Contribution of fluvial wetlands to nitrogen retention in urbanizing coastal watersheds in New England across multiple scales

Basic Information

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Publications

1. Rosengarten, D. 2014. Spatial and temporal variability of nitrate cycling in a New England headwater wetland and stream. Department of Earth Sciences, College of Engineering and Physical Sciences, University of New Hampshire, Durham, NH, 184 pages.
2. Wilderotter, S. 2015. Parameterization of transient storage and nutrient retention in coastal New England wetlands. Department of Earth Sciences, College of Engineering and Physical Sciences, University of New Hampshire, Durham, NH, 235 pages.

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Problem

Surface water quality in rapidly urbanizing coastal watersheds in New England is at risk due to excess anthropogenic nutrient inputs, which threaten downstream water uses and could lead to fluvial and estuarine eutrophication (Bricker et al. 1999, Caraco and Cole 2003). Fluvial wetlands, which are biologically reactive and have long residence times (Vidon and Hill 2001), can remove excess nitrate, thus providing an important ecosystem service (Wollheim et al. 2005, Rabalais et al. 2009). Flow-through wetlands consist of an advective main channel, plus slow-flowing off-channel areas collectively termed "transient storage." Wetlands with higher lateral connectivity between the main stream channel and transient storage are especially important because they may retain more nitrate than wetlands that receive little direct stream discharge (Racchetti et al. 2011). However, wetland connectivity and reactivity is still poorly understood, thus limiting our ability to predict the impact of future changes in land use and climate change on watershed retention of nitrogen inputs.

Project Objectives
1) Determine contribution of wetland-dominated stream reaches to surface transient storage as a function of inundation and season
2) Quantify nitrate uptake rates among different types of surface transient storage as a function of season.
3) Scale biogeochemical and hydrologic insights to wetland-dominated reaches throughout New England
4) Share results with local and regional policy makers

Methods

This project focused on eight wetland-dominated reaches (Figure 1) in four different watersheds in coastal New Hampshire and Massachusetts, with preference given to wetlands that
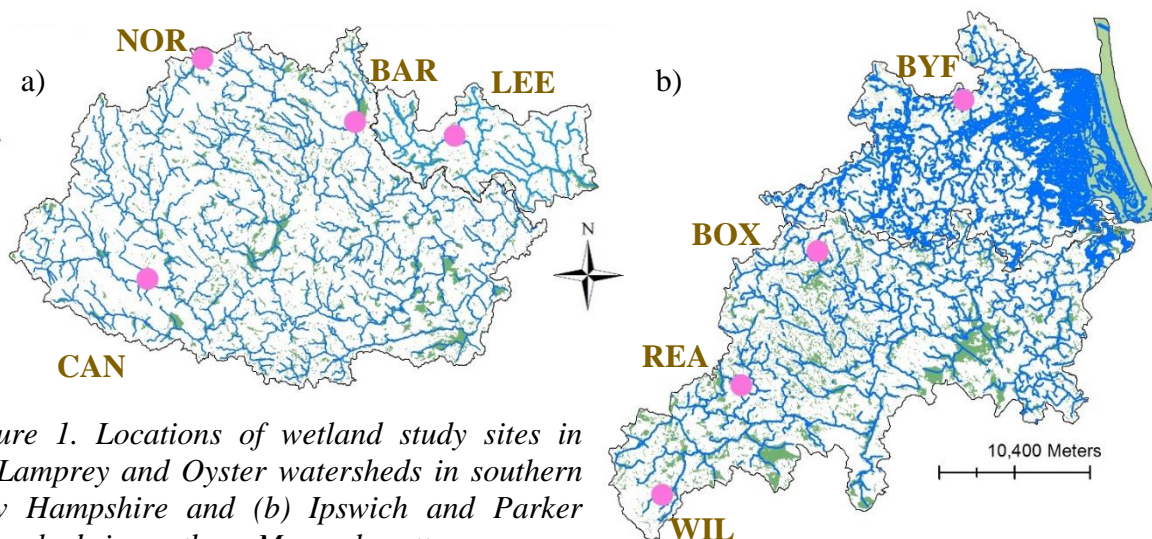
Figure 1. Locations of wetland study sites in (a) Lamprey and Oyster watersheds in southern New Hampshire and (b) Ipswich and Parker watersheds in northern Massachusetts.

