the water column in this area.

The source of this release is likely the P that accumulated in the soils during the time the area was used for celery production, as well as the wetland history of the area. Phosphorus amendments in agricultural areas can accumulate in both biotic and abiotic compartments of the ecosystem (Reddy et al., 2005) due to the incorporation of P in organic matter and the adsorption of P by soil and sediments (Sharpley et al., 2013). Soil and sediment accumulation of P has been observed as a result of agricultural operations, including dairy ranching (Dunne et al., 2011), poultry production (Slaton et al., 2004), and the production of crops (Townsend and Porder, 2012) such as celery (Steinman and Ogdahl, 2011). Erosion, land development (Sharpley et al., 2013), reflooding (Kinsman-Costello et al., 2014), decreased external P loading (Fisher and Reddy, 2001), and changes in concentration gradients (Pant and Reddy, 2003) can mobilize this

accumulated P and result in a flux of P from the sediment to the water column. A concentration gradient was established in the west pond cores once the high P sediments were exposed to the relatively low P concentration in Bear Creek water, resulting in P release due to diffusion. This was not the case when west pond sediments were exposed to west pond water, as the P concentration in the water column was relatively high, and the sediments and water column were already in an equilibrated state. Indeed, distinct water column characteristics can be seen when examining the water in the two areas as measured in the field, as well as when comparing the characteristics of the water used to refill the core tubes. As a result, we observed a much smaller release of P in the cores where west pond sediments were exposed to west pond water as compared to when west pond sediments were exposed to Bear Creek water.

In several instances in my study, SRP maximum apparent release rates and maximum concentration increases in sediment cores from the west pond are reported as being larger than those measured for TP. Although this may appear to be an error, as SRP is indeed a component of TP, it is important to note that absolute SRP concentrations were always lower than TP concentrations, even though the maximum rates of increase and maximum concentration increases were sometimes greater. To explain, TP and SRP release rates in my study were sometimes calculated over different time periods in order to capture the maximum apparent rate. This contributed to SRP release rates exceeding TP release rates in some cases. Additionally, sediment SRP release rates as well as concentration increases can exceed TP release naturally, as was observed in multiple sediment cores in my study. In brief, this can occur when core water column SRP increases, but the concentrations of additional components of TP, such as sorbed and complexed inorganic or organic P decrease over the incubation time. This can then cause the maximum release rates and maximum concentration increases of TP to be lower in relation to

that of SRP. Although sorbed and complexed P fractions were not directly measured in my study, calculations in which water column SRP concentrations were subtracted from TP concentrations in the same core tube over the incubation time revealed multiple instances in which components of TP that were not directly measured decreased from initial concentrations over the incubation period. Because SRP release rates and concentration increases were typically similar if not larger when compared to TP release rates and concentration increases, this highlights the fact that the majority of the P being released from west pond sediments in certain cases is SRP. SRP is an extremely reactive and bioavailable form of P when compared to sorbed and complexed organic and inorganic P in aquatic ecosystems (Welch and Jacoby, 2004). This indicates even more pointedly the negative impacts that hydrologic reconnection of the two ponds to Bear Creek, without proper consideration of the ponds as P sources, could potentially have on downstream water quality.

In contrast to the west pond, my work indicates that reconnecting the east pond to Bear Creek will not significantly increase P release rate; however, P will still be released from the sediment to the water column. The lack of a water source effect in the east pond may be related to prior dredging, which removed much of the enriched sediment, exposing sediments that may have high P adsorption capacities. Dredging has been used to decrease internal nutrient loading in lakes, and has been shown to significantly reduce water column P concentrations in lakes when coupled with a reduction in external loading (Does et al., 1992; Kleeberg and Kohl, 1999). The relatively high concentrations of Ca and Fe in the east pond sediments may also have limited the amount of P release in this area. In wetlands, P solubility is largely regulated by the presence of Fe and Ca (Reddy et al., 1999), and Fe:P ratios greater than 15:1 have been shown to significantly predict and limit the release of soluble P from oxic sediments in shallow lakes

(Jensen et al., 1992). Yet, this ratio has proven to be a coarse indicator of potential P dynamics as measurements of total Fe and P include forms that may be unavailable for adsorption (Rydin et al., 2000), and the specific form of P in the sediment will also strongly influence its mobility under anoxic conditions (Pilgrim et al., 2007), as well as its solubility and bioavailability (Psenner et al. 1988). Despite these caveats, Fe:P ratios in the sediments of my study area were on average lower than the coarse threshold of 15:1; however, Fe:P ratios were significantly higher in the east pond than the west, potentially contributing to the smaller degree of P release I observed in the east pond. In alkaline environments, forms of Ca such as calcite or calcium hydroxide can bind P and form insoluble compounds such as apatite and hydroxyapatite (Cooke et al., 1993; Reddy et al., 1999). My study sites were somewhat alkaline, ranging in pH from 7.8 to 9.2, indicating the potential for this retention mechanism to occur. However, P binding to Ca may be a short-term phenomenon, as large percentages of this bound P can be released if water column pH decreases to less than ~8 (Diaz et al., 1994). In my study area, the removal of sediment P and organic matter by dredging, as well as the presence of high concentrations of Ca and Fe in the east pond sediments, could account for decreased concentrations of P in east pond water as well as low P release from the east pond sediment.

