TAKING NITROGEN BY STORM: SPATIAL AND TEMPORAL CONTROLS ON NITROGEN PROCESSING IN A SMALL RESERVOIR

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TAKING NITROGEN BY STORM: SPATIAL AND TEMPORAL CONTROLS ON NITROGEN PROCESSING IN A SMALL RESERVOIR

BY

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TAKING NITROGEN BY STORM: SPATIAL AND TEMPORAL CONTROLS ON NITROGEN PROCESSING IN A SMALL RESERVOIR

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This research was conducted in N’dakinna (homeland), the ancestral and current homeland of the Abenaki, Pennacook, and Wabanaki peoples (People of the Dawnland). UNH and the field sites for this work are located within the Peskategwa watershed (branched river with fast-flowing waters). We acknowledge and honor with gratitude the land, waterways and the alnobak (people) who have stewarded N’dakinna throughout the generations. These peoples currently lack federal recognition or rights to this continually unceded land which was stolen centuries ago and is perpetually denied return.

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ABSTRACT
Nitrate inputs pose a threat to aquatic ecosystems, leading to eutrophication, algal blooms, and habitat loss in downstream coastal marine and estuarine habitats. Rivers and streams can attenuate nitrogen between inputs and coastal outputs, moderating ecosystem harm. While nitrogen dynamics in streams and rivers have been studied for decades, less is known about the wetlands through which they flow, namely small reservoirs. Storms can have a large influence on nitrogen processing in reservoirs through hydrologic changes and introduction of new solute sources, but are poorly understood. To understand the spatial and temporal variability of nitrogen processing in a small reservoir, this study made use of high-frequency sensors and spatial sampling within a small coastal dammed reservoir in New Hampshire, USA. This reservoir is not a nitrogen sink, rather acts as a transformer from inorganic to organic nitrogen forms. Inorganic nitrogen is retained temporarily, and exported later as dissolved organic nitrogen, offsetting retention of nitrate. The production of dissolved organic nitrogen and the undersaturation of nitrogen gas indicates that retention in this system occurs via plant and microbial assimilation rather than denitrification. In addition, nitrate is retained during storms due to increased delivery and connectivity to biologically active areas of the reservoir. These areas were found to be responsible for overall reservoir biogeochemical responses for some forms of nitrogen but not for others. Storms had a significant effect on nitrate and dissolved organic nitrogen processing, but there was no evident effect of storm size on nitrogen processing. This works contributes to our need to understand the biogeochemical role of small reservoirs within the landscape in the face of widespread dam removal and land use change.
CHAPTER I: INTRODUCTION

Nitrate is a threat to aquatic ecosystems

Reactive nitrogen levels have increased globally 120% since 1970 due in large part to demand for agricultural fertilizer (Sutton et al., 2008). The global increase in reactive nitrogen has in turn increased inputs to freshwater systems by 6-50x (Carpenter et al., 1998). Anthropogenic nitrogen inputs pose a threat to aquatic ecosystems by altering biological processes in rivers, streams, and reservoirs (Carpenter et al., 1998). Nitrate is a reactive inorganic form of nitrogen which enters waterways from sources such as wastewater treatment plants, leaky septic tanks and fertilizer runoff (Kaushal et al., 2011). Nitrate loading from the landscape can lead to eutrophication, algal blooms, and habitat loss in freshwater systems as well as downstream coastal marine and estuarine habitats (Bernot & Dodds, 2005; Deegan et al., 2012; Robert W. Howarth & Marino, 2006; Orth et al., 2006). Lastly, nitrate pollution can lead to poor drinking water quality (Smith et al., 1999). Understanding the temporal and spatial controls on nitrogen processing is important in improving our understanding of nitrogen dynamics in waterways and maintaining long-term health of these important ecosystems.

Nitrogen processing in rivers and streams

Rivers and streams can retain nitrogen between inputs and coastal outputs, moderating ecosystem harm. Retention of inorganic nitrogen by river networks varies across systems, ranging from 27-72% (Schmadel et al., 2019; Wollheim et al., 2006). Nitrate is removed from aquatic systems through denitrification or plant assimilation (Saunders & Kalff, 2001). Denitrification converts nitrate to atmospheric N₂ gas, and typically accounts for 16-43% of nitrate removal in streams (Mulholland et al., 2004, 2008). Primary producers and heterotrophic
bacteria can also assimilate nitrate, retaining it temporarily or long-term (Saunders & Kalff, 2001). While nitrogen dynamics in streams and rivers have been studied for decades, less is known about the impounded waters through which they flow.

**Nitrogen processing in reservoirs**

While nitrogen removal can occur through the fluvial network (Wollheim et al., 2018), impoundments also play an important role in removing nitrogen, responsible for 64% of the total nitrogen retained in a river network (Saunders & Kalff, 2001). Reservoirs are impounded waters behind humanmade dams. They can decrease incoming nitrogen inputs by 2-70%, depending on nutrient availability (Stanley & Doyle 2002). Another study found that lakes and reservoirs removed 39-76% of their input nitrogen (Alexander et al., 2002). When modeled globally, nitrogen removed by reservoirs and lakes is comparable to that which is removed by rivers and streams, 20-35 Teragrams/year (Harrison et al., 2009).

Reservoirs are capable of removing nitrate inputs from their contributing watershed, due to their high surface area to volume ratio and potentially favorable redox conditions (Boyer et al., 2006; Harrison et al., 2009). Denitrification and assimilation are processes which are mediated by sediment-water contact, and are enabled by greater residence times (Powers et al., 2013; Seitzinger et al., 2002). Previous research suggests that reservoirs may be particular hotspots for removal processes due to this unique morphology and biogeochemistry (Seitzinger et al., 2002; Stanley & Doyle, 2002). However, when considering nitrogen removal on the river network scale, models suggest that reservoirs do not remove more nitrogen per unit area than their advective counterparts (Seitzinger et al., 2002).

Recent models suggest that small reservoirs may play a disproportionately large role in watershed nitrogen removal when compared to large reservoirs (Cheng & Basu, 2017; Gold et
A study which incorporates data from 300,000 small reservoirs in the northeastern United States shows that small reservoirs are responsible for 34% of the nitrogen removed by the river network (Schmadel et al., 2019). However, these models were based on abundance and morphology of small reservoirs and assumed similar biological functionality between small and large reservoirs. Small reservoirs have a comparable total global surface area to large reservoirs, and are far more numerous (Downing et al., 2006). As such, including small reservoirs is crucial for modeling nitrogen removal by lentic ecosystems globally (Harrison et al., 2009). This research contributes to our understanding of small reservoirs, which could ultimately benefit global nitrogen estimates.

**Different forms of nitrogen may have different fates**

Studies on the mass balance of nitrogen in reservoirs have predominantly been focused on nitrate (Alexander et al., 2002; Cheng & Basu, 2017; David et al., 2006; Johnson et al., 2015). Nitrate is a widespread nonpoint source pollutant in aquatic systems, and dominates the inorganic nitrogen pool in aquatic systems (Camargo & Alonso, 2006). However, considering only inorganic nitrogen provides an incomplete picture of the fate of nitrate in reservoirs. The dissolved nitrogen pool contains both inorganic forms, such as nitrate and ammonium, and organic forms, classified as dissolved organic nitrogen (DON). DON is a subset of dissolved organic matter (DOM), a set of dissolved molecules which contain nitrogen and carbon, thus acting as both nutrient and energy source (Wymore et al., 2015). DON can be derived from terrestrial sources (such as leaf litter) or aquatic sources (such as algal decomposition) (Johnson et al., 2013). This study incorporates organic forms of nitrogen in addition to inorganic forms to identify multiple fates of nonpoint source nitrate in this reservoir ecosystem.
Impact of storms on reservoir nitrate removal

Capturing hydrological variability is important in understanding the role of reservoirs in nitrogen processing. Most of our scientific understanding of nitrate removal comes from periodic sampling during baseflow conditions, when we can assume steady state conditions. These measurements and estimates do not account for variability due to storm events. Models show that watersheds export more anthropogenic nitrogen when precipitation and discharge increase, such as during storm events (Han et al., 2009; Howarth et al., 2006). Annual precipitation in seacoast New England is projected to increase by 12-17% by the end of the century, with an increase in storm frequency and intensity (Wake et al., 2011). Further, urbanization of a watershed increases vulnerability of watershed nitrogen retention to climate variability (Kaushal et al., 2008). This reinforces the need for greater understanding of the influence of storms on aquatic ecosystems.

