Biogeochemical Hotspots:

Role of Small Water Bodies in Landscape Nutrient Processing

by

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Author's Declaration

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Statement of Contributions

I would like to acknowledge my co-authors Drs. Kimberly Van Meter and Nandita Basu who contributed to the research described in this thesis.

Abstract

Increased loading of nitrogen and phosphorus from agricultural and urban intensification has led to severe degradation of inland and coastal waters. Lakes, reservoirs, wetlands, and streams retain and transform these nutrients, thus regulating their delivery to downstream waters. While the processes controlling nitrogen and phosphorus removal from the water column are relatively well-known, there is a lack of quantitative understanding of how these processes manifest across spatial scales.

This thesis explores the relationship between hydrologic and biogeochemical controls on nutrient processing in a lentic water body (lakes, reservoirs, and wetlands). Here, our work revolves around three research questions: 1) What are the emergent patterns between nutrient processing rates and residence times in lentic systems? 2) What are the underlying mechanisms contributing to the observed patterns? 3) What is the relative magnitude of nutrient retention as a function of wetland size? These questions are addressed through a meta-analysis of existing literature, the development of a modelling framework, and an analysis through upscaling of the results.

Within the meta-analysis, we synthesized data from 600 sites across the world and various lentic systems (wetlands, lakes, reservoirs) to gain insight into the relationship between hydrologic and biogeochemical controls on nutrient retention. Our results indicate that the first-order reaction rate constant, k [T^{-1}], is inversely proportional to the hydraulic residence time, τ [T], across six orders of magnitude in residence time for total nitrogen, total phosphorus, nitrate, and phosphate. This behavior prompted the hypothesis that the consistency of the relationship points to a strong hydrologic control on biogeochemical processing. Specifically, we hypothesized that small systems have a higher sediment surface area to water volume ratio that would facilitate the biogeochemical processes of the system.

To validate the hypothesis, we developed a two-compartment model that links the major nutrient processes with system size: the water column and the reactive sediment zone are coupled through a mass exchange process, with nitrogen being removed through denitrification in the sediments and phosphorus transferring to long term storage via particle settling. The model analyses validated our hypothesis by replicating the empirical inverse k-τ relationship through deterministic modelling. Additionally, we demonstrated the inverse relationship between the sediment surface area to water volume ratio and size through an analysis of the bathymetric relationships.

Finally, we focused on wetland systems that have been relatively less studied, and upscaled the k-τ relationships to the landscape scale using a wetland size-frequency distribution. Results highlight the disproportionately large role of small wetlands in landscape scale nutrient processing, such that for the same wetland area removed, the nutrient removal potential lost is larger when smaller wetlands are lost. The disproportionately larger role of small wetlands in landscape scale nutrient processing is important given previous research on the preferential loss of smaller wetlands from the landscape.

Through the use of a cross-system meta-analysis that spanned multiple orders of magnitude of system size, we were able to quantify multi-scale behavior that is less apparent when studying individual systems. Our study highlights the need for a stronger focus on small lentic systems as potential nutrient sinks in the landscape due to their high reactivity rates in comparison to larger water bodies. With a growing recognition that wetlands play a critical role in landscape nutrient cycling, our work will help policy makers and water managers to better understand the suite of functions that is associated with the different size classes and types of wetlands.

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Acknowledgements

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Chapter 1 – Introduction

1.1   Background and Motivation

Over the last century, human activities have dramatically altered global nutrient cycles, leading to both negative ecosystem impacts as well as threats to human health [*Vitousek et al.*, 1997; *Filippelli*, 2008; *Gruber and Galloway*, 2008]. Specifically, increased fertilizer use and cultivation of crops have accelerated the transport of nutrients such as nitrogen (N) and phosphorus (P) and consequently increased eutrophication of both inland and coastal waters [*Tilman et al.*, 2001; *Anderson et al.*, 2002; *Smith*, 2003]. Rivers, lakes, wetlands, and reservoirs typically act as important net sinks of nitrogen and phosphorus during their transport across the landscape, and thus can prevent further deterioration of receiving waters [*McClain et al.*, 2003; *Groffman et al.*, 2009; *Powers et al.*, 2014].

There has been a large body of research quantifying the role of the river network in both watershed and global scale nutrient retention [*Peterson et al.*, 2001; *Seitzinger et al.*, 2002; *Wollheim et al.*, 2006; *Alexander et al.*, 2009; *Botter et al.*, 2010; *Basu et al.*, 2011; *Ye et al.*, 2012]; however, relatively less has been done to quantify the role of lakes and reservoirs [*Harrison et al.*, 2009], and even less research has quantified the role of natural and constructed wetlands in global nutrient processing [*Saunders and Kalff*, 2001]. Many global studies have either omitted or only indirectly included wetlands [*Piña-Ochoa and Álvarez-Cobelas*, 2006; *Seitzinger et al.*, 2006], yet wetlands are one of the largest sinks of anthropogenic nitrogen and phosphorus. A recent review suggests that 64% of reactive nitrogen removal in US freshwaters systems occurs in wetlands, while 28% occurs in lakes and reservoirs, and only 8% occurs in streams and rivers [*Baron et al.*, 2013]

Both nitrogen and phosphorus have complex biogeochemical pathways that facilitate the internal cycling between different species of the nutrient; however, the scope of this thesis focuses primarily on the input-output dynamics of a water body or its net retention. Nitrogen retention

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within a water body, defined as the difference between nitrogen inputs and outputs in a given system, is impacted by three key processes: permanent loss to the atmosphere via denitrification, sedimentation of organic particles, and biological uptake by plants and microbes [*Saunders and Kalff*, 2001]. Of these, denitrification is considered to be the dominant pathway for nitrogen retention in water bodies. Aquatic systems are often considered to be the hotspots of denitrification in watersheds, given the availability of anoxic bottom sediments, which promote microbial activity [*Seitzinger et al.*, 2006]. Phosphorus retention, similarly defined as the difference between phosphorus inputs and outputs, includes sedimentation of both inorganic sediment-bound and organic forms of phosphorus and biological uptake by plants and microbes [*Søndergaard et al.*, 2003]. Unlike N, phosphorus does not have removal mechanisms that permanently remove the nutrient from the water column within the water body; however, lakes, reservoirs, and wetlands are considered hotspots for phosphorus retention given their slower velocities, which provide enhanced opportunities for settling.

While the processes contributing to nutrient retention are well-established, a major limitation to research in global nutrient cycling is the difficulty in measuring or quantifying nutrient removal rates across diverse ecosystems [*Groffman et al.*, 2006]. Large-scale synthesis efforts are required to understand the dominant controls on nutrient removal and spatiotemporal patterns in the removal rate constants. Research on the role of river networks in global nutrient cycles has identified factors such as stream temperature, the supply of biogenic nutrients, respiration rates and contact time of water with sediments as the key variables affecting nutrient retention [*Boyer et al.*, 2006; *Alexander et al.*, 2009]. Both mass balance and stream tracer studies have revealed an inverse relationship between nutrient retention potential and stream depth, thus leading to a higher nutrient retention potential of small streams compared to larger rivers [*Seitzinger et al.*, 2002; *Peterson et al.*, 2001; *Alexander et al.*, 2000; *Botter et al.*, 2010; *Basu et al.*, 2011; *Ye et al.*, 2012]. In a study of five drainage ditches in Sweden, for example, phosphorus retention rates were found to decrease with increases in the depth and flow of the watercourse [*Olli et al.*, 2009]. Similar

results have also been observed for both nitrogen and phosphorus in reach-scale isotope tracer studies by *Ensign and Doyle* [2006] and *Marcé and Armengol* [2009].

Studies in lakes and reservoirs have also demonstrated the disproportionately greater role of small systems in nutrient and carbon cycling. For example, *Crisman et al.* [1998] found oxygen concentrations to be lower in ponds and small lakes, enhancing greenhouse gas emission and carbon sequestration. *Downing et al.* [2010] found that rates of organic carbon burial in small lakes and reservoirs exceeded those of larger lakes by more than an order of magnitude. Similarly, *Harrison et al.* [2009] found that small reservoirs (< 50 km^2) accounted for 84% of nitrogen removal in all reservoirs, and that small lakes account for 65% of the nitrogen removal in all lakes. As with lotic ecosystems, *Hejzlar et al.* [2006] synthesized data to estimate the phosphorus retention of approximately 200 lakes and reservoirs, finding an inverse relationship between the phosphorus removal rate constant and residence time. Similarly, *Brainard and Fairchild* [2012] studied small constructed ponds and found that the area-specific sediment accumulation rates were inversely proportional to the pond surface area.

While the stream, lake, and reservoir communities have converged on recognizing the significantly greater role of smaller systems in global nutrient processing, there has been relatively less research exploring the role of system size on nutrient processing for wetlands. One of the most exhaustive meta-analyses on wetlands [*Jordan et al.*, 2011] found a positive relationship between nitrogen retention and nitrogen loading over several orders of magnitude of both wetland area and nitrogen loading rates. They estimated worldwide reactive nitrogen removal by wetlands to be approximately 17% of anthropogenic nitrogen inputs, though they did not explore the role of wetland size on nutrient processing. A meta-analysis of 186 wetland sites, however, found a negative correlation between wetland size and water quality [*Ghermandi et al.*, 2010]. Further, in a review of 17 constructed wetlands receiving agricultural runoff in Europe, *Braskerud et al.* [2005] found specific particulate phosphorus retention (g P retention/m^2/year) to decrease as

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wetland area increased. However, these studies linking wetland size to water quality are relatively sparse compared to literature related to streams and lakes.

In North America, interest in the landscape-scale role of small wetlands has grown in recent years in response to two U.S. Supreme Court decisions indicating that small, geographically isolated wetlands can only be afforded protection under the U.S. Clean Water Act if they demonstrate a "significant nexus" with nearby rivers or other surface water systems [*Leibowitz*, 2003; *Tiner*, 2003; *Marton et al.*, 2015; *Cohen et al.*, 2016; *Golden et al.*, 2016]. Thus, lawmakers have placed scientists and engineers in the position of demonstrating whether small wetlands have significant hydrologic or biogeochemical connectivity with other surface waters [*Leibowitz et al.*, 2008]. Interest in the role of wetland size in providing key ecosystem services has also increased in recent years with increased efforts to restore previously drained wetlands and to construct new wetlands to improve water quality [*Mitsch and Day*, 2006; *Zhi and Ji*, 2012]. *Mitsch et al.* [2005], for example, used a simple empirical model to provide an estimate of the extent of new wetland creation necessary in the Mississippi River Basin to remove 40% of nitrogen loading to the Gulf of Mexico. But as pointed out by many authors [*Semlitsch and Bodie*, 1998; *Downing*, 2010; *Ghermandi et al.*, 2010]: the functionality of a wetland is not uniform across systems, and thus wetland restoration must focus not only on goals related to total wetland area, but also to the type, landscape position, and morphometry of the wetlands being restored [*Van Meter and Basu*, 2015]. To better direct restoration efforts, a better understanding of how wetland attributes alter nutrient processing is required; currently, such information is lacking [*Marton et al.*, 2015]. Our goal is to address this knowledge gap by quantifying the role of small and large wetlands in nutrient processing.

1.2 Objectives

The overall goal of the work presented in this thesis is to quantify the role of the size of lentic systems (lakes, reservoirs, wetlands) on landscape-scale nitrogen and phosphorus processing. It is our hypothesis that similar to lakes, reservoirs, and stream systems, small wetlands play a disproportionately large role in global nutrient processing. More specifically, we hypothesize that the greater ratio of reactive area to water volume in small water bodies leads to greater nutrient removal, by area, than that found in larger water wetlands. In testing this hypothesis, we focus on the following three questions in the subsequent chapters:

- What are the emergent patterns between nutrient processing rates and water residence times in lentic systems?
- What are the underlying mechanisms contributing to the observed pattern?
- What is the relative role of wetland size in landscape nutrient processing?

In **Chapter 2**, the existing literature relating to nutrient processing in the both lotic and lentic systems is presented. Here, the methods of quantifying and modelling these systems and highlight the need to quantify nutrient removal wetlands in the context of the different water bodies are summarized. In **Chapter 3**, our methods used in the data synthesis and meta-analysis, the two-compartment model used to mechanistically test our hypothesis, and upscaling analysis to quantify landscape scale nutrient processing are presented. In **Chapter** 4, the results and discussion related to our analyses are presented. Finally, **Chapter 5** summarizes our work with some comments on future directions.

Chapter 2 – Literature Review

2.1   Introduction

In this thesis, we explore the impacts of hydrology, biogeochemistry and bathymetry on nutrient removal in a range of aquatic systems. Various methods for quantifying nutrient retention have been developed, including the nutrient spiraling concept and the advection-dispersion-reaction equation as well as its associated forms. In this section, we summarize the various parameters typically measured during field or experimental studies that are used in these models. Finally, we compare the similarities and differences in methodologies used to model nutrient retention in lentic and lotic ecosystems and the need to frame nutrient processing in wetlands within the context of other aquatic ecosystems.

2.2   Nutrient Dynamics in Diverse Ecosystems

Inland water bodies receive large quantities of excess nutrients generated from terrestrial ecosystems, and both lentic systems (slow-moving water bodies such as lakes, reservoirs, and wetlands) and lotic systems (fast-moving water bodies such as streams and rivers) function as key reactive interfaces for both nitrogen and phosphorus removal from the water column [*McClain et al.*, 2003]. All future references of nutrient removal or retention in this thesis refers to the removal of nitrogen or phosphorus from the water channel. Interestingly, the biogeochemical processes that govern nutrient removal are similar across lentic and lotic systems, even though the hydrological processes are unique between them.

Terrestrial ecosystems receives nitrogen through biological nitrogen fixation, fertilizer inputs and atmospheric deposition [*Galloway et al.*, 2004]. Once on land, nitrogen can be immobilized by bacteria, used by vegetation, or be exported through the watershed through various pathways [*Seitzinger et al.*, 2006; *Gruber and Galloway*, 2008]. Overland runoff or leaching to the

underlying aquifer will eventually transport dissolved nitrogen to inland aquatic ecosystems and finally the ocean – often with detrimental effects [*Vitousek et al.*, 1997; *Gordon et al.*, 2008]. Importantly, nitrogen removal from the water column can occur along these transport pathways via the process of denitrification, which transforms nitrate in the water column into nitrogen gas or nitrous oxide by bacteria and releases it to the atmosphere[*Seitzinger et al.*, 2006]. Denitrification can occur in soils across the terrestrial ecosystem, in the groundwater system, as well as in aquatic ecosystems [*Seitzinger*, 1988; *Vitousek and Howarth*, 1991; *Howarth et al.*, 1996]. Although terrestrial soils and the underlying groundwater account for 31% (168 Tg) of global denitrification and lakes and rivers only 11% (66 Tg), *Seitzinger et al.* [2006] found that the rate of denitrification in lakes and rivers on a per area basis was approximately 10 times greater than the terrestrial ecosystems in their synthesis of global scale denitrification. High denitrification rates in aquatic ecosystems are facilitated by several factors typically found in the sediment zone of these systems: strong redox gradients due to the mixing of groundwater and surface water, availability of organic carbon, and relatively anoxic conditions that denitrifying bacteria need to thrive [*Seitzinger et al.*, 2006; *Fennel et al.*, 2009].

The phosphorus cycle differs from the nitrogen cycle in that there are no significant atmospheric pathways and there are no 'permanent' removal mechanisms from the water column [*Filippelli*, 2008; *Ruttenberg*, 2014]. Additionally, phosphorus typically exists in two major forms: sediment-bound phosphorus and dissolved phosphorus [*Pierrou*, 1976]. Phosphorus typically enters the terrestrial ecosystem through physical or chemical erosion of phosphorus-bearing minerals (such as apatite) or anthropogenic inputs such as fertilizer [*Ruttenberg*, 2014]. Once in the soils, phosphorus may be used by plants if bio-available, stored as sediment-bound phosphorus until eroded by overland flow, or leached into groundwater [*Follmi*, 1996; *Filippelli*, 2008]. Unlike nitrogen, phosphorus is only retained in the watershed via storage (whether in biomass or sediments). These storage pools can be temporary in nature, as biomass will eventually die and become active in the cycle again, and sediment phosphorus can be re-released under reducing

conditions and high pH [*Christophoridis and Fytianos*, 2006; *Filippelli*, 2008]. The settling of particulate phosphorus in aquatic ecosystems, however, serves as an important sink of phosphorus in watersheds.

