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Small Reservoirs as Nitrogen Transformers: Accounting for Seasonal Variability in Inorganic and Organic Nitrogen Processing

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Key Points:

- Small reservoirs were not a significant nitrogen sink over annual timescales when considering both inorganic and organic forms of N
- Seasonal variability in nitrogen processing led to small reservoirs acting as temporary sinks or sources for different forms of nitrogen
- In contrast to previous predictions, small dam removals do not always lead to greater nitrogen exports to coastal ecosystems

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Abstract

Anthropogenic nitrogen (N) inputs to the landscape have serious consequences for inland and coastal waters. Reservoirs are effective at mitigating downstream N fluxes but measurements have generally focused on large reservoirs and have not considered seasonal variability or all N forms. In this study, we conducted an N mass balance in eight small reservoirs (surface area <0.55 km^2) in coastal New England over annual time periods, including both inorganic and organic forms of N. We found that small reservoirs have high capacity for dissolved inorganic N (DIN) retention during low and moderate discharge, but are roughly in balance for DIN at higher discharge. Because proportional DIN retention occurred when N inputs were at their lowest, their effect on downstream N fluxes is small over annual time frames. Further, dissolved organic N (DON) was also evident during low flow late in the warm season. Accounting for DON production, the net effect of reservoirs on total dissolved N (TDN) fluxes was limited. These transformations between inorganic and organic N should be considered when evaluating the effect of small reservoirs on TDN fluxes over seasonal and annual timescales. With dam removal becoming a common solution to aging, unsafe dams, their ability to retain or produce N must be scrutinized at longer time scales while accounting for the complete N pool to better comprehend the effect their reservoirs have on downstream waters.

Plain Language Summary

Excess nitrogen in the environment can negatively impact both freshwater and coastal ecosystems. However, water bodies such as reservoirs have been shown to reduce the amount of nitrogen flowing downstream. This has led to the idea that if reservoirs are removed, there will be more nitrogen exported downstream. Many studies on reservoir influence on nitrogen flowing downstream have not explicitly included small reservoirs, transformations between forms of nitrogen, or seasonal variability of nitrogen processing. We found that while small reservoirs do decrease inorganic nitrogen during the warm season, organic nitrogen is also produced, leading to a lesser impact on total nitrogen. Dissolved inorganic nitrogen retention is highest during low flows. When flows are higher and nitrogen transport is greater, small reservoirs are not as biologically active, leading to very little nitrogen being transformed. We conclude that small reservoirs are not a nitrogen sink when accounting for transformations between nitrogen forms and accounting for nitrogen processing across all seasons. Removal of small reservoirs will likely not lead to increased annual nitrogen exports to coastal areas.

1. Introduction

Human activities have significantly altered the global nitrogen (N) cycle, primarily due to the production of food and energy (Fowler et al., 2013; Galloway et al., 2004). Anthropogenic N is transported from the terrestrial landscape into aquatic networks (Boyer et al., 2006), with serious consequences for both coastal and freshwater ecosystems (Boesch, 2002; Davidson et al., 2012; Erisman & Larsen, 2013). However, river networks are very effective in reducing downstream N fluxes, preventing a large proportion of this anthropogenic N from reaching the coast (Seitzinger, Styles, et al., 2002; Wollheim, Peterson, et al., 2008; Wollheim, Vörösmarty, et al., 2008). Within aquatic networks, channelized streams are well-studied, and much is known about their role in N cycling at both the reach and river network-scales (Bernhardt et al., 2005; Helton et al., 2018; Mulholland et al., 2008; Stewart et al., 2011). N retention in ponded water bodies within river networks, including reservoirs, is also substantial (David et al., 2006; Garnier et al., 1999; Gold et al., 2016; Harrison et al., 2009; Saunders & Kalff, 2001; Seitzinger, Styles, et al., 2002; Seitzinger et al., 2006, 2010), suggesting reservoirs are largely beneficial in terms of reducing N loads to downstream ecosystems.

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Large reservoirs have been preferentially studied compared to small reservoirs despite small reservoirs having a greater abundance and wider distribution relative to their large counterparts (Graf, 1993, 1999; Magilligan et al., 2016; Smith et al., 2002). There are an estimated 2.6 million small (surface area $<10^4$ m^2), artificial water bodies distributed throughout the contiguous US, with about 25.7% of these impoundments on the east coast (Graf, 1999; McDonald et al., 2012; Renwick & Sleezer, 2006; Smith et al., 2002). Reach-scale analyses have found that small water bodies can also greatly reduce downstream fluxes of constituents, including nitrate (Cheng & Basu, 2017; Fairchild & Velinsky, 2006; Ignatius & Rasmussen, 2016). Modeling and geospatial studies further suggest that the abundance of small water bodies, coupled with their nitrate-retaining potential, may have an outsized influence on river network- and regional-scale N budgets (Cheng & Basu, 2017; Gold et al., 2016; Schmadel et al., 2018, 2019). However, these studies often consider the mass balance of nitrate only and not of other forms of N, particularly organic nitrogen.

Most studies examining the effects of reservoirs on N processing have emphasized the fate of dissolved inorganic N (DIN) via storage or denitrification, which converts nitrate (NO_3^-) to N_2O or inert N_2 gas. This is a reasonable simplification as anthropogenic loading in suburban river networks (>40% human land use) is mostly in the form of inorganic N (Wollheim, Peterson, et al., 2008; Wollheim, Vörösmarty, et al., 2008) and therefore, mitigation of DIN is an important ecosystem service that reservoirs provide. However, organic N is a major component of the total N budget in most fluvial systems (Berman & Bronk, 2003; Bronk et al., 2007; Campbell et al., 2000) and few studies taking place in reservoirs have considered organic N separate from DIN. In one study on all N forms in a small agricultural reservoir in the Midwestern US, Powers et al. (2013) found that NO_3^- and ammonium (NH_4^+) generally declined while dissolved organic N (DON) fluxes increased. The omission of DON may lead to the conclusion that reservoirs are stronger N sinks than if all N forms are considered. More studies in small reservoirs that encompass the entire N cycle and integrate all seasons are needed to address their role in river network-scale N cycling, particularly as many small dams are being removed for a variety of reasons.

Many studies have emphasized reservoir N processing during the warm season. Summers are biologically active time periods with high potential for NO_3^- retention (Bosch et al., 2009; Fairchild & Velinsky, 2006; Gooding & Baulch, 2017; Ignatius & Rasmussen, 2016; Powers et al., 2013; Richardson & Herrman, 2020). However, to more accurately assess reservoir N dynamics relevant to coastal fluxes, budgets developed over the entire year allow for accounting for temporal variability in flow, influxes, and biological activity. Improved understanding of reservoir N budgets and dynamics requires regular, frequent sampling performed year-round and including both the inorganic and organic components of the dissolved N pool. Further, multiple small reservoirs, encompassing a range of physical, hydrological, and physicochemical reservoir conditions, will aid in developing general relationships.

Understanding how small reservoirs regulate N fluxes is important for a number of reasons such as how their removal affects N exports downstream and to coastal areas. This is acutely important in coastal New England where dam removals are more commonly becoming the solution to aging infrastructure (Doyle et al., 2008; Magilligan et al., 2016). However, dam removals are a controversial topic particularly since their effect on N fluxes to the coast are not yet fully understood (Gold et al., 2016; Lewis et al., 2021; Maavara et al., 2020; Stanley & Doyle, 2003). Many dam removal studies have focused on physical or hydrological effects, sediment regimes, and fish passage, leaving a gap in the current understanding surrounding the biogeochemical consequences of dam removal (Bednarek, 2001; Bellmore et al., 2017; Lewis et al., 2021; Maavara et al., 2020).

In this work, we address the question *How do small reservoirs influence nitrogen fate and transport seasonally and over annual time periods?* We hypothesized that small reservoirs retain nitrogen, but less than expected based on inorganic N alone because a proportion of inorganic N retention is transformed to organic forms and because most N loads occur during high flows outside the biologically active period. To test this hypothesis, we evaluated nitrogen mass balances in small reservoirs in coastal New England, analyzing the entire dissolved N pool across seasons and multiple years. Annual time periods provide a fuller understanding of the effect of small reservoirs on downstream N fluxes, accounting for processes that vary seasonally and affect the entire N pool. As many small reservoirs, particularly those in the northeastern US, are being removed (Magilligan et al., 2016), having a more complete comprehension of the effect of reservoir loss due to dam removals on nitrogen fluxes will help managers of small dams and coastal areas make the best decisions regarding their fates (e.g., Balch, 2020; VHB, 2020).