High-frequency sensors provide valuable insights into aquatic ecosystem function, capturing complex coupled hydrological and biogeochemical processes, and daily and seasonal variability (Burns et al., 2019). A high-frequency sensor approach can capture more temporal variability of nitrate transport, revealing concentration-discharge relationships, different sources, and spatial heterogeneity (Carey et al., 2014, Fazekas et al., 2020). When studying the effect of storms, high-frequency data can help identify the timing and relative contribution of different stream inputs, status as a source- or transport-limited ecosystem, and mass balance of solutes without assuming steady-state conditions (Carey et al., 2014; Koenig et al., 2017; Fazekas et al., 2020).

Storms can have a large influence on nitrogen processing in reservoirs through hydrologic changes and introduction of new solute sources (Carey et al., 2014; Koenig et al., 2017; Talbot et al., 2018). Delivery of nitrate to ponded reservoir waters is mediated by storm
runoff and hydrologic connectivity (Bende-Michl et al., 2013). Elevated runoff from storm events transports nitrate from the landscape to the river network where it can be retained (Koenig et al., 2017; Talbot et al., 2018). At the same time, increased flow increases hydrologic connectivity between the main advective flow path and the biologically active side pools of the reservoir (Carey et al., 2014; Death et al., 2015). In a source-limited ecosystem, retention capacity is increased with delivery of nutrients such as nitrate (Basu et al., 2011). Increased hydrologic connectivity and nutrient runoff during storms delivers nitrate to plants and microbes within the reservoir ecosystem, where it can be retained through denitrification and assimilation. However, these responses can vary, and previous research has studied their threshold behavior.

When supply outweights demand for nutrients such as nitrate, retentive capacity becomes saturated and greater amounts are exported downstream (Wollheim et al., 2018). This threshold can be applied to storm events, where nitrate removal may decline with increasing flow as demand is overwhelmed (Peterson et al., 2001; Wollheim et al., 2018). Increased flow during a storm event decreases residence time of a reservoir, which may lower the capacity of the reservoir to retain nitrate.

*Spatial heterogeneity of a reservoir*

In exploring the role of reservoirs as nitrate removers, it is important to consider the diversity of ecological and hydrological conditions within a reservoir. Reservoirs contain transient storage zones (TSZ), areas within aquatic systems that are somewhat isolated from the main channel with highly reduced flow velocity (Stewart et al., 2011). In high-nutrient systems, surface transient storage in fluvial wetlands retain more nitrate than headwater stream channels, suggesting TSZ are a hotspot for nitrate retention (Wollheim et al., 2014). Some biological and hydrological controls of nitrate removal in TSZ have been identified, such as nitrate loading and
delivery, area, size, and connectivity between TSZ and the main channel (Briggs et al., 2010; Stewart et al., 2011). However, there is chemical, biological, and geomorphological variability between transient storage zones, underlining the need to capture more of the spatial heterogeneity within a reservoir.

By measuring a suite of solutes and gases across a range of distances from the main advective path of the reservoir, we can identify the relative contribution of different areas of the reservoir on different parts of the nitrogen cycle. Monitoring different N species (nitrate, ammonium, nitrous oxide, dinitrogen gas, and total dissolved nitrogen) from the main advective area to more transient storage dominated area can provide a finer resolution to identify the predominance of different nitrogen cycle processes. For example, nitrate concentration can be lowered through denitrification, but can increase due to nitrification. Nitrous oxide (N\textsubscript{2}O) is produced as a byproduct of denitrification, so can be used in proportion with nitrate to delineate the relative importance of denitrification and nitrification.

Research directions
To better understand the role of small reservoirs in nitrate retention, this paper sought to answer: (1) Is the reservoir a source or a sink for nitrogen? (2) How do storm events affect nitrate mass balance within a reservoir? and (3) How do the hydrological and biological controls of nitrogen processing vary spatially? I hypothesized that the reservoir would be a nitrogen sink, based on previous research showing the retention of nitrogen in reservoirs. Given the tradeoffs between nutrient delivery and residence time, I hypothesized that removal of nitrate would increase during small storm events compared to baseflow, but decrease relative to baseflow during large storm events. Delivery and retention during small storms were expected to outweigh export due to decreased residence time, and export during large storms was expected to outweigh
retentive capacity, which decreases retention. Lastly, I hypothesized that delivery and
biogeochemistry of transient storage zones would determine overall reservoir biogeochemistry,
due to their greater residence time and biological activity. Findings will enhance our
understanding of nitrogen processing in aquatic ecosystems across spatial and temporal scales.
CHAPTER II: METHODS

Overarching approach
To understand whether a small reservoir acts as a source or sink of different nitrogen species over the course of two years, we used an instantaneous mass balance of inputs and output to the reservoir. We explored in more detail the mass balance of nitrate during a storm event using high-frequency nitrate sensors. To capture spatial heterogeneity and more detailed nitrogen cycling patterns of the reservoir, we sampled a series of solutes and gases at several points within the reservoir (Figure 1). These water quality and solute concentrations were measured in-situ or with the use of laboratory analysis. We performed an Analysis of Covariance (ANCOVA) to determine if storms had a significant effect on biogeochemical patterns within the reservoir.

Study Area
This study took place in the Mill Pond, a coastal dammed reservoir in Durham, New Hampshire, USA. The Mill Pond is situated at the mouth of the Oyster River watershed, which drains an area of 50.6 km² (Figure 2). The Mill Pond dam is a head-of-tide dam and the impounded waters have a surface area of 0.08 km². Land use of the watershed is 17% developed (suburban and urban), 3.7% impervious surfaces, 10% agricultural land, 58% forest, and 12% wetlands. Three major inputs flow into the Mill Pond reservoir: Hamel Brook (HAM) (watershed area = 1.8 km²), College Brook (CLGB) (watershed area = 2.3 km²) and Oyster River (ORR) (watershed area = 43.2 km²). The output of the reservoir is at the dam (OMPD). Land use of the input flows is variable, ranging from 12% developed in Oyster River to 46% developed (Hamel Brook) to 69% developed (College Brook). Overall, the watershed has 17% developed land cover (Strafford County Planning Commission 2010).
When defining the Mill Pond reservoir for internal sampling, I included only the impoundment which is downstream of the three major inputs and immediately upstream of the dam, covering a surface area of 0.03 km$^2$. Hamel Brook contains impounded waters that cover the other 0.05 km$^2$. When sampling inputs for mass balance calculations, the Hamel Brook site is upstream of the impounded Hamel Brook waters, functionally treating that reach between inputs and outputs as reservoir.

The Oyster River watershed is part of the larger Piscataqua River watershed. The receiving estuary, Great Bay, is nitrogen-impaired due to elevated nitrogen inputs from the watershed (Scott et al., 2017). Inputs from nonpoint sources such as fertilizer runoff and leaky septic tanks account for 50% of the dissolved inorganic nitrogen that enters the Great Bay watershed (PREP, 2018). In Great Bay, excess nutrients are a main cause of eelgrass decline, a native habitat that is important for ecological health and economic stability (PREP, 2018). The Great Bay watershed is home to several small dams, 10 of which have been removed since 2004, and at least 2 more which are being considered for dam removal (American Rivers). Two head-of-tide dams have been removed, from the Exeter River in 2016 and the Bellamy River in 2019 (American Rivers). Dam removals are occurring due to obsolescence and increasing cost of maintenance. Understanding the role of reservoirs in aquatic nitrogen processing can aid future decisions regarding dam removal.

**Instantaneous Mass Balance**

We identified changes in nitrogen concentrations between reservoir inputs and output using an instantaneous mass balance approach (Figure 3). Primary surface water inputs and an output of the Mill Pond reservoir were sampled within several hours of each other, between the hours of 9:00am and 5:00pm, monthly between March 2018 and January 2020, excluding winter...
periods due to ice cover at the dam outflow. Flow conditions captured with the mass balance approach range from 0.14 to 3.7 m$^3$s$^{-1}$. The past ten years (2010-2020) have shown an average annual precipitation of 831 mm. The two years throughout which I sampled, 2018 and 2019, both had above average precipitation, at 1016 and 1270 mm respectively (National Weather Service).

Sampling for the mass balance approach included nitrate (NO$_3^-$), ammonium (NH$_4^+$), chloride (Cl$^-$), dissolved oxygen (DO), temperature, and total dissolved nitrogen (TDN). Mass balance for dissolved organic nitrogen (DON) was established by subtracting inorganic nitrogen (NO$_3^-$ + NH$_4^+$) from TDN. Chloride is a conservative solute, and used to check the hydrologic mass balance to be able to isolate changes due to biological processes. Quantifying differences using the ratio of reactive solute to chloride measured during steady state conditions represents changes in concentration due to biological effect alone. Dissolved oxygen and temperature were included as dominant environmental controls of biological processes (Wiegner & Seitzinger, 2004). Dissolved organic nitrogen (DON) was calculated by subtracting the concentration of inorganic nitrogen forms (NO$_3^-$ and NH$_4^+$) from total dissolved nitrogen (TDN).