Retention processes for nitrogen and phosphorus are typically modeled as first-order reactions, although more complex process-based models that consider saturation kinetics and second-order dependencies do exist [*Hamilton and Schladow*, 1997; *Bicknell et al.*, 2001; *Wade et al.*, 2002; *Gu et al.*, 2007]. First-order fluxes are characterized by a rate constant (e.g. *k*) multiplied by the mass or concentration of a chemical constituent. While first-order equations allow for simple analytical solutions of models and thus less computation time, they may be only applicable under certain conditions. For example, denitrification may more closely resemble a Michaelis-Menten function (linearly increasing at low concentrations until a plateau due to saturation); as well, there may be dependencies on the availability of other chemical constituents (such as oxygen or organic carbon) [*Heinen*, 2006]. Consequently, models of these first-order processes can be modified to accommodate different biogeochemical factors. *Heinen* [2006] synthesized over fifty models that quantified denitrification and found that approximately 65% of them followed first-order kinetics. Amongst these models, additional modifiers such as soil saturation, temperature, pH level, and nitrate availability have been formulated.

Similarly, the settling and sorption of phosphorus is not truly linear in the environment. Linear settling rates are based on the assumption that lakes are dilute and that the sediment particles do not interact with each other [*Di Toro*, 2001]. While the kinetics of phosphorus sorption can be modelled using a linear isotherm, they can also be modelled using Michaelis-Menten type functions, or dependencies on iron concentrations, pH, etc. [*Weber et al.*, 1992; *Limousin et al.*, 2007; *Song et al.*, 2007]. In the present study, we do not explicitly model sorption, but treat settling as a dominant, first-order process, which implicitly assumes that phosphorus will be adsorbed onto sediment. Accordingly, our focus herein is on literature that employs first-order modeling

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approaches to simulate nutrient retention processes in different aquatic ecosystems. The impacts of such assumptions are summarized in the subsequent chapters.

The biogeochemical processes that are within the nitrogen and phosphorus are complex and continues to be the subject of intense research. While aquatic ecosystems are often thought of as net nutrient sinks in the landscape, there are instances in which these systems act as net nutrient sources. Net source dynamics may manifest seasonally and be caused by the dominance of certain internal processes or the reduction of the main removal processes [*Morris*, 1991]. Net export of reactive nitrogen in water bodies across long time scales tend to be uncommon, as described by the meta-analysis performed by *Jordan et al.* [2011] and the work by *Seitzinger et al.*, [2006]. There have been documented cases of net nitrogen export in some cases such as in a marsh ecosystem undergoing coastal erosion [*Childers and Day*, 1990] or water diversions [*DeLaune et al.*, 1989]. Other aquatic ecosystems such as salt marshes or mangrove wetlands have also been observed to exhibit net nitrogen export behaviours due to the transport of particulate nitrogen in detritus or dissolved nitrogen in shallow pore water due to tidal movement [*Valiela et al.*, 1978; *Aziz and Nedwell*, 1986]; however these types of systems are not explored in our work.

Within the nitrogen cycle, nitrification (the oxidation of ammonia to nitrite and nitrate through nitrogen fixating plants or bacteria) is a source pathway of nitrogen in a water body. Nitrification is an aerobic process, which requires the presence of oxygen to proceed, can often be found in shallower regions of a water body [*Dunnette and Avedovech*, 1983; *Pauer*, 2000]. Water bodies that may experience oxygenation of the bottom sediments will consequently see a reduction of denitrification and experience an increase of nitrification and thus nitrates [*Cebron et al.*, 2003]. Lake Superior, which has been observed to be 'increasingly nitrifying' in recent years, is a prime example of the competing nitrogen processes at work. The steadily increases of nitrate export from Lake Superior has been largely attributed to several factors: (1) low loading of organic carbon, thus limiting the denitrification process; (2) the lake water is considered to be an oxidizing

environment and nitrate is favoured, and (3) the low productivity of the lake limits uptake of nitrogen [*Sterner et al.*, 2007]. Though Lake Superior has strong nitrification fluxes and relatively weak denitrification, the lake continues to be a net nitrogen sink in annual or long-term budgets [*Sterner et al.*, 2007].

The phosphorus cycle is highly dynamic and water bodies may become phosphorus sources due to a range of factors. Physically speaking, phosphorus that is stored within the sediment zone may be washed out during extreme hydrological events such the spring snow melt [*Gibson et al.*, 2001; *van der Perk et al.*, 2007]. There are also biogeochemical factors that may lead to net phosphorus export. The sorption of phosphorus is a reversible process that can result in phosphorus release from the sediments depending on a variety of factors such as pH and the redox conditions within the water. It has long been recognized that lakes, especially those that undergo seasonal turnover, have fluctuating oxic conditions in the sediment zone [*Boström et al.*, 1988]. In general, there has been a longstanding paradigm in limnology in which oxygenated waters promote phosphorus fixation to iron whereas anaerobic conditions causes the dissolution of iron-phosphorus complexes back into the water column [*Mortimer*, 1942; *Christophoridis and Fytianos*, 2006]; there has been increasing recognition that additional factors such as the binding material and bacteria that are active in the phosphorus cycle prevent the use of oxygen as the sole controlling factor of internal phosphorus loading [*Hupfer and Lewandowski*, 2008]. Similarly, studies in wetlands have documented a saturation effect that reduces the efficiency of phosphorus retention. *Richardson et al.* [1996] observed that short-term processes such as uptake by periphyton and plants can remove phosphorus from the water column quickly, but are limited in total magnitude due to biophysical constraints. *Richardson et al.* [1996] also note that loads greater than 1 g P m^{-2} yr^{-1} often resulted in drastic increases of output phosphorus concentrations due to the exceedance of the assimilative capacity of the wetland system.

Since the scope of the work in this thesis will focus on larger spatial scales (watershed and landscapes) as well as longer time scales (steady-state behavior and greater than a year to average out seasonal patterns), the remainder of the literature review, as well as the thesis, will focus on the nutrient removal dynamics of water bodies, while recognizing that can be instances of nutrient export at shorter time-scales.

2.2.1   Nutrient Retention Rates in Lotic Systems (Streams)

The importance of streams in watershed nutrient cycling is increasingly being recognized, and we have come far from the days of treating lotic systems as mere conduits of contaminants that lead to the oceans [*Howarth et al.*, 2002]. Some early work on stream nutrient cycling by *Robinson et al.* [1979], *Cooke and White* [1987], *Mulholland* [1992], and *Jansson et al.* [1994] explored dominant controls on nitrogen export and retention in streams, including loading, land use, and the characteristics of the sediment bed. More recently, the research community has expanded the spatial scales of interest to watersheds and continents. Most notably, *Alexander et al.* [2000] found that in-stream loss rates scale inversely with stream depth across the Mississippi River Basin. In other words, the smaller, headwater streams are more reactive than their larger counterparts downstream. *Peterson et al.* [2001] and *Mulholland et al.* [2008a] further explored these relationships through extensive isotope tracer tests and quantified the rapid uptake of nutrients in lower-order headwater streams.

This loss rate-depth dependence has been explained using the concept of nutrient spiraling through the hyporheic zone [*Newbold et al.*, 1982]. Stream systems are not simply the visible water channel but include the surrounding flood plain and underlying hyporheic zone. The hyporheic zone is the interface between groundwater and surface water and consequently is a site of strong redox gradients and critical biogeochemical processes. Within the nutrient spiraling framework, the spiral begins when nutrients are brought to the sediment zone through hyporheic flow, then is

assimilated from the pore water into benthic biomass in the hyporheic zone, and then are either retained permanently via denitrification or burial, or mineralized back into the water column [*Newbold et al.*, 1982; *Ensign and Doyle*, 2006]. This cycling or spiraling between the aqueous, biological, and mineral forms of the nutrient and the transfer between the water column and sediment zone was a large deviation from the original conceptualization of through-flow only in the water channel [*Ensign and Doyle*, 2006]. The mass transfer between the compartments are facilitated by the natural bedform morphology and meanders of a stream, which forces the flow of the water and soluble contaminants into the sediment zone [*Gooseff et al.*, 2006].

Systems with high hyporheic exchange will bring a greater proportion of water and nutrient mass to enter the reactive zone in the sediments [*Harvey et al.*, 1996a] ; small streams (or those of lower stream order) have been observed to have higher hyporheic exchange fluxes [*Gomez-Velez and Harvey*, 2014]. This was seen again at the Mississippi river basin scale by *Gomez-Velez et al.* [2015], where catchments with high gradients, hydraulic conductivity, and thus high hyporheic exchange were observed to have lower nutrient export.

The traditional approach for measuring reach-scale nutrient retention and nutrient spiraling is through the use of mass balance studies. In these studies, nutrient isotopes or inorganic forms of nutrients are injected into the stream, and the spatiotemporal changes in concentrations are measured at a downgradient location to quantify retention [*Bencala et al.*, 1984; *Triska et al.*, 1989]. Some of the earliest tracer studies aiming to parameterize the nutrient spiralling model were conducted by *Newbold et al* [1983] and *Mulholland et al.* [1985], who used ^{32}P isotopes. The Lotic Intersite Nitrogen experiment by *Mulholland et al.* [2008a] quantified the denitrification rates of 72 streams in 8 distinct biomes across the conterminous United States through the use of ^{15}N isotopes. *Ensign and Doyle* [2006] synthesized 52 injection and tracer studies and found that the loss rates normalized by area were relatively constant across stream orders in the river network. These studies were able to quantify the nutrient removal rates by measuring changes in

concentration over a characteristic length scale and using various mathematical models or metrics, as described below.

2.2.1.1 Methods of Modelling Nutrient Retention in Streams

The nutrient spiraling model can be summarized using several simple metrics. *Newbold et al.* [1982] presented the concept of the spiraling length, *S*, which is the characteristic length that a nutrient particle must travels to complete one spiral (from dissolved form in water to particulate phase to organic phase and back to aqueous phase). This spiraling length, *S*, can be quantified by using the uptake rate constant, *k*, and the stream velocity, *u*, where $S = u/k$ [*Ensign and Doyle*, 2006]. Thus systems with a low spiraling length are considered to be more efficient in using nutrients. Other commonly used forms of these parameters are discussed in **Section 2.2.3**.

A process-based model that is commonly used to characterize nutrient retention in the literature is the advection-dispersion-reaction equation (ADRE) [*Bencala and Walters*, 1983; *Runkel*, 1998; *Roig and Shrestha*, 1999; *Jones and Mulholland*, 2000]. This model provides three modes of transport for a contaminant: advective transport with the flow of water, dispersion or diffusive transport due to concentration gradients, and a reactive pathway due to a general biogeochemical reaction. As described below, there have been two common modifications to the ADRE in the stream literature: 1) the addition of the hyporheic exchange and 2) the simplified plug flow reactor model (PFR). More complex nutrient spiraling models that explicitly account for biological uptake in the channel and hyporheic zone do exist, but it has been demonstrated that at long-term scales (at annual or greater time scales) settling (for P) and denitrification (for N) are the dominant retention processes (see *DeAngelis et al.* [1995] or *Jones and Mulholland* [2000]). Furthermore, while more complex models provide more flexibility and fewer assumptions, the number of parameters may lead to issues of equifinality and difficulties in isolating the interactions between

state variables and outputs [*Snowling and Kramer*, 2001; *Robson et al.*, 2008]. In this thesis, we will thus focus only on two forms of the ADRE model:

(1) The ADRE with hyporheic exchange, also known as the One-Dimensional Transport with Inflow and Storage model (OTIS) model was originally developed to model the tracers under the influence of surface and groundwater interactions on water quality in streams [*Bencala and Walters*, 1983; *Harvey et al.*, 1996b]. This modeling framework has been widely used in stream systems where the groundwater-surface water exchange constitutes an important component of nitrogen cycling [*Botter et al.*, 2010; *Basu et al.*, 2011; *Stewart et al.*, 2011] and can be used to link the physical geometry to nutrient retention in a parsimonious manner. This model can be written as:

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2} - kC - \alpha(C - C_{HZ}) \tag{1a}$$

$$\frac{\partial C_{HZ}}{\partial t} = R\alpha(C - C_{HZ}) - k_s C_{HZ} \tag{1b}$$

where C is the concentration of the contaminant in the channel [M/L^3], t and x are time [T] and space [L], v is the mean velocity of the advective flow [L/T], D is the dispersion coefficient [L^2/T], k is a biogeochemical reaction in the channel [1/T], C_{HZ} is the concentration in the hyporheic zone [M/L^3], α is a mass exchange coefficient [1/T], R is the ratio of the cross-sectional area of the main channel to the hyporheic zone [-], and k_s is the biogeochemical reaction rate constant in the hyporheic zone [1/T].

(2) The PFR model is a simplification of the ADRE model in that it removes the dispersive term and assumes that the contaminant moves as a 'plug' through the system. In this model, it is common to use the apparent uptake velocity v_f [L/T] to quantify nutrient uptake in streams assuming first-order kinetics. This parameter also spatially and temporally averages the nutrient spiraling mechanisms into a constant. The PFR equation and its associated analytical solution are:

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} - \frac{v_f}{h}C \tag{2a}$$

$$C = C_o e^{-\frac{v_f}{h}\tau} \tag{2b}$$

where v_f is the nutrient uptake velocity [L/T] and h is the mean depth of the channel [L], C_o is the initial concentration at the inlet [M/L^3], and τ is the mean water residence time [T].

The PFR model has been used extensively in stream literature at watershed and continentals scales due to its simplicity and its spatiotemporal averaging of the fine-scale processes. SPARROW, the commonly used watershed model [*Smith et al.*, 1997] uses the PFR approach, as have studies by *Runkel and Chapra* [1993], *Boyer et al. [2006], Wollheim et al.* [2008], *Basu et al.* [2011], etc., to name only a few. In addition, *Wollheim et al.* [2006] used the PFR model as the basis for a river network model to determine the relative roles of stream order on nutrient removal. They found that small streams remove more nutrient mass on a per length basis while larger streams remove more total nutrient mass due to longer residence times and because most of the land (and nutrient mass) will eventually drain through the large streams.

2.2.2 Nutrient Retention Rates in Lentic Systems (Lakes, Reservoirs and Wetlands)

Numerous studies have focused on nutrient processing and removal in lentic water bodies [*Nichols*, 1983; *Dillon and Molot*, 1990; *Saunders and Kalff*, 2001; *Jeppesen et al.*, 2005; *Brett and Benjamin*, 2007; *Downing*, 2010; *Maavara et al.*, 2015]. For nitrogen, the importance of nitrate reduction in the sediment bed was addressed in many early studies such as those by *Keeny et al.* [1971] and *Seitzinger* [1988]. For phosphorus, the mass flux of particulate phosphorus into long-term sediment storage has also been widely recognized as a dominant process for phosphorus removal [*Chapra*, 1975; *Vollenweider*, 1975]. Wetlands, and especially constructed wetlands,

have also been a subject of interest as sites for removing nutrients from runoff or wastewater [*Tilton and Kadlec*, 1979; *Nichols*, 1983].

Limnological research was initially more strongly focused on phosphorus removal, stemming from the seminal work of *Schindler* [1977], who observed the limiting effects of phosphorus from a lake-scale experiment, and the early work by *Smith* [1983] observing N:P ratios on lake ecosystem health. However, more recently there has been a shift to consideration of other nutrients and to larger scales. *Downing* [2010], for example, has quantified the disproportionate importance of small lakes and ponds in global carbon removal. Similarly, *Harrison et al.* [2009] and *Harrison et al.* [2012] described the collective importance of small lakes and reservoirs in global nitrogen and silica cycles respectively (those smaller than 50 km^2). They estimated that the smaller systems remove 20 to 27% more nitrogen per unit area and 97 to 670% more silica per unit area than larger water bodies. The authors also note that these estimates are due to the difficulty of quantifying the number of small water bodies and the assumption of loading in grids enter small lakes within their model during upscaling. *Harrison et al.* [2009] and *Harrison et al.* [2012], using a regression based model, did not focus on the results pertaining to small lakes and reservoirs nor postulate a mechanistic reason for this phenomena. This modelling result was treated as a curiosity and also speaks to the need of furthering our understanding of these systems.