Given that the sediments of both ponds will release P, albeit to different degrees, there are water quality implications for downstream water bodies. It is likely that a substantial amount of P released from sediments within the two ponds would reach Bear Lake due to the short distance between the ponds and the lake. In response to excess algal growth and elevated P concentrations, Bear Lake was placed on the Section 303(d) list of impaired and threatened waters as part of the Federal Clean Water Act in 2008 (MDEQ, 2008b). As required, the state of Michigan then developed a Total Maximum Daily Load (TMDL) for the lake, stipulating a 50%,

or 848 lb/yr, reduction in the external load of P, in order to reduce the seasonal (April-September) TP average from 0.044 to 0.03 mg L^{-1} P in the water column (MDEQ, 2008a). However, my work indicates that reconnection of the two ponds to Bear Creek will likely result in more P reaching Bear Lake, unless the restoration design takes into consideration the ponds as potential sources of P.

Hydrologic reconnection also has implications beyond those related to nutrient exchange. When two previously separated biological communities mix, species can coexist or be added or subtracted (Livingston et al., 2013), which can then influence biogeochemical processes in the area where mixing occurs. With respect to species addition, the migration of fish species from Bear Creek and Bear Lake into the ponds could potentially increase nutrient release. Studies have shown that P excretion from fish can constitute a large fraction of the P load in lakes (Persson, 1997), in addition to the direct release of N and P by benthic feeding fish, such as carp (Breukelaar et al., 1994). Conversely, reconnection of the ponds to Bear Creek would likely stimulate deposition of suspended sediments in the two ponds, which would increase nutrient retention; sedimentation of nutrients bound to particles is common in wetlands (Reddy and DeLaune, 2004), and wetlands of sufficient size can significantly reduce the amount of total suspended solids in the water column during flood events (Koskiaho, 2003). Reestablishment of wetland vegetation in the ponds could also aid in retention of N and P due to their ability to take up and store N and P in their biomass (Reddy and DeLaune, 2004). However, the majority of nutrients stored in the aboveground biomass will be released after a short time due to the relatively short cycles of growth and senescence in wetland plants (Richardson, 1985).

Previous work has found that elevated temperatures can increase the release of P from sediments (Holdren and Armstrong, 1980; Steinman et al. 2009), and limit the amount of P

adsorption by sediment particles (Redshaw et al., 1990); however, this result was not observed in my study. The studies cited above attribute increased P release and decreased P adsorption to reducing conditions created by the stimulation of benthic microbial respiration at higher temperatures. The depletion of sediment oxygen can then result in facultative microorganisms reducing ferric iron, a major mineral associated with P binding, by using it as an electron acceptor during metabolism (Reddy et al., 1999). The reduction of Fe results in the release of previously bound P. Because the water column of my sediment cores was maintained in an oxic condition, this may have negated the impacts of increasing microbial activity on sediment oxygen concentrations, and masked the potential effect that increasing temperatures would have on the anoxic/oxic boundary in the sediment. Additionally, the relatively small temperature difference between my two treatments coupled with the large amount of inter-site variability in sediment chemistry and physical properties throughout my study area may have limited my availability to detect a significant impact due to temperature.

In contrast to the increased release of P due to the simulated reconnection of Bear Creek to the west pond, I observed no consistently significant impact of water source on N dynamics in either pond. Yet, previous work has found that restoring wetland hydrology to a former agricultural unit resulted in that area acting as a significant source of NH₄-N and dissolved organic N (Ardón et al., 2010). Although I did not observe a strong response of N concentrations due to water source treatment, I was still able to observe consistent patterns of N dynamics in my core tubes. These dynamics represent microbial reactions that occur as part of the aquatic N cycle; however, they may not be indicative of what will happen in the two ponds in situ. I contend that the inverse relationship in NH₃-N and NO₃-N dynamics in my study could be explained by the interacting processes of ammonification in the anoxic sediment and nitrification