We collected samples at all sites on 28 different days over the course of two years. The equations above were applied to each sample day, for NO$_3^-$, NH$_4^+$, DON, TDN and Cl$^-$. To assess changes between upstream and downstream of Mill Pond reservoir, the percent (%) change was calculated using the following equation, based on the conservation of mass:

\[
Eq. 1) \ % \ change = (Output - Input) / Input \times 100
\]

Concentrations were scaled with the contributing watershed area of each site as a proxy for discharge. The use of watershed area as the scaling factor (as opposed to discharge itself) is an approximation that assumes all studied watershed areas contribute a similar amount of runoff:

\[
Eq. 2) Input = WA_{ORR} \times C_{ORR} + WA_{HAM} \times C_{HAM} + WA_{CLGB} \times C_{CLGB} + WA_{DIRECT} \times C_{CLGB}
\]
\[ Eq. 3) \text{Output} = W_{\text{OMPD}} A * C_{\text{OMPD}} \]

where \( WA \) is watershed area and \( C \) is concentration measured at the site. \( \text{Input} \) represents the sum of all input sites, including direct inputs to the reservoir from surrounding land (Figure 4). Due to difficulty in measuring concentration from surrounding land, direct input area is multiplied by the concentration from College Brook (CLGB) as a proxy for concentration of direct inputs. This site was chosen as the proxy because it is the site with the most similar land use.

The impounded Hamel Brook and Oyster River converge upstream of the reservoir and can be measured together at Oyster River at Hamilton Smith Chapel (OHC). Samples were taken at OHC in order to pair consistently with high-frequency sensors during their deployment, and due to logistical constraints. Eight sampling days utilized OHC and CLGB as their inputs (Figure 4). In this case, the output was calculated the same way, using equation 3.

\[ Eq. 4) \text{Input} = W_{\text{OHC}} A * C_{\text{OHC}} + W_{\text{CLGB}} A * C_{\text{CLGB}} + W_{\text{DIRECT}} A * C_{\text{CLGB}} \]

If the percent change of chloride is closer to zero, the mass balance accounts for sources and sinks. If the difference is farther from zero, the mass balance does not account for all sources and sinks, and interpretation of reactive solutes should be more careful. To test for the conservation of chloride as compared to nitrate, the absolute value of % change chloride was plotted against absolute value of % change nitrate. Absolute value was used to demonstrate amount of change and because direction of change was not informative for this test.

To observe trends over a seasonal scale, average summer fluxes were determined by calculating a flux amount (kilograms/day) of nitrate, dissolved organic nitrogen, and total dissolved nitrogen from all sample days between June and August. Because assimilative demand varies seasonally (due to algae growth), I designated my calculation of summer fluxes for the
growing season only (Berman & Bronk, 2003). In 2018, four (4) sampling days were averaged and in 2019, five (5) sampling days were averaged.

The instantaneous mass balance approach assumes stable flow conditions. Therefore, this approach cannot be used to determine mass balance during storm events. For this, we used paired deployments of high-frequency sensors to establish a mass balance estimate.

**High-Frequency Mass Balance**

To establish a mass balance for non-steady state conditions such as those during storms, we used paired deployments of high-frequency sensors. Submersible Ultra-Violet Nitrate Analyzers (SUNA) (Satlantic, Inc.) and water-level sensors (Onset, Inc.) were deployed concurrently to account for temporal variability of nitrate concentration and flow conditions throughout storm events, and establish a high-frequency mass balance. Mass balance for a baseflow period (9/28/19-10/1/19) and a storm event (9/25/18-9/28/18) was established using deployed SUNAs at the input(s) and output to the reservoir. Three SUNAs were placed at three of the four sampling sites: HAM, OMPD, and ORR. Storm event scale nitrate inputs from College Brook (CLGB) were estimated using the site-specific relationship between storm runoff and nitrate previously established (Wollheim et al., 2017).

SUNAs were programmed to measure nitrate every 15 minutes. They measure absorbance between 200 and 240 nm, and convert absorbance to NO$_3$-N concentration. They were calibrated before deployment, and sensors had either an optical screen wiper or were manually cleaned once per week to avoid biofouling. High-frequency sensors (Onset, Inc.) were also installed at each site to continuously measure water level and specific conductance throughout the study period. Specific conductance was used as a conservative tracer to isolate biological processes controlling nitrate. Water-level sensors were used to weight each 15-minute nitrate measurement with a flow measurement from the same time to quantify fluxes throughout
the storm event. Rating curves were established using concurrent measurements of water level and discharge for a range of flow conditions at each site (Appendix 3). The storm event occurred as three successive pulses, which were counted as one event. The baseflow period that followed was designated starting at the break in the falling limb of the hydrograph as the flow returned to baseflow (Figure 5).

*Internal Sampling*

To investigate the biogeochemical dynamics within the reservoir responsible for changes between inputs and outputs, we collected samples from 11 points within the reservoir at varying distances from the channelized section (hereafter *distance*) (Figure 1). These points accounted for the dam outflow as well as two locations within the channelized area of the reservoir, one at the transition from the river input to the impoundment, and one just upstream of the two large transient storage zones. Each transient storage zone, A and B, contained three points with increasing distance, to track how solute concentrations changed with increasing influence from the transient storage zones. Internal samples were collected using a paired baseflow-stormflow approach. Five summer storms were captured from July 2018 and June to October 2019. Paired sampling for each storm represented the antecedent base flow condition, and a post-storm condition. These five storm events ranged from .34 to 2.69 m$^3$s$^{-1}$, capturing the complete range of summer storms in these years. (Table 1, Figure 6).

Samples collected at each internal point were collected between 9:00am and 5:00pm from a depth of approximately one foot below the surface. Samples included solutes (DOC, TDN, NO$_3^-$, NH$_4^+$ and Cl$^-$), water quality measurements (dissolved oxygen, temperature, specific conductance), and dissolved gases (N$_2$ and N$_2$O). Concentration of dissolved organic nitrogen (DON) was established by subtracting concentrations of inorganic nitrogen (NO$_3^- +$ NH$_4^+$) from
concentrations of TDN. Measured gases and solutes are products or byproducts of nitrogen processes in aquatic systems. Where some processes have multiple chemical indicators, coupled or decoupled concentration patterns can better isolate a process. Geographic coordinates were recorded for each sampling location, and distance from main advective flow path was found using geographic information systems (GIS).

Sample analysis
Water samples were taken for the mass balance and internal sampling. These included all solutes (DOC, TDN, NO$_3^-$, NH$_4^+$, all major anions and cations), water quality measurements (dissolved oxygen, temperature, specific conductance), and dissolved gases (N$_2$:Ar, N$_2$O).

Solutes were sampled in situ with a rinsed syringe and filtered through a .45 µm filter into an acid-washed 60mL bottle, then frozen for future analysis. Major anions and cations, including NO$_3^-$ were analyzed using ion chromatography (Dionex ICS-1000). DOC and TDN were analyzed with catalytic oxidation using a Shimadzu TOC-V with TNM-1 analyzer. NH$_4^+$ was analyzed on a SmartChem 200 colorimeter. Water quality measurements (dissolved oxygen, temperature, specific conductance) were taken in situ using a handheld sonde (Yellow Springs Instrumentation, Inc.).

N$_2$:Ar samples were collected in triplicate vials using a sampler that ensures no contact with the atmosphere, then analyzed using membrane-inlet mass spectrometry (MIMS) (Bay Instruments, Reisinger et al., 2016). These data were corrected to account for equilibrium at the temperature and pressure of the sample, as well as the gas exchange coefficient (Hall & Madinger, 2018). Data are reported as disequilibrium:

Eq. 5) N$_2$:Ar disequilibrium = N$_2$:Ar$_{sample}$ - N$_2$:Ar$_{saturation}$
N₂:Ar disequilibrium can be used as an indicator of denitrification and nitrogen fixation. When disequilibrium is less than zero, nitrogen gas is undersaturated, and nitrogen fixation is occurring. When disequilibrium is greater than zero, nitrogen gas is supersaturated, indicating that denitrification is occurring.

N₂O samples were collected in 60mL syringes then equilibrated with ambient air or helium immediately prior to lab analysis by shaking for three minutes. Samples were analyzed using gas chromatography in the Water Quality Analysis Lab and Trace Gas Biogeochemistry Lab at the University of New Hampshire. Following sample analysis, N₂O data were corrected to account for equilibrium concentration, Bunsen solubility coefficient, and Henry’s Law coefficient to find the concentration and percent saturation of each sample. Atmospheric pressure at the time of sampling was measured from a nearby site (Wednesday Hill Brook, Lee, NH, USA).

