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The Role of Small Reservoirs in Reducing Reactive N Export Via Denitrification

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THE ROLE OF SMALL RESERVOIRS IN
REDUCING REACTIVE N EXPORT VIA
DENITRIFICATION

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Abstract

Reactive nitrogen (N), which harms ecosystem health, has been increasing in the biosphere, leading to higher N export to coastal ecosystems. Although man-made reservoirs can be significant sources of greenhouse gases, they can also retain N, thus reducing N export. Because many dams are relics from industrial hydropower, their removal is becoming increasingly common. It is therefore crucial to understand the ecological tradeoffs of man-made reservoirs. While previous studies have examined nutrient budgets and denitrification at inputs and outputs of large reservoirs, small reservoir dynamics remain understudied. In this study, we measured inputs and outputs of NO_3 and N_2 at two small coastal reservoirs and assessed reasons for changes by sampling internally within the reservoirs. We hypothesized that denitrification is high in small reservoirs due to lower dissolved oxygen. While we found evidence of denitrification in one reservoir the second reservoir showed evidence of N fixation. Fixation was evident within the reservoir where low NO_3 concentrations and high algal growth occurred, suggesting that NO_3 was being assimilated, limiting algal growth, and allowing the occurrence of N fixing algae. As a result, reservoirs may not always remove N, but may at times be a source of additional N. As dam removal decisions continue, the role of reservoirs in N export should be carefully considered.

1 Introduction

Reactive nitrogen (N) has been increasing in the biosphere since the industrial and agricultural revolutions (Green et al., 2004), leading to higher export of N from land to streams and streams to the ocean (Seitzinger et al., 2010). Excess N in coastal ecosystems can cause harmful algal blooms and hypoxic conditions, which have been documented in coastal ecosystems worldwide (Diaz and Rosenberg, 2008). The flux of N to the ocean is altered by dams which retain sediments and alter transport from the headwaters to the ocean. There are over 14,000 dams in the northeast USA and, as many are relics from hydropower, dam removal is becoming increasingly common (Dartmouth College, 2016); it is crucial to understand the ecological impacts of man-made reservoirs. Although reservoirs have been cited as significant sources of greenhouse gases to the atmosphere (Deemer et al., 2016; Song et al., 2018; Prairie et al., 2018), reservoirs have also been shown to retain N (Wollheim et al., 2008), thus reducing N export. Reservoirs tend to have lower dissolved oxygen (D.O.) than channels, which may promote denitrification, microbial anaerobic respiration which converts NO_3 to inert N_2 gas and N_2O (Beaulieu et al., 2011). While N_2O is a potent greenhouse gas, its production in beaver ponds, which are similar to small reservoirs, has not been shown to be significantly higher than in streams (Lazar et al., 2014), suggesting that denitrification typically goes to completion, producing inert N_2 gas.

While previous studies have examined nutrients budgets from the inputs and outputs of large reservoirs (Teodoru and Wehrli, 2005; Powers et al., 2015; Xu et al., 2018), small reservoir dynamics remain understudied and could represent an important knowledge gap. Further, the internal mechanisms within reservoirs that set denitrification rates, and how they differ among small vs. large reservoirs, are also not well characterized. Denitrification occurs primarily in the sediment (Reisinger et al., 2016) under reducing, or low oxygen conditions,

and is favored by high NO_3 and organic carbon (Knowles, 1982). Key relationships have found denitrification to be limited by hydrological conditions that affect contact with sediment: decreasing with stream depth (Alexander et al., 2007) and increasing with residence time (Seitzinger et al., 2002), but other mechanisms remain understudied. In this study, we sampled an indicator of denitrification, $\text{N}_2:\text{Ar}$, using a new technology, Membrane Inlet Mass Spectrometry (MIMS), which provides more precision than measuring N_2 alone. We measured NO_3 concentration, D.O., and water temperature at the inputs and outputs of two small reservoirs and conducted internal sampling across a range of conditions within each reservoir to determine reasons for changes. We hypothesized that denitrification is evident in both shallow reservoirs during the summers due to low dissolved oxygen, leading to a decline in nitrate concentrations between inputs and outputs.