have one channelized stream inlet and one channelized stream outlet. The eight wetlands used in this study are of varying sizes and shapes. Wetland geometrical characteristics were calculated from delineation of aerial photography (Figure 2) for all eight study wetlands plus a randomly chosen subset of 50 wetlands in the neighboring Charles, Concord, Merrimack, and Piscataqua-Salmon watersheds. Watershed area was delineated Light Detection and Ranging (LiDAR) digital elevation models. Wetland area and main wetland channel length were delineated from aerial photography based on vegetation differences. National Wetland Inventory (NWI) datasets were used to obtain another measurement of wetland area. Specifically, all NWI polygons that shared a boundary with the target wetland were combined to create one large polygon. Wetland length was obtained by smoothing the main channel length. Average wetland width was then calculated from the wetland area divided by the length of the main channel. Width-to-length ratio was calculated as the wetland width divided by wetland length. Finally, sinuosity was measured as the length of the main channel divided by the
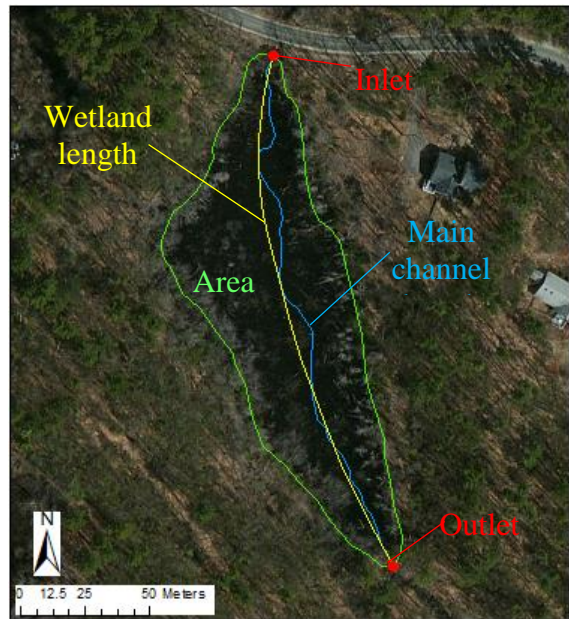

Figure 2. Aerial photograph of wetland site BOX in Boxford, MA, showing delineated geometrical parameters. Flow is from north to south; tracer was released at the wetland inlet and recorded exiting the wetland at the outlet.

smoothed length of the wetland. All geographical analyses were performed using ArcMap 10.1 Spatial Analyst Toolbox.

Wetland connectivity was measured with the use of whole-reach slug releases of the nontoxic fluorescent tracer dye rhodamine WT (RWT). Tracer releases were performed during 2014 and 2015 during baseflow conditions. Three of the eight sites were studied multiple times to examine seasonal changes in baseflow connectivity, resulting in 19 studies in total. During each study, rhodamine was released into the stream feeding the wetland, then measured *in-situ* at the
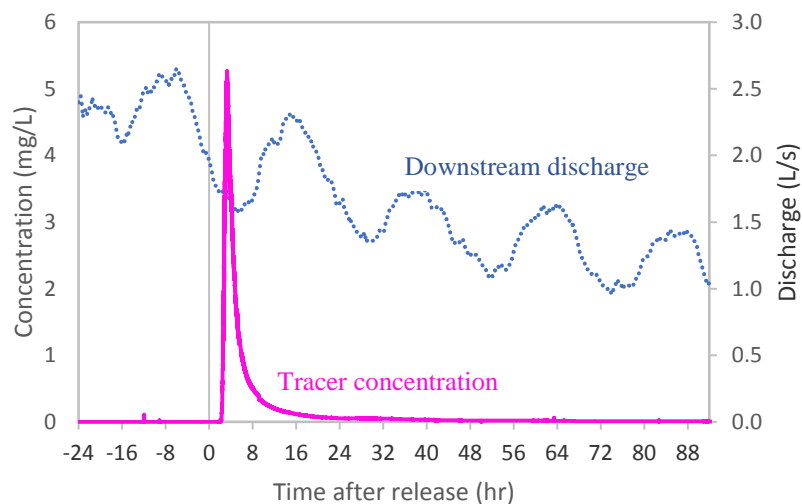

Figure 3. Continuous breakthrough curve of rhodamine WT (RWT) tracer concentration measured at the outlet of wetland study site BAR from June 18-23, 2014. The peak tracer concentration reached the outlet 3.5 hours after the release. Half of the dye exited by 9.7 hours. Discharge generally declined during the steady period.