Early models of wetlands stem from the constructed wetland literature and generally use the PFR formulation to describe nutrient retention (*Kadlec and Knight* [2009], *Mitsch et al.* [1995], *Griffin et al.* [1999], *Arheimer and Wittgren* [2002], *Carleton and Montas* [2010]). More complex models that consider the wetland to be comprised of different compartments like the surface water, littoral zone, macrofauna, top and deep soil exist as well (e.g. *Kadlec and Hammer* [1988], *Hantush et al.* [2012], *Paudel and Jawitz* [2017], etc.). The model type used in the studies are often directed by the research question at hand. Those using the simpler input-output model such as the PFR formulation typically are interested in the overall behavior and the influence of relatively few

controlling factors; conversely, complex models are able to quantify the interaction of multiple processes and the presence of feedback loops at the cost of needing many parameters or constraints. The goal of this thesis falls under the former category; the next sections will summarize the use of the parsimonious input-output models to describe lentic system behavior.

2.2.2.1 Methods of Modelling Nutrient Retention in Lentic Systems

Similar to modelling nutrients in stream, there are many levels of complexity that can be added to a model to capture more complex interactions among the biophysical and ecosystem controls on nutrient removal. In their simpler forms, models can simulate water column dynamics alone, while more complex approaches can extend to additional compartments such as sediments, macrophytes and periphyton [*Paudel and Jawitz*, 2012].

The most basic models focus on the water column, with the sediment being treated as a boundary (e.g. *Hejzlar et al.* [2006], *Kelly et al.* [1987], *Vollenweider* [1975]). Limnologists studying phosphorus retention commonly use the Vollenweider equation [1975], which conceptualizes the lake as a continuously stirred tank reactor (CSTR) with an effective removal rate constant σ (also referred to as the volumetric rate constant $k_{v,C}$, $[T^{-1}]$) that can be estimated based on the percent removal R and the mean water residence time τ (**Table 1**). In its most basic form, the CSTR equation can be written as:

$$V\frac{dC}{dt} = QC_o - QC - k_{v,C}CV \qquad (3)$$

where V is the volume of the water column $[L^3]$, C_o is the concentration in the inflow $[ML^{-3}]$, C is the nitrogen concentration in the water column and outflow $[ML^{-3}]$, and Q is the flow $[L^3T^{-1}]$.

CSTRs, or well-mixed reactors, are diffusion-dominated systems, with any mass entering the system being assumed to be instantaneously mixed within the water body, such that the

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concentration within the water body and the outflow are the same. Modeling a lentic system as a CSTR is a widely accepted practice in the limnologic literature. *Brett and Benjamin* [2007] conducted a review and found hundreds of studies citing the original Vollenweider model or some variant of the CSTR model to describe phosphorus retention. The Vollenweider approach has also been adapted to other systems – as an example *Spieles and Mitsch* [1999] used the Vollenweider model for nitrogen in wetlands and *Dettmann* [2001] for nitrogen in estuaries. By adding other mass fluxes such as a sedimentation term, other studies such as those by *Sonzogni et al.* [1982] and *Maavara et al.* [2015] used the CSTR formulation for phosphorus in lakes and reservoirs.

Another group of models focus only on the sediment, with the water column providing a boundary condition to the sediment model (e.g. *Reed et al.* [2011], *Hantush* [2007], *Katsev et al.* [2006]). Commercial models such as the HYDRUS Wetland Module and COMSOL operate in a similar manner [*Orellana et al.*, 2012]. HYDRUS and COMSOL solve the Richard's equation for water flow and couple advective-dispersive transport processes to contaminant flow [*Langergraber*, 2016]; however these models are highly parameterized and are more tailored to subsurface systems, with the surface water being treated as a boundary condition.

There are also more complex limnologic models such as Minlake [*Riley and Stefan*, 1988], the wetland model by *Kadlec and Hammer* [1988] and eutrophication models (*Arhonditsis and Brett* [2005]) that couple nutrient processes in the water column to the sediment zone, but these models have the added complexity of hydrodynamics, spatial dimensions, or ecological feedbacks that are beyond the scope of what can be parameterized from a data synthesis.

2.2.3 Nutrient Retention Rate Constants across Aquatic Ecosystems

Modelling studies attempting to replicate field studies or predict future behavior of a specific water body or its internal processes at small scales tend to require more precise spatiotemporal resolution

and may necessitate additional parameters to account for effects of temperature, pH, etc. [*Snowling and Kramer*, 2001]. On the other hand, studies quantifying the behavior of systems at larger scales such as watersheds or even continents will encounter issues of expensive computational simulations because of model complexity [*Beven*, 2000; *Beven and Freer*, 2001]. In the case of larger scales, the first-order rate constant approach is often considered sufficient to describe the behavior of water bodies as many processes may be averaged spatially or temporally – thus organization from complexity may emerge so that dominant behaviours may be quantified at these scales with simple rate constants [*Turcotte*, 2007; *Jenerette et al.*, 2012; *Sivakumar and Singh*, 2012; *Bras*, 2015]. The scope of this thesis more closely aligns with the second category and thus the CSTR and PFR models were explored.

Traditionally, CSTR models have been used for lentic systems and PFR models for lotic systems. There has been much overlap of the models when modelling a particular type of water body. For example, the widely cited NiRReLa model by *Harrison et al.* [2009], which quantifies global nitrogen retention in lakes and reservoirs, applies the PFR formulation. Similarly, the most commonly used approach in the constructed wetland literature is to conceptualize the system as a PFR [*Kadlec*, 2000; *Werner and Kadlec*, 2000; *Rousseau et al.*, 2004].

While the original nutrient spiraling model for streams by *Newbold et al.* [1982] presents an areal rate constant k_a [LT^{-1}] in the form of uptake velocity, there is also a large body of work that uses the volumetric constant $k_{v,P}$ [T^{-1}] (example papers for both can be found in **Table 1**). The choice of rate constant typically depends on the research question at hand and may be a matter of convenience. The relation between the two rate constants can be expressed as $v_{f,i} = k_{a,i} = hk_{v,i}$ where h [L] is the depth of the water body, $i = c$ or p for CSTR and PFR formulations [*Kadlec and Wallace*, 2009]. The areal rate constant $k_{a,i}$ or $v_{f,i}$ is a biological measure of removal that is independent of the surface water hydrology, while spatiotemporal variations in hydrology are considered in the volumetric rate constant [*Alexander et al.*, 2000; *Ensign and Doyle*, 2006;

Wollheim et al., 2006; *Alexander et al.*, 2009; *Marcé and Armengol*, 2009]. The areal rate constant is mainly affected by biogeochemical controls such as dissolved oxygen, redox potential, organic content and microbial activity [*Boyer et al.*, 2006], and has been shown to be relatively independent of stream order. The independence of the areal rate constant with respect to the depth and volume of a system makes it a weaker choice when comparing the effects of system size on its nutrient processing and points to the choice of the volumetric rate constant within our work to explore the controls of system size.

Interestingly, tracer tests on a number of treatment wetlands have shown that the flow regimes actually lie between the extremes of a PFR and a CSTR [*Kadlec*, 1994], and thus studying these two end-member systems enable us to constrain the system response. The simplicity of the equations allows us to calculate these rate constants as a function of R and τ (for the volumetric rate constant) or R and hydraulic loading rate q (for the areal rate constant).

Table 1. Comparison of commonly used first-order removal rate constants

Removal Rate Constant Name	Units	Steady State Removal/Retention Equation	Example Usage in Papers in Different Disciplines
CSTR Model			
Apparent removal velocity ($v_{f,c}$)	$[LT^{-1}]$	$k_{a,c} = v_{f,c} = \left(\dfrac{R}{1-R}\right)q$	Lakes and reservoirs: Sonzogni et al. [1982], Dillon and Molot [1996] for P; Kelly et al. [1987] for N
Volumetric rate constant ($k_{v,C}$), Vollenweider rate constant (σ)	$[T^{-1}]$	$k_{v,c} = \left(\dfrac{R}{1-R}\right)\dfrac{1}{\tau}$	Lakes and reservoirs: Hejzlar et al. [2006] for P, Vollenweider [1975] for P;
PFR Model			
Areal rate constant ($k_{a,p}$), Uptake velocity ($v_{f,p}$)	$[LT^{-1}]$	$k_{a,p} = v_{f,p} = -\ln(1-R)q$	Lakes and reservoirs: Harrison et al. [2009] for N, Knight et al. [2003] for P, Wollheim et al. [2008] and Beusen et al. [2015] for N and P; Constructed wetlands: Kadlec and Wallace [2009] for N and P; Rivers: Wollheim et al. [2006] for N
Volumetric rate constant ($k_{v,p}$), time specific uptake rate	$[T^{-1}]$	$k_{v,p} = \ln(1-R)\dfrac{1}{\tau}$	Constructed wetlands: Carleton et al. [2007] for N and P; Rivers: Alexander et al. [2009] for N

where R is the fraction of nutrient retained [-], q is the hydraulic loading rate $[LT^{-1}]$ and τ is the mean water residence time $[T]$. The subscripts a and v indicate the areal and volumetric rate constants, the p and c refer to the PFR and CSTR models.

2.2.4 Damkohler Number: A Ratio to Unite Hydrology with Biogeochemistry

The Damkohler number, *Da,* is a dimensionless ratio between a hydrological time scale (for example the water residence time τ_w [T]) and a reaction time scale (for example the inverse of the volumetric rate constant $\tau_{rxn} = 1/k$ [T]); the ratio can be generally written as τ_w /τ_{rxn}. A Damkohler number equal to 1 indicates that the transport and reaction timescales are balanced, while $Da < 1$ indicates transport limitation, and $Da > 1$ implies reaction rate limitation where biophysical conditions are limiting for the reaction [*Harvey et al.*, 2013]. In other words, the reaction times are much smaller than transport or exposure times, and thus the nutrient will be removed fully from the water column under reaction rate limiting conditions. Conversely, if reaction times are larger

than transport times, there is insufficient time for reactions to occur (and often assumptions of equilibrium are not met) in transport limiting conditions.

Lansdown et al. [2015] sampled a transverse cross-section of a streambed and found that deep locations characterized by hyporheic exchange flows had a *Da* greater than 1 (i.e. reaction rate limited). These hotspots had more reducing conditions and lower oxygen levels that promoted better denitrification. *Harvey et al.* [2013] similarly found that the hyporheic zone was largely reaction limited in their study site. *Ocampo et al.* [2006] applied the *Da* framework to hillslopes and riparian zones and found that the slope of the system acted as a major control on nutrient attenuation. The flatter hillslope, which had longer transport times, would consequently be reaction limited whereas the nitrate would behave similarly to a conservative tracer in the steep hillslope due to insufficient reaction time. The use of the Damkohler number provides a concise way to summarize a system's behavior in a non-dimensional manner and thus allows one to compare different types of water bodies that span multiple orders of magnitude in size.

2.3   Small Wetlands as Biogeochemical Hotspots in Landscapes

The inverse relationship between nutrient processing rates and the size of a system has been more fully studied in the stream literature [*Wollheim et al.*, 2006; *Alexander et al.*, 2009; *Olli et al.*, 2009; *Basu et al.*, 2011]. However, there has been less focus on such phenomena in lentic systems. Recent work by *Holgerson and Raymond* [2016] and *Downing* [2010] quantified the relatively large role of small ponds and lakes in global carbon cycling and generating greenhouse gases; *Harrison et al.* [2009] also quantified the greater role of small lakes in removing nitrogen at global scales. Nitrogen and phosphorus retention of wetlands as a function of size, unfortunately, has not been addressed fully in the literature.

The need to quantify how nutrient processes scale with size in wetlands grows as wetland loss continues: while it is relatively easy to remove or drain a wetland, restoring wetlands is a costly and complex endeavor that requires years of ecological succession before the intended functions may manifest [*Kentula*, 2000; *Mitsch and Day*, 2006]. A recent study estimated that there has been a 40% reduction of wetlands globally in the 20th century with an overall loss of 83% since the 1800s [*Davidson*, 2014]. Regionally, these losses may be even greater due to competing land use change due to urbanization and agricultural usage. For example, the Prairie Pothole Region (PPR), an approximately 700,000 km^2 area across the central US and Canada, has lost an estimated 65% of wetlands primarily due to drainage of wetlands for cropland from the 1800s to the mid-1980s; southwestern Ontario has similarly lost 72% of wetlands since pre-settlement to urban and agricultural expansion [*Ducks Unlimited Canada*, 2010]. In a previous study, *Van Meter and Basu* (2015) quantified the historical and current size-frequency functions of depressional wetlands in the southernmost lobe of the PPR (Iowa), and found that, in addition to an overall loss of wetlands across the size classes, there has been a preferential loss of smaller wetlands in upland locations and may allude to a preferential loss of biogeochemical processes in the landscape

Indeed, small, geographically isolated wetlands (GIWs) are considered to be at particular risk of drainage due to both a lack of legislative protections and general patterns of land development, i.e. the smallest wetlands are the easiest to drain, and their importance in landscape functionality (whether hydrologically, biogeochemically or ecologically) is easily underestimated [*Van Meter and Basu*, 2015]. GIWs are defined as wetland systems that do not have an apparent surface connection to a nearby water body (such as a river or lake) and thus are completely surrounded by uplands [*Leibowitz*, 2015]; however, it should be noted that many GIWs are connected through subsurface pathways or are seasonally connected for a portion of the year and form wetland complexes and thus are not 'visibly' connected or deemed to be useful [*Leibowitz and Vining*, 2003; *Johnson et al.*, 2010]. Many distinct wetland systems fall under this category such as vernal pools in forests, the playa formations in the southwestern US, desert spring wetlands, the coastal

Carolina and Delmarva bays, cypress domes, ponds, and wetlands of the Prairie Pothole Region – many of which tend to be small systems in the landscape [*Tiner*, 2003; *Mushet et al.*, 2015].

Recently, GIWs have seen significant *reductions* of legal protection in the USA following two US Supreme Court rulings: Solid Waste Agency of Northern Cook County v. U.S. Army Corps— SWANCC (2001) and Rapanos v. U.S. (2006). With these rulings, federal protection for GIWs were abolished unless a 'significant nexus' in relation to the physico-chemical or biological integrity of navigable waters can be proven [*EPA and U.S. Army Corps of Engineers*, 2003; *Mushet et al.*, 2015]. More locally, some wetlands in southern Ontario are protected by the Ontario Planning Act [2016] and the associated Provincial Policy Statement (PPS) [2014] as well as the Greenbelt Act [2009] and Conservation Authorities Act [2011]. Specifically, the PPS does not permit the development or alterations of provincially significant wetlands with some exceptions to infrastructure projects. While provincially significant wetlands are based on an aggregate score of ecosystem and human utility vales, the evaluation system may deem wetlands as not significant if they do not reach a threshold score; 'wet lands' that are periodically saturated but used in agricultural settings are not considered to be wetlands in the PPS [*Ontario and Ministry of Municipal Affairs and Housing*, 2014].

There has been criticisms of the GIW and 'significant' terminology as it precludes the idea of "connectivity continua," as systems may have different degrees of connectivity in hydrological, biogeochemical and ecological connection. The term GIW implies that these systems are functionally isolated from the landscape [*Mushet et al.*, 2015]; 'significant wetlands' are implied to be the only systems to be truly beneficial A growing number of recent studies have begun to explore the collective effect of wetlands in landscapes but with a growing emphasis on the role of size, location, and type on its functionality in hydrological, biogeochemical, and ecological cycles. *Cohen et al.* [2016] presented a framework in which the different wetland types classified by connectivity and relative location to the stream network perform unique functions in the landscape.

GIWs that are primarily disconnected from the surface water network have been shown to stabilize water table the regional [*McLaughlin et al.*, 2014; *Cohen et al.*, 2016; *Golden et al.*, 2016]; occasionally connected GIWs provide both sediment and bank storage as well as habitats for waterfowl [*Craft and Casey*, 2000]; riparian wetlands exert a strong influence on streamflow generation and floodplain morphology [*Junk et al.*, 1989].