in the oxic water column. First, water column NH₃-N/NH₄-N concentrations increased over the incubation time due to the mineralization of organic N in the sediment. Because of this, NH₃-N/NH₄-N concentrations reached sufficient levels that facilitated the proliferation of nitrifying microbes which use NH_3-N/NH_4-N as a substrate. Subsequently, we observed a decrease in NH_3-N/NH_4-N as a substrate. N/NH₄-N concentrations and an increase in NO₃-N concentration due to this reaction. This is a textbook example of two reactions that occur in the N cycle; however, the increase of NH₃-N/NH₄-N concentrations that was observed in my sediment cores may not be an accurate representation of what would happen in the two ponds as much of NH₃-N/NH₄-N produced due to mineralization would be taken up by algal cells in the water column, and not allowed to concentrate. Because my cores were a closed system, were incubated in the dark, and the majority of algal cells were filtered out of the water column, this may have prevented normal algal NH₃-N/NH₄-N uptake and allowed NH₃-N/NH₄-N concentrations to rise in the water column. Although this response may not be an accurate representation of what would happen in situ in the two fields, it can still serve as a demonstration of the microbial transformations that occur in the aquatic N cycle. However, direct measurements of N cycling processes are needed to confirm the mechanisms at work.

The contrasting fates of N and P in agricultural systems also could help explain why I observed no significant impact of water source on N dynamics. Unlike P, which has the tendency to accumulate in the soils and sediments of agricultural systems due to its binding to soil minerals (Hill and Robinson, 2012; Sharpley et al., 2013), reactive N is relatively more mobile, and can be lost from an ecosystem through volatilization to gaseous forms of N or transport of soluble reactive N in groundwater (Robertson and Vitousek, 2009). Consequently, there may be

a relatively smaller buildup of legacy N compared to P in agricultural systems, and because of this a smaller risk of release in response to changes in hydrology.

In addition to the lack of an effect from water source treatment, temperature also had no significant impact on N release in either pond. This may be partly due to the fact that temperature affects many different, and sometimes opposing, transformations in the aquatic N cycle such as mineralization, nitrification, and denitrification (Kadlec and Reddy, 2001). Thus, temperature may have stimulated multiple opposing microbial N transformations, resulting in a zero net difference of source/sink dynamics. Again, I observed large amounts of inter-site variability within each pond; this variability in sediment characteristics likely affected N dynamics, and possibly hindered my ability to find statistically significant effects on nutrient flux among my four treatment combinations.

Seasonality is generally recognized as a major influence on ecosystem functioning in wetlands (Kadlec and Reddy, 2001); yet, in general I did not see a large disparity in nutrient dynamics between my two seasonal experiments, besides the decrease in the magnitude of P concentrations in October compared to July. This may be because the temperature differences were relatively modest (23 vs. 17°C); a larger temperature difference may very well have produced different results. It has been shown that seasonal changes in temperature have a part in controlling soil moisture and biogeochemical processes regulating organic matter decomposition, enzyme activity, dissolved organic matter production, and the emission of various gasses (Reddy and DeLaune, 2004). Additionally, because my experiments were performed in the laboratory, many other seasonal changes that effect wetlands were not able to be incorporated. Seasonal hydrologic changes have been shown to strongly impact sediment redox state (Reddy and DeLaune, 2004), plant growth, and nutrient loading (Kadlec and Reddy, 2001). Additionally, the

seasonal growth and senescence patterns of wetland plants can also influence nutrient dynamics and result in greater nutrient retention in the growing season, with subsequent nutrient release when the plants senesce and decompose (Kröger et al., 2007).

Conclusions

Intact sediment cores from two flooded fields that were formerly used for celery farming were used to estimate the dynamics of N and P in response to hydrologic reconnection and climate warming. My results showed that sediments from the two ponds have the potential to contribute P to the water column once the two areas are reconnected to Bear Creek due to the presence of legacy P; however, reconnection significantly increased P release only in the west pond. The flux of N from both ponds was not consistently and significantly influenced by reconnection. In addition, increased incubation temperatures did produce a consistently significant effect on the flux of N or P from either pond in this study. Overall, the effects of warming on nutrient dynamics were much less pronounced than effects related to previous land use.

Because the reconnected wetlands would discharge to a water body that is already impaired due to high P concentrations, any restoration design must take into consideration water quality as well as habitat improvement. Preventative measures such as chemical amendments or dredging may potentially remove or bind a large amount of the P that is present, and make the area more suitable for P retention. This study reinforces the need to study sediment nutrient content and release prior to any wetland restoration, especially when the proposed restoration area is on agricultural land.
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Chapter III

Conclusions and Synthesis

High quality sustainable freshwater resources are essential to all life on earth. In addition to the fundamental provision of drinking water, freshwater resources also provide services such as the facilitation of large scale industrial production, irrigation, flood control, hydroelectric power production, recreation, the production of various foods, and essential habitat for large amounts of plant and animal life (Jackson et al., 2001; Baron et al., 2002). In spite of these benefits, large scale human activities such as agriculture, fossil fuel combustion, and land development (Crutzen, 2002) have negatively impacted water quality through eutrophication (Smith, 2003), wetlands loss (Millennium Ecosystem Assessment, 2005), and climate change (Schindler, 2001). As a result, water quality is declining on a global scale (Millennium Ecosystem Assessment, 2005; Welch and Jacoby, 2004).