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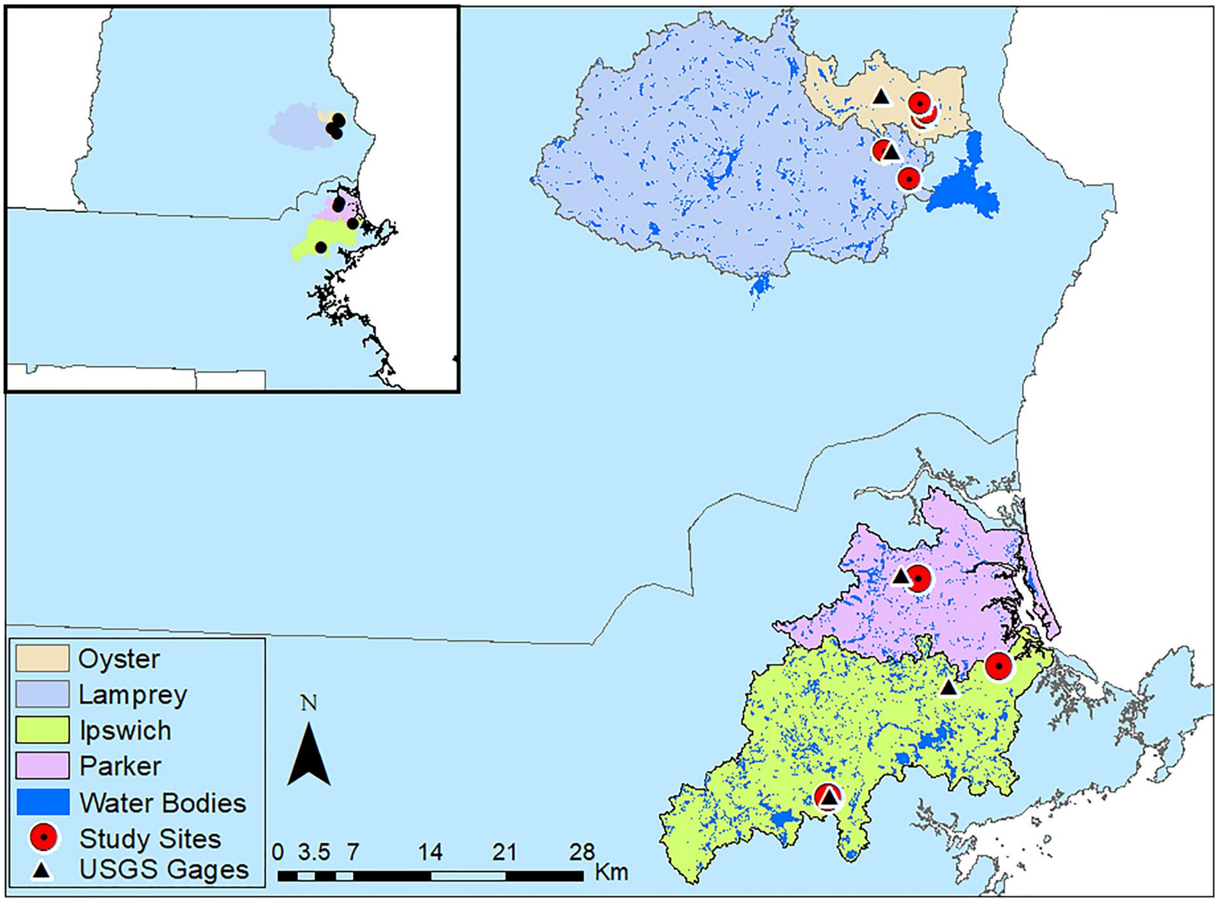

Figure 1. Locations of study sites within their respective watersheds in MA and NH, water body polygons from MA and NH hydrology geospatial data sets, and the locations of the nearest USGS stream gages.

2. Materials and Methods

2.1. Study Sites

Eight small reservoirs included in this study were located in four watersheds across two New England states (Figure 1). Three of these reservoirs were sampled regularly over 5 years, while the other five were sampled for 2 years but were included to test the generality of findings. The reservoirs spanned a range of drainage areas (1.1–549.1 km^2), surface areas, (0.004–0.527 km^2), and land cover (Table 1). The three intensively measured reservoirs were in northeastern Massachusetts in the Parker and Ipswich River watersheds. Two of these were located at the head of tide on both the Parker and Ipswich Rivers; a third was the uppermost reservoir on the Ipswich mainstem. These three reservoirs were within the domain of the Plum Island Ecosystems Long-Term Ecological Research (PIE LTER) site. The other five small reservoirs were located in southeastern New Hampshire, within the Lamprey and Oyster River watersheds and included the head of tide dams on the Lamprey and Oyster Rivers, the second mainstem dam on the Lamprey River, and two small impoundments in the Oyster River watershed. The latter two were located on Little Hale Creek and Beards Creek, first and second order streams, respectively.

2.2. Sampling Design

We used a mass balance approach for determining instantaneous N retention or export for each water body on a given day. To ensure changes in the mass balance of N between inputs and outputs were due to internal processing and not a result of either hydrological imbalance or direct inputs to the reservoir, we used the mass balance of chloride as criteria for including the N mass balance for any given sample day (see below). Sampling began at

Table 1
Site Characteristics of the Study Reservoirs

Site	Site abbreviation	Watershed	Dam age (years)	Mean depth (m)	Drainage area (km^2)	Surface area (km^2)	Mean annual Q ($m^3\ s^{-1}$)	Number of inputs	Mean residence time (days)	% developed	% forested	% wetland
Macallen Dam	MCLN	Lamprey	134	4.07	549.1	0.527	9.43	3	0.4	8.5	68.2	13.1
Wiswall Dam	LMPD	Lamprey	110	3.16	475.3	0.195	8.16	1	1.1	7.9	70.3	11.7
Ipswich Mills Dam	ID	Ipswich	113	2.85	387.5	0.130	6.57	2	1.5	34.6	35.1	23.1
South Midleton Dam	SMD	Ipswich	121	1.27	113.8	0.061	1.88	1	2.1	53.5	22.6	20.8
Parker River Dam	PD	Parker	46	0.76	63.9	0.162	1.25	2	0.9	18.3	50.1	23.3
Oyster Mill Pond Dam	OMPD	Oyster	108	1.42	50.6	0.092	0.92	3	0.6	16.6	59.2	11.7
Beards Creek Dam	BRDS	Oyster	68	3.48	8.3	0.062	0.15	2	0.1	49.1	37.8	4.8
Little Hale Dam	LH	Oyster	70	0.75	1.1	0.004	0.02	1	0.6	51.1	42.9	4.7

Note. Mean depth (m) was estimated from reservoir volumes reported by the U.S. Army Corps of Engineers National Inventory of Dams and reservoir surface areas determined from GIS for all sites except Little Hale (LH). Depth at LH was estimated from observations made in person. Land cover for all sites was determined from the 2016 National Land Cover Data Set. Dam ages are for the current dam configuration although certain sites have a longer history of being dammed.

all reservoirs in MA and NH in June 2015 and concluded October 2019 for the sites in MA and February 2016 at the NH sites. The three MA sites could be explored for the full effects of seasonality, while the NH sites provide an assessment of the generality of the relationships. Sampling took place every other week to monthly (Figure 2). Water chemistry samples were collected at the reservoir outflows as well as each input. Five reservoirs had multiple inputs (Table 1) which were weighted for a combined input estimate (see below). Samples were filtered in the field using Whatman GF/F filters with a nominal pore size of 0.7 μm and stored on ice until returned to the lab where they were frozen until analysis. Samples were analyzed for anions (NO_3^-, Cl^-, SO_4^-, Br^-) via ion chromatography on a Dionex Ion Chromatograph; NH_4^+ using a colorimetric method on a SmartChem Chemistry Analyzer; and total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) via high-temperature oxidation on a Shimadzu TOC-V. DON was calculated as the difference between TDN and DIN ($NO_3^- + NH_4^+$). Particulate N was not explicitly considered in this study. For each sample collected, water temperature and dissolved oxygen were measured in the field with a YSI ProODO handheld instrument while electrical conductivity and specific conductance were measured on a YSI Pro30 handheld instrument.