**Statistical Analyses**

To see how chemistry changed as distance increased, linear regression models were fitted for NO₃:Cl, N₂:Ar disequilibrium, DON:Cl and N₂O against distance (Appendix 2). A logarithmic transformation was applied to NO₃:Cl to improve linear regression fit. A best fit linear model was determined for each of the two dominant transient storage zones within the reservoir, A and B. The slope was used as an indicator of presence and strength of different biological processes. To test for the difference in slope between flow conditions (baseflow vs. stormflow), one-way Analysis of Covariance (ANCOVA) tests were performed. For log NO₃:Cl, DON:Cl, N₂O, and N₂:Ar disequilibrium, ANCOVA tests determined if flow condition had a significant effect on the change in concentration with distance. Flow condition was categorized as presence or absence of a storm for the ANCOVA tests. Inputs to the ANCOVA were
evaluated using a homogeneity of regression slopes test, Shapiro-Wilks test, and the presence of outliers. All data are reported with indications of each assumption they met (Appendix 2). Homogeneity of regression is determined by the insignificance (p> .05) of the interaction between the independent variable and the covariate (Kassambara, 2018). The Shapiro-Wilks test assumes normality of residuals in the input data if it is not significant (p> .05) (Kassambara, 2018). Lastly, outliers are defined as cases with standardized residuals greater than 3 in absolute value (Kassambara, 2018). All data manipulation and statistical analyses were performed in R (R Core Team, 2020) using packages tidyverse (Wickham et al., 2019), ggpubr (Kassambara, 2020), rstatix (Kassambara, 2020), broom (Robinson et al., 2020), and car (Fox and Weisberg, 2019) following a template written by Kassambara (2018).
CHAPTER III: RESULTS

Chemistry

Mean chloride concentration ranged from 47.7 mg/L to 65.6 mg/L across all sites except College Brook (CLGB), which was much greater, averaging of 249.3 mg/L (Table 2). Nitrate (NO$_3$-N) ranged from an average of 0.1-0.6 mg/L across all sites, with CLGB being the highest. (Table 2). Ammonium (NH$_4$-N) concentrations ranged from 16.1 ug/L in the reservoir to 53.2 ug/L at CLGB, with the other sites falling between. Total dissolved nitrogen (TDN) concentration averaged 0.2 mg/L to 0.8 mg/L and dissolved organic nitrogen (DON) averages fell between 0.1 and 0.3. Non-purgeable organic carbon (NPOC) mean concentrations ranged from 4.9 to 7.1 mg/L. Mean dissolved oxygen (DO) ranged from 63.6 % saturated in the reservoir to 91.8 % saturated at Oyster River (ORR). Nitrous oxide (N$_2$O) means were consistently 0.2-0.3 µM (Table 2). Average chloride, nitrate, ammonium, and TDN concentrations show an apparent relationship with land use, displaying higher concentrations in sites characterized by higher urban land use such as College Brook and Hamel Brook. Dissolved oxygen is lower in the impounded sites (OMPD and Internal) than in more advective sites, such as CLGB, HAM, and ORR. OHC falls between, with both impounded and advective characteristics at times.

Instantaneous mass balance

When interpreting instantaneous mass balance figures, negative values indicate consumption, while positive values indicate production. Chloride mass balance values were close to zero, with the highest value being 33.6% (Figure 7). When plotting absolute value of % change chloride against absolute value of % change nitrate, all but 4 points included in the mass balance indicated that nitrate was more reactive than chloride and does not behave
conservatively (Figure 8). A line of best fit reveals that there is close to no relationship between change in chloride and change in nitrate ($m=0.03, R^2=0.01$). NO$_3$-N is almost always lower at the output than input, with percent (%) change values across the sampling period ranging from increases (max = 40.6%) to declines (max decline = -81.96%) with a median decline -37.79% (Figure 9). The greatest NO$_3$-N declines tend to occur in the summer months (Figure 9).

Dissolved organic nitrogen (DON) passing through the reservoir tends to be close to balanced, but with 6 time periods where large increases occurred. DON values range from increases (max=300.6%) to decreases (-26.1%), with a median decline 6.6% (Figure 10). DON increases occur mainly in the summer months (Figure 10). As a result of the NO$_3$ and DON imbalances tending to offset one another, total dissolved nitrogen (TDN) balanced close to zero, ranging from increases (max=59.1%) to decreases (min=-32.44%), with a median decline of -11.029 (Figure 11).

The average summer uptake of nitrate by the reservoir (kg/d) during summer 2018 (n=4) and summer 2019 (n=5) show a negative tendency, indicating less nitrate flux at the output than input (Table 3). DON flux averages (kg/d) for summer 2018 and 2019 both show a positive tendency, indicating more at the output than input (Table 3). TDN flux averages (kg/d) for summer 2018 is positive, while average value for summer 2019 is negative (Table 3). These values are not statistically different from one another, as shown by the standard deviation reported in parentheses.

*High-frequency mass balance*

During stormflow, there was a decrease of nitrate from the inputs to the output (Figure 5). Fifteen-minute fluxes were integrated for the storm period, where the reservoir retained 22.99 kg/storm. The storm lasted 3.92 days, so during the storm event, the reservoir retained 5.87
kg/day. (Figure 5). A period of gradual decrease of flow followed the storm event, during which the reservoir retained 2.97 kg/day. The high-frequency mass balance captured a low- to intermediate-sized storm for this watershed (Figure 12).

**Internal reservoir dynamics**

A linear regression was fitted for each solute (NO$_3$:Cl, N$_2$O, N$_2$:Ar, DON:Cl) against distance into the side pool from main advective path (hereafter distance), for each zone of the reservoir and each sampling day (e.g. Figure 13). Each plot indicates zone (A or B) as well as condition (baseflow or stormflow) within each event. There are five storm events, each with a corresponding baseflow and stormflow. For NO$_3$:Cl and DON:Cl, a logarithmic transformation was applied for improved fit.

For log NO$_3$:Cl, 18 out of 20 NO$_3$:Cl slopes were negative (p<.05 for n=6), indicating decreasing log NO$_3$:Cl at increasing distance (Figure 14, Appendix 1 Table 1). This result is consistent with the mass balances indicating the reservoir as a whole is a nitrate sink. Differences between slopes (stormflow minus baseflow) showed steeper slopes during stormflow for 7 out of 10 conditions, indicating greater retention during storm events. The difference between slopes shifts from negative to positive as the difference between Q (storm minus base, as a proxy of storm size) increases, indicating less retention during larger storms (Figure 15). However, the linear fit is very weak (R$^2$=.01).

For log DON:Cl, slopes are very flat, though 16 out of 18 slopes were slightly negative (Figure 14). Only two relationships were significant (p<.05) (Appendix 1 Table 2). This indicates homogeneity of DON:Cl within the reservoir. There is no visible pattern shown in slope differences between stormflow and baseflow, signifying very little effect of storms on DON:Cl. As storm size increases, the differences between slopes from stormflow to baseflow decreases,
becoming more negative ($R^2=0.8$). This indicates that more DON is consumed during large storm events (Figure 15).

For N$_2$:Ar disequilibrium, 8 out of 13 slopes were negative, signifying a decrease in N$_2$:Ar disequilibrium as distance increases (Figure 14). However, none of these relationships is significant (Appendix 1 Table 3). Only two storms were included in this analysis. The first storm event (July 2018) displayed negative differences between storm and base flow, showing an increase in fixation. For the other storm event (August 2019), both differences were positive, showing negative slopes becoming positive. This displays a shift from fixation to denitrification. As storm size increases, the difference between slopes increases, shifting from negative to positive ($R^2=.22$) (Figure 15). This shows a shift toward denitrification during large storms.

For N$_2$O, 11 out of 16 slopes were negative (Figure 14). However, none of the linear regression fits were significant and slopes are very close to zero (Appendix 1 Table 4). Half (n=5) of the differences between baseflow slope and stormflow slope were negative, half (n=5) were positive. In this case, negative differences indicate negative slopes becoming more negative, and most of the positive differences indicate a shift from a negative slope to a positive slope. There is no effect of storms on change in slope between baseflow and storm flow ($R^2=.01$) (Figure 15).