In response to this global decline, many environmental restoration projects have been initiated that aim to improve water quality. Naturally occurring wetland ecosystems typically improve water quality; thus, because large areas of wetlands have been degraded and destroyed throughout history, wetland restoration and creation is viewed as a viable way to facilitate water quality improvement (Zedler, 2000).Yet, the effectiveness of wetland restoration can be limited by prior land use of the restoration area—hence, rehydration of previously drained agricultural areas as part of restoration may have negative impacts on water quality (Pant and Reddy, 2003; Duff et al., 2009; Ardón et al., 2010; Kinsman-Costello et al., 2014). Additionally, changes in hydrology and temperature due to climate change are seen as major threats to natural and restored wetlands (Ferrati et al., 2005), and have the possibility to alter wetland biogeochemistry and associated ecosystem services (Erwin, 2009).

Changes in hydrology

Previous studies have demonstrated that drained agricultural areas can release nutrients in response to flooding, but relatively less is known in regards to how flooded agricultural areas will respond to changes in hydrology. My study indicated that hydrologic reconnection of a stream and floodplain within a flooded agricultural area can potentially stimulate nutrient release, and thus have negative impacts on downstream water quality. In the west pond of my study area, I clearly observed that hydrologic reconnection to Bear Creek will significantly increase the flux of P from the sediment to the water column in that area. West pond sediment cores flooded with Bear Creek water released TP at rates and concentrations that were significantly greater than when west pond cores were flooded with west pond water. Indeed, west pond TP release rates approached ~60 mg $m^{-2} d^{-1}$ when flooded with Bear Creek water. Overall, west pond TP release rates ranged from ~6 to ~60 mg $m^{-2} d^{-1}$ when considering both water source treatments, indicating a consistent potential for P release. Although hydrologic reconnection did not stimulate increased P flux in the east pond, I also observed a release of P from the sediment to the water column in this area regardless of water source treatment (~2 to ~5mg TP $m^{-2} d^{-1}$). In comparison to other systems, Carter and Dzialowski (2012) measured TP release using intact sediment cores incubated under anoxic conditions from 17 reservoirs of varying trophic status conditions and found that mean TP release rates ranged from ~2 to ~36 mg m⁻² d⁻¹. Additionally, Nürnberg and Lazerte (2004) report mean sediment TP release rates under anaerobic conditions

ranging from ~0 to ~30 mg m⁻² d⁻¹ when analyzing 91 small lakes ranging from oligotrophic to hyper-eutrophic. The release rates I measured when sediments from the two ponds were flooded with Bear Creek water and incubated under *aerobic* conditions further illustrate the large potential of my study area overall, and the west pond especially, to be a large and significant P source.

To more clearly examine and illustrate how reconnection could impact water quality and the load of P supplied to Bear Lake, I used my data to calculate different scenarios of potential TP loading that would occur if the two ponds are reconnected to Bear Creek. In order to do this, I first calculated average sediment TP release rates for both ponds using data from my sediment coring experiment in Chapter II. This calculation was based on an estimate of average TP release rate over the entire incubation time. This calculation is in contrast to the maximum release rates that were calculated in Chapter II, which are unlikely to persist over long time periods in nature, and hence would have likely overestimated true potential loading. In brief, average TP release rates were calculated using the change from initial to final water column TP concentration for sediment cores that were flooded with Bear Creek water in July and October experiments. Because there was no significant effect of temperature on P release, release rates from cores incubated at ambient and $+2^{\circ}$ C temperature treatments were combined to determine the mean average release rate (n=4). From this, I then calculated maximum, mean, and minimum, average TP release rates. Maximum, mean, and minimum average release rates (mg TP $m^{-2}d^{-1}$) were then converted into loadings (lbs TP d⁻¹), in order to be consistent with the format of the Bear Lake TMDL. These daily loadings were then extrapolated to calculate the amount of loading that would be expected to occur using three different scenarios of loading days per year. The three scenarios were 270 days, 182 days, and 91 days, representing liberal, moderate, and conservative

periods of release. I did not include 365 days, as it is highly unlikely release is occurring during winter months due to the cold temperatures (cf. Steinman et al. 2009). Additionally, I incorporated three scenarios in which I varied the percentage of the TP load leaving the pond sediments that would actually reach Bear Lake. The three scenarios of load percentage reaching Bear Lake were 100%, 50%, and 10%. Again, because of the short distance between the ponds and Bear Lake, it is likely that a higher rather than lower percentage of TP released by the ponds would enter the lake basin. Finally, from the calculations of average release rates, average daily loadings, period of loading, and percentage TP reaching Bear Lake, I estimated the amount of TP that would be expected to enter Bear Lake upon reconnection of the two ponds to Bear Creek on an annual basis. Although the designations used in this analysis are somewhat arbitrary, it nonetheless helps to visualize a wide range of potential P loading from the ponds to Bear Lake, and allows for estimates of uncertainty.