There are further studies examining the coupled nature of nutrient and hydrological cycles in GIWs within landscapes. *Marton et al.* [2015] synthesized the morphometric factors affecting the nutrient removal potential in GIWs and outlined a framework of biogeochemical reactivity in the context of connected and isolated wetlands in the landscape. The authors present the conceptual relationship between the nutrient removal processes as a function of its position in the landscape. They postulate that GIWs, and in particular small wetlands, are much more reactive than wetlands that are connected or adjacent to the stream network due to their soil surface area to storage volume ratio. Other contributing factors such as wetland perimeter-area ratios as well as the position, slope, and abundance within a watershed allow different types of wetlands to remove different nutrient constituents: in other words, different classes of wetlands can provide unique benefits and only a distribution of wetland classes will provide full functionality and ecosystem benefits [*Marton et al.*, 2015].

Thus, it is imperative that the functionality and behavior of these GIWs are quantified so that we can better understand how to protect our water resources and how to direct restoration efforts. Both *Verhoeven et al.* [2006] and *Mitsch et al.* [2005] quantified the potential of wetland restoration on catchment nutrient removal in Sweden and the Mississippi River Basin respectively. However, these studies did not focus on the role of size in nutrient removal but rather the total area that is required to improve water quality. Consequently, there remains a critical need to understand how the size of a wetland system can affect its nutrient processing ability so that we can manage the entire range of wetlands (based on size, connectivity, etc.) in a holistic manner.

2.4 Summary

Research in the lotic literature and in lake research have seen clear relationships between the biogeochemical functions of the water body and the size of the system while there has been fewer studies in wetlands literature. The need to directly quantify the role of size has increased with the surge of interest in understanding the functionality of GIWs and whether they are 'significant nexuses'.

Cross-system comparisons and meta-analyses (such as those conducted by *Alexander et al.* [2000]*, Harrison et al.* [2009]*, Downing et al.*[2010]*, Jordan et al.* [2011] that were previously discussed in this chapter) can help to identify interesting dynamics that are often missed when focusing on individual systems and have been used extensively in lotic literature as well as lakes research. The main benefit of meta-analyes are that emerging patterns emerge as the mean response of numerous data points that span a range of behavior whereas trends within a local system can be confounded by factors or be data limited. For example, *Seitzinger et al.* [2006] synthesized denitrification rates as a function of nitrogen loading and showed that there is a positive linear relationship across a range of ecosystems – a conclusion that may have been attributed to other local variables if the data originated from a single system. As such, there is a clear opportunity to explore how wetlands are able to remove or retain nutrients as a function of size through a meta-analysis of different systems across a wide range of spatial scales.

Chapter 3 – Methods

In **Chapter 3**, the methods for the various analyses conducted in the study are presented. **Section 3.1** describes the global meta-analysis on nutrient processing in wetlands, lakes, and reservoirs. The mechanistic modelling framework used to test the hypotheses is presented in **Section 3.2**. Finally, the upscaling analysis from individual wetland to the landscape scales are detailed in **Section 3.3**.

3.1   Cross-System Synthesis of Nutrient Processing in Lentic Systems

A database of water bodies and their nutrient processing capabilities was compiled through a literature review in Scopus in 2015 using a combination of the keywords "nutrients", "nitrogen", "nitrate", "phosphorus", and "phosphate" to constrain the nutrient constituents and the keywords "wetland", "lake", "pond", and "reservoir" to constrain the water body type. Studies providing data on hydraulic residence times as well as input/output concentrations and mass loads were included in the database and used in subsequent analyses (full data table in Supplementary Materials). Additionally, the North American Treatment Database v2.0 (NADB) was used for additional constructed wetland data prior to 1994 [*Knight et al.*, 1994]. A total of 1604 data points representing approximately 600 sites were included in the analysis (**Figure 1**).
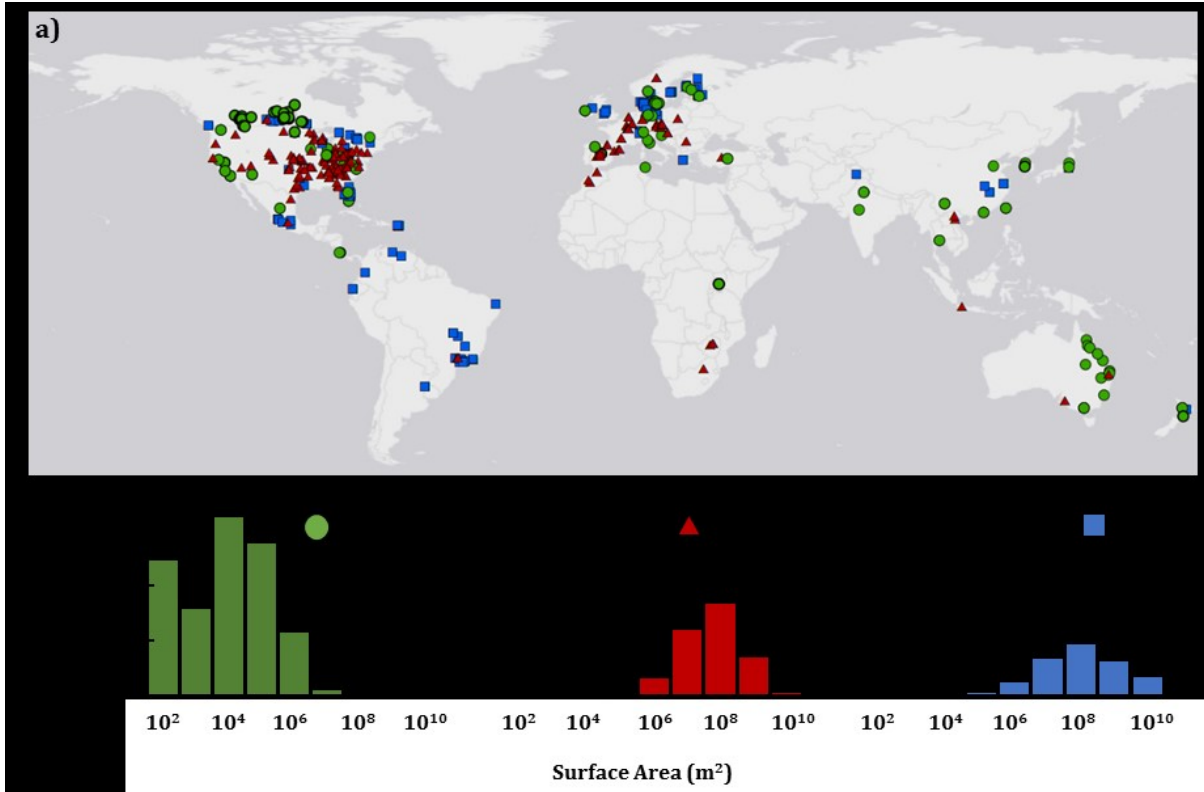
Figure 1. a) Locations of the study sites and the size distribution of b) wetlands, c) reservoirs, and d) lakes used in the analysis

3.2　　　　Estimating Rate Constants for Nutrient Retention

Nutrient retention (R) in wetlands, lakes and reservoirs refers to the removal processes in the water body, and is generally estimated as the difference between the input and output fluxes:

$$R = \frac{M_{in} - M_{out}}{M_{in}} \qquad (4)$$

where M_{in} and M_{out} are the measured mass fluxes at the inlet and outlet of the system, in units of mass per time [MT^{-1}].

To draw on the literature of different disciplines and systems of variable spatial scales in a comparable framework, we fitted the input-output loadings of lakes, reservoirs and wetlands into

the PFR and CSTR models to determine the effective volumetric removal rate constant. The use of a single effective rate constant to represent removal in lentic and lotic systems is common practice in most watershed models (as examples, see NiRReLa [*Harrison et al.*, 2009], SPARROW [*Smith et al.*, 1997]), despite the existing complexities and uncertainties related to removal at the local scale. All nutrient removal pathways (such as sedimentation and denitrification) were implicitly assumed to be incorporated into an effective removal rate constant within this framework under steady-state conditions (with seasonal and other effects averaged into the constant). Both $k_{v,P}$ and $k_{v,C}$ were calculated; however, the latter is presented only in the supplemental material for simplicity; all subsequent references of k in this paper refer to the volumetric PFR removal rate constant ($k_{v,P}$) unless specified. The k values that are derived from the data synthesis are the mean response of the spatiotemporal variability that may arise from hydroclimatic variability (such as the daily evapotranspiration rates and precipitation) and fluctuations in the controlling biogeochemical parameters (such as temperature, pH, available organic carbon material, oxygen levels).

3.3   Mechanistic Two-Compartment Model of Lentic Systems

3.3.1 Model Formulation

Similar to the OTIS modeling approach in lotic systems, a two-compartment sediment-water interaction model was developed in which an advective water column is coupled to a sediment zone by first-order mass transfer processes. The computational domain of the model includes the water column and a certain reactive depth d_r [L] of the benthic sediments (see **Figure 2**). The lotic system (wetland, lake, or reservoir) is modeled as a completely mixed reactor of volume V_w [L^3] and a steady flow rate Q [L^{3}T^{-1}]. The reactant of interest (N or P) enters the reactor as dissolved or suspended in the water column and leaves the reactor through the outflow. There is mass exchange between the reactant in the water column and the sediment, with a mass exchange rate coefficient

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α [T^{-1}]. In this model, denitrification in the benthic sediments is assumed to be the primary mechanism for long-term removal of nitrate, whereby nitrate is converted to gaseous N$_2$, N$_2$O or NO and released to the atmosphere [*Alexander et al.*, 2000; *Seitzinger et al.*, 2002; *Boyer et al.*, 2006; *Mulholland et al.*, 2008b]. Similarly, settling of sediment-bound phosphorus is considered to be the primary process responsible for the phosphorus removal [*Reddy et al.*, 1999; *Hejzlar et al.*, 2006; *Withers and Jarvie*, 2008]. Uptake by biota is not generally considered to be part of long-term removal since biologically-associated nitrogen and phosphorus is often recycled until ultimate burial via settling. Settling of phosphorus is described following the equations proposed by *Chapra* [1975]. Note that the goal of this study is not to develop the most comprehensive model for nitrogen and phosphorus cycling in lotic systems, but to demonstrate using a parsimonious modeling framework that the emergent patterns observed in the data synthesis can be explained using some basic principles.

The mass balance equations for the system can be written as:

For nitrogen:

$$\frac{dC_w}{dt} = \frac{Q}{V_w}C_o - \frac{Q}{V_w}C_w - \alpha(C_w - C_r) \tag{5a}$$

$$\frac{dC_r}{dt} = + \frac{V_w}{WA*d_r}\alpha(C_w - C_r) - k_{den}C_r \tag{5b}$$

For phosphorus:

$$\frac{dC_w}{dt} = \frac{Q}{V_w}C_o - \frac{Q}{V_w}C_w - \alpha(C_w - C_r) - C_w v_s SA \tag{6a}$$

$$\frac{dC_r}{dt} = + \frac{V_w}{WA*d_r}\alpha(C_w - C_r) \tag{6b}$$

where C_o is the N (or P) concentration in the inflow [ML^{-3}], C_w is the N (or P) concentration in the water column and the outflow [ML^{-3}], V_w is the volume of the water column [L^3], k_{den} [T^{-1}] is the intrinsic volumetric denitrification rate constant in the sediment, C_r is the N (or P) concentration in the pore water [ML^{-3}], WA is the wetted contact area [L^2], d_r is the effective reactive depth [L], v_s is the settling velocity for sediment-bound phosphorus [LT^{-1}] and SA is the surface area [L^2]. Note that the settling velocity v_s is a physically based parameter describing the net flux between downward sedimentation and upward sediment release or desorption.
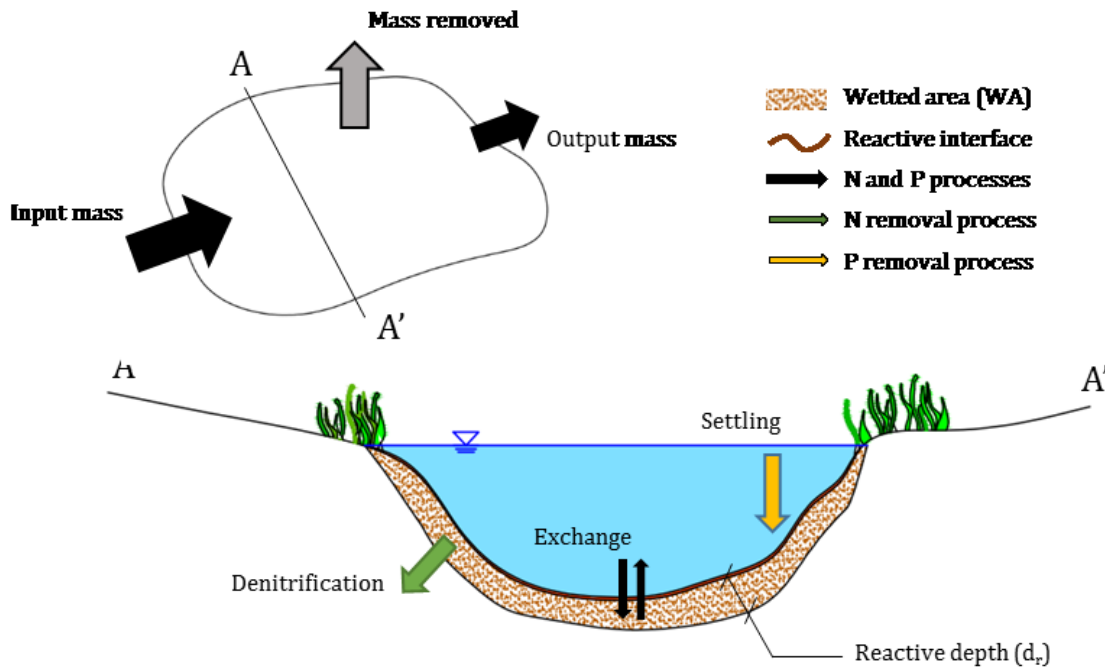
Figure 2. Plan and cross-sectional view of the two-compartment (sediment-water) model for nutrient mass removal

The coupled equations were solved at steady state to simulate the long-term input and output dynamics of nitrogen and phosphorus in these systems. The steady-state concentrations in the water column and the sediment pore water were obtained as a function of input concentration C_o, flow rate Q, wetted area WA, water column depth d, and volume of the water column V_w. Finally, the modelled steady-state output concentration C was used with the volumetric PFR equation (**Equation 4**) to determine the effective volumetric rate constant k.

3.3.2 Model Parameters

Our overall goal was to use the model to generate the removal rate constant k as a function of surface area SA. To achieve this goal, the range of SA values observed in the data analyses was discretized into six equally spaced bins ranging from 10^1 to 10^{11} m^2 on a logarithmic scale to cover the range of data. For each of the six area classes, the mean area was calculated, and empirical values of flow, input loading and system depth were obtained by using the equations from the regression analyses (see **Table 5**). A cylindrical bathymetry was then assumed to calculate V_w and WA from the mean surface area and depth parameters. The reactive depth d_r was assumed to be equal to 30 mm based on the zone of active denitrification seen in field studies [*Harvey et al.*, 2013]. To test the model sensitivity to the parameters, a local perturbation test was performed by changing a single parameter by 10% and comparing the percent change of output concentrations to the base case parameter set (**Supplementary Table S1**). The model is most sensitive to v_s, followed by k_{den}, d_r, and WA. The model is relatively insensitive to the other parameters. The methods used to account for the uncertainty that may stem from the wide variability of v_s and $k_{den,}$ are described in the following paragraph and sections. While the model is moderately sensitive to WA and d_r, we will not be exploring the effects of these parameters due to the low variability associated with these parameters given a wetland size class.

Both the intrinsic denitrification rate constant in the sediment k_{den} and the settling rates of phosphorus v_s have high degrees of variability in the environment. *Mulholland et al.* [2008b] measured the intrinsic denitrification rates in sediments from stable nitrogen isotopes across a wide range of biomes. They injected ^{15}N into the stream and measured the resulting concentrations across a characteristic length scale and derived various nutrient spiraling metrics including the sediment denitrification rate. These values had an asymmetric distribution that ranged between 0.002 to 4.8 hr^{-1} (mode = 0.01 hr^{-1}). Several authors have summarized phosphorus settling rates (for inorganic and organic P) for numerous lentic systems and their associated descriptive statistics

[*Chapra*, 1975; *Dillon and Molot*, 1996; *Hejzlar et al.*, 2006]. Similarly, *Battin et al.* [2008] conducted a synthesis of tracer experiments across a wide range of climatic zones (such as Arctic, semi-arid, tropical, temperate, etc.) and have provided a dataset of mass exchange coefficients. These mass exchange coefficients ranged from 0.02 to 16 hr^{-1} and are also skewed towards the mode of 0.36 hr^{-1}. Using these published datasets (**Figure 3**), lognormal probability distributions were fitted to the intrinsic denitrification rate, phosphorus settling rate, mass exchange coefficients datasets (summarized in **Table 2**) and were used in the subsequent Monte Carlo analysis.