**Internal Gradient Analysis of Covariance**

Across the entire data set, storms significantly affected the relationship between NO$_3$:Cl and distance from main advective path across all events (p=.009) (Appendix 2 Table 1). Furthermore, after adjustment for storms, distance significantly affected NO$_3$:Cl across all events (p= 1.59 E-07). Tests for linearity were used and show linear relationships between the covariate
and the response variable (Appendix 2 Figures 1-4). There was homogeneity of regression slopes and no outliers in any given corresponding storm event. All storms had normality of residuals except for the overall dataset and one sampling. The interaction between distance and NO₃:Cl after removing effects of storms was significant for both zones on all days except for one sampling (Appendix 2 Table 1).

The relationship of storms on DON:Cl across all events together was significant (p=.002874) (Appendix 2 Table 2). However, the overall dataset did not have homogeneity of regression slopes or normality of residuals, and had outliers. When analyzing each event separately, there was no significant effect of storm on DON:Cl. However, after adjusting for storm, the overall dataset (p=3.33 E-07), displays a significant relationship between distance and DON:Cl (Appendix 2 Table 2).

N₂:Ar declines with distance across all sample times combined (p=.032). However, there is no normality of residuals (Appendix 2 Table 3).

The overall relationships between storms and N₂O and distance and N₂O adjusting for storms were not significant (p=.1992, .152). The overall dataset did not show normality of residuals and did have outliers (Appendix 2 Table 4).
CHAPTER IV: DISCUSSION

Discussion overview
This study evaluated the role of small reservoirs in nitrate retention by measuring the spatial and temporal variability of nitrogen processing. The reservoir was not a sink for nitrogen across flow conditions. The reservoir acts as a transformer from inorganic to organic nitrogen, with dissolved organic nitrogen (DON) production in the reservoir offsetting the retention of nitrate. Nitrate is retained during small to intermediate storms, and shows no relationship to storm size. In addition, storms have a significant effect on nitrate and DON processing within the reservoir. The production of DON and the undersaturation of nitrogen gas indicates that retention in this system occurs via plant and microbial assimilation rather than denitrification. Lastly, transient storage zone dynamics are consistent with the nitrate sink and provide an additional source of nitrogen through fixation. Transient storage dynamics are not consistent with reservoir DON production seen in the mass balance.

Reservoir is not a consistent nitrogen sink
Contrary to other studies on reservoirs, this small coastal reservoir is not a sink for nitrogen across all flow conditions. We found the Mill Pond to be a sink for nitrate, but often a source for dissolved organic nitrogen (DON). This results in total dissolved nitrogen (TDN) being relatively balanced. This reservoir acts as a transformer from inorganic to organic nitrogen. Although previous studies have assumed nitrate retention, our study shows nitrate transformation to organic forms, resulting in balanced total dissolved nitrogen. Studying multiple forms of nitrogen revealed unexpected fates of nonpoint source nitrate in this reservoir ecosystem.
Nitrate (NO₃) was almost always lower at the outflow of the reservoir than the observed levels flowing in, suggesting the pond is effectively retaining nitrate (Figure 9). Three dates show positive values, indicating that the reservoir is a source of nitrate on those days. These values occur twice in the summer and once in the late fall. In a similar study, % change NO₃ in two reservoirs ranged from -73% to 15% (Tomaszek & Koszelnik, 2003). Retention tends to be higher during the summer months, sometimes approaching 100% (Figure 9). Increased nitrate retention during the summer months has been observed in other temperate systems (Powers et al., 2013; Tomaszek & Koszelnik, 2003). This pattern is likely due to the seasonal effect of algal biomass on nitrate transformation (Powers et al., 2013).

High algal biomass supports a high assimilatory demand for nitrate (Caraco et al., 1998), potentially explaining the decline in nitrate through the reservoir. Low dissolved oxygen levels in the reservoir provide favorable redox conditions which contribute to high nitrate demand via denitrification (Piña-Ochoa & Álvarez-Cobelas, 2006). However, mass balance at the reservoir scale cannot distinguish these fates. If nitrate is assimilated, it is stored in the reservoir. From there, it can be leached as dissolved organic nitrogen (DON), remineralized to NH₄, or settled as particulate organic nitrogen (PON) (David et al., 2006). DON and PON can both be metabolized further or return to the water column and be exported downstream after being stored (Jani & Toor, 2018).

At the same time nitrate is retained, there are periods of time where the reservoir produces dissolved organic nitrogen (DON) (Figure 10), suggesting that some retained nitrate is ultimately returned to the water column as DON (Johnson et al., 2013). This aligns with previous findings that high DON export is seen across wetland systems (Mulholland 2003). Production of DON is highest in the summer months (Figure 10). This is likely due to uptake of nitrate into
algal biomass, which temporarily stores it as the plant is living. Algae release DON through leaching while they are living, and also during decomposition (Jani & Toor, 2018).

The reservoir as a whole is nearly balanced for total dissolved nitrogen (TDN) due to the offset of nitrate and DON mass balances across seasons and flow conditions (Figure 11). Thus, this reservoir does not retain nitrogen as hypothesized based on earlier studies (Schmadel et al., 2019; Seitzinger et al., 2002; Stanley & Doyle, 2002). Rather, it acts as a transformer of inorganic nitrogen to organic nitrogen. Previous studies have established that nitrate can be assimilated by autotrophs (such as algae) or heterotrophs (such as microbes) (Caraco et al., 1998; Johnson et al., 2013). Once nitrate is assimilated into algal or microbial biomass, DON can be leached (Jani & Toor, 2018).

*DON export from reservoirs*

While previous work often excludes organic nitrogen, one study was found which measured DON in addition to nitrate when quantifying solute mass balance of a reservoir (Powers et al., 2013). The results of their work showed that while DON response was variable, reservoirs were a net source of DON. This response is in line with the findings of our study, and reinforces the importance of including both organic and inorganic nitrogen in mass balance models. There is more error associated with DON concentration than other solutes, as it cannot be measured directly. Rather, it is calculated by subtracting inorganic nitrogen from total dissolved nitrogen, as described in the methods.

DON produced internally in the pond is likely very labile and readily used by microbes downstream, therefore contributing similarly to nitrogen pollution of the estuary as nitrate (Caraco et al., 1998). There are many forms of DON with a wide range of environmental origins (Johnson et al., 2013). The origin and range of molecules within DON can determine how labile,
or biologically available, it is (Wiegner & Seitzinger, 2004). While both DON and nitrate can be harmful to downstream ecosystems, DON’s potential harm relative to nitrate is unknown. In the context of this study system, the organic nitrogen that is produced may still cause ecosystem harm, even though nitrate is retained in the reservoir.

*Nitrate is retained during storm events*

There was retention of nitrate during a storm event, (Figure 5). The retention during this storm was 40%, comparable to nitrate retention seen in the instantaneous mass balance. In the baseflow period following the storm event, retention occurred, but at a lesser rate (Figure 5). During this time, 32% of incoming nitrate was retained, in range with values found through the instantaneous mass balance, but less than that during the storm event. As the storm event captured was characterized as a small- to intermediate-sized storm, this finding supports my hypothesis that retention would increase during small storms (Figure 6). During a storm event, increased concentrations of nitrate and increased connectivity to the source-limited areas of the reservoir allow for retentive processes throughout the reservoir to occur. This finding is supported by a previous study showing that concentrations decrease with increased flow in source-limited systems (Basu et al., 2011).

Landscape runoff increases during storms, delivering nitrate to waterways (Kaushal et al., 2008). Impervious surfaces mobilize storm runoff, further increasing storm nitrate delivery from the landscape. Impervious surfaces comprise only 3.7% of the entire watershed. However, that number increases closer to the reservoir itself, such as within the College Brook watershed, where impervious surfaces comprise 27.6%. In addition, increased flow and water level alter flowpaths within a reservoir, resulting in greater connectivity between transient storage zones and the main advective path (McMillan et al., 2018).
Storms affect transient storage zone influence on nitrate in the reservoir when all storm events are tested together (Appendix 2 Table 1). However, storms tended have no significant effect on the relationship between distance from the main advective path (hereafter distance) and NO$_3$:Cl concentration during individual storm events. This suggests that there is considerable variability between storm events, and no universal response. More specific storm metrics could be used to determine what storm characteristics influence biogeochemical processing in a reservoir. These could include season, storm size, and antecedent condition. Storm size was examined further in this study.

Nitrate retention shows no strong relationship with storm size, which does not support the original hypothesis. Slopes between NO$_3$:Cl and distance tended to become steeper and more negative during storm events, displaying greater nitrate removal during storms. When considering storm size, the difference in slopes shifts from negative to positive, indicating less retention during larger storm events (Figure 15). However, the relationship between the change in NO$_3$:Cl slope and storm size was very weak ($R^2$=.01), so the effect of storm size on slope difference cannot be determined. The difference between DON:Cl slopes decreased with increasing storm size, indicating that more DON was consumed during large storm events ($R^2$=.8) (Figure 15). However, given the spatial homogeneity of DON:Cl within the reservoir, shifts in slope between baseflow and stormflow are likely negligible.