2 Methods

We sampled inputs and outputs of NO_3 and N_2 (as $\text{N}_2:\text{Ar}$) at both reservoirs weekly from May through July, 2018 and conducted one round of internal spatial sampling within each reservoir in mid-July. NO_3 concentration was sampled using grab samples that were analyzed for $\text{NO}_3\text{-N}$ concentration using Ion Chromatography (IC) in the UNH Water Quality Analysis Lab. Dissolved N_2 was quantified using $\text{N}_2:\text{Ar}$ ratios measured with Membrane Inlet Mass Spectrometry (MIMS) which were then compared to the ratio at equilibrium calculated for the given water temperature at the time of sampling. The difference between the measured $\text{N}_2:\text{Ar}$ ratio and the ratio at equilibrium, the disequilibrium, was used to determine whether denitrification ($\text{N}_2:\text{Ar} > \text{equilibrium}$) or N-fixation ($\text{N}_2:\text{Ar} < \text{equilibrium}$) was dominating. Specific conductance, dissolved oxygen (D.O.), and water temperature were measured using a Yellow Springs Instruments (YSI) handheld sensor.

2.1 Study Sites

The study was conducted at the Mill Pond Reservoir in Durham, NH (Figure 1) and the Bellamy Reservoir in Dover, NH (Figure 2) from May through July, 2018. Mill Pond inputs: College Brook (I), Oyster River (K) and Hamel Brook (N) and Mill Pond output (A) were sampled once a week. Internal sampling of Main Zones, which are within the main flow of the reservoir, and Transient Storage Zones, which are the side pools where some stream flow is retained before returning to the main channel and flowing downstream, occurred on July 10th and 18th (Figure 1).

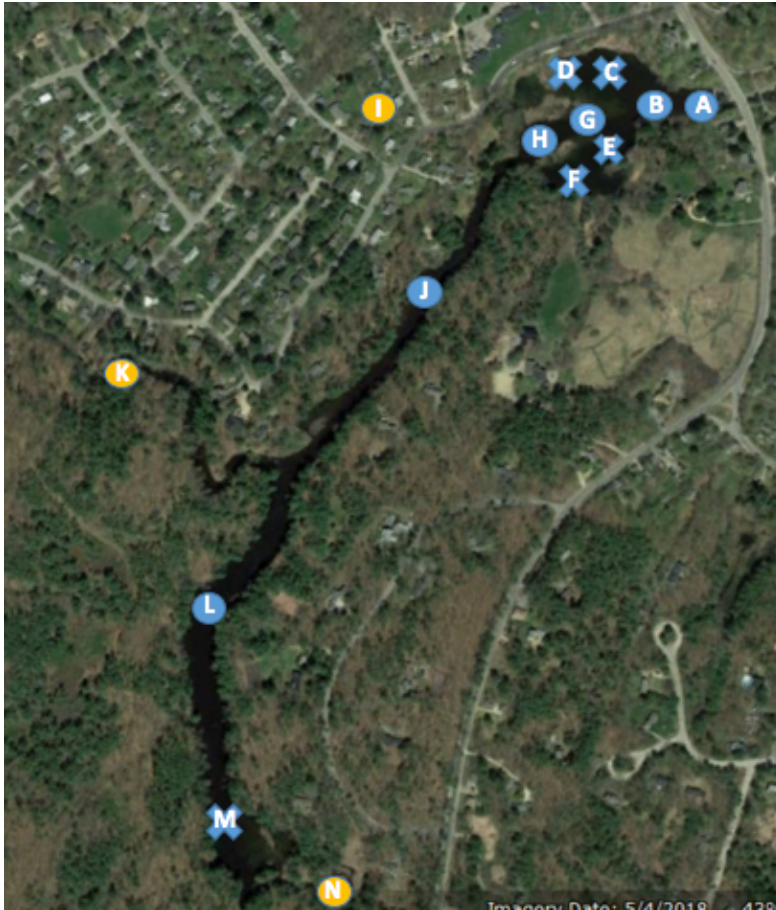


Figure 1. Mill Pond Reservoir inputs (yellow), Main Zones (blue circles) and Transient Storage Zones (crosses) sampled May through July, 2018 in Durham, NH.

Bellamy Reservoir input, Bellamy River upstream (K), and output, Bellamy Reservoir downstream (A), were sampled weekly. A small tributary (E) was sampled for specific conductance and dissolved oxygen weekly and twice for NO_3 and $\text{N}_2:\text{Ar}$ on the other side of the highway (Figure 2) and sampled further downstream (Figure 2) during internal sampling. Internal sampling of Main Zones and Transient Storage Zones occurred on July 12th.



Figure 2. Bellamy Reservoir inputs (yellow), Main Zones (orange circles), and Transient Storage Zones (crosses) sampled May through July, 2018 in Dover, NH.