An instantaneous mass balance of the flux of each N form (discharge × concentration) was performed by estimating each inflow and outflow flux:

$$F_{\text{in}} = \sum_{i=1}^{n} C_i\, Q_i$$

$$F_{\text{out}} = C_o Q_o$$

where n = the number of inputs to the reservoir, C is concentration, and Q is discharge, i is input, and o is output. Q is approximated for each sample location from the nearest USGS gage scaled to that locations drainage area. The proportional change in each N species was then calculated as:

$$\Delta N = (F_{\text{in}} - F_{\text{out}})/F_{\text{in}}$$

where ΔN is the proportional change in an individual N species between the reservoir input(s) and output.

Verification that flow is at equilibrium among inputs and outputs and that all inputs are accounted for was accomplished using the mass balance of chloride (Cl^-), a conservative tracer. Because Cl^- tends to be transported conservatively in aquatic ecosystems (Cox et al., 2007; Stream Solute Workshop, 1990), the Cl^- mass balance indicates whether there is a hydrologic cause for an imbalance. If the Cl^- mass balance is approximated, here operationally assumed to be plus or minus 20%, then we include the estimate of the N mass balance for that sample day. The ±20% threshold was chosen because we did not have confidence that there was not a hydrologic imbalance if the Cl^- imbalance was outside that threshold. If the Cl^- and N imbalances were both within ±20%, we have confidence in the conservation of hydrology, but still uncertainty that the N imbalance is not due to solely biological reasons. However, we have the greatest confidence in the N imbalance when the Cl^- imbalance is within the 20% threshold and the N imbalance is outside that threshold. N mass balances within plus or minus 20% are considered as not different from 0. While almost 30% of the sampling events were excluded due to Cl^- imbalance, there was still a large range of flows within the ±20% threshold. The assumption of hydrologic equilibrium may be violated especially during extreme low flow periods (when inflow is small relative to volume) or times when reservoirs with multiple tributary inputs do not have uniform runoff (i.e., differential timing of return to equilibrium). In these cases, biological and hydrological reasons for the N imbalance cannot be discerned from one another and are therefore excluded from further analysis.

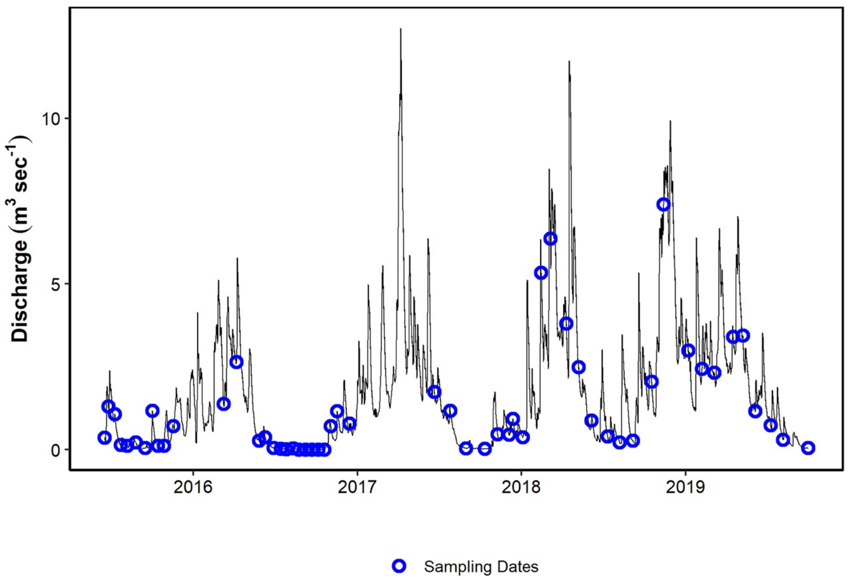

Figure 2. Hydrograph of the outflow of South Middleton Dam measured from the nearest USGS gage (01101500). Open circles indicate the daily discharge of each sampling date.

The study reservoirs vary in the number of inputs, with some having only the main river input and others having up to two additional small tributary inputs. The assumption of hydrologic equilibrium is least likely to be violated with fewer inputs and most violated in reservoirs with multiple inputs and small drainage area (Table 1).

Functions were fit to the relationships between ΔN and hydraulic load to understand the response of ΔN to flow. Hydraulic load is discharge scaled by reservoir surface area and calculated as:

$$\mathrm{HL} = Q/\mathrm{SA}$$

where Q is the mean daily flow for a particular sampling date ($m^3\ sec^{-1}$) and SA is reservoir surface area (m^2). Three different models were fit to each relationship. Power functions were fit as this model has previously been used to describe the relationship between N removal and hydraulic load (e.g., David et al., 2006; Seitzinger et al., 2006; Seitzinger, Styles, et al., 2002). However, power functions do not cross the x-axis and therefore cannot represent both N retention and N production. As such, logarithmic functions were also fit to the ΔN and hydraulic load relationships as they can describe both N retention and N production but logarithmic functions have not been previously described in the literature as representative of these relationships. Finally, four parameter logistic models were fit to the ΔN versus hydraulic load relationships. The logistic regressions can describe both N retention and N production and have a theoretical basis in the literature (Wollheim et al., 2018). Model fits were compared using their root mean square error (RMSE), Akaike Information Criterion (AIC), and Bayesian Information Criterion (BIC).

2.3. Statistical Analyses

Statistical analyses included the above-mentioned regressions between ΔN and hydraulic load as well as t-tests to compare both N inputs in large and small reservoirs. ANOVA was used to compare mean ΔN across seasons and ΔN residuals to water temperatures. Linear regressions were also performed to investigate the effect of water chemistry and physicochemical variables such as water temperature and dissolved oxygen saturation; physical variables including reservoir surface area, drainage area, mean depth, and land cover; as well as hydrological variables such as discharge and hydraulic load on ΔN. Statistical analyses were performed in R (R Core Team, 2023).

To demonstrate reservoir N retention across the flow regime over annual times scales we used a frequency analysis sensu Doyle et al. (2005) and Doyle (2005). The frequency analysis was applied to the three most intensively studied reservoirs with results presented from the reservoir behind the South Middleton Dam (SMD), the site with the most data. The frequency analysis accounts for the timing of inputs combined with the proportional

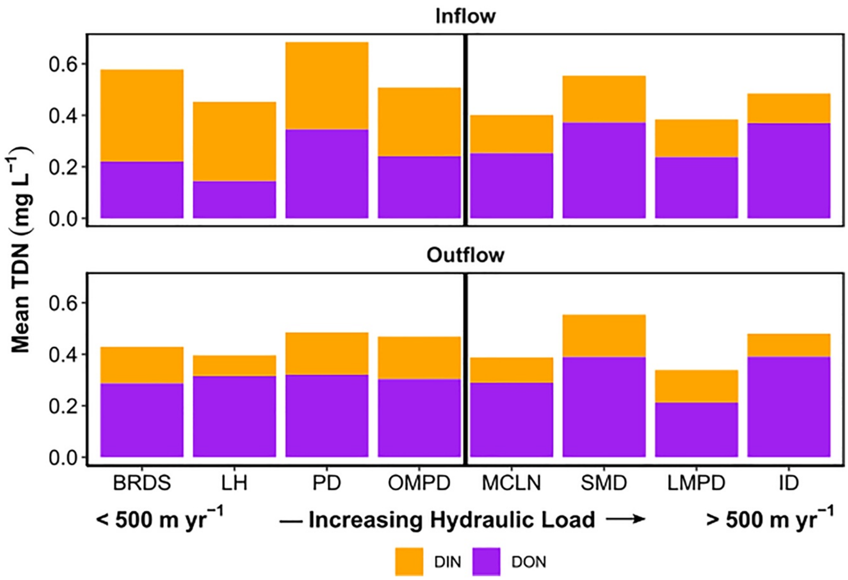

Figure 3. Mean composition of the TDN pool at reservoir inflows and outflows (top and bottom panels, respectively) as DIN and DON concentrations. Reservoirs to the left of the black vertical bar have mean annual hydraulic loads less than 500 m yr^{-1} while those to the right of the black bar have mean annual hydraulic loads greater than 500 m yr^{-1}.

retention (or source) of N form as a function of discharge to derive the mass of N form retained (or sourced). The integral under the frequency distribution of mass of N retained corresponds with the annual N retention.