As storm size increases, the difference between N$_2$:Ar disequilibrium slopes increased, shifting from negative to positive ($R^2$=.22) (Figure 15). This shift could indicate less fixation or greater denitrification during larger storms. While denitrification is not a dominant process in this system, delivery of nitrate during storms could stimulate some denitrification. There is no effect of storm size on the difference of N$_2$O slopes ($R^2$=.01) (Figure 15).
**Reservoir system is nutrient source-limited**

Nitrate uptake in the side pools leads to very low measured concentrations of nitrate. The undersaturation of N₂:Ar at low nitrate levels indicates the presence of nitrogen fixation as an important process at this site (Figure 16). It appears that these zones are nitrogen limited, and fix nitrogen, introducing new nitrogen to the system. Nitrogen fixation occurs in environments with ample light, limited access to inorganic nitrogen, and enough phosphorus (Scott et al., 2009). Other studies show that areas which transition from a river to reservoir can be hot spots for nitrogen fixation (Scott et al., 2009). The presence of nitrogen fixation indicates that the reservoirs is nitrogen source-limited, requiring bacteria to fix their own nitrogen to access essential nutrients. In a similar study, two reservoirs which retained nitrogen were found to be source-limited as well (Tomaszek & Koszelnik, 2003). More fixation is occurring in transient storage zones within the reservoir, indicating that these areas in particular are source-limited (Figure 16). Source-limited systems are nitrogen depleted, therefore better at retaining nitrate (Basu et al., 2011). This aligns with other results showing the retention of nitrate in transient storage zones (Figure 14).

Nitrogen fixation requires phosphorus, so the presence of nitrogen fixation suggests that the reservoir is not phosphorus limited. This reservoir system is high sedimemented, and likely carries sorbed phosphate in those sediments (Krom & Berner, 1980). The sorbed phosphate can become mobile in anoxic sediments, such as during the summer when water temperature increases and sediment oxygen decreases (Watson et al., 2018). Once the phosphate is desorbed, algae can use it as a nutrient. In this case, the system is no longer phosphorus-limited, and becomes nitrogen-limited, thus supporting nitrogen fixation.
Denitrification is not an important process in this reservoir system as we had originally hypothesized. Denitrification has been an important process in other reservoirs systems due to low dissolved oxygen, which led me to hypothesize that nitrogen removal was occurring primarily via denitrification (Saunders & Kalf, 2001). Nitrate is retained in this system, but the transformation from nitrate to DON indicates retention via assimilation rather than removal via denitrification (Figures 10 and 11). In addition, N₂:Ar disequilibrium values tend to be negative, indicating nitrogen fixation, or around zero, indicating equilibrium (Figure 16). Relatively little denitrification is occurring, as seen by the few positive values of N₂:Ar disequilibrium.

*Transient storage zones control biogeochemical reservoir response*

Evidence of assimilation within the reservoir supports the hypothesis that transient storage zones control overall reservoir response. Nitrate is retained in the shallow, vegetated side pools of the reservoir, regardless of flow condition (Figure 14). For all internal sampling days that have an overlapping instantaneous mass balance value, NO₃:Cl is negative, indicating retention. This shows that dominant processes occurring in the transient storage zones are consistent with those seen on the ecosystem level as well.

The role of transient storage zones in reservoir function is evident for NO₃:Cl. However, there is less continuity with DON:Cl, displaying very little change within the reservoir while showing net production in the mass balance. This could be due to a temporal lag between nitrate storage and DON export. Nitrate can be assimilated and stored for a range of time scales, and not be immediately exported as DON (Berman & Bronk, 2003). When referencing the mass balance of DON:Cl for a given storm event, there may be disconnect in timing of these reactions due to short term retention in biomass that is leaching slowly or has not been leached yet.
Nitrous oxide (N\textsubscript{2}O) concentration displays very little spatial heterogeneity within the reservoir (Figure 14). Concentrations of N\textsubscript{2}O do not change into the side pools, indicating little evidence of denitrification. The relationships between distance and N\textsubscript{2}O concentration are not significant (Appendix 1 Table 4). This supports previous findings that denitrification is not a dominant process in this system. N\textsubscript{2}O is a byproduct of denitrification and nitrification (Senbayram et al., 2012). If denitrification were a more dominant process, we would see more N\textsubscript{2}O increases in association with nitrate declines (Laursen & Seitzinger, 2004). However, N\textsubscript{2}O is consistently supersaturated across the reservoir system (Figure 17). Though there is little evidence elsewhere for denitrification, N\textsubscript{2}O is also a product of nitrification, a dissimilatory process through which ammonium is converted to nitrate. Ammonium mass balance does not help evaluate whether nitrification is happening (Figure 18). As such, it is difficult to determine the governing process of supersaturated N\textsubscript{2}O. Supersaturation of N\textsubscript{2}O may be occurring outside the reservoir, as N\textsubscript{2}O in sediments or groundwater can remain in surface waters before being released (Beaulieu et al., 2011). While transient storage zones are shown to influence overall reservoir signal for NO\textsubscript{3}:Cl, their influence on other solutes and gases is less apparent.

\textit{Future directions}

This study incorporated organic forms of nitrogen in addition to inorganic forms to reveal multiple fates of nonpoint source nitrate in a reservoir ecosystem. The fate and transport of nitrogen could be studied further through incorporating particulate forms, which would account for assimilated nitrate exported as algal biomass. This could be especially revealing for this system since assimilation into algal biomass could cause accumulation of particulate organic nitrogen (PON) when algae die and decay (Bronk et al., 1994). Laboratory analysis for particulate nitrogen (PN) would contribute to our understanding of the role of particulates, and allow us to calculate total nitrogen (TN), revealing the summative nitrogen budget. By
considering DON and TDN mass balance in addition to nitrate, this study identified more specific nitrogen processes, creating a more holistic picture of nitrogen dynamics within small reservoirs.

Use of paired high-frequency sensors across a range of flow conditions would provide further insight on storm characteristics and controls on reservoir biogeochemistry. Antecedent condition, season, storm duration, storm size, and land use are all storm metrics which influence biogeochemical response. Capturing temporal variability across scales remains a challenge to our understanding of aquatic biogeochemistry. These pursuits are imperative for a climate future with more frequent and stronger storms.

Transport metrics between transient storage and main advective path of the reservoir could be better quantified using a hydrologic tracer, such as Rhodamine WT. Using high-frequency sensors, we can establish breakthrough curves for different areas of the reservoir, and quantify residence time and hydrologic connectivity during different flow conditions. This would provide insight on the delivery and fate of solutes to transient storage zones.
CHAPTER V: CONCLUSIONS

Findings from this study suggest that small reservoirs are not always nitrogen sinks, and can act as transformers of nitrogen from inorganic to organic forms. Findings further suggest that reservoirs retain nitrate during large storms, and that storms have a significant effect on processing of nitrate and dissolved organic nitrogen. Lastly, transient storage processes are consistent with overall ecosystem nitrate retention. These findings contribute to our understanding of the variable role of reservoirs in nitrogen processing, which has implications for dam removal decisions. Dam removals across the northeast United States are driving landscape shifts with unknown consequences. New England is home to >14,000 small dams (Gold et al., 2016). More than 175 of these dams have been removed, 94% of which have been removed since 1990 (American Rivers).

Dam removal has become a favorable management strategy primarily due to the economic cost of maintaining obsolete infrastructure (Pohl, 2002), and concerns for fish passage and ecosystem connectivity (Bednarek, 2001). Several environmental criteria are evaluated when considering dam removal (Bednarek, 2001). Due to the lack of research on the effects of dam removal on nitrogen processing, nitrogen is typically not considered. Although there is a perceived tradeoff between improved fish passage and nitrogen retention capability when considering dam removal, a previous model suggests only 10% of New England dams are high priority for both criteria (Gold et al., 2016). Within the nitrogen-impaired Great Bay watershed, 10 dams have been removed since 2004, and at least 2 others are being considered for dam removal, including the Mill Pond Dam (American Rivers). Furthermore, the Mill Pond dam,
located at the study site, is being considered for removal. The increasing popularity of dam removal could have considerable effects on regional nitrogen balance.