3 Results

$N_2:Ar$ disequilibrium was generally positive in all stream and tributary inputs for both reservoirs, as well as at the outflow of the Bellamy Reservoir (Figure 3). $N_2:Ar$ disequilibrium at the Bellamy outflow was not much higher than the inflow (Figure 3). However, $N_2:Ar$ disequilibrium was negative at the outflow of Mill Pond (Figure 3).

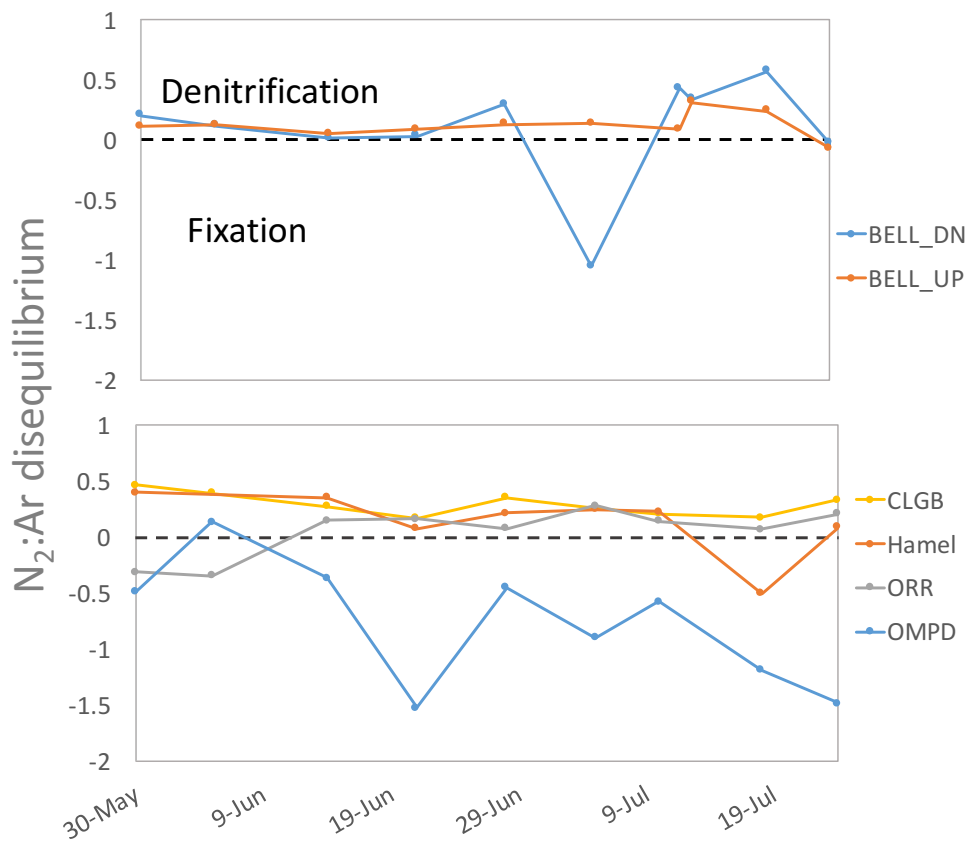


Figure 3. $N_2:Ar$ disequilibrium over time in the Mill Pond (top) and Bellamy Reservoir (bottom) watersheds from May through July, 2018. Positive values indicate a possible denitrification signal and negative values indicate a possible fixation signal.

$N_2:Ar$ was more negative at lower NO_3-N concentration across all sites (Figure 4). College Brook generally had the highest NO_3-N concentration and had positive $N_2:Ar$ disequilibrium throughout the study (Figure 4). Mill Pond transient storage sites had the lowest NO_3-N concentrations and the most negative $N_2:Ar$ disequilibrium (Figure 4).