Figure 4. Conceptual model of the (a) single-zone and (b) multiple-zone model geometries used to parameterize transient storage connectivity α and size A_s. Red color represents the conservative tracer added to the main channel, which advects and disperses in the main channel and is also transferred to and from the lateral transient storage zones.
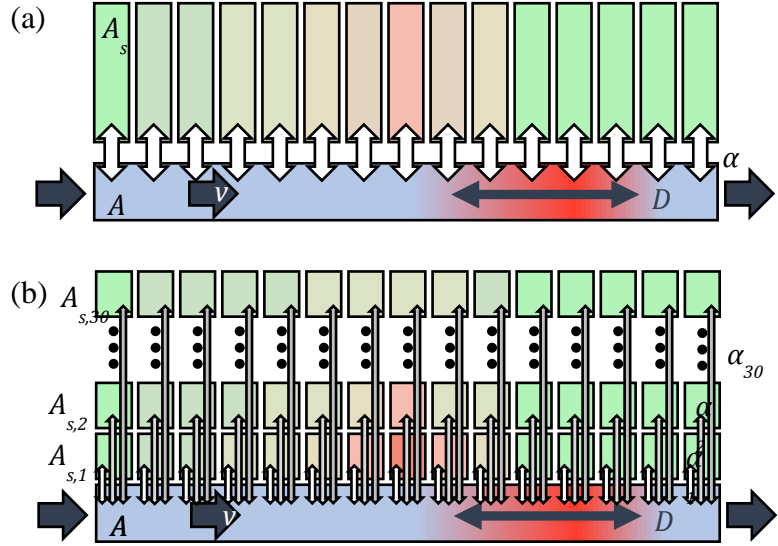
wetland11 outlet with a Turner C3 fluorometer set to record every 15, 30, or 60 seconds for at least 2 and typically 5 times the advective time scale of the wetland channel (Figure 3). Measured fluorescence at the wetland outlet was converted to excess rhodamine concentration using calibration curves and accounting for background fluorescence, instrument fouling, retardation, and photodegradation. Additionally, stage was measured at the inlet and outlet of each wetland at 12-15 minute intervals and converted to a continuous discharge record.

Tracer flux exiting the wetland was calculated by multiplying together tracer concentration and stream discharge (Figure 3). The mass of tracer recovered was calculated by integrating exit flux over time. The residence time distribution (RTD) of tracer in the wetland was calculated by dividing the exit flux by the mass recovered. The detention time (median travel time within the wetland) was calculated as the first moment of the RTD, and the variance was calculated as the second moment of the RTD. Because studies occurred during steady base-flow conditions, it was assumed that the movement of the introduced fluorescent tracer was representative of other dissolved substances (in particular, dissolved inorganic nitrogen) also moving through the wetland at the same time.

Transient storage characteristics at the reach scale were determined from inverse modeling of reach-scale tracer RTDs using the transient storage model STAMMT-L (Haggerty 2009). This approach conceptually divides the wetland into a main advective channel that exchanges water with stationary transient storage zones. The number of transient storage zones was specified in advance, and their size and connectivity were estimated by optimizing parameter values to obtain the best fit between the observed tracer RTD and a semi-analytical solution to the underlying partial differential transport equations. Different transient storage models were compared (Figure 4), including a single-zone model and multiple-zone models with 30 different zones (cf. Haggerty 2009); preliminary testing showed no difference in model parameter estimates for 30, 40, 50, or 60 zones.

Nitrate samples were collected at the inlet and the outlet of each wetland once during each tracer study. Samples were filtered in the field, placed on ice, then analyzed at the UNH Water Quality Analysis Laboratory using standard methods. Nitrate flux at the wetland inlet and outlet was calculated by multiplying concentration measurements by stream discharge. The change in

nitrate flux from the inlet to the outlet provided an estimate of net reach-scale nitrate production or release.

Reach-scale nitrate uptake rate constants was estimated by combining the optimized transport parameters determined from the slug releases of rhodamine with the observed inlet and outlet fluxes of nitrate. Specifically, the models were re-implemented assuming steady discharge conditions and the measured inlet flux of nitrate. The nitrate uptake rate constant was increased until the steady modeled outlet concentration matched the measured outlet concentration. Two scenarios were considered to apportion uptake between the main channel and the storage zones. First, whole-wetland uptake rate constants were calculated assuming the same rate constant for both the channel and the storage. Second, maximum storage uptake rate constants were determined by assuming no uptake in the channel, which forced all the uptake to occur in the storage zones.

To determine the fate of nitrogen in different wetland compartments, *in-situ* nutrient addition experiments were undertaken at three study sites (BAR, BOX, and WIL) using benthic chambers that isolated a portion of the water column and substrate, including macrophytes. Chambers were deployed at each site in the wetland channel and two contrasting storage zones, with the goal of quantifying the magnitude and rate of nitrate uptake in different wetland riparian compartments. A disadvantage of chambers is that only a small portion of each environment is studied; to improve our spatial coverage, three chamber replicates were performed in each environment. Chamber experiments were performed during June and October 2015, to contrast net production/release of nutrients during growing and senescence periods (Stewart et al. 2011).