Daily input fluxes of N over the entire study period were estimated using the composite model from the R "loadflex" package (Appling et al., 2015) which implements a LOADEST (Runkel et al., 2004) regression model via the R "rloadest" package (Runkel & De Cicco, 2017) combined with interpolation performed on the model residuals to better fit the range of the observations. Applying the effective discharge analysis to each form of N (Doyle, 2005), we estimated the frequency distribution as a function of discharge of N inputs, the proportional change N between the input and output (using the relationships derived above), and the frequency distribution in the change in N mass flux (Δ Flux). Integration of frequency distribution of Δ Flux relative to the integral of inputs provides an estimate of the total proportion of inputs that are gained or lost due to internal processing within the reservoir.

3. Results

3.1. Mean Reservoir Input and Output Concentrations

Reservoirs outflows generally had lower TDN concentrations, much lower DIN concentrations, and higher DON concentrations compared to their inflows. Inputs to reservoirs with mean annual hydraulic loads >500 m yr^{-1} had lower TDN concentrations (mean = 0.72 ± 0.30 mg L^{-1}) compared to reservoirs with lower mean annual HL (<500 m yr^{-1}) (mean = 1.18 ± 0.72 mg L^{-1}); (Two-sample t-test: $t = -4.87$, df = 103, $p < 0.001$) (Figure 3) suggesting that dilution or upstream retention may have already occurred in the larger watersheds. Additionally, reservoirs with high mean annual HL had similar DON concentrations, resulting in higher proportions of DON in the inputs (mean = 75.8% DON), while reservoirs with lower mean annual HL were comprised mainly of DIN (mean = 30.2% DON).

Mean DIN concentrations were lower in the outflow than in the inflow, especially in reservoirs with lower mean annual HL (HL < 500 m yr^{-1}: inflow = 0.60 mg L^{-1}, outflow = 0.13 mg L^{-1}; HL > 500 m yr^{-1}: inflow = 0.19 mg L^{-1}, outflow = 0.16 mg L^{-1}) (Figure 3). In contrast, mean DON concentrations were higher in the outflow compared to the inflow (HL < 500 m yr^{-1}: inflow = 0.24 mg L^{-1}, outflow = 0.31 mg L^{-1}; HL > 500 m yr^{-1}: inflow = 031 mg L^{-1}, outflow = 0.32 mg L^{-1}) (Figure 3). While most sites exhibited decreases in DIN concentrations and slightly smaller increases in DON concentrations resulting in net decreases in TDN,

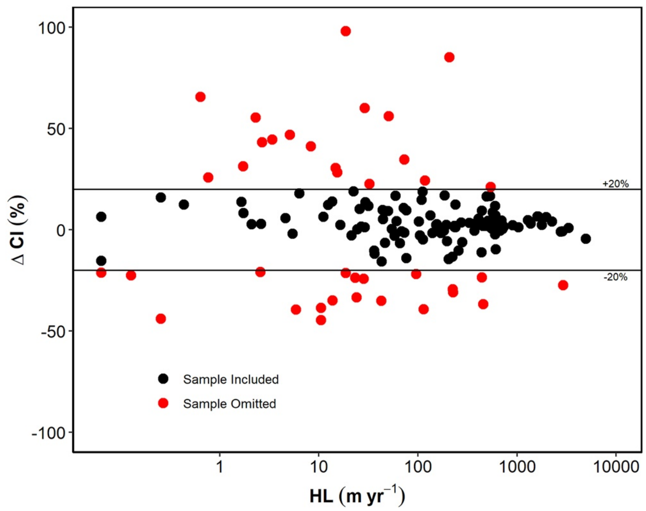

Figure 4. Mass balance of chloride at all study reservoirs. Horizontal lines are the thresholds used to determine whether Cl was conserved between inputs and outputs. N mass balances coinciding with Cl mass balances between −20% and +20% were included in analyses (black symbols) while those that fell outside of that range were omitted (red symbols).

LMPD and PD experienced both lower DIN and DON concentrations. Thus, based on the mean change in concentration only, it would appear that TDN retention on a total mass basis is relatively high, especially in those reservoirs with high DIN inputs (i.e., those with smaller drainage areas).

3.2. Nitrogen Retention and Transformations in Small Reservoirs

The chloride mass balance identified 45 of 153 sampling events in the study reservoirs that did not meet our criteria for inclusion in the nitrogen mass balance analysis. The remaining events spanned a wide range of flow conditions. Sampling events where differences in chloride concentrations between inflow and outflow were greater than ±20% were not included as changes in N could not be attributed to internal processing only and not due in part to hydrological imbalances or direct inputs to the reservoir (Figure 4). Many of these omitted samples were collected after rain events or during times of extremely low flows lending support to transient hydrological factors (e.g., differential inputs from tributaries, disproportionate local inputs, extremely long lags between input and output) acting as a more dominant influence on mass balances for a given sample day (Figure 2). By including only points where the hydrological mass balance was within 20%, we assume greater confidence and credibility in the N mass balance. Henceforth, only mass balances that meet these criteria are discussed. The acceptance of a chloride imbalance of ±20% implies that an N imbalance within this range is more uncertain (possibly not different from 0), whereas N imbalances outside the 20% threshold indicate reservoir source or sink.

Hydraulic load on the day of sampling was a major determinant of N retention. Reservoirs at low hydraulic loads (i.e., low flow, HL < 10 m yr^{-1}) showed a greater likelihood of decreased DIN concentrations, that is, DIN retention (Figure 5a), while DON concentrations were more likely to increase, though DON imbalances were often <20% (Figure 5b). The net effect on TDN concentration was moderate retention (40%–60%) at low hydraulic loads (Figure 5c). High hydraulic loads (>1,000 m yr^{-1}) led to little change in DIN, DON, or TDN concentration, almost always falling within the 20% threshold based on the chloride mass balance. Intermediate hydraulic loads (10–1,000 m yr^{-1}) showed the greatest variability across flow conditions and seasons with small reservoirs generally acting as DIN sinks, but transitioning into a greater probability of no change or acting as sources as HLs increase. Intermediate hydraulic loads were also generally when reservoirs had the highest probability of being a large source (>20% increase) of DON.