The results of the above calculations show that reconnecting the two ponds to Bear Creek without accounting for the potential for P release could add large and wide ranging amounts of TP to Bear Lake (Table 3.1, Table 3.2). Overall, the calculations indicate that the west pond has the potential to contribute 10-959 lbs TP yr⁻¹ (Table 3.1) to Bear Lake, and the east pond can potentially contribute 0.4-15 lbs TP yr⁻¹ (Table 3.2). Again, this difference in loading between the two ponds likely relates to the previous dredging of the east pond and its effects on sediment TP and mineral content. Considering that just the Bear Creek TP load was estimated to be 1,529 lbs TP yr⁻¹ (MDEQ, 2008), the addition of TP from the pond after reconnection could increase the Bear Creek TP load by over 60% at the highest load scenario (i.e. to ~2,500 lbs TP yr⁻¹). In order to reach the TMDL stipulated goal of 0.03 mg L⁻¹ TP in the Bear Lake water column, it was estimated that the entire load of P of the lake would need to be reduced from 3,387 to 1,458

lbs TP yr⁻¹ (MDEQ, 2008). Hence, reconnecting the ponds to the creek without any nutrient reduction mitigation measures would likely exacerbate the eutrophication and harmful algal bloom conditions in Bear Lake, and seriously limit the community's ability to meet the TMDL target for TP. Overall, it is clear that reconnecting the two ponds to Bear Creek without proper restoration would produce effects counteractive to the TMDL and to water quality goals for Bear Lake.

Table 3.1. Summary of results illustrating the additional TP load that would be added to Bear Lake once Bear Creek is reconnected to the west pond when considering a range of: average release rates; average daily loads; period of loading; and percent of the load reaching Bear Lake.

West Pond																											
	Maximum									Mean										Minimum							
Avg. release rate $(mg TP m^{-2}d^{-1})$	18.09									10.87									5.75								
Avg. daily load (lbs TP d ⁻¹)	3.55									2.13									1.13								
Period of yearly loading (days)	270			182			91				270			182		91			270			182			91		
Percent load reaching Bear Lake (%)	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10
Load (lbs TP yr ⁻¹)	959	479	96	646	323	65	323	162	32	576	288	58	388	194	39	194	97	19	305	152	30	205	103	21	103	51	10

Table 3.2. Summary of results illustrating the additional TP load that would be added to Bear Lake once Bear Creek is reconnected to the east pond when considering a range of: average release rates; average daily loads; period of loading; and percent of the load reaching Bear Lake.

East Pond																											
	Maximum									Mean										Minimum							
Avg. release rate (mg TP m ⁻² d ⁻¹)	0.53									0.48									0.38								
Avg. daily load (lbs TP d ⁻¹)	0.057									0.051									0.041								
Period of yearly loading (days)	270			182			91			270			182			91			270			182			91		
Percent load reaching Bear Lake (%)	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10	100	50	10
Load (lbs TP yr ⁻¹)	15	7.6	1.5	10	5.1	1	5.1	2.6	0.5	14	6.9	1.4	9.3	4.6	0.9	4.6	2.3	0.5	11	5.5	1.1	7.4	3.7	0.7	3.7	1.9	0.4

It is well known that historic human activity and the legacy of previous land use influences ecosystem structure and function (Foster et al., 2003). Often, the specific land use history of an area can delay or prevent environmental recovery, as well as result in a disparity between expected environmental improvements and reality (Carpenter, 2005; Meals et al., 2010; Jarvie et al., 2013). Previous work has indicated that historic agricultural land use has had a significant impact on terrestrial and aquatic ecosystems worldwide (Foster et al., 2003). One significant impact of agricultural land use is legacy nutrient buildup in soil (Slaton et al., 2004; Dunne et al., 2011; Townsend and Porder, 2012; Mattingly and Orrock, 2013; Sharpley et al., 2013), as is the case in my study area where sediment TP concentrations averaged \sim 3750 mg kg⁻¹ in the west pond, and ~960 mg kg⁻¹ in the east pond. As evidenced by this study and others (Pant and Reddy, 2003; Steinman and Ogdahl, 2011), this buildup of nutrients can impact source/sink nutrient dynamics in restored wetland areas. In addition to the effects of legacy nutrients on wetland restoration, agricultural nutrient enrichment can also have other broad ecological impacts and influence terrestrial and aquatic invasive plant colonization (Chambers et al., 2008; Kuhman et al., 2011), community composition (Leibold, 1999; Molofsky et al., 2013), and ecosystem biodiversity (Isbell et al., 2013; Brönmark and Hansson, 2002). Thus, it is important that all associated components of a restoration effort consider the specific deficiencies and challenges represented within a proposed restoration area before beginning the project (Hobbs, 2007).