Table 2. Fitting parameters for lognormal probability distributions

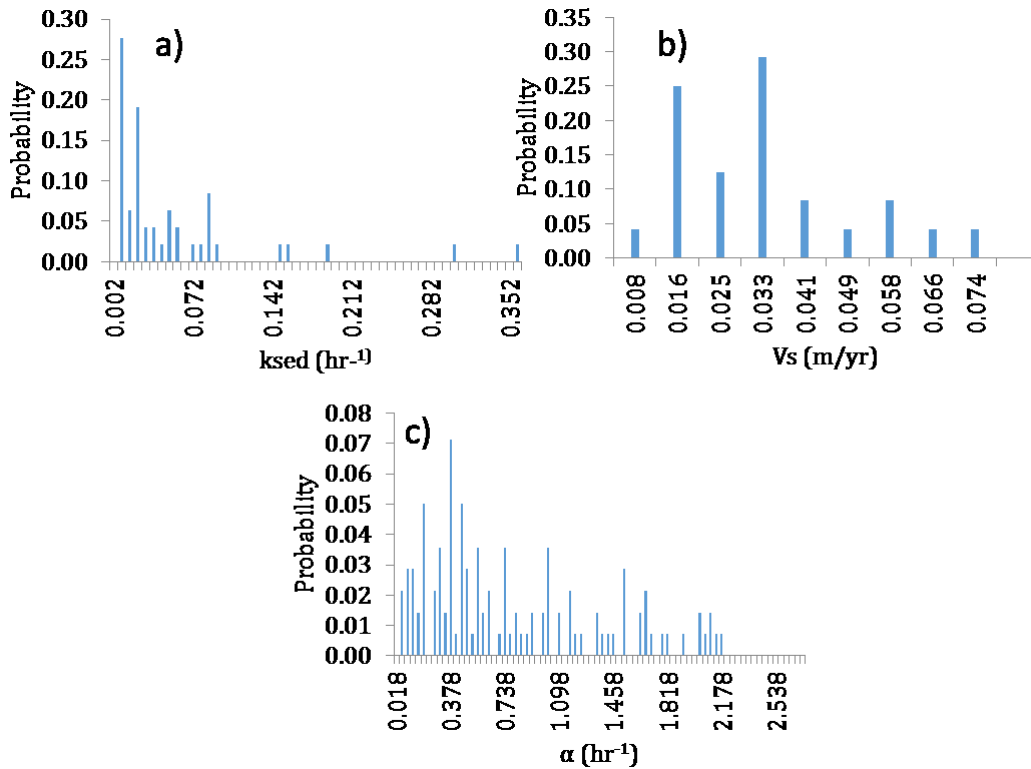|	μ_{ln}	σ_{ln}
k_{den} (hr^{-1})	-3.64	1.7
v_s (m/d)	-3.1	2.35
α (hr^{-1})	-0.35	0.6

Figure 3. Histograms of a) sediment denitrification rate constant, b) phosphorus settling rate, c) mass exchange coefficient [*Dillon and Molot*, 1996; *Hejzlar et al.*, 2006; *Battin et al.*, 2008; *Mulholland et al.*, 2008b]

3.3.3 Monte Carlo Analysis

Due to the uncertainty in the model variables, a Monte Carlo analysis (MCA) was used to quantify the range of likely model outputs. MCA is an iterative algorithm that requires one or more state variables to be described as probability distributions (**Figure 4**). For each iteration, a new random variable is drawn from each statistical distribution to create a unique subset of parameters and used in the model to generate a feasible output variable. This process is repeated so that a distribution of likely output values are generated and can be characterized by descriptive statistics (such as mean, median, etc.). The output distribution can be used to bound the output with confidence intervals based on the percentiles of the distribution.

A MCA analysis is typically run until the output distribution is considered stable (e.g. no significant changes to the mean or variance with increasing iterations). To ensure such conditions were met, the model was run 10,000 times for each size class using the values of L_o, Q, V_w, and WA, and the probability distributions for the intrinsic denitrification rate constant k_{den}, phosphorus settling velocity v_s, and the mass exchange coefficient α (**Figure 4**). The modeled output mass loadings were then used to calculate the median and 95th percentile values for R as well as the effective removal rate constant k for each size class (see **Table 4**). The 5th and 95th percentile of extreme values from the final set of outputs were used as the confidence intervals for the median value. The k values obtained for the six size classes were used to create the modeled k-τ relationship, which was then compared with results from the meta-analyses.
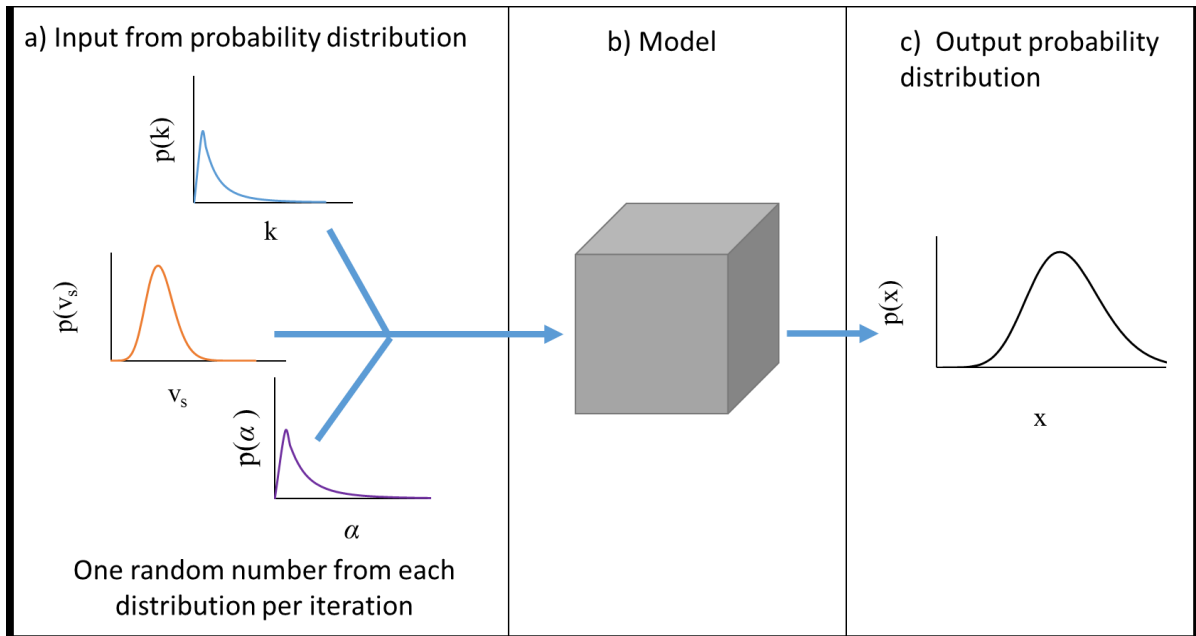
Figure 4. Schematic of Monte Carlo simulation process. Steps a) and b) will be run multiple times to generate the final output distribution.

3.4   Scaling Up: From Individual Wetlands to Landscape Scale Nutrient Removal

The results of the data synthesis were upscaled to the landscape scale to determine the relative role of different sized wetlands in removing nutrients from the water column. The focus of this analysis was on wetlands; however similar conclusions should hold for other water bodies. The size-frequency function of lakes and reservoirs also follows an inverse power-law distribution [*Downing et al.*, 2006] and the loading-size as well as the *k-τ* relationships of lakes and reservoirs were found to be consistent with the wetland relationships. Lakes and reservoirs were omitted due to the lack of fine-resolution datasets that would allow the results to be upscaled concurrently for the same area as the wetlands.

3.4.1   Regression Relationships for Scaling

The total mass of nutrients removed L_r [MT^{-1}] in wetlands as a function of surface area *SA* can be described using the following equations:

$$L_r = R(SA) \times L_o(SA) \times N(SA) \tag{7}$$

$$R(SA) = 1 - e^{-k(SA)\tau(SA)} \tag{8}$$

where L_o is mass loading into the system [MT^{-1}], N is the number of water bodies with a given surface area and R is the fraction of mass removed given the system surface area [-]. Note that $L_o(SA)$, $k(SA)$, and $\tau(SA)$ relationships were developed based on the data synthesis described in **Section 3.1**. The form of **Equation 8** is derived from the plug flow reactor model relationship (See **Table 1**). The $N(SA)$ relationship was based on a distribution of wetlands found in the prairie pothole region in Iowa. A previous study had used high-resolution (1 m resolution) LIDAR data to estimate the number of water bodies as a function of surface area in the Des Moines Lobe in Iowa [*Van Meter and Basu*, 2015]. This size-frequency distribution was chosen as there have been few studies that have quantified the distributions of small wetlands at such a fine spatial resolution within landscape scales. Global datasets such as the HydroLAKES database which characterizes the area, volume, and residence times of lakes are truncated at waterbodies less than 10 ha in area [*Messager et al.*, 2016] – thus would not be useful when attempting to quantify the truly smaller systems. The Des Moines Lobe landscape is part of the Prairie Pothole Region, which has numerous depressional features with surface areas ranging from 100 m^2 to 5×10^4 m^2 [*Van Meter and Basu*, 2015]. Analyses by *Van Meter and Basu* [2015] showed that there is a power law relationship between the number of depressional wetlands in the lobe and their surface areas (**Figure 5**; $N = 2 \times 10^{10} \times SA^{-1.67}$; p <0.001; $r^2 = 0.99$). Or in other words, the smallest wetlands are found more frequently in the landscape than their larger parts; small wetlands sized 10^3 m^2 have a frequency three orders of magnitude higher than those sized 10^5 m^2 in the Des Moines lobe landscape. These depressional landscapes, much like lakes and other earth system features, follow a power-law distribution which speaks to the fractal nature of the erosional processes and form

these features and thus the relationship's lack of dependence on spatial scale [*Downing et al.*, 2006; *Seekell and Pace*, 2011; *Seekell et al.*, 2013].
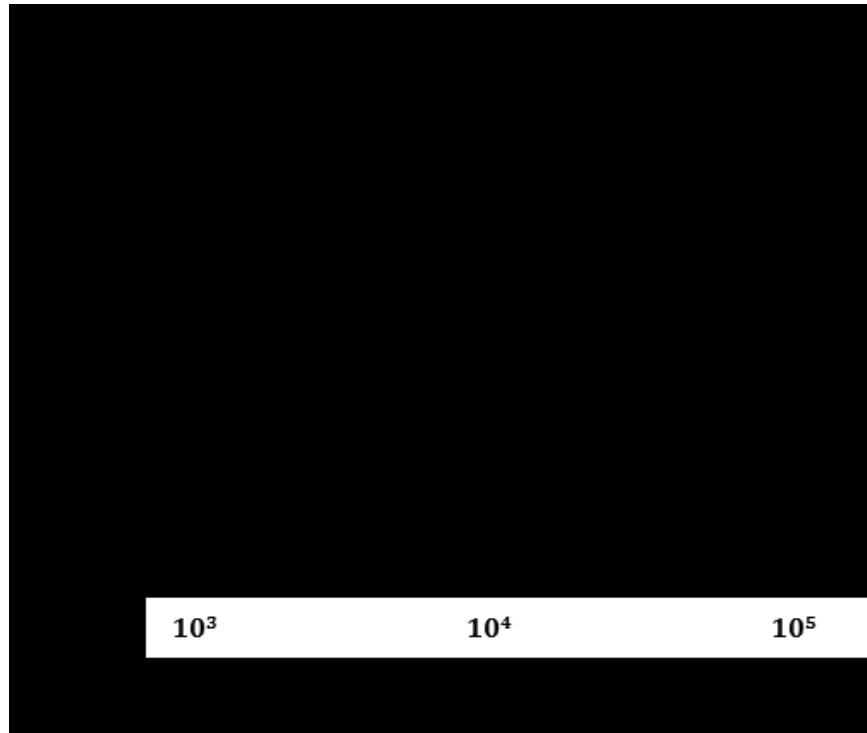
Figure 5. Historical size-frequency relationship for depressional wetlands in the Des Moines Lobe, Iowa, USA *[Van Meter and Basu, 2015]*.

3.4.2 Monte Carlo Analysis

Similar to the MCA used to quantify the uncertainty of the model outputs in **Section 3.2**, a Monte Carlo approach was also used when solving **Equation 7** to develop estimates of the cumulative mass removed for each wetland size class. The surface areas used in the analysis ranged between 10^2 and 10^5 m^2 to model the wetland sizes found in the Des Moines Lobe; thus, the wetlands were divided into six equally sized bins (10^2 to $10^{2.5}$, $10^{2.5}$ to 10^3 m^2, etc.).

To describe the associated uncertainties for each wetland size class, lognormal probability distributions were fitted to the associated removal rate constants k, hydraulic residence times τ, and mass loading L_o found in each size class. Specifically, the range of values that were found in

the data synthesis for each parameter were separated into each size class. A distribution was then fitted to the subsets of each parameter of each bin for use in the MCA.

The Monte Carlo analysis was run using 10,000 simulations for each bin to generate a range of probable values for the mass loading removed L_r by drawing on a new parameter set from the various probability distributions each time. The interquartile values of mass removal for each size class were determined and used as the bounds around the median values.

3.4.3 Denitrification Potential Loss at the Landscape Scale

Since wetlands are typically hotspots of nitrogen removal in the landscape, loss of wetlands is analogous to a Denitrification Potential Loss (DPL) of the landscape. In this section, the question whether DPL is greater when smaller wetlands are preferentially lost in the landscape, or is it larger when we preferentially lose the larger ones is asked. This is relevant because previous research has shown that humans preferentially drain smaller wetlands in the landscape [*Van Meter and Basu*, 2015]. The cumulative DPL loss was estimated by semi-analytically integrating the *Lr-SA* relationship derived in **Section 3.3.1** using different intervals of integration using the following equation:

$$\int_{SA_i}^{SA_{i+1}} L_r \, dSA = \int_{SA_i}^{SA_{i+1}} R(SA) \times L_o(SA) \times N(SA) dSA \tag{9}$$

where SA_i and SA_{i+a} create discrete bounds that are equally sized on a logarithmic scale from 10^2 to $10^5 \, m^2$. In this analysis, twelve bins were created: 10^2 to $10^{2.5}$, $10^{2.5}$ to $10^{2.75}$ … $10^{4.75}$ to $10^5 \, m^2$ to span the range of system sizes found in the Des Moines Lobe (**Section 3.4.2**).

Two scenarios were created to simulate wetland loss: Scenario one describes the progressive loss starting with the small size classes towards the large size classes, Scenario two simulates the

preferential loss of large wetlands first. The DPL was then normalized to the total denitrification potential of the original landscape to determine the fractional DPL due to wetland loss.

Chapter 4 – Results and Discussion

4.1 Results of Data Synthesis

4.1.1 Percent Nutrient Removal for the Different Water Bodies

A total of 355 wetlands, 138 reservoirs and 117 lakes were synthesized in this study. The means and standard deviations of percent removal of TN, TP, nitrate and phosphate were calculated for the lakes, reservoirs and wetlands (**Table 3**). A standard two sample t-test assuming unequal variances was used to compare the means between each constituent and system. The samples are independent, assumed to follow a normal distribution (given the Central Limit Theorem with large sample sizes) and the data are continuous – thus satisfying the assumptions of the statistical test. Overall, the percent removal does not vary significantly between systems (all wetlands, lakes, and reservoirs) and across constituents, ranging between 32% and 65% ($p<0.05$). Natural wetlands had a wider variance in means (except nitrate) compared to other systems; however, there were not many natural wetland data points relative to the other systems due to the difficulty in quantifying the hydrological and bathymetrical parameters in these systems.