This research highlights the importance of considering nitrogen dynamics in dam removal decisions. Recommended considerations for stakeholders and consultants involved with dam removal decisions include measuring both inorganic and organic forms of nitrogen at inputs and outputs over a representative range of flow conditions. This would identify if nonpoint source nitrate is attenuated within the reservoir, as well as if it is removed or retained and exported later as dissolved organic nitrogen (DON). In addition, measurements taken over a range of flow conditions would capture some of the biogeochemical variability introduced to aquatic systems by storms. Access to high-frequency sensors remains a likely barrier to capturing storm dynamics. Incorporation of nitrogen dynamics in dam removal considerations would greatly improve our ecological understanding of freshwater reservoir systems, and the impact of dam removal on regional nitrogen budgets.
REFERENCES


consumption and nitrous oxide production in rivers measured at the whole-reach scale. *Freshwater Biology*, 49(11), 1448–1458. https://doi.org/10.1111/j.1365-2427.2004.01280.x


**Tables**

*Table 1:* Dates and maximum flow of five storm events captured using the internal sampling. Each storm event was sampled twice, once during the preceding baseflow and once during the falling limb of the storm. Peak flow values show range of storm size captured. Flow values are from of USGS gage station 1073000, located in the Oyster River watershed, and are the flow at the storm peak, not the flow at the storm sampling time.

<table>
<thead>
<tr>
<th>Storm #</th>
<th>Baseflow</th>
<th>Stormflow</th>
<th>Q at peak (cms)</th>
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<td>1</td>
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Table 2: Average concentrations for measured solutes and gases shown for each sample site included in this study. All internal samples are averaged together.

<table>
<thead>
<tr>
<th>Site</th>
<th>CI (mg/L)</th>
<th>NO₃ (mg/L)</th>
<th>NH₄ (µg/L)</th>
<th>DON (mg/L)</th>
<th>TDN (mg/L)</th>
<th>NPOC (mg/L)</th>
<th>DO (%)</th>
<th>N₂O (µM)</th>
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</thead>
<tbody>
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**Table 3:** Average summer flux (kg/d) for nitrate (NO$_3^-$), dissolved organic nitrogen (DON) and total dissolved nitrogen (TDN). For 2018, n=4 sampling days averaged; for 2019, n=5. Standard deviation is reported in parentheses.

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<td>-2.19 (3.32)</td>
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**FIGURE 1:** Site map of internal samples, with zones A and B indicated. Output site highlighted yellow. Baseline concentration determined by averaging the two channelized points, colored orange. Distance from main advective path used as a metric to evaluate spatial heterogeneity and biological processes. Each zone has three sampling points at variable distances from the main advective path. Direction of flow is toward the yellow dot. Orthomosaic made by Alexandra Evans (2019).
Figure 2: Study sites used to monitor water quality and develop a mass balance for the Mill Pond. Sites are located in Durham, NH, USA. Ponded waters of Hamel Brook are downstream (northwest) of HAM, before Hamel Brook and Oyster River converge. Oyster River at Hamilton Chapel (OHC) is located downstream of that convergence. Map by Eliza Balch. Shapefiles sources from NH GRANIT and the National Hydrography Dataset.
Figure 3: Conceptual map of the ecological black box, where inputs and outputs provide a proxy for internal sampling. The high-frequency mass balance and instantaneous mass balance follow this design. Orthomosaic made by Alexandra Evans (2019).
Figure 4: Sites and components of the instantaneous mass balance approach. The input component was satisfied using CLGB+HAM+ORR, CLGB+OHC, or CLGB2+OHC. Local inputs were factored in using concentration of CLGB or CLGB2 as a proxy for concentration of runoff inputs from the surrounding landscape.
**Figure 5:** High-frequency fluxes during a fall stormflow period followed by a baseflow period (September 2018). Established using a concurrent deployment of Submersible Ultraviolet Nitrate Analyzer (SUNA) sensors at HAM, ORR, and OMPD. The sum of input fluxes minus the output flux determines the baseflow high-frequency mass balance (kg/day). Output flow (Q) is established using high-frequency in-situ stage sensors and applying a site-specific rating curve relationship between stage and flow. Dotted line delineates stormflow period and a baseflow period discussed in the text. CLGB flux for storm period calculated using site-specific relationship of storm event runoff to storm event nitrate flux (kg/storm) (Wollheim et al. 2017). CLGB flux for falling limb period calculated using concurrent grab sample of nitrate and discharge at CLGB.
**Figure 6:** Flow hydrograph of USGS gage station 1073000, located in the Oyster River watershed. Arrows indicate the storm events that were captured using the internal sampling. Storms occurred on 7/18/18, 6/12/19, 6/24/19, 8/31/19, and 10/20/19.
Figure 7: Percent change of chloride (Cl) between the inputs and output of Mill Pond, Durham, NH.
Figure 8: Absolute value of percent change of chloride vs. absolute value of percent change nitrate, to assess validity of mass balance model. 1:1 line represents conservative behavior solutes. Line of best fit shown in blue (m=.03). Points represent sampling days included in the mass balance analysis.
Figure 9: Percent change of nitrate (NO₃) between the inputs and output of Mill Pond, Durham, NH.
Figure 10: Percent change of dissolved organic nitrogen (DON) between the inputs and output of Mill Pond, Durham, NH. Annotated values indicate additional points which fall outside the plot range.
Figure 11: Percent change of total dissolved nitrogen (TDN) between the inputs and output of Mill Pond, Durham, NH.
Figure 12: Flow hydrograph of USGS gage station 1073000, located in the Oyster River watershed. Arrow indicates the storm event captured using the paired high-frequency mass balance approach. Storm is small- to intermediate- sized, and occurred 9/25/18.
**Figure 13**: Linear regression fit slope analysis example. Concentration plotted against distance from channel for each zone on every sampling day. Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Figure 14: Slopes of log NO$_3$-Cl, log DON:Cl, N$_2$:Ar disequilibrium, and N$_2$O vs. distance into the side pool for all sampling days and both zones (A and B). Numbers indicate a storm set, or corresponding baseflow and stormflow samplings. Standard error shown with black bars.
Figure 15: Difference in Q (storm Q-base Q) vs. difference in slope (storm slope-base slope) for the following solutes: NO$_3$:Cl, DON:Cl, N$_2$:Ar disequilibrium, and N$_2$O concentration. Each point represents one zone (A or B) during a storm event.
Figure 16: Relationship between nitrate (NO$_3$) and N$_2$:Ar disequilibrium for all internal, input, and output sites.
Figure 17: Equilibrium concentration of $\text{N}_2\text{O}$ vs. measured concentration of $\text{N}_2\text{O}$ for each sample. 1:1 line plotted to denote equilibrium. Points above the 1:1 line are considered supersaturated.
Figure 18: Percent change of ammonium (NH₄) between the inputs and output of Mill Pond, Durham, NH.
APPENDICES
**APPENDIX 1**

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**Appendix 1 Table 1**: Slopes of the linear relationship between log NO$_3$-Cl and distance from main advective path into the reservoir transient storage. Storm sets include corresponding pre-storm baseflow and falling limb stormflow sampling sets. Significant linear relationships indicated with *.

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### Appendix 1 Table 2: Slopes of the linear relationship between log DON:Cl and distance from main advective path into the reservoir transient storage. Storm sets include corresponding pre-storm baseflow and falling limb stormflow sampling sets. Significant linear relationships indicated with *.

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Appendix 1 Table 3: Slopes of the linear relationship between N₂:Ar disequilibrium and distance from main advective path into the reservoir transient storage. Storm sets include corresponding pre-storm baseflow and falling limb stormflow sampling sets. Significant linear relationships indicated with *.

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Appendix 1 Table 4: Slopes of the linear relationship between N$_2$O concentration and distance from main advective path into the reservoir transient storage. Storm sets include corresponding pre-storm baseflow and falling limb stormflow sampling sets. Significant linear relationships indicated with *.