In my study, N release was generally unaffected by the different water source treatments, which may be related to the contrasting fates of excess N and P in agricultural systems. Unlike P, which has the tendency to accumulate in the soils and sediments of agricultural systems when excess concentrations are applied due to its binding to soil minerals (Hill and Robinson, 2012;

Sharpley et al., 2013), reactive N is highly mobile in the biosphere, and excess N not taken up by crops can be lost from an ecosystem through processes such as volatilization to gaseous forms of N, and transport of soluble reactive N in groundwater (Robertson and Vitousek, 2009). Confounding effects of my experimental design also may have hindered my attempts to draw conclusions in regards to the effects of reconnection and temperature on N dynamics within my study site. As noted above and in Chapter II, the N cycle is mediated by many different biological processes that occur under specific environmental conditions. Because my study was conducted in the lab under controlled environmental conditions, the N dynamics I observed may not be a realistic example of what may occur in my study area. The sediment cores used in my study were a closed system and incubated in the absence of light; because of this, it is possible that the inverse relationship in NH₃-N and NO₃-N dynamics that was observed could be explained by the interacting processes of ammonification in the sediment and nitrification in the oxic water column as conditions within the core tube changed over the incubation period (Taylor and Townsend, 2010). Thus, I propose that the initial increase in NH₃-N from ammonification was followed by both a decrease in NH₃-N and an increase in NO₃-N, as the conditions became more favorable to nitrifying microbes in the water column. Although these are both transformations that occur in the aquatic N cycle, it is unclear if these N dynamics are an artifact of the experimental set-up, or representative of in situ conditions. More work is needed to examine the impact of temperature and hydrology on nitrogen dynamics, as other studies have observed a significant effect of hydrologic reconnection and temperature on wetland N dynamics (Ardón et al., 2010; Kadlec and Reddy, 2001)

Many studies have been performed with the intent of identifying the nutrients that exert the most control over primary productivity in freshwater ecosystems. This research is beneficial for enhancing our biological knowledge of freshwater environments, and also informs us as to what nutrients should be controlled when trying to limit eutrophication. Because costs are higher to control both N and P, rather than just one of the two nutrients individually, the results of this type of work have the potential to have a broad economic impact on water quality improvement related projects (Schindler, 2012). The P limitation paradigm holds that P is the main nutrient controlling freshwater primary productivity (Schindler, 1974; Schindler et al., 2008). In recent history, this paradigm has strongly influenced the understanding, management, and legislation in regards to freshwater eutrophication, resulting in actions centered on the control of P. However, as research on nutrient limitation has continued, more recent work has begun to challenge the P paradigm, with the recognition that both N limitation (Lewis and Wurstbaugh, 2008; North et al., 2007) and co-limitation by N and P (Elser et al., 2007) are more common and widespread than previously thought. Indeed, simultaneous enrichment by N and P can lead to dramatically higher levels of production than when N or P are supplied individually (Elser et al., 2007). Although critics of N limitation point out issues of study scale, community succession, and gradual changes in biogeochemical cycles (Schindler, 2012), it is becoming apparent that management of both N and P is the most effective method to attempt to limit eutrophication and improve water quality in many water bodies (Conley et al., 2009). Thus, wetland restoration in the context of improved nutrient retention and water quality should consider both N and P.

Changes in climate

In my study, increased temperatures did not produce a consistently significant influence on the dynamics of N and P. However, other studies have shown that rising temperatures, and changes in hydrology and weather patterns due to climate change (Mitsch and Hernandez, 2013), are expected to alter wetland biogeochemical processes and wetland sustainability (Burkett and Kusler, 2000; Kadlec and Reddy, 2001). Due to the effects of temperature on microbial metabolism, climate warming has the capacity to alter the cycling of N and P, potentially affecting the source/sink dynamics of these elements in wetlands (Kadlec and Reddy, 2001). Previous work has also found that increases in temperature can stimulate the release of P from sediments (Holdren and Armstrong, 1980; Steinman et al., 2009), and limit the amount of P adsorption by sediment particles (Redshaw et al., 1990). The above studies attribute the observation of increased P release to reduced sediment oxygen concentrations resulting from increased benthic microbial respiration at higher temperatures. Redox-driven reactions will result in the release of phosphorus that is associated with ferric (Fe⁺³) hydroxide (Mortimer, 1941). Increased P release in response to elevated temperatures could also be a result of thermally sensitive sediment processes related to P dynamics such as diffusion coefficients or rates of iron oxidation, mineralization, or adsorption (Anthony and Lewis, 2012).