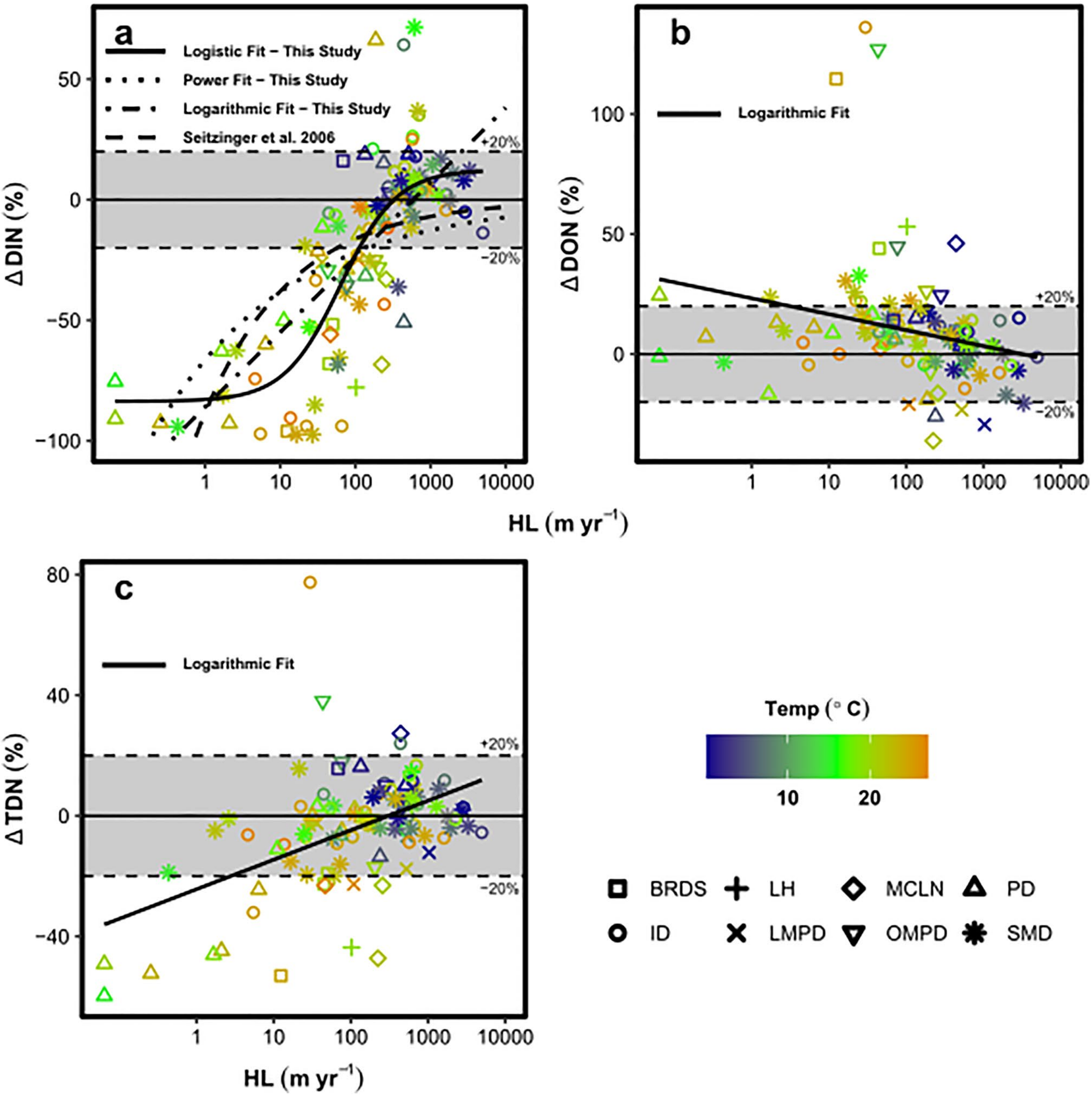

Figure 5. Relationships between differences between inflow and outflow concentrations of (a) DIN, (b) DON, and (c) TDN, and hydraulic load for all sample times that met the 20% chloride threshold. A negative percent change indicates retention of a species while a positive percent change is indicative of production. Best fit statistical relationships are shown in solid lines. In (a) the commonly used DIN retention relationship for reservoirs reported by Seitzinger, Styles, et al. (2002) is also shown. Note that *y*-axes have different scales for each N species. Color of individual points represents water temperature in the outflow at the time of sampling. Shaded band indicates the ±20% Cl^- threshold.

The net change in DIN concentration between inflows and outflows was significantly related to hydraulic load with the best model fit resulting with a four-parameter log-logistic (FPL) regression (Table 2):

$$\Delta \mathrm{DIN} = -83.62 + \frac{96.08}{1 + \exp\left(\frac{1.80 - \log_{10}(\mathrm{HL})}{0.37}\right)}$$

where ΔDIN is the percentage change in DIN concentration (retention or production) between inflow and outflow and HL is the hydraulic load (m yr^{-1}) calculated from mean daily discharge for the day of sampling (scaled to per year) and reservoir surface area (Figure 5a).

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Table 2
Equations and Summary Statistics for Three Different Models Fit to the DIN Percent Change Versus Hydraulic Load Relationship, Including the Root Mean Square Error (RMSE), As Well As the Equation and RMSE for the Seitzinger et al. (2006) "N Removed" Versus Hydraulic Load Relationship

Model	Equation	RMSE	AIC	BIC
Four-Parameter Logistic	$\Delta\text{DIN} = -83.14 + 95.13/\left(1 + \exp\left(\left(1.80 - \log_{10}(\text{HL})\right)/0.36\right)\right)$	24.01	8.31	21.81
Power	$\Delta\text{DIN} = -66.43 * \text{HL}^{-0.24}$	31.3	62.61	70.71
Logarithmic	$\Delta\text{DIN} = -85.96 + \log_{10}(\text{HL}) * 31.02$	26.38	25.04	33.14
Seitzinger et al. (2006)	$\Delta\text{DIN} = -88.453 * \text{HL}^{-0.3677}$	63.23	NA	NA

Note. Also shown are the Akaike Information Criterion (AIC) and the Bayesian Information Criterion (BIC). Also included are the results of applying the Seitzinger et al. (2006) "N Removed" versus hydraulic load relationship assessed with RMSE only. Power and FPL regressions did not converge for relationships between either DON or TDN with HL.

For DIN, the FPL model performed better than both a power function (sensu Seitzinger et al., 2006; Seitzinger, Styles, et al., 2002) and a logarithmic function (which, like the FPL model, can cross $y = 0$) based on the AIC, BIC and RMSE (Table 2). Despite the FPL model having more parameters, AIC indicated it was the better model (AIC = 8.31 for FPL, and >25 for the others). Direct application of the Seitzinger, Styles, et al. (2002) and Seitzinger et al. (2006) function (as done throughout New England reservoirs in Gold et al. (2016)), would have been least effective for predicting ΔDIN from hydraulic load based on RMSE, indicating that explicitly including small reservoirs strengthens the analysis of the role of reservoirs on downstream N concentrations.

While during low HLs (~flows) small reservoirs reduced DIN concentrations, at these HLs they acted as sources of DON, though generally not enough to offset retention of DIN. DON production was greatest at moderate HLs (Figure 5b). The negative log-linear relationship between ΔDON and HL was statistically significant, but explained relatively little of the variability ($p = 0.01$, $r^2 = 0.06$):

$$\Delta\text{DON} = -6.65 * \log_{10}(\text{HL}) + 23.26$$

where ΔDON is the percent change in DON concentration between the inflow and outflow and HL is hydraulic load. Power and FPL regressions between ΔDON and HL did not converge so comparisons between models could not be made and the log-linear regression was used to describe the relationship.

The net result of DIN and DON changes indicated TDN retention at low HLs (Figure 5c). The positive log-linear relationship between ΔTDN and HL was statistically significant ($p < 0.001$, $r^2 = 0.24$):

$$\Delta\text{TDN} = 9.79 * \log_{10}(\text{HL}) - 24.32$$

where ΔTDN is the percent change in TDN concentration between small reservoir inflow and outflow and HL is hydraulic load. Similar to DIN, the greatest TDN retention occurred at low HL. Like DON, the greatest variability in ΔTDN was at moderate HL and TDN production was greatest at the highest HLs. Like DON, power and FPL models could not be fit to the relationship between ΔTDN and HL and the log-linear model was used to describe this relationship.

The overall mean ΔDIN was a decrease of 21.3% and ranged from a maximum decrease of 97.4% to a maximum increase of 71.5% (Figure 6). Mean ΔDON was an overall increase of 9.4% and ranged from a decrease of 36.2% to an increase of 136.1% (Figure 6). Mean ΔTDN was a decrease of 3.9% with a range of a maximum decrease of 59.7% to a maximum increase of 77.5% (Figure 6). Mean ΔTDN across all sites indicated small reservoirs were a moderate sink for TDN only during the summer and relatively balanced during the remainder of the year (Figure 6).

Seasonality was evident, as warmer temperatures corresponded with the lowest flows and HL, resulting in higher DIN retention (warmer colors in Figure 5), while cooler periods with highest flows and HL resulted in little net change (bluer colors in Figure 5). Across all sites, mean ΔDIN was highest during the summer followed by autumn. Moderate production of DIN (based on means) was evident during the winter, while no change occurred in spring (Figure 6). ΔDIN was significantly and negatively related to water temperature but water temperature explained little of the variability in ΔDIN ($p < 0.001$, $r^2 = 0.18$). Residuals from the relationship between ΔDIN and HL were not significantly related to temperature, however, as determined by one-way ANOVA ($F(1, 102) = 1.685$, $p = 0.20$). Thus, the greatest proportional DIN retention took place during the low flow parts of the year when HL is low, residence times are long, and biological activity is high.