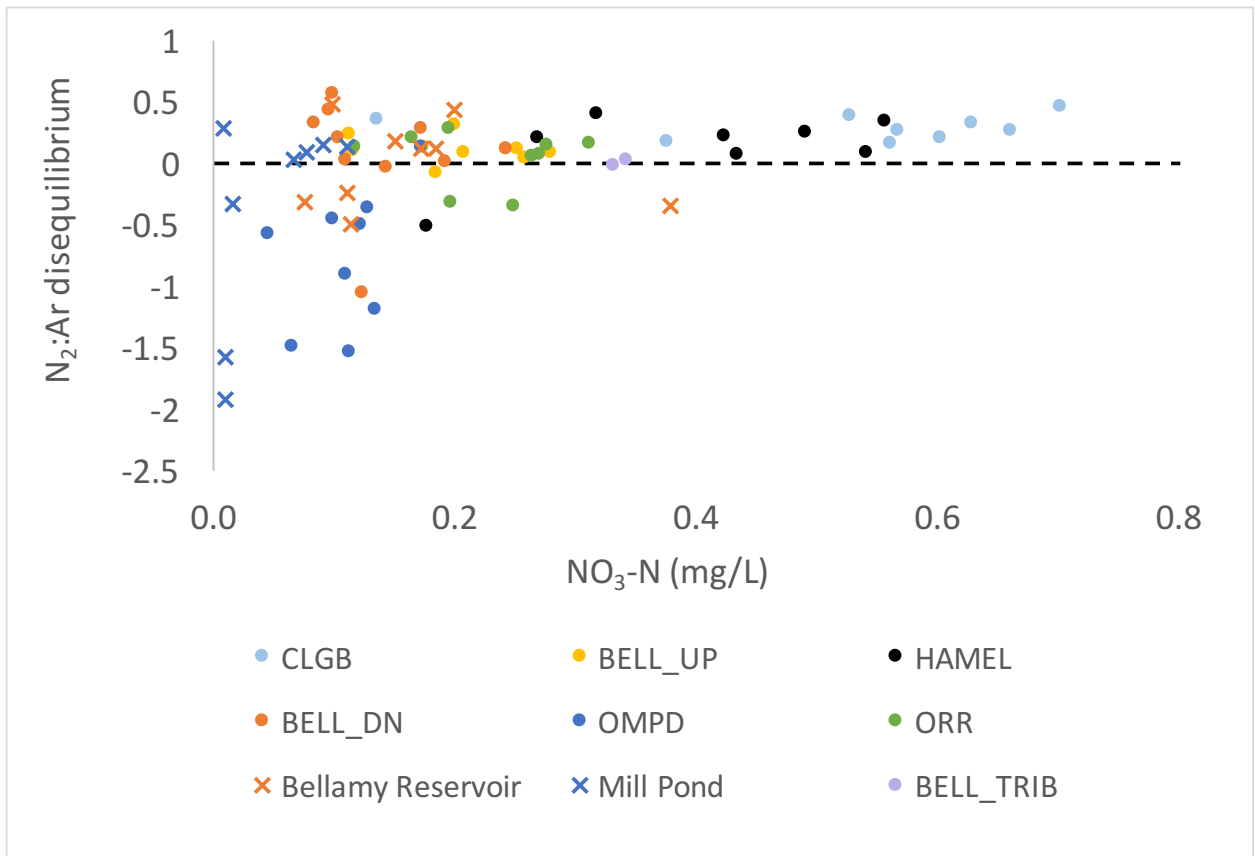


Figure 4. $\text{N}_2\text{:Ar}$ disequilibrium vs. $\text{NO}_3\text{-N}$ concentration for weekly samples and one round of internal samples (x's) in the Mill Pond and Bellamy Reservoir. Positive values indicate a possible denitrification signal and negative values indicate a possible fixation signal.

Average dissolved oxygen and $\text{N}_2\text{:Ar}$ disequilibrium were lower in the Transient Storage Zones than the Main Zones in both Mill Pond and the Bellamy Reservoir (Table 1). $\text{NO}_3\text{-N}$ concentration was lower in the Transient Storage Zones than the Main Zones in Mill Pond, but was slightly higher in the Bellamy Reservoir Transient Storage Zones, compared to the Main Zones, despite lower D.O. (Table 1). $\text{N}_2\text{:Ar}$ disequilibrium was slightly positive in the Main Zones of the Bellamy Reservoir and slightly negative in the Transient Storage Zones (Table 1) with an overall positive $\text{N}_2\text{:Ar}$ signal for the reservoir at the Bellamy downstream (Figure 3). $\text{N}_2\text{:Ar}$ was slightly positive in the Main Zones of Mill Pond and negative in the Transient Storage Zones in Mill Pond (Table 1); the net effect for the entire reservoir is negative

N₂:Ar disequilibrium, as observed at OMPD (Figure 3), indicating that fixation may predominate.

Table 1. NO₃-N concentration Dissolved Oxygen and N₂:Ar disequilibrium in the Main Zones and Transient Storage Zones from internal sampling in the Bellamy Reservoir and Mill Pond in mid-July.