In regards to N, various microbial N transformations such as organic N mineralization, nitrification, as well as denitrification, all proceed more rapidly at higher temperatures to a point (Kadlec and Reddy, 2001). Thus, the effects of warming temperatures could potentially result in zero net change in wetland N dynamics due to the relative acceleration of multiple opposing transformations within the microbial N cycle. Additional work needs to be done to determine the overall net effect on source/sink N and P dynamics in natural wetland environments in response to warming temperatures, as well as what the effects may be in restored wetland environments.

In addition to the vulnerability of wetland biogeochemistry to elevated temperatures, wetlands are also by nature susceptible to changes in hydrology. Consequently, predicted

changes in hydrology due to climate change have the potential to impact wetlands species diversity, biogeochemistry, and sustainability (Millennium Ecosystem Assessment, 2005). In Great Lakes coastal wetlands, climate change is expected to cause a decline in water levels to some extent (Hayhoe et al., 2010), however, there are issues with the methodologies used to calculate these predictions (Lofgren et al., 2011). If water levels do indeed drop, it has been shown that this effect may facilitate the spread of invasive or nuisance species, which can potentially influence community composition, biodiversity, and ecosystem function (Lishawa et al., 2010). Precipitation changes due to altered weather patterns may also lead to the loss of wetlands in certain areas due to drying out, such as prairie pothole and vernal pool wetlands (Erwin, 2009). Additionally, when extended drying periods are followed by extreme precipitation events, this may impact wetland biogeochemistry and stimulate nutrient release due to redox-driven dynamics associated with sediment desiccation followed by inundation (Steinman et al., 2012). Therefore, the combined effects of rising temperatures and changes in hydrology due to climate change represent a large threat to many components of wetland biogeochemistry, ecology, and sustainability.

Finally, although I did not see a large disparity in my results between the July and October experiments, this may be because the temperatures I used were relatively warm and the differences were relatively modest (23 vs. 17°C); a larger temperature difference may very well have produced different results. Seasonal hydrologic changes have been shown to strongly impact sediment redox state (Reddy and DeLaune, 2004), plant growth, and nutrient loading (Kadlec and Reddy, 2001). Additionally, seasonal changes in temperature have a part in controlling soil moisture and biogeochemical processes regulating organic matter decomposition, enzyme activity, dissolved organic matter production, and the emission of various gasses (Reddy

and DeLaune, 2004). Finally, the seasonal growth and senescence patterns of wetland plants can influence nutrient dynamics and result in greater nutrient retention in the growing season, with subsequent nutrient release when the plants senesce and decompose (Kröger et al., 2007). Thus, seasonality should be considered when studying wetland areas in regards to restoration, and potential changes in the future.

Potential solutions

Management techniques to control water column nutrient concentrations and sediment nutrient release are plentiful and diverse, and each technique has its own associated advantages and disadvantages. Several common management techniques for lakes and wetlands include phytoremediation, chemical inactivation, artificial sediment aeration, and dredging (Cooke et al., 2005). Phytoremediation, or the use of plants and their associated microbes to remove pollutants, is one of the less expensive and more publicly supported nutrient concentration management techniques (Pilon-Smits, 2005). In order for phytoremediation to be successful, however, plant biomass must be removed annually after each growing season, which leads to increased ecosystem disturbance and habitat loss. Additionally, it may take longer to reach restoration goals using phytoremediation when compared to other management techniques (Schnoor et al., 1995). Chemical inactivation of nutrients using compounds such as aluminum sulfate (alum) is another commonly used management technique, but the efficacy of alum application is variable (Cooke et al. 2005). Alum application results in the removal of P through the coagulation/entrapment of phosphorus containing particulates, precipitation of insoluble AlPO₄, and by sorption of P on the surfaces of aluminum hydroxide (floc) polymers that form a cap on

the sediment surface (Kennedy and Cooke, 1982). Negatively, alum application can adversely impact benthic invertebrates in the short term after application (Steinman and Ogdahl, 2006), and can produce effects toxic to aquatic organisms when applied in water bodies that have a pH of below ~6 or above ~8 (Kennedy and Cooke, 1982; Cooke et al., 1993). Artificial hypolimnetic oxidation, when sufficient sediment iron is present, has proven to significantly increase the rate of P sedimentation from the water column (McQueen et al., 1986), and reduce the concentration of ammonia in the water column during stratification (Liboriussen et al., 2009). Yet, sediment oxidation can increase hypolimnetic temperatures (Liboriussen et al., 2009), and potentially have an adverse effect on populations of cold water benthic fauna (Jyväsjärvi et al., 2013). Finally, dredging is one of the most effective management techniques for controlling excess nutrient concentrations (Cooke et al., 2005) because it removes the top layer of sediment that contains the majority of nutrients and organic matter, and has a long-term beneficial impact. When external loading of nutrients is small, dredging has been shown to significantly reduce water column P concentrations in lakes (Does et al., 1992; Kleeberg and Kohl, 1999). Adversely, sediment dredging is costly, and is extremely disruptive to benthic habitat.