Table 3. Mean removal (%) of constituents by system

	TN	NO_3^-	TP	PO_4^{-3}
All Wetlands	49.4 ± 25.4	60.8 ± 29.5	49.0 ± 28.8	52.3 ± 30.5
CSF	47.1 ± 21.8	52.0 ± 28.2	39.8 ± 29.3	49.8 ± 26.5
CSSF	51.0 ± 26.3	65.3 ± 29.4	51.7 ± 28.4	53.8 ± 32.0
NW	17.5 ± 14.4	58.7 ± 26.1	27.9 ± 26.1	26.3 ± 19.2
Lakes	44.0 ± 27.4	59.4 ± 28.2	50.2 ± 25.5	65.2 ± 27.7
Reservoirs	31.8 ± 20.6	46.9 ± 24.0	47.8 ± 25.6	64.7 ± 18.9

Note: Natural Wetlands (NW), Constructed Subsurface (CSSF) and Constructed Surface Flow (SF) wetlands are subsets of the total wetlands.

4.1.2 Nutrient Removal Rate Constants as a Function of System Size

The volumetric nutrient removal rate constants k of all four constituents (TN, NO_3^-, TP, PO_4^{-3}) follow a significant inverse relationship with the residence time of the system ($p<0.001$).

Residence time can be a surrogate for system size, where longer residence times indicate larger water bodies. Within the dataset, water residence time has a significant positive relationship with surface area (p<0.002) and is illustrated in **Figure 6** (τ=1.44xSA$^{0.23}$). It was assumed that confounding factors such as managed flows, relative magnitude of groundwater exchange, and preferential flowpaths which cause variance in this relationship will not significantly alter the slope of this relationship at longer time scales.
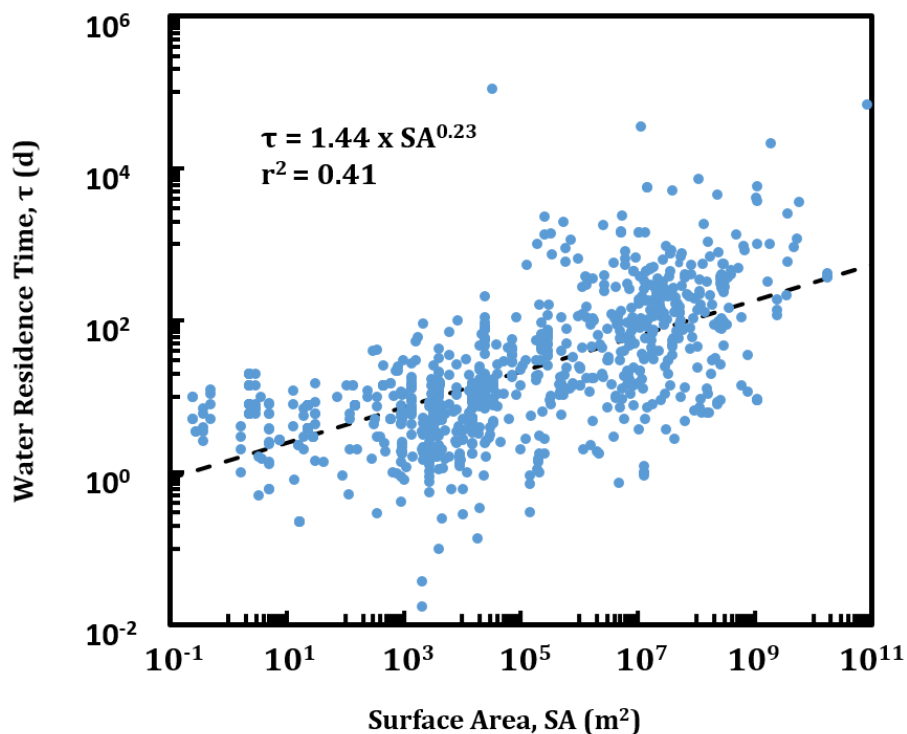
Figure 6. Water residence time (τ) versus surface area (SA) regression based on entire dataset from meta-analysis.

The data all follow a power law function that is consistent across six orders of magnitude for residence times. The inverse relationship holds whether a CSTR or a PFR model is assumed to describe the reaction kinetics. **Figure 7** and **Table 4** show the values based on the PFR model, while **Supplemental Figure S1** shows the similar results obtained under the CSTR assumption. The strong relationship between the rate constant and the water residence time for the variety of system types (wetlands, lakes or reservoirs, as well as their trophic state, climate, nutrient loading,

etc.) suggests that there is a common physical constraint acting as the primary modifier of the relevant biogeochemical processes. The physical constraint altering biogeochemical processing could likely be attributed to the wetted sediment area (total area of sediment that comes into contact with water) to water volume ratio, with larger water bodies having a smaller ratio, and thus smaller effective rate constants. In the following section, a model analysis is used to explore this hypothesis.

Figure 7. Removal rate constant (k) versus hydraulic residence time (τ) for a) total nitrogen (TN), b) nitrate (NO_3^-), c) total phosphorus (TP), d) phosphate (PO_4^{3-})

The effective removal rate constants were also regressed against surface area (**Figure 8**). Again, there were significant inverse relationships between k and SA across all four constituents. It should be noted that the best fits were weaker with surface area and the r^2 values ranged from 0.13 to 0.52 but the downward slopes remained significant. The lower r^2 values point to other drivers of the

relationship such as depth and water residence time. However, surface area is an important proxy for these factors as it is the parameter most easily collected from aerial imagery and for use in watershed or global analyses as both depth and flow typically requires field measurements.

It is likely that the hydraulic residence time serves as a better proxy for the sediment area-volume ratio as τ can be derived from the volume, surface area, as well as the flow of the system. Thus, the hydraulic residence time better integrates the hydrology and the geometry of the system than simply the surface area.
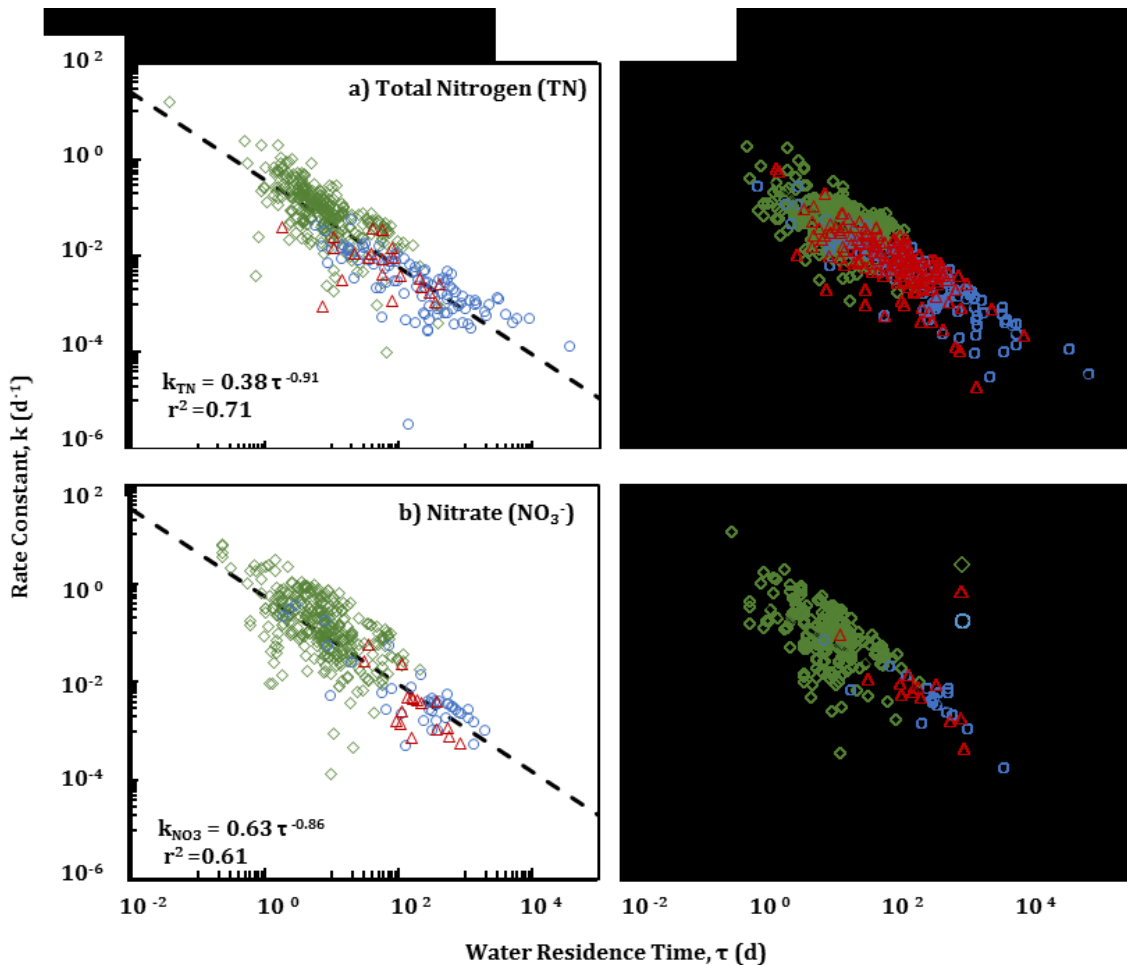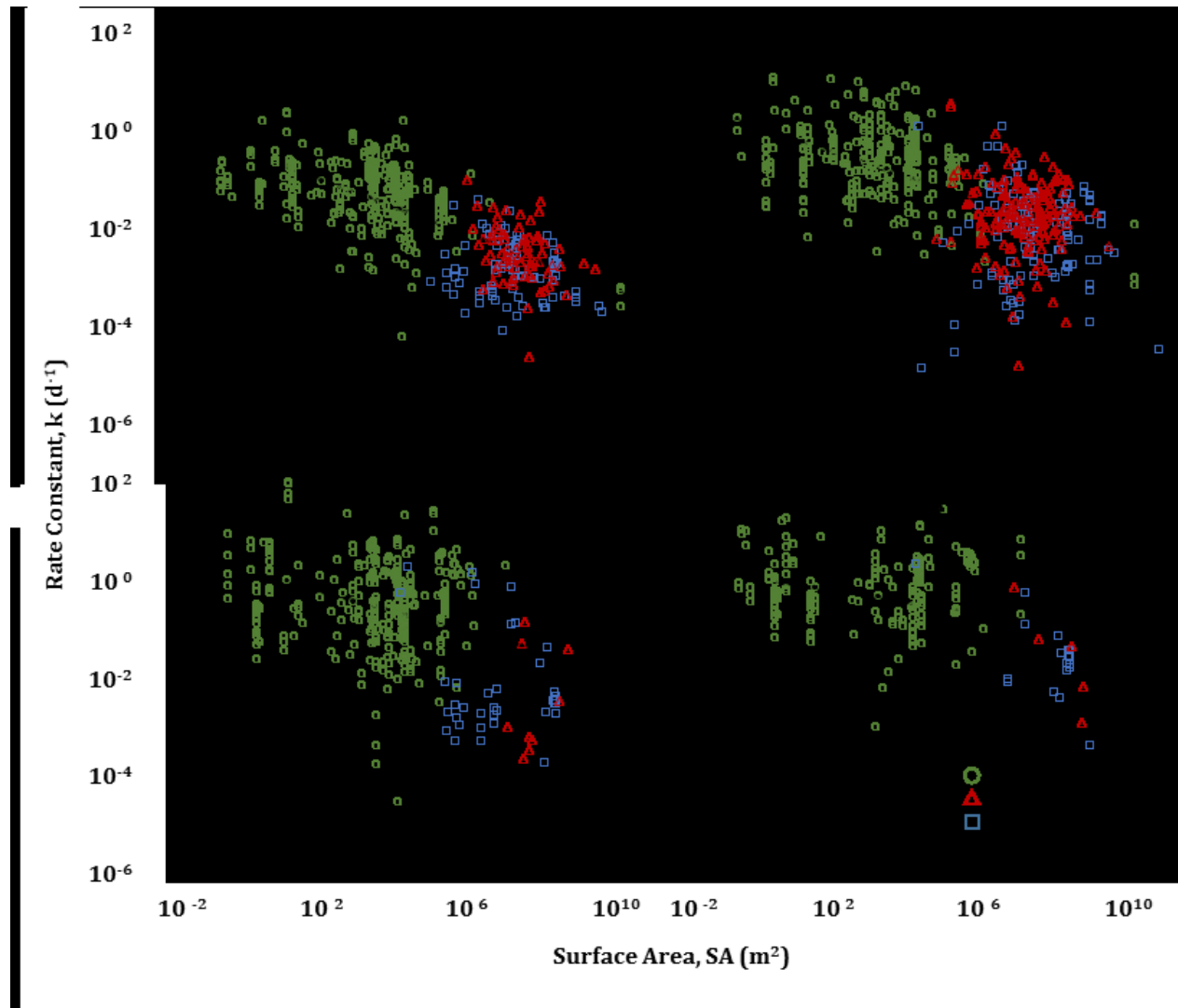

Figure 8. Removal rate constant (k) versus surface area (SA) for a) total nitrogen (TN), b) nitrate (NO_3^-), c) total phosphorus (TP), d) phosphate (PO_4^{3-})

While all available data on lotic systems were used to develop a single regression equation for each constituent in **Figure 7**, also explored the individual relationships between effective removal rate constants and residence times for lakes, reservoirs, surface and subsurface flow constructed wetlands were also explored (**Table 4**). All the different water body types show statistically significant power function relationships between the effective removal rate constant and the residence times (**Table 4**). For TN, the constant of the relationship was an order of magnitude higher for wetlands than for lakes and reservoirs, and the slope for wetlands was also slightly greater. A higher constant and a steeper slope for wetlands indicate that (a) smaller wetlands are disproportionately more reactive than smaller lakes or reservoirs; (b) the surface area to volume ratio is a more critical control for wetlands. Similar patterns are observed for TP, with wetlands having a greater constant and steeper slope compared to lakes and reservoirs. The patterns for nitrate and phosphate are much less apparent; however, the dataset is also much more sparse for these two constituents.

Table 4. Summary of k-τ regression analyses for lakes, reservoirs and wetlands

Element	System	n	Constant	Exponent	p	r^2
TN	Lakes	102	0.048	-0.55	<0.001	0.392
	Reservoirs	74	0.053	-0.60	<0.001	0.427
	Wetlands	357	0.375	-0.78	<0.001	0.475
	CSSF	95	0.413	-0.80	<0.001	0.292
	CSF	249	0.295	-0.65	<0.001	0.414
	NW	9	0.169	-1.10	<0.001	0.848
NO_3^-	Lakes	40	0.184	-0.72	<0.001	0.724
	Reservoirs	17	0.884	-1.09	<0.001	0.564
	Wetlands	338	0.540	-0.73	<0.001	0.374
	CSSF	106	0.365	-0.60	<0.001	0.171
	CSF	220	0.635	-0.75	<0.001	0.392
	NW	12	1.009	-1.08	<0.001	0.900
TP	Lakes	117	0.186	-0.78	<0.001	0.807
	Reservoirs	178	0.175	-0.73	<0.001	0.546
	Wetlands	332	0.306	-0.71	<0.001	0.404
	CSSF	63	0.228	-0.62	<0.001	0.226
	CSF	255	0.289	-0.66	<0.001	0.332
	NW	7	0.256	-1.01	<0.001	0.913
PO_4^{3-}	Lakes	18	0.122	-0.60	<0.001	0.763
	Reservoirs	13	0.803	-0.95	<0.001	0.791
	Wetlands	209	0.321	-0.67	<0.001	0.279
	CSSF	53	0.388	-0.76	<0.001	0.298
	CSF	149	0.306	-0.65	<0.001	0.245
	NW	4	0.190	3.02	0.73*	0.075

Note: Natural Wetlands (NW), Constructed Subsurface (SSF) and Constructed Surface Flow (SF) wetlands are subsets of the total wetlands. The number of SSF and SF wetlands may not add up to the total number of wetlands due to unclassified or hybrid wetland types. *Exponent value not significant

Table 5. Summary of regression analysis for various parameters derived from data synthesis. All water body types were included in the analysis. Regression parameters are all significant (p<0.001).