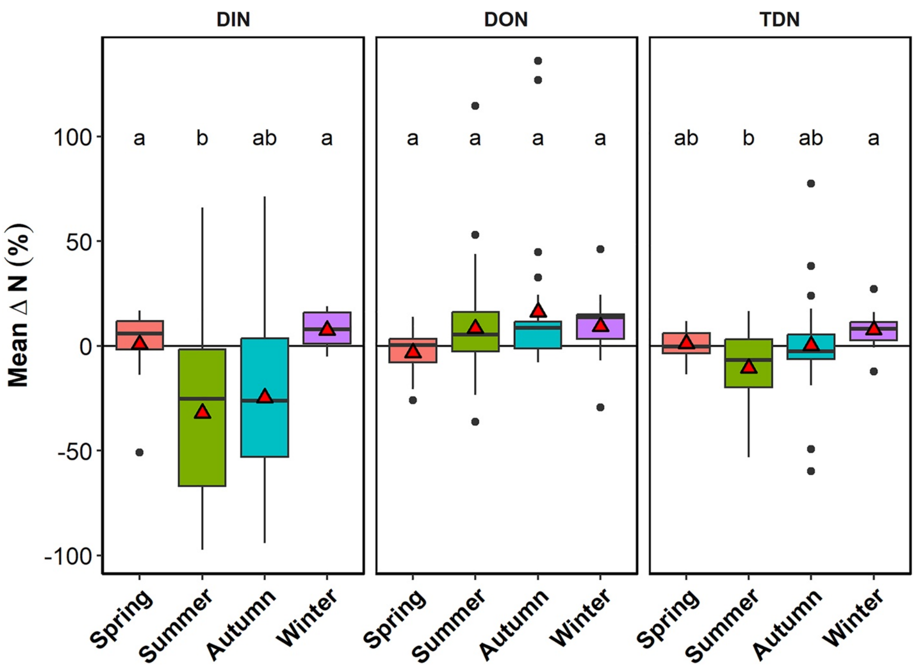

Figure 6. Boxplots of the percent change in N species across seasons showing the median, first and third quartiles, and whiskers extending to 1.5 times the interquartile range. Points outside the range of the whiskers are plotted individually. Also shown are letters designating differences in groups as determined by Tukey's HSD. Mean values for ΔN are shown in red triangles for each species and season.

While water temperatures typically corresponded with flow and HL and DON production was generally higher at low flows and HL (Figure 5b), seasonal differences in the proportional change in DON were not observed (Figure 6). Tukey's HSD test indicated that there were no significant differences in mean ΔDON across seasons although mean ΔDON was highest during the autumn and lowest (slight decrease in DON) during the spring. There was also no significant relationship between water temperature and ΔDON ($p = 0.40$, $r^2 = 0.01$). As determined by one-way ANOVA, residuals between the ΔDON and HL relationship were not significant ($F(1, 102) = 0.021$, $p = 0.88$). However, DON production was greatest at intermediate flows that occurred largely during the end of summer to early autumn.

Seasonal effects were observed in the proportional change in TDN concentrations with ΔTDN corresponding with the warmer, low flow and HL time of year (Figure 5c). Across all sites, mean ΔTDN indicated the greatest TDN retention during the summer and the greatest TDN production taking place during the winter while there were no significant differences between spring and autumn (Figure 6). The relationship between ΔTDN and water temperature was significant but explained little of the observed variability ($p = 0.002$, $r^2 = 0.09$). Similar to the relationships between the residuals of the ΔDIN and ΔDON relationships with HL, one-way ANOVA determined that there was no significant relationship between the residuals of the ΔTDN and HL relationship with temperature ($F(1, 103) = 1.786$, $p = 0.18$).

3.3. Net Effect of Small Reservoirs on Annual Downstream TDN Fluxes

The frequency analysis was applied to the three intensive reservoirs, but we present results for SMD only, the reservoir for which we had the most data. Similar results occurred for the other reservoirs. N Inputs of each form were similar across flow conditions with the greatest inputs occurring at intermediate flow (Figure 7, solid red line). The maximum input for all three species was at flows greater than mean annual flow at SMD (Figure 7, vertical black line). ΔN relationships indicate DIN retention, DON production, and moderate retention of TDN fluxes at low flows while at intermediate flows, these relationships suggest little change in fluxes (Figure 7, dashed green line). The product of the relationships between N inputs and Δ*N* with flow demonstrate the impact of reservoirs on downstream fluxes for the different forms of N. At low flows, when ΔN is high, N inputs are low while at higher flows when N inputs are high, Δ*N* is closer to zero (Figure 7, blue ribbons). This leads to a negligible impact on fluxes of all forms of N at annual time scales.

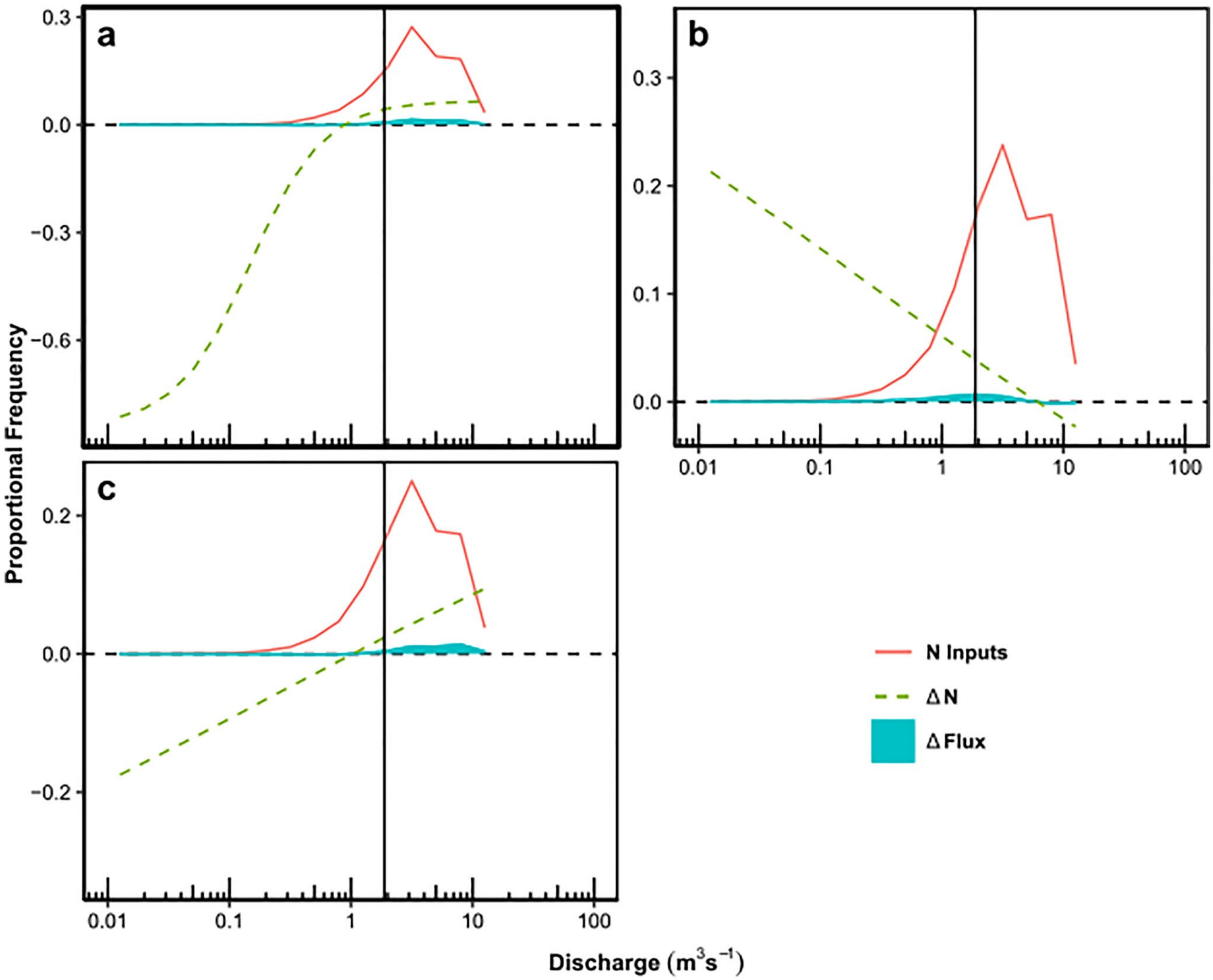

Figure 7. Distribution of annual N inputs to South Middleton Dam (SMD) over various flow categories (N Inputs), mean proportional change in N fluxes at SMD for each flow category (ΔN), and the distribution of annual change in N flux from SMD for each flow category (the product of N Inputs and Δ N; Δ Flux) for (a) DIN, (b) DON, and (c) TDN. The integration under the shaded delta flux indicates the total annual change in flux due to internal reservoir processes. Vertical black lines indicate mean annual flow at SMD.