Based on the results of my study, I support the previous suggestion to dredge the enriched sediments in both ponds and apply alum in order to manage the excess P in the restoration area (Steinman and Ogdahl, 2013). This is reasonable due to the large amounts of P in the sediment of the west pond especially, as well as the elevated concentrations of P in the water column. However, water column pH will have to be monitored closely because the pH I measured was on average >8 in both ponds during both experiments. When alum is applied at pH levels above or below an approximate range of 6-8, it can lead to increased aluminum solubility and toxicity (Kennedy and Cooke, 1982). The addition of a buffer solution to the water prior to alum

treatment can manipulate pH into a range acceptable for application and reduce the possibility of aluminum toxicity.

Summary

Overall, my results showed that the two ponds involved in this study have the potential to contribute P to the water column once they are reconnected to Bear Creek due to the presence of legacy P; however, reconnection significantly increased sediment P release only in the west pond. This is likely because the east pond was previously dredged, while the west pond was not. The flux of N from both ponds was not consistently and significantly influenced by reconnection. This observation may be due to differences in how N and P accumulate and are removed from the sediment, as well as possible confounding effects of my study design. In addition, increased incubation temperatures did not consistently and significantly affect the flux of N or P from either pond in this study. Although I was not able to detect a significant impact of temperatures and other effects of climate change such as alteration of precipitation patterns and increased extreme weather events may influence wetland nutrient dynamics.

Because the concentrations of sediment and water column P are so high in the two ponds, the area will not be suitable in its current state to serve as a sink of the Bear Creek P load if it is hydrologically reconnected. The sediments within the ponds will in fact be a net contributor of P to Bear Creek and downstream Bear Lake if reconnection occurs without proper remediation. Hence, reconnecting the ponds to the creek without any nutrient reduction mitigation measures would likely exacerbate the eutrophication and harmful algal bloom conditions in Bear Lake, and

seriously limit the community's ability to meet the TMDL target for TP. Preventative measures such as chemical additions, phytoremediation, or dredging may potentially remove or bind a large amount of the soluble P that is present. In the case of this specific restoration, I support the previous suggestion to dredge the enriched sediments in both ponds and apply alum in order to manage the excess P in the restoration area. Additionally, before reconnection, I recommend verifying that water column P concentrations in the two ponds are consistently below 0.03 mg L⁻¹, which is the target concentration in the Bear Lake TMDL, and that the sediments will not release any appreciable amount of P to the water column. Preferably, the sediments would have the potential to retain P when reconnection occurs. The establishment of wetland vegetation in the two ponds prior to reconnection may also aid in sediment and nutrient retention.

Finally, my work supports the idea that the application of scientific research to real world environmental problems not only provides academic insight, but also increases the rigor and success of associated environmental restoration efforts (Omeron, 2003). In general, it is understood that including and developing the scientific research basis for restoration is essential if current and future restoration efforts are to be successful (Hobbs, 2007). Yet, in addition to scientific research based aspects of environmental restoration, it is also important to consider the socio-economic side of restoration efforts. Indeed, it has been suggested that perhaps the greatest need in environmental restoration currently is for the development of a synthetic approach in which we can integrate the ecological and socio-economic aspects of the issues surrounding environmental restoration and the setting of restoration goals (Hobbs, 2007). Beyond setting restoration goals, additional areas for collaboration between the two interests may include, but are not limited to: choosing areas for restoration; determining pre, during, and post restoration monitoring; and choosing the technical restoration design (Figure 3.1). Although this does not

guarantee success, it sets the stage for a well thought out and designed project which considers the specific goals of the restoration, community needs/desires in the area, as well as ways to measure restoration success and distribute the results to interested individuals (Hobbs, 2007). In addition to the environmental and community benefits of successful restoration, the gained understanding of ecosystem processes and scientific theory resulting from the research associated with these projects benefits academia, and serves to enrich the growing literature concerning environmental restoration and its associated techniques. Thus, all groups involved in restoration benefit by working together. In an era where the effects of humanity on the environment are rapidly expanding (Crutzen, 2002), environmental restoration and the recovery of lost ecosystem services is increasingly necessary on a global scale. Hence, restoration efforts should be thoughtfully considered and designed in order to provide not only the maximum amount of environmental and ecological improvement, but also address associated socioeconomic needs.



Figure 3.1. Conceptual model diagraming the various questions that should be addressed as part of environmental restoration efforts, as well as whether those questions fit under the umbrella and responsibility of scientific research, or as part of the socio-economic concerns of the project.

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