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<th>Std. Error</th>
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Appendix 1 Figure 1: Linear regression fit slope analysis of log NO$_3$:Cl during storm event 1 (7/10/18-7/18/18). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 2: Linear regression fit slope analysis of log DON:Cl during storm event 1 (7/10/18-7/18/18). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 3: Linear regression fit slope analysis of N₂:Ar disequilibrium during storm event 1 (7/10/18-7/18/18). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 4: Linear regression fit slope analysis of log NO$_3$:Cl during storm event 2 (6/10/19-6/12/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 5: Linear regression fit slope analysis of log DON:Cl during storm event 2 (6/10/19-6/12/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 6: Linear regression fit slope analysis of N₂:Ar disequilibrium during storm event 2 (6/10/19-6/12/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 7: Linear regression fit slope analysis of N$_2$O concentration during storm event 2 (6/10/19-6/12/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 8: Linear regression fit slope analysis of log NO$_3$:Cl during storm event 3 (6/20/19-6/24/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 9: Linear regression fit slope analysis of log DON:Cl during storm event 3 (6/20/19-6/24/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 10: Linear regression fit slope analysis of N₂:Ar disequilibrium during storm event 3 (6/20/19-6/24/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 11: Linear regression fit slope analysis of N$_2$O concentration during storm event 3 (6/20/19-6/24/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 12: Linear regression fit slope analysis of log NO₃:Cl during storm event 4 (8/28/19-8/31/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 13: Linear regression fit slope analysis of log DON:Cl during storm event 4 (8/28/19-8/31/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 14: Linear regression fit slope analysis of N$_2$:Ar disequilibrium during storm event 4 (8/28/19-8/31/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 15: Linear regression fit slope analysis of \( \text{N}_2\text{O} \) concentration during storm event 4 (8/28/19-8/31/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 16: Linear regression fit slope analysis of log NO$_3$:Cl during storm event 5 (10/16/19-10/20/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 17: Linear regression fit slope analysis of log DON:Cl during storm event 5 (10/16/19-10/20/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 18: Linear regression fit slope analysis of N$_2$:Ar disequilibrium during storm event 5 (10/16/19-10/20/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 1 Figure 19: Linear regression fit slope analysis of N$_2$O concentration during storm event 5 (10/16/19-10/20/19). Concentration plotted against distance from channel for each zone (A or B) on every sampling day (base or storm). Linear regression analysis fits a line to the relationship, and the slope of that line is used as a metric for spatial patterns of biological processes within the reservoir.
Appendix 2 Table 1: Summary of metrics and results of one-way Analysis of Covariance to determine effect of storms on the relationship between distance and log NO$_3$ :Cl (slope). HRS is homogeneity of regression slopes; N means insignificant, therefore there is homogeneity. SW is Shapiro Wilks test to determine normality of residuals. N means insignificant, therefore there is normality. Out is presence of outliers, where N means there are none. Storm p-value indicates the significance of the influence of storm on the effect of distance on log NO$_3$ :Cl. Dist-storm p-value is the influence of distance on log NO$_3$ :Cl after adjustment for storm. Significant values **bolded**.
### Appendix 2 Table 2: Summary of metrics and results of one-way Analysis of Covariance to determine effect of storms on the relationship between distance and DON:Cl (slope).

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HRS is homogeneity of regression slopes; N means insignificant, therefore there is homogeneity. SW is Shapiro Wilks test to determine normality of residuals. N means insignificant, therefore there is normality. Out is presence of outliers, where N means there are none. Storm p-value indicates the significance of the influence of storm on the effect of distance on DON:Cl. Dist-storm p-value is the influence of distance on DON:Cl after adjustment for storm. Significant values **bolded.**
Appendix 2 Table 3: Summary of metrics and results of one-way Analysis of Covariance to determine effect of storms on the relationship between distance and N₂:Ar disequilibrium (slope). HRS is homogeneity of regression slopes; N means insignificant, therefore there is homogeneity. SW is Shapiro Wilks test to determine normality of residuals. N means insignificant, therefore there is normality. Out is presence of outliers, where N means there are none. Storm p-value indicates the significance of the influence of storm on the effect of distance on N₂:Ar disequilibrium. Dist-storm p-value is the influence of distance on N₂:Ar disequilibrium after adjustment for storm. Significant values **bolded**.
Appendix 2 Table 4: Summary of metrics and results of one-way Analysis of Covariance to determine effect of storms on the relationship between distance and N$_2$O concentration (slope). HRS is homogeneity of regression slopes; N means insignificant, therefore there is homogeneity. SW is Shapiro Wilks test to determine normality of residuals. N means insignificant, therefore there is normality. Out is presence of outliers, where N means there are none. Storm p-value indicates the significance of the influence of storm on the effect of distance on N$_2$O concentration. Dist-storm p-value is the influence of distance on N$_2$O concentration after adjustment for storm. Significant values **bolded**.
Appendix 2 Figure 1: Linearity tests show linear regression analysis of the relationship between the covariate (storm) and the response variable (log NO$_3$Cl). Variables with a linear relationship are fit to be inputs for an analysis of covariance (ANCOVA).
Appendix 2 Figure 2: Linearity tests show linear regression analysis of the relationship between the covariate (storm) and the response variable (DON:Cl). Variables with a linear relationship are fit to be inputs for an analysis of covariance (ANCOVA).
Appendix 2 Figure 3: Linearity tests show linear regression analysis of the relationship between the covariate (storm) and the response variable (N$_2$:Ar disequilibrium). Variables with a linear relationship are fit to be inputs for an analysis of covariance (ANCOVA).
Appendix 2 Figure 4: Linearity tests show linear regression analysis of the relationship between the covariate (storm) and the response variable (N$_2$O concentration). Variables with a linear relationship are fit to be inputs for an analysis of covariance (ANCOVA).
Appendix 3 Figure 1: Rating curve used to estimate discharge using stage height at College Brook (CLGB) for the high-frequency mass balance. Rating curve established over several years and compiled from measurements made by the United State Geological Survey in 2014 and measurements made since then. Measurements of stage height since 2014 were made using a water level logger (Onset, Inc.) and discharge (Q) was measured using a doppler water velocity sensor and physical dimension measurements across a cross section of the river. For this project, estimations were made using the 2015-2020 segment for low flows, and the upper curve of the Final 2013-2015 segment (red dash) for high flows.
Appendix 3 Figure 2: Rating curve used to estimate discharge using stage height at Hamel Brook (HAM) for the high-frequency mass balance. Stage height was measured using a water level logger (Onset, Inc.) and discharge (Q) was measured using a doppler water velocity sensor and physical dimension measurements across a cross section of the river.
Appendix 3 Figure 3: Rating curve used to estimate discharge using stage height at Mill Pond Dam (OMPD) for the high-frequency mass balance. Rating curve established by United States Geological Survey in June 2014.
Appendix 3 Figure 4: Rating curve used to estimate discharge using stage height at Oyster River (ORR) for the high-frequency mass balance. Stage height was measured using a water level logger (Onset, Inc.) and discharge (Q) was measured using a doppler water velocity sensor and physical dimension measurements across a cross section of the river.

\[ y = 7.4279x^{7.7883} \]

\[ R^2 = 0.707 \]
Appendix 4 Figure 1: Percent change of dissolved oxygen (%DO) between the inputs and output of Mill Pond, Durham, NH.
Appendix 4 Figure 2: Percent change of the ratio of non-purgeable organic carbon (NPOC) to total dissolved nitrogen (TDN) between the inputs and output of Mill Pond, Durham, NH.
Appendix 4 Figure 3: High-frequency fluxes during a summer baseflow period (July 2019). Established using a concurrent deployment of Submersible Ultraviolet Nitrate Analyzer (SUNA) sensors at OHC and OMPD (Figure Map). The sum of input fluxes minus the output flux determines the baseflow high-frequency mass balance (kg/day). Output flow (Q) is established using high-frequency in-situ stage sensors and applying a site-specific rating curve relationship between stage and flow. Flow data for OMPD are extrapolated for 7/10/19-7/13/19 using a linear best fit of preceding flow during a period with no precipitation in the watershed. CLGB flux calculated by applying the average concentration of four grab samples from baseflow periods two weeks before or after this period to the flow at CLGB over the time period. Nitrate input measured at OHC, and flow data applied from measurements at ORR + HAM, two rivers which converge upstream OHC (Figure Map).
Appendix 5 Figure 1: Time series of non-purgeable organic carbon (NPOC) (mg/L) for all sites over the course of the sampling period.
Appendix 5 Figure 2: Time series of water temperature (C) for all sites over the course of the sampling period.
Appendix 5 Figure 3: Time series of dissolved oxygen (% saturation) for all sites over the course of the sampling period.
Appendix 5 Figure 4: Time series of methane (CH4) concentration (µM) for all sites over the course of the sampling period.
Appendix 5 Figure 5: Time series of dissolved organic carbon (DOC) concentration (mg/L) for all sites over the course of the sampling period.
Appendix 5 Figure 6: Time series of total dissolved nitrogen (TDN) concentration (mg/L) for all sites over the course of the sampling period.
Appendix 5 Figure 7: Time series of NO$_3$-N concentration (mg/L) for all sites over the course of the sampling period.
Appendix 5 Figure 8: Time series of N₂O % saturation for all sites over the course of the sampling period.
Appendix 5 Figure 9: Time series of $\text{N}_2$:Ar disequilibrium for all sites over the course of the sampling period.
Appendix 5 Figure 10: Time series of total dissolved nitrogen concentration (mg/L) for all sites over the course of the sampling period.