Regression Equation	r^2
$Q = 41.6 \times SA^{0.91}$	0.87
$d = 0.13 \times SA^{0.21}$	0.50
$L_o = 0.05 \times SA^{0.45}$	0.44
$\tau = 1.51 \times SA^{0.23}$	0.40

4.1.3 Hydrologic versus Biogeochemical Controls on Nutrient Removal Rates

The balance between hydrologic and biogeochemical controls on removal rates can be expressed most succinctly by the dimensionless Damkohler number Da, defined as the ratio between the transport and the reaction timescales ($\tau / (1/k)$). A Damkohler number equal to 1 indicates that the transport and reaction timescales are balanced, while $Da < 1$ indicates transport limitation, and $Da > 1$ implies reaction rate limitation where biophysical conditions are limiting for the reaction [*Harvey et al.*, 2013]. For this study, a large fraction of the Da values were less than 1 across all systems (**Figure 9**), suggestive of a transport-limited system. The reaction rate constant, however, is not the intrinsic reaction rate in the sediment, but is modified by the sediment-area to water volume ratio as described in **Section 3.3**. Thus, a transport limitation implies access limitation to the reactive sediment zone where denitrification or sediment entrapment occurs removing the element (N or P) from the water column.
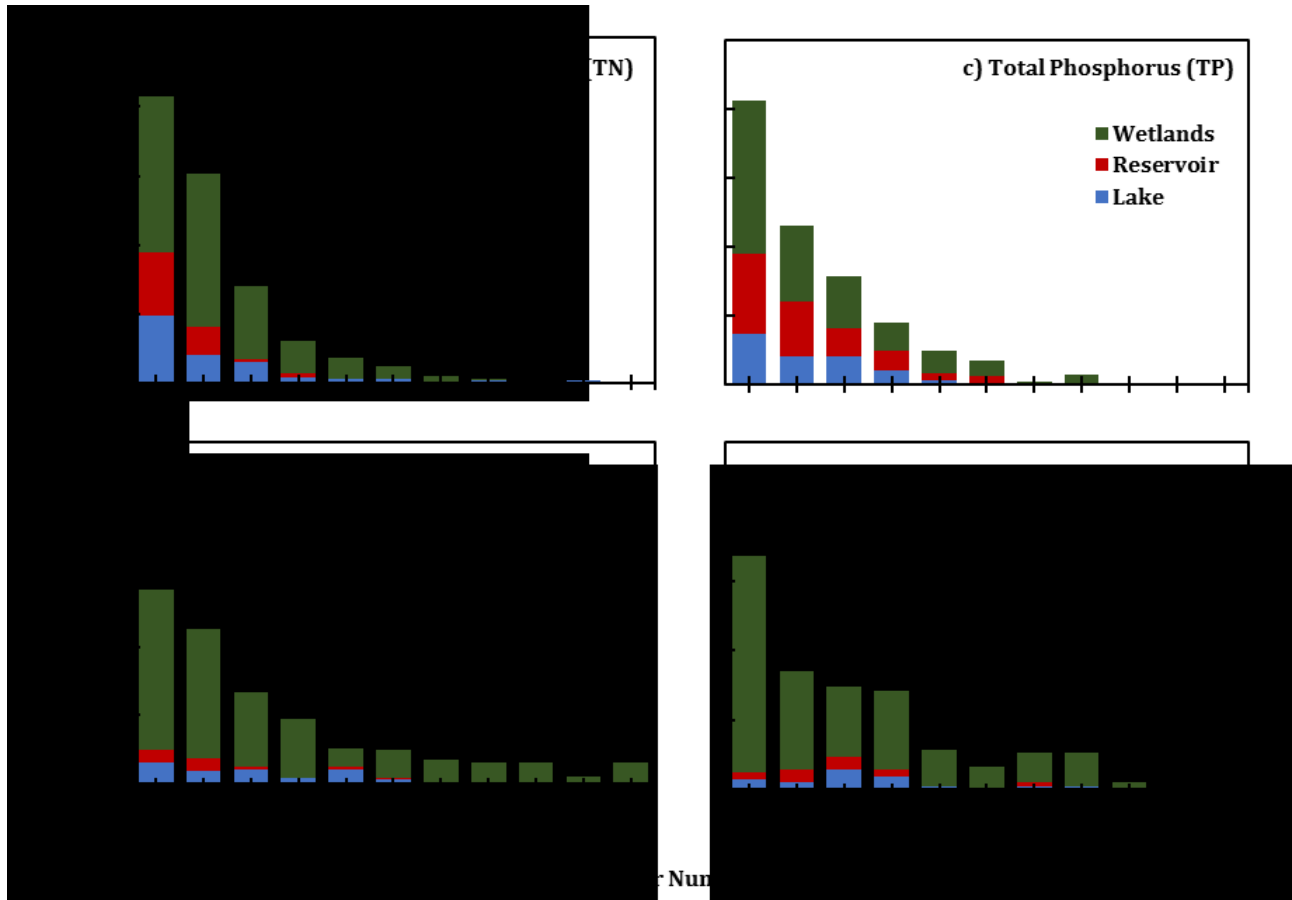

Figure 9. Frequency distributions for the Damkohler number ($\tau/(1/k)$)

4.2   Results of Model Analysis

The regression relationships developed from the entire dataset for Q and d with surface area (**Table 5**) were used with the lognormal distributions for k_{den} and v_s to run the model 10,000 times for each size class, and the values of the volumetric rate constant k was plotted as a function of residence time (**Figures 10a** and **b** for nitrogen and phosphorus respectively). These modeled-derived relationships were then compared with the data-derived relationship between k and residence time. The 95% confidence intervals on the modeled relationship capture the variability in the data adequately well with 94% of the TN data and 77% of the TP data falling within the model-derived bounds (**Figures 10a** and **b**). The correspondence between the modeled and data-derived relationships confirm our hypothesis that the greater surface area to volume ratio of the smaller water bodies is the primary factor contributing to their larger rate constants.

It is interesting to note that for nitrogen, the mean value of the intrinsic rate constant in the sediment (k_{den}) used in our model is equal to 0.63 d^{-1}, which is close to the k values from systems with lower residence times, and larger contact area to volume ratios. With increasing size of the water body and residence times the effective rate constant decreases following a power function to as low as 0.001 d^{-1}. Thus, the intercept of the k-τ relationship is indicative of biogeochemical control, while the slope is controlled by hydrology. In other words, the intrinsic rate constant in the sediment is a primary control on the intercept, with the effective k of small systems approaching k_{den}; the water residence time (which largely controls how much of the water and nutrient comes into contact with the sediment and for how long acts) as a further modifier that reduces the intrinsic rates. For phosphorus, the mean v_s value of 16 m/year and the 95% CI range between 3.3 and 79 m/year falls within the observed ranges reported in the literature (12-36 m/yr [*Hejzlar et al.*, 2006], 16 m/yr [*Chapra*, 1975], 6-81 m/yr [*Dillon and Molot*, 1996].

The variance around the median may be attributed to some of the assumptions made in the model conceptualization. The hydrology of the system is assumed to be driven only by a generic point

inflow and is discharged by a point outflow. Other fluxes such as groundwater exchange with the surrounding uplands or aquifers are neglected, as are seasonal non-point sources of water such as snowmelt or flood events. These dynamics are difficult to capture in a generalized modelling framework yet they can modify the nutrient dynamics of the system. For example, groundwater often has a different oxygen concentration than that of the sediment bed (may depend on if the groundwater is sourced from deep or shallow aquifer, and if the discharge is near the edge or bottom of the water body) and will alter the redox gradient and modify the denitrification rates in the system [*Stoliker et al.*, 2016]. Similarly, the oxic level of the sediments determine the source-sink dynamics of sorbed P. In oxic conditions, iron hydroxides are strongly bonded and limit the diffusive flux between the water-sediment interface; in anoxic conditions, the phosphorus is released [*Van Cappellen and Berner*, 1988; *Slomp et al.*, 1996, 1998].
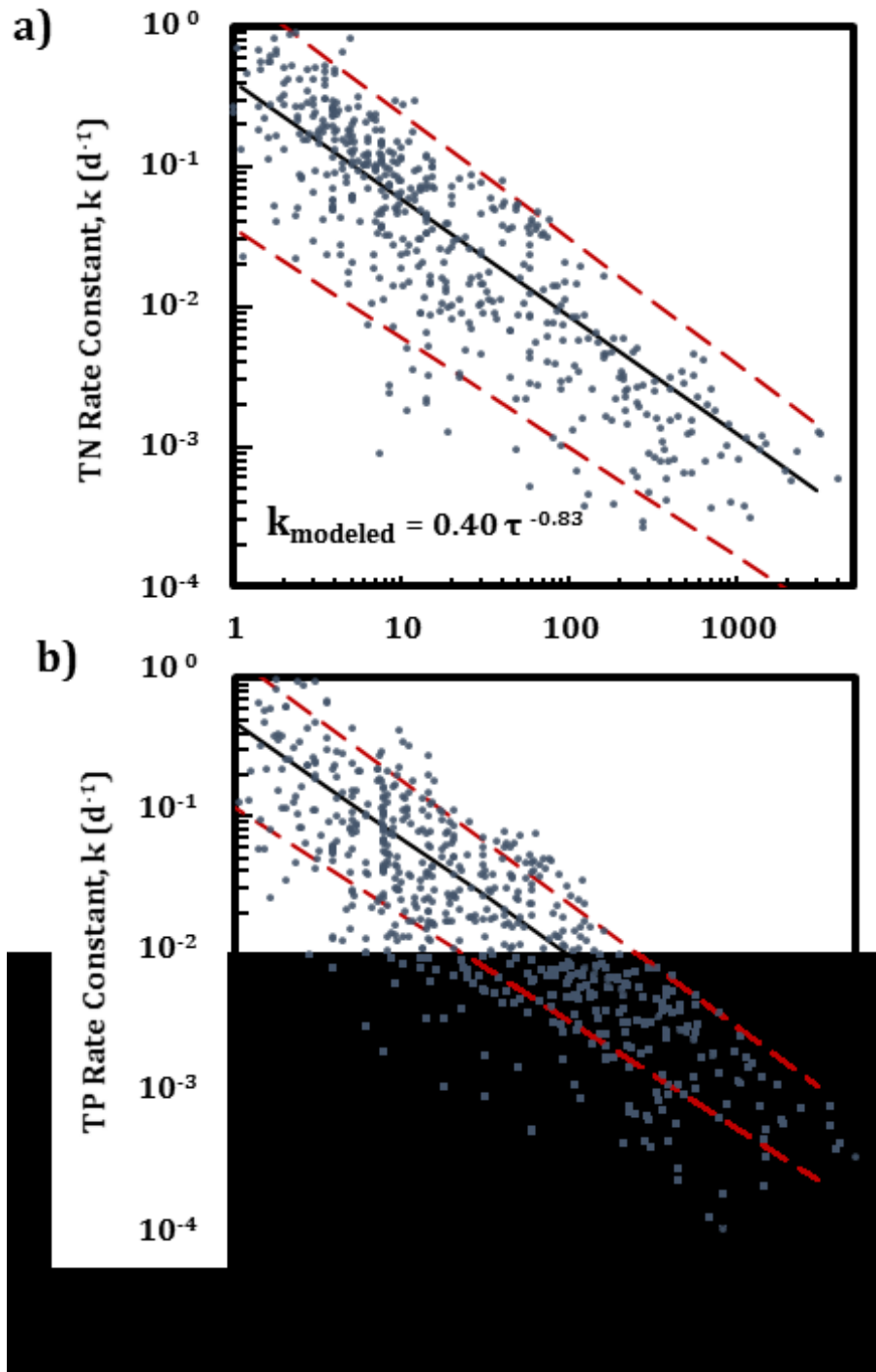
Figure 10. Comparison between the model-estimated k-τ relationship (solid line) and data from meta-analyses for a) total N and b) total P. Scatter plot is data based on meta-analyses, while the lines are modeled values. The black solid line is the median value, while the red dashed lines are the 95% confidence intervals of the k-τ relationship derived from Monte Carlo simulations. The black horizontal dashed line in 4a is the intrinsic sediment denitrification constant that captures the biogeochemical control on the relationship.

4.3   Exploring Dominant Controls on the Observed Inverse *k-SA* Relationship

Both the data and model results reveal an inverse relationship between the water residence time (or surface area) and the effective nutrient removal rate constant. The cause of this behaviour can likely be attributed to the higher ratio of wetted sediment area and the volume of water (*WA:V* ratio) in small water bodies. As discussed previously, the sediment zone is a critical part of the nitrogen and phosphorus cycles where denitrifying bacteria can remove nitrogen and is the storage zone for sediment bound P. Here, the relationship between the *WA:V* ratio and size using an analytical expression is shown.

The model described above assumes a cylindrical bathymetry for ease of calculations. The wetted area term serves as a link between the bathymetry and the removal processes in the system. To determine a relationship between the size of a water body and wetted area, the bathymetric relationship developed by Hayashi and van der Kamp [2000] was used:

$$\frac{y}{y_o} = \left(\frac{r}{r_o}\right)^p \tag{10}$$

where y and r are the maximum depth and radius of the water body [L], y_o and r_o are the depth and radius at a reference depth [L] and p is a shape factor. The shape factor describes the slope of the water body where $p=1$ creates a cone and p approaching infinity creates a cylinder (**Figure 11**). Surface area-wetted area-volume relationships were developed by integrating the bathymetric equation (i.e. the slope profile) around the vertical axis.
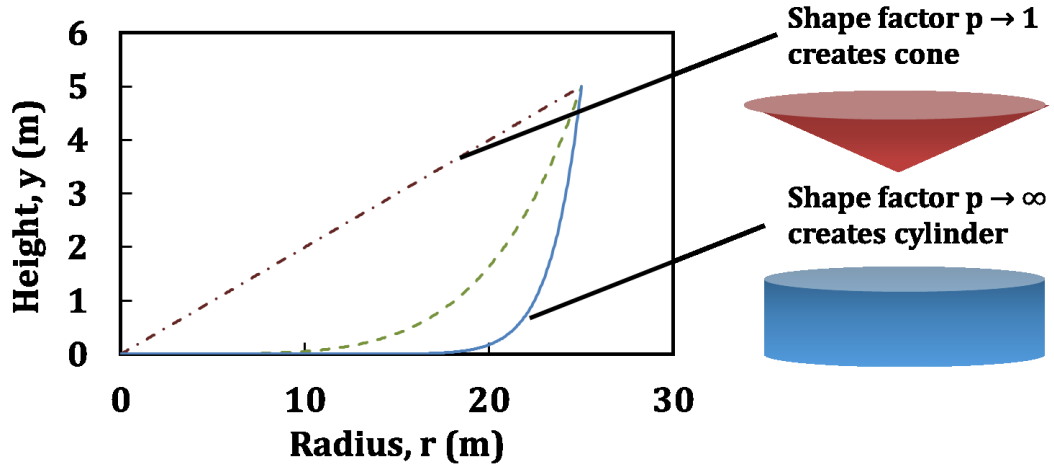
Figure 11. Example slope profile of symmetric basin following $y = y_o(r/r_o)^p$

The effect of varying bathymetry was explored by calculating the wetted area – volume ratio of the water body. As such, the wetted contact area (S_y) and volume (V) were calculated using **Equations 11 and 12** respectively:

$$S_y = 2\pi \int_{y_1}^{y_2} r(y) \sqrt{1 + \left(\frac{dr}{dy}\right)^2}\, dy \tag{11}$$

$$V = \pi \int_{y1}^{y2} y(r)^2\, dy \tag{12}$$

where *Sy*, which represents the wetted contact area and is the surface of revolution along the y-axis, *r* is the radius as a function of depth (based on **Equation 10**), *V* is the volume of the solid of revolution along the y-axis.

A common metric for the biological richness and diversity of a wetland is the perimeter-area ratio [*Helzer and Jelinski*, 1999; *Fairbairn and Dinsmore*, 2001]. The same metric can also be used in determining wetland hydrological behaviour. Studies such as those by *Millar* [1971] and *Hayashi and Rosenberry* [2002] found that the water level recession in wetlands are highly dependent on the perimeter-area ratio which accounts for the higher surface areas allowing for evapotranspiration or groundwater exchange. Thus, it should follow that nitrogen and phosphorus

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removal dynamics in lentic systems, which are greatly dependent on the hydrological processes and pathways, should also be dependent to analogous metrics such as the wetted area-volume ratio.