Site	NO ₃ -N (mg/L)	Dissolved Oxygen (%)	N ₂ :Ar disequilibrium
Bellamy Reservoir Main Zones	0.13	85.1	0.108
Mill Pond Main Zones	0.07	78.5	0.134
Bellamy Reservoir Transient Storage Zones	0.15	7.2	-0.188
Mill Pond Transient Storage Zones	0.01	5.9	-1.123

4 Discussion

The trend of decreasing $N_2:Ar$ as NO_3-N concentration decreased is consistent with N-fixation being an important process in Mill Pond. Algal production was very high in the Transient Storage Zones (Appendix 1), which suggests high N demand, resulting in low NO_3 concentrations. As a result, the algal production could have been dominated by N-fixers, resulting in high rates of N-fixation, and depletion of $N_2:Ar$ relative to equilibrium. Mill Pond had a higher abundance of algae, and macrophytes in general, than the Bellamy Reservoir (Appendix 1) which could explain the fixation signal if algae were assimilating NO_3 . The fixation signal observed in Mill Pond contradicts our hypothesis that denitrification would dominate in reservoirs due to lower dissolved oxygen, which did occur in both reservoirs. Importantly, it is also inconsistent with previous studies that have cited reservoirs as zones that retain reactive N (Wollheim et al., 2008). This may indicate that internal dynamics of shallow reservoirs, particularly primary production and NO_3-N concentration, are important drivers to the fate of incoming nitrate.

Perhaps the best representation of internal dynamics is the Transient Storage Zones. Generally, the main zones within the reservoirs behaved similarly to the inputs, with higher $N_2:Ar$ disequilibrium and higher dissolved oxygen. Transient Storage Zones had low dissolved oxygen, indicating reduced conditions. The role of nitrogen as a nutrient, energy source (NH_4), and terminal electron acceptor under reduced conditions (Helton et al., 2015) remains unexplored in this study, since only NO_3-N concentration have been measured so far (other forms of nitrogen are yet to be analyzed). Similarly, nitrification cannot be ruled out as a process that was producing NO_3 in the Transient Storage Zones of the Bellamy, where NO_3-N concentration was higher than in Transient Storage Zones in Mill Pond. Data on NH_4 will address this possibility.

Perhaps the most interesting finding is that the reservoirs behaved differently under similarly reduced conditions. D.O. was low in both reservoirs, especially Transient Storage Zones, as hypothesized, but fixation occurred in Mill Pond while denitrification occurred in the Bellamy Reservoir. NO_3 concentrations in Mill Pond Transient Storage Zones were the lowest measured during the study, across all sites, but NO_3 concentrations in the Bellamy Transient Storage Zones were similar to the Main Zones. It is possible that local urban inputs of NO_3 were high enough to promote denitrification in the Bellamy Reservoir. Another possibility is that the Bellamy Reservoir is Phosphorus-limited while Mill Pond is not. This could explain why a N fixation signal was not seen in the Bellamy; if phosphorus was the limiting nutrient to growth, NO_3 would not be in high demand for fixation.

This study was conducted during the summer months when primary productivity was high; a longer-term study would provide an interesting comparison across seasons. The transition of systems from reservoirs with longer residence times into naturally flowing channels is also important to consider as dam removal becomes increasingly common and would be a valuable research question for a future study. The Sawyer Mill Dam, which is a two-part dam that formed the Bellamy Reservoir, was partially removed after the study took place with the second part scheduled to be removed in 2019. The Mill Pond dam can no longer handle high flows and the town of Durham has allocated \$300,000 to study the effects of its removal (Conley, 2019). Thus, both reservoirs may soon become naturally flowing channels with different biogeochemistry than their former reservoir inputs and output.

Small reservoirs and internal dynamics remain understudied. The unexpected N-fixation, despite low D.O. in Mill Pond suggests that internal dynamics are important to consider when studying reservoir systems. The possibility of reservoirs behaving as additional reactive N sources also necessitates nutrient cycling and reactive N export being considered in dam removal decisions.

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Appendix 1

Table 2. Macrophyte abundance (relative to reach) and type of macrophytes present at internal sampling locations in the Bellamy Reservoir.

Site	Zone type	Amount	Macrophyte type		
			Algae	Grass	Lilies
B	Main	Medium	X		
C	Transient	Medium	X	X	
D	Transient*	Low	X	X	X
E	Input	Low	X	X	
F	Main	Medium	X	X	
G	Main	Low	X	X	
H	Main	Low	X	X	
I	Main*	Low		X	
J	Main	Low	X		

Table 3. Macrophyte abundance (relative to reach) and type of macrophytes present at internal sampling locations in Mill Pond.

Site	Zone type	Amount	Macrophyte type		
			Algae	Grass	Lilies
B	Main	Low	X		
C	Transient	Medium	X		X
D	Transient	High	X		X
E	Transient	Medium	X		X
F	Transient	High	X		X
G	Main	Low	X		
H	Main				
J	Main	Low	X		
L	Main	Low	X		
M	Transient	High	X		X