SMD did not considerably alter the downstream flux of TDN over annual time scales. While TDN retention proportion were relatively high at low flows (40%), most annual TDN inputs predominantly occur at intermediate flows when retention has declined. N inputs to the reservoir for all three N species mostly occurred at discharge above 0.5 $m^3 s^{-1}$ at which the retention or source curves had already approached zero (Figure 7). This indicates a mismatch between the timing of when N processes are most impactful and N fluxes, reducing the impact of internal N processing within small reservoirs over annual time scales. For all three N species considered, this translates to an increase in DIN fluxes of 4.5%, an increase in DON fluxes of 2.5%, and an increase in TDN fluxes of 4.1%. However, given the uncertainty in the approach, these increases in N fluxes are likely not different from zero, rather suggesting that there is no change in flux due to small reservoirs.

4. Discussion

4.1. DIN Retention in Small Reservoirs

The relationship between ΔDIN and hydraulic load was similar to what has been previously reported in the literature in that DIN percent retention is high at low hydraulic loads and asymptotes at high hydraulic loads. However,

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the relationship for ΔDIN and hydraulic load in this study suggests that high DIN retention in small reservoirs is maintained through moderate discharge before transitioning during intermediate discharge and asymptoting at high discharges, leading to an S-shaped relationship as well as small reservoirs having the potential to be both sources and sinks for DIN. In situations where sizable headwater impoundments (e.g., mill ponds, farm ponds, etc.) where ratios of drainage area to reservoir surface area are low, this high DIN retention can take place at higher HL (Kellogg et al., 2010). However, headwater reservoirs intercepting small proportions of the landscape and receiving low N inputs have little impact on N exports at the larger watershed scale.

Relationships between the percent change in DIN with reservoir hydrological characteristics (e.g., hydraulic load) have been generally used to characterize only its permanent removal (i.e., assumed to be denitrification). Seitzinger, Styles, et al. (2002) compiled DIN, TN, and NO_3^- data from 23 lakes and reservoirs, combined with data from 10 channelized rivers, to develop a power function for estimating proportional N removal as a function of hydraulic load (Figure 5a). David et al. (2006) added 23 years of annual NO_3^--N data from a single reservoir to the data from Seitzinger, Styles et al. (2002) to develop a new power law relationship between NO_3^- removal and hydraulic load for streams, rivers, and reservoirs. However, small reservoirs that experience HL lower than those reported for larger reservoirs indicates that high DIN retention occurs at the lowest HL and is maintained through moderate HL. There is much variability in intermediate HL where DIN retention decreases rapidly before asymptoting at higher HL, revealing an S-shaped curve. As such, a power function was not the best fit (Figure 5a, Table 2). Therefore, a four-parameter logistic regression was appropriate to fit the sigmoidal nature of the relationship to characterize these upper and lower asymptotes as well as the ability of small reservoirs to act as both sources and sinks.

The use of a logistic regression in describing the relationship between DIN retention and HL has not been previously reported in the literature. Small reservoirs were able to maintain a similarly high rate of DIN retention through moderate HL. At the lowest HLs, high assimilation or denitrification rates coupled with small inputs result in high proportional DIN retention (Gooding & Baulch, 2017; Richardson & Herrman, 2020). Under these circumstances, the lower end of the reservoirs may become supply limited because any upstream DIN inputs are retained rapidly in the upper end of the reservoir (Wollheim et al., 2018). As discharge slowly increases, high retention proportions at the reservoir scale are maintained because previously N limited sections now receive DIN (Schmadel et al., 2020; Wollheim et al., 2018). With further increases in discharge, DIN supplies to reservoirs increase at a faster rate than DIN demand, eventually saturating the system (Bernot & Dodds, 2005; Wollheim et al., 2018). The sigmoid retention relationship better characterizes this dynamic that is not accounted for using power or logarithmic functions insofar that it explains small reservoirs DIN demand keeping up with supply before becoming saturated.

4.2. DON Sources in Small Reservoirs

Small reservoirs can increase concentrations of DON in outflowing waters, particularly at intermediate hydraulic loads and during autumn. DON increases are not likely due to terrestrial DON inputs entering directly to the reservoir, as the average amount of outflow drainage area unaccounted for by the upstream drainage was 3.8%. Therefore, the DON released likely originates from either organic matter stored in the reservoir, N fixation, atmospheric deposition, or internal autochthonous sources that transform DIN into DON (Bernhardt et al., 2005; Bronk et al., 1994; Fowler et al., 2015). Stored organic sources include DON leachate from terrestrial organic matter like leaves transported to and deposited in the reservoir, while autochthonous DON is released via exudation from primary producers, breakdown of individual cells, as well as the consumption and subsequent excretion by zooplankton (Berman & Bronk, 2003).

DON in freshwater ecosystems is often allochthonous and is primarily composed of humic substances (Berman & Bronk, 2003; Bronk et al., 2007; Wiegner et al., 2006). However, in temperate regions during the warm season, particularly those experiencing increased nutrient inputs, autochthonous production can be dominant (Pagano et al., 2014). This autochthonous DON source should be evident during the warm, low flow months of the warm season when primary productivity, via aquatic macrophytes and phytoplankton is at its greatest (Bronk, 2002; Bronk et al., 2007). Yet, increases in outflow DON concentrations are not observed until later in the summer and autumn at intermediate flows (Figure 5b). These DON dynamics are similar to those found for headwater wetlands by Flint and McDowell (2015). This suggests that, like DIN, DON is rapidly consumed when reservoirs are N limited and increased exports do not occur until DON supply is greater than demand or DON is exported before it can be consumed (Wollheim et al., 2018).

This study did not explicitly consider the bioavailability of the DON produced by small reservoirs but DON has the potential to be highly bioavailable and an important N source for both freshwater and marine organisms (Bronk et al., 2007; Seitzinger, Sanders, & Styles, 2002). While we did not quantify the bioavailability or lability of DON, C:N ratios were used to infer dissolved organic matter (DOM) sources and the likely lability of the DON released. Outflowing C:N ratios in small reservoirs ranged from 19.8 to 25.3, similar to C:N ratios found for northern mixed forests by Aitkenhead and McDowell (2000). However, Gong et al. (2018) found that submerged, floating, and emergent aquatic macrophytes had an overall C:N ratio that was similar to terrestrial DOM of 23.6 ± 16.0 with floating-leaved vegetation being the most N enriched (16.8 ± 5.9), emergent vegetation being the most depleted (25.4 ± 18.6), and submerged macrophytes having C:N ratios between floating-leaved and emergent (20.5 ± 8.6). DON exported from the small reservoirs was not likely due to algal production as algal DOM has a highly enriched C:N signal (7.6 ± 1.52) compared to terrestrial DOM and aquatic macrophytes (Hillebrand & Sommer, 1999; O'Brien & Wehr, 2010).

4.3. Net Effect of DIN and DON Dynamics on TDN Concentrations

The combination of DIN reductions and DON production results in relatively little change in outflowing TDN concentrations. Large reductions in DIN at low HL, combined with slight increases in DON, translated to modest decreases in TDN concentrations while moderate increases in DIN concentrations at high HL, coupled with slight decreases in DON concentrations, led to very little change in TDN concentrations at those higher flows. As sampling events with ΔCl^- outside of $\pm 20\%$ were omitted, we have confidence that differences between inflow and outflow N concentrations were the result of internal processing and not due to differences between inflow and outflow discharge or direct local N inputs.

Intermediate HL was the least predictable as the proportional changes in both DIN and DON were highly variable. During these moderate HLs, both DIN and DON production and retention were observed. The balance between supply and demand of N can shift depending on reservoir conditions, and the net effect can become evident in the overall mass balance because flows are high enough to transport excess to the outflow. Intermediate flows are also when N processing is the most evident (Wollheim et al., 2018). At low HL, autochthonous DON is rapidly consumed due to high demand (Wiegner et al., 2006), so when DON production is high and HL is low, elevated DON is not evident in outflowing concentrations. At high flows, outflowing DON concentrations are indistinguishable from inflowing concentrations and ΔDON is within the margin of uncertainty. During intermediate flows and particularly during the warm season, DON supply is greater than demand, leading to an observed increase in outflow concentrations. This increase is a function of the reduced residence time associated with the higher flows and reduction in reservoir retention efficiency (Akbarzadeh et al., 2019; Seitzinger et al., 2005).