The wetted contact area-volume ratio, regardless of the shape of the system, is higher for smaller systems (**Figure 12**). This relationship supports the hypothesis that a controlling factor to the overall reactivity of the system is dependent on size due to the contact area-volume ratio. The effect is most apparent for small water bodies: accounting for system bathymetry will be more important when modelling the biogeochemical processes for small systems. However, this relationship tends to converge at larger scales where the wetted area approaches unity with volume due to the relatively small magnitude of depth.
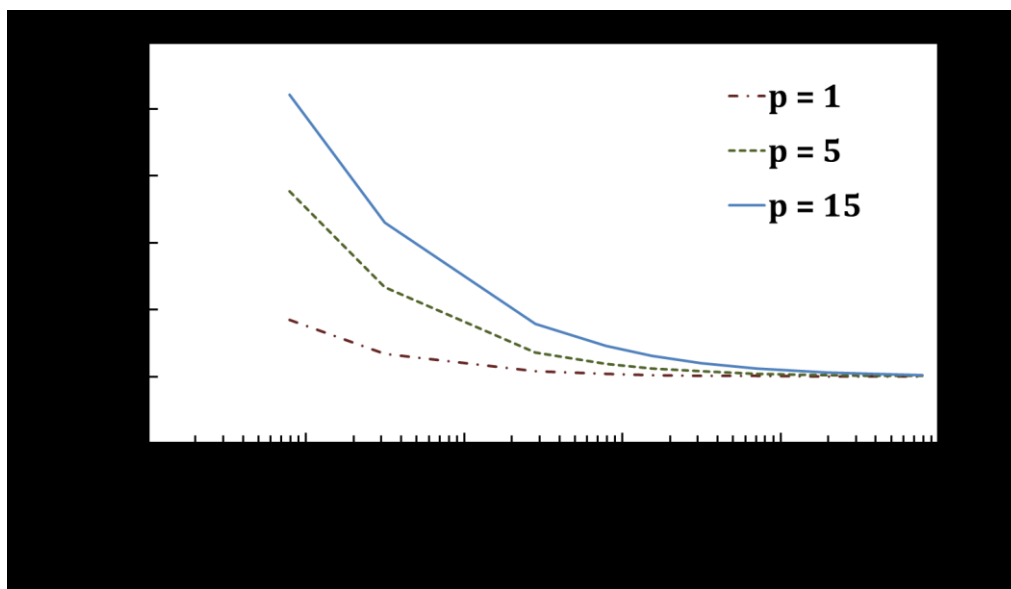
Figure 12. Decreasing wetted area-volume ratio as a function surface area

The shape of the water body is another factor that can affect the wetted area-volume ratio. Systems that are more conical in shape tend to have a higher ratio when compared to cylindrical systems. However, the conical and cylindrical are end members of likely scenarios with most systems having concave bathymetries but the negative relationship between the wetted area-volume ratio and surface area still holds true.

4.4   Nutrient Removal Potential Loss at the Landscape Scale

The TN mass removed by wetlands belonging to different size classes, and the cumulative fraction of mass removed are presented in **Figure 13**. The results clearly demonstrate that in a landscape with a distribution of wetland sizes the smaller wetlands remove a greater amount of TN than the larger ones. In fact, approximately 50% of the TN loading is removed by wetlands smaller than $10^{2.5}$ km^2. The disproportionate removal by the smaller systems occur due to their high removal rate constants coupled with a higher frequency of smaller water bodies on the landscape (**Figure 13**). The results are very similar for the other constituents (TP, nitrate and phosphate) since the *k-τ* relationships are not significantly different for the different species. It is important to note again that the similarity in the *k-τ* relationships for the four constituents with very different biogeochemical properties points to the strong hydrologic controls that overwhelm the site-specific biogeochemistry.

To explore the effect of the preferential loss of smaller water bodies, we calculated the fractional denitrification potential lost as a function of fractional loss in wetland area. When smaller wetlands are lost preferentially (green line in **Figure 14**), a greater fraction of the denitrification potential is lost, even when the same amount of wetland area is lost, compared to the case when larger wetlands are lost preferentially (red line in **Figure 14**). Thus, for the same fractional area of wetlands lost in the landscape, a greater fraction of the denitrification potential will be lost if we lose smaller versus larger wetlands.

The observation of a greater fraction of nutrients removed by smaller wetlands is significant, especially in the context of the current loss of protection for smaller wetlands on the landscape. Regions such as the historically wetland-rich Prairie Pothole Region have indeed seen a disproportionate loss of small wetlands to agriculture [*McCauley and Jenkins*, 2005; *Van Meter and Basu*, 2015]. Urban landscapes have lost water bodies with a preferential loss of smaller

systems relative to the surrounding undeveloped land [*Steele et al.*, 2014; *Steele and Heffernan*, 2014]. This disappearance of small wetlands thus has significantly impacted landscape-scale nutrient-processing potential and thus must be better taken into account with regard to wetland protection and wetland restoration efforts.
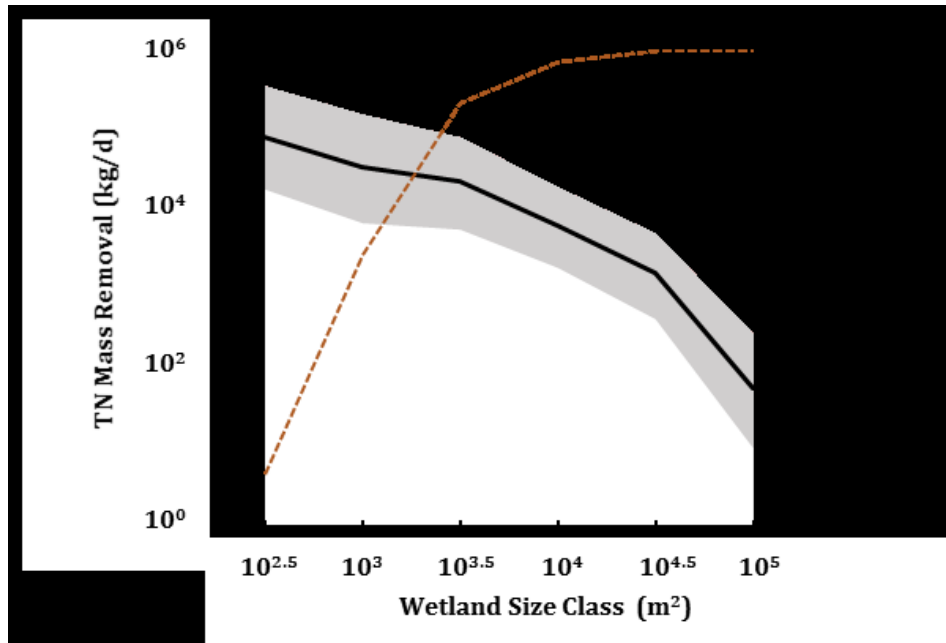
Figure 13. The TN mass removed (solid line) and the cumulative fraction of mass removed (dashed line) by each size class, given the wetland size frequency distribution of the Des Moines Lobe, and the *k-τ* relationship from the data synthesis. The grey shaded area indicates the interquartile range estimated based on Monte-Carlo simulations.
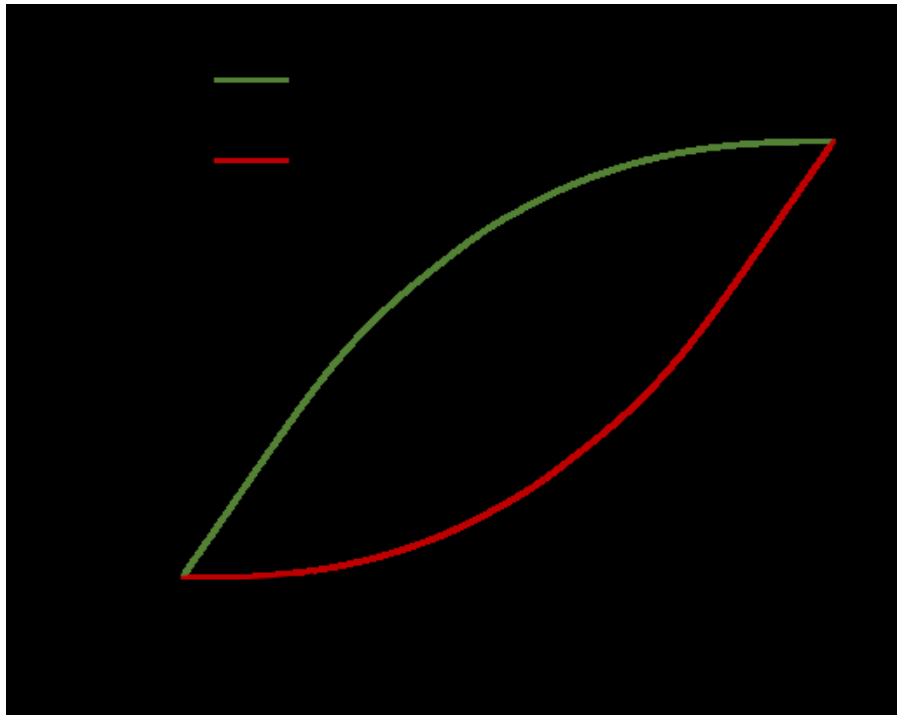
Figure 14. Fractional denitrification potential lost as a function of fractional wetland area lost, given the wetland size frequency distribution of the Des Moines Lobe and the k-τ relationship from the data synthesis. For the same fractional area lost, the loss is greater if smaller wetlands are lost preferentially.

Chapter 5 – Conclusions

5.1   Summary

Wetlands often function as critical sinks of nutrients in the landscape, and thus significant research has focused on understanding the biogeochemical cycling of nutrients in wetlands over the last few decades. However, most studies have focused on individual wetlands, making it difficult to extend these findings to wetlandscapes, which are composed of a distribution of wetlands. Similar challenges exist with other aquatic systems - in fact, research comparing small streams with larger rivers has highlighted differences in nutrient cycling in these systems [*Alexander et al.*, 2000]. Our goal in the present study was to explore nutrient retention potential across various wetland types and sizes, and to place these results in the context of other lentic systems, namely lakes and reservoirs.

we examined the retention rate constants for total nitrogen, nitrate, total phosphorus and phosphate in lakes, wetlands and reservoirs through a meta-analysis of data from over 600 sites. A strong inverse relationship (power function) was apparent between the volumetric first-order nutrient removal rate constant (k, $[T^{-1}]$) and the mean residence time (τ, $[T]$) across six orders of magnitude in residence times. The consistency of the relationship across constituent and system types alludes to an underlying physical mechanism that leads to the emergent inverse k-τ relationship. Specifically, the similarities in the effective removal rate constants between a biologically mediated nutrient (N) and a physically mediated nutrient (P) suggests the dominance of hydrologic controls on biogeochemical functioning.

To test the hypotheses that hydrologic controls dominate the nutrient removal rate constant, we developed a two-compartment sediment-water model that simulated denitrification as the primary removal mechanism for nitrogen and settling as the primary removal mechanism for P. The model was able to replicate the k-τ relationship observed in the data synthesis, thus supporting the

hypothesis that larger water bodies with longer residence times have smaller first-order removal rate constants.

Finally, we explored the role of small versus large wetlands on nutrient retention at the landscape scale. The historical size frequency distribution of wetlands in the Des Moines Lobe in Iowa was used for this analysis. The results from this analysis demonstrate the disproportionately larger role that small wetlands have in total nutrient removal at the landscape scale. For example, wetlands smaller than $10^{2.5}$ m^2 accounted for approximately 50% of TN removal when analyzing systems up to 10^5 m^2 in size. The results also showed that for the same wetland area lost, the total denitrification potential lost is larger when smaller wetlands are lost than when larger ones are lost. These results are important to consider in the context of wetland protection and wetland restoration efforts, since, as highlighted by *Van Meter and Basu* [2015], anthropogenic disturbances have not only contributed to a loss of overall wetland area, but have also in a preferential loss of smaller wetlands. These smaller wetlands on the landscape provide critical watershed functions, and thus warrant greater protection than is currently provided [*Marton et al.*, 2015; *Cohen et al.*, 2016]. This study, for the first time, quantifies the disproportionately larger role smaller wetlands can play in landscape nutrient processing, and highlights the need for valuing and protecting these smaller, often ignored, landscape features.

5.2   Future Work

The meta-analyses focused on the long-term nutrient reduction behavior of water bodies and identified small water bodies as 'hotspots' in watershed biogeochemical cycles. However, water bodies are dynamic systems that will exhibit distinct seasonal or short-term activity. These 'hot moments' have been identified to be just as important in furthering our understanding of the nitrogen and phosphorus cycles [*McClain et al.*, 2003; *Groffman et al.*, 2009]. Additional work will need to be done to couple existing hydrological models that capture the dynamics of the

aquifer-wetland interface [*McLaughlin et al.*, 2014] or to further existing catchment scale biogeochemical models to include wetland dynamics and other nutrients [*Porporato et al.*, 2003]. There remains an opportunity to also couple nutrient cycles (e.g. C, N, P) together within the catchment scales to quantify the interaction of these ecohydrological processes.

A direct extension of this thesis will be to introduce the concept of spatial and temporal connectivity between these reactive interfaces in the catchment. The transient nature of hydrological connectivity of wetlands and its surrounding upland influences the biogeochemistry of the system [*Groffman et al.*, 2009; *Golden et al.*, 2014]. In particular, geographically isolated wetlands may work in networks and exhibit hydrologic threshold behaviors that need to be quantified so that these systems, which are often co-located in agro-ecosystems and subject to excess nutrient loading, can be better understood.

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Appendix 1 – Additional Relationships from Data Synthesis

A well-mixed reactor (CSTR) assumption yields significant inverse relationships between the removal rate constant and the hydraulic residence time similar to the plug-flow assumption.
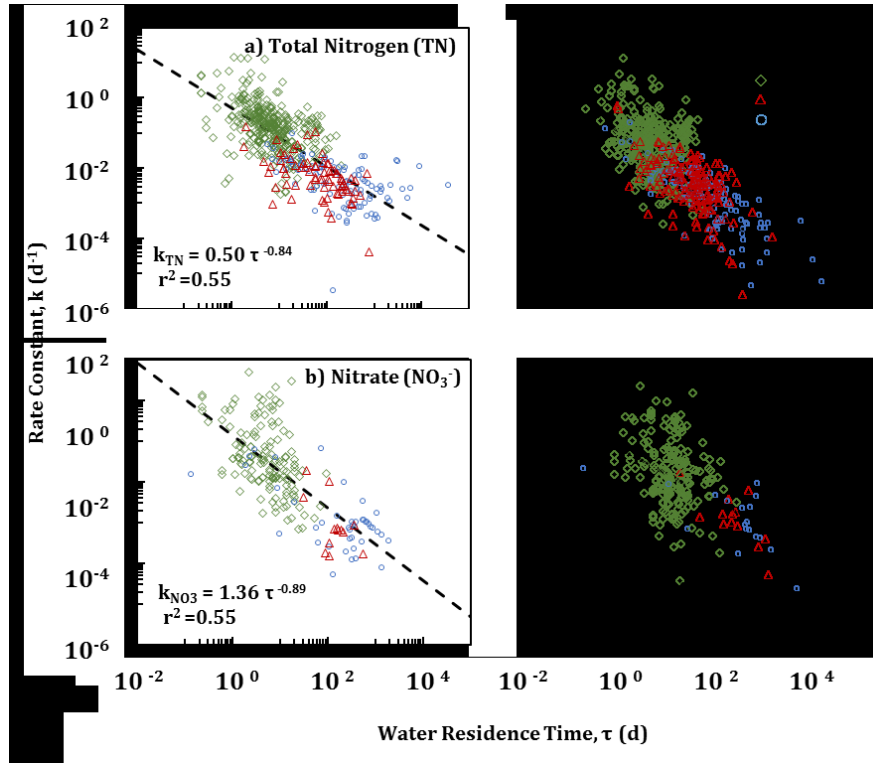

Figure S1. Removal rate constant ($k_{v,c}$) – hydraulic residence time relationships (τ) for a) total nitrogen (TN), b) nitrate (NO_3^-), c) total phosphorus (TP), d) phosphate (PO_4^{3-}). Same as Figure 7 but with CSTR model.

Table S1. Local sensitivity to parameter perturbation of 10%

Parameter	|% Change|
v_s	5.06
d_r	1.60
WA	1.60
Q	1.44
d	0.01
α	0.01
V_w	0.01