Small reservoirs also experienced temporal differences in net N processes. Maximum DIN retention occurred during the summer and autumn (Figure 6). Kong et al. (2019), using high-frequency data, found that a reservoir in Germany had the greatest NO_3^--N retention during the summer and that retention followed patterns in Chl-*a* concentrations. They attributed NO_3^--N retention to a three-step process in which N was taken up by algae, algal cells proliferated, followed by their mortality and sedimentation (Kong et al., 2019). However, generally we saw no evidence of proliferation of algal cells due to no observed increase in Chlorophyll *a* (J. Buonpane, unpublished data), an indicator of the presence of algal cells (Fiedler et al., 2015; Paul et al., 2017), nor was there an enrichment of the outflow DOC:DON to levels associated with algal DOM (Gong et al., 2018; Hillebrand & Sommer, 1999; O'Brien & Wehr, 2010). Therefore, algal production is unlikely to be the cause of either DIN retention or DON release. However, while Balch (2020) did find that N fixation occurred at OMPD, this reservoir was DIN limited, had sufficient phosphorous availability, and evidence of algal growth, giving N fixers a competitive advantage (Scott et al., 2009). The other small reservoirs did not have similar conditions likely to induce substantial N fixation. In contrast, submerged and emergent macrophytes were abundant which likely assimilated a considerable amount of DIN (Manolaki et al., 2020; Preiner et al., 2020; Racchetti et al., 2017), especially during early summer when they were adding much biomass (Manolaki et al., 2020; Racchetti et al., 2017). Similarly, N deposition was a small proportion of total inputs to the small reservoirs, however, this source would cause an increase in outflow N concentrations, causing an underestimation of retention of riverine inputs.

While macrophytic N uptake was likely responsible for DIN retention during the summer, high DIN retention in the autumn months was more likely to be the result of elevated ecosystem respiration (ER). Reservoirs are both sources and sinks of organic matter (Clow et al., 2015; Kraus et al., 2011; Shaughnessy et al., 2019). Roberts and Mulholland (2007) attributed large autumnal organic matter inputs in a temperate stream to leaf fall while Bernal et al. (2012) similarly found that large stocks of organic matter accumulated in two Mediterranean-climate streams during the late summer and early autumn due to inputs from riparian vegetation. Temperate streams and reservoirs also receive large inputs of leaf litter during the autumn (Bernhardt et al., 2005; Tranvik et al., 2009), in addition to inputs from macrophyte senescence (Preiner et al., 2020). This has been shown to induce high rates of ER and consumption of DIN arising from declines in NO_3^- due to enhanced denitrification rates in anoxic sediments as well as elevated NO_3^- concentrations found in suburbanized watersheds (Acuña et al., 2004; Argerich et al., 2008; Bernal et al., 2012; Mulholland et al., 2008; Roberts & Mulholland, 2007). However, we do not know the net effect of mineralization versus denitrification and in the low DO water, the NH_4^+ produced will not be nitrified so denitrification may be limited.

During the summer and autumn, DON production offset DIN retention (Figure 6). As a result, a small proportion of TDN was retained during the summer, while there was no change during autumn. And while algal cells have been shown to release DON (Bronk, 2002), senescence of macrophytes, which may begin when water levels in shallow reservoirs decline during summer (Landers, 1982; Wu et al., 2021), has also been shown to contribute to water column DON. Lu et al. (2018) found that sediment drying and rewetting in reservoirs and lakes due to water level fluctuations (e.g., drawdowns, abstractions, fluctuations in precipitation and runoff) led to macrophytes shifting between DON sources and DIN sinks. The small reservoirs in this study experienced water level fluctuations arising primarily from seasonal variability in precipitation, suggesting that this these cumulative seasonal effects on both biology and hydrology are responsible for the observed DON dynamics.

The retention of DIN during the summer when both inland and coastal aquatic systems are vulnerable to elevated N concentrations (Diaz & Rosenberg, 2008; Wells et al., 2015) along with the release during the winter when biota are largely dormant (Contosta et al., 2017; Lee et al., 2007) is an important benefit provided by small reservoirs. Release as DON, which is generally less reactive than DIN (Berg et al., 2001; Bronk et al., 2007), later in the year, also occurs when primary producers are largely dormant (Caffrey et al., 2014; Cloern & Jassby, 2008). While permanent N removal is not always the dominant process, the temporary storage of N prevents it from reaching vulnerable ecosystems when they are the most susceptible to enhanced N inputs.

4.4. Effect of Small Reservoir Nitrogen Transformations on Downstream Fluxes

While small reservoirs had significant effects on N concentrations at times, their impact on downstream N fluxes over annual time scales was minimal. The small reservoirs had the greatest effect on N concentrations at low discharge when N inputs were at their lowest. Therefore, when small reservoirs had the greatest potential to impact N fluxes, inputs were too low to make a significant difference to N fluxes over annual time scales (Figure 7). At higher HL when N inputs were greater, small reservoirs had less retention potential and in fact, acted as N sources, leading to increased fluxes at annual time scales. At the very least, while small reservoirs have the capacity to reduce N concentrations, particularly during the low flow warm seasons, we have no evidence that the reservoirs reduce N fluxes at longer time scales.

For the Ipswich River watershed, Wollheim, Peterson, et al. (2008) and Wollheim, Vörösmarty, et al. (2008) found, using a river network scale flow frequency analysis, that despite DIN removal nearing 100% during low flow periods, annual removal percentages only ranged from 15% to 33% due to most DIN inputs occurring during high flow periods when biological and hydrological conditions were not optimal for high removal. In terms of DIN retention, low discharges are dominant due to large surface area to volume ratios and longer residence times relative to higher flows (Doyle, 2005). However, N inputs are greatest at high flows. A similar dynamic occurs for DIN retention in these small reservoirs. The mismatch in the timing of retention and inputs limits DIN retention at annual timescales.

The inclusion of DON sheds additional light on the function of small reservoirs in regulating downstream N fluxes at annual timescales. The net effect of the observed DIN and DON dynamics resulted in a slight calculated increase in annual TDN fluxes. However, because the percentage change in export was relatively small, we can only state with certainty that the system is in near balance for TDN. The FPL regression for ΔDIN and logarithmic regression for ΔTDN both indicated that at HL ~ 300 m yr^{-1}, reservoirs can transition from sinks to sources of DIN and TDN while reservoirs were net sources of DON at all HLs observed in this study. This shows the importance of these intermediate HLs which must be considered in assessments of dam removal feasibility.

5. Conclusions

While small reservoirs have the ability to reduce inflowing N concentrations in certain seasons, we found that small reservoirs were not an effective net sink for N fluxes at annual time scales as is commonly assumed. While during the warm season large reductions in DIN fluxes were observed, inputs are very small at this time. This percent change in DIN flux at low flows needs to be considered alongside flow regime (e.g., Figure 7). When small reservoirs are their most reactive, flows are low enough that the effect on downstream fluxes is minimal over longer, annual timescales.

At the same time, seasonal variability in N processing led to small reservoirs acting as both sinks or sources depending on the N species. For example, the retention of DIN in small reservoirs during the warm season prevents this N from reaching vulnerable downstream aquatic ecosystems during critical times of year. This benefits these downstream ecosystems because this is when primary producers, such as macrophytes and algae, are the most responsive to N inputs. Following senescence later in the year, this N is then exported from small reservoirs as either leached DON or mineralized DIN, when it is less likely to result in adverse ecological impacts. The lag leading to release of N during the winter months allows for the export of N during times when downstream ecosystems are less susceptible to elevated N fluxes, providing a significant benefit for inland and coastal aquatic ecosystems.

Dam removals have increased in recent years (Magilligan et al., 2016) and studies have found that these dam removals are likely to lead to greater N exports to coastal ecosystems (e.g., Gold et al., 2016). At annual timescales, we suggest that small reservoirs may not affect fluxes much. Thus, if small run of the river dams are removed, the loss of their reservoirs will not affect N exports to coastal systems. However, their impact in summer may be beneficial, and so location of reservoirs relative to different estuaries of varying N sensitivity is important to consider.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Reservoir input and output water chemistry data including dissolved inorganic nitrogen, dissolved organic nitrogen, and total dissolved nitrogen, as well as outflow water temperature and daily average discharge are available at the Environmental Data Initiative online data repository at https://doi.org/10.6073/pasta/aab85a3ba288e5c12df228bf91221be2 (Whitney et al., 2023).

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