The chambers (Figure 5) were re-circulating, submerged, sealed from the atmosphere, open-bottom chambers, similar in design to those used by O'Brien et al. (2012). The chamber footprint was round with an area of 0.017 m^2; the depth of enclosed water in the chamber ranged from 10 to 25 cm. An innovation in chamber design was the use of 3-way valves on tubing that allowed remote sampling, preventing disturbance of the benthic sediment directly adjacent to the chamber. Following the method of O'Brien et al. (2012), the chamber experiments were run at midday for 3–5 hours. Oxygen, pH and temperature in the chamber were continuously monitored during the experiment to verify that conditions in the chamber remained stable (Figure 6a). Chambers were excluded from further analysis when measured dissolved oxygen concentration decreased below 1.3 mg/L.

During nutrient addition experiments, nitrate and bromide were injected into each chamber, and the concentration of both reactive nitrate and conservative bromide were monitored over time (Figure 6b). Bromide was used to allow the estimation of nitrate loss due to transport out of the chamber into the sediment. Samples were filtered in the field, placed on ice, then analyzed at the UNH Water Quality Analysis Laboratory using standard methods. Observed decreases in the ratio of the concentration of nitrate to the concentration of bromide were used to estimate zero-order consumption

Figure 5. Chamber deployment in main channel at study site BOX on June 19, 2015, showing the 3-way valve system (on top of peristaltic pump) that allowed remote sampling.

(or production) rates, first-order uptake rate constants, and uptake velocities. Specifically, zero-order consumption rates were estimated using the negative slope of a straight line fit to the concentration ratio over time. First-order rate constants were estimated only for chambers exhibiting net consumption; rate constants were estimated using the slope of a straight line fit to the natural logarithm of the concentration ratio over time. The uptake velocity was calculated by multiplying the first-order rate constant by chamber depth.

Following each chamber deployment, sediment cores were obtained from the footprint of each chamber. The fraction of dry mass lost following ignition in a muffle furnace for 400°C for 24 hours was used to estimate organic carbon content.
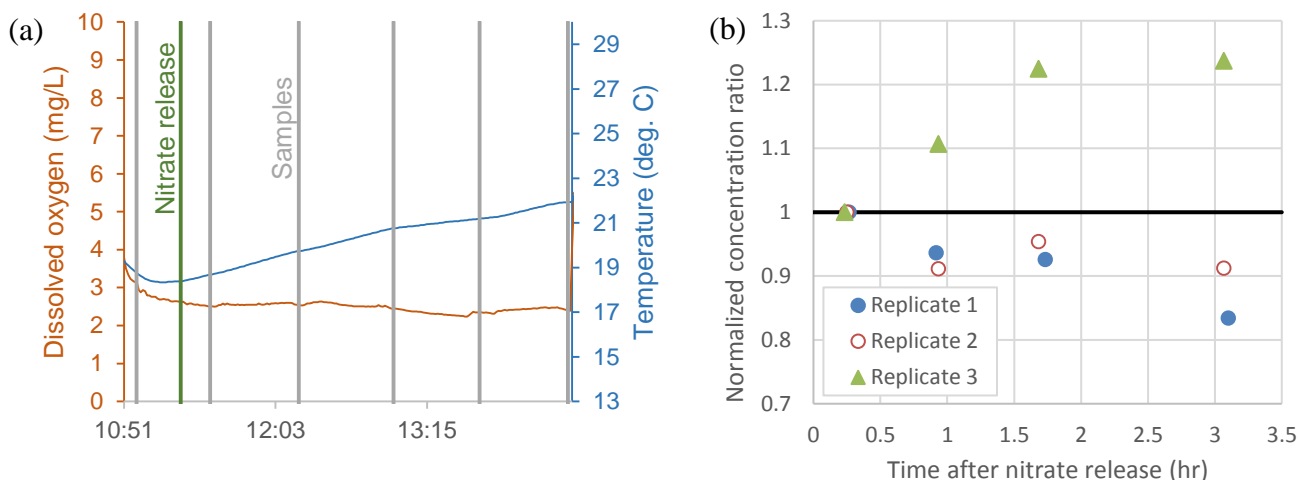

Figure 6. Chamber deployments on 6/30/2015 in transient storage near outlet at site WIL. (a) Time series of dissolved oxygen concentration and temperature within replicate #3 during the time the chamber was sealed. Vertical bars indicate the timing of the nitrate and bromide release and sampling. (b) Nitrate-to-bromide concentration ratio normalized by initial nitrate-to-bromide concentration ratio within each of the 3 chamber replicates.

Principal findings and significance
Objective 1: Determine contribution of wetland-dominated stream reaches to surface transient storage as a function of inundation and season.

The watershed area of the study wetlands ranged from 0.5 to 210 km^2. Wetland area ranged from 2,400 to 40,00 m^2, NWI area ranged from 1,200 to 52,000 m^2, wetland length ranged from 120 to 650 m, average width ranged from 18 to 50 m, width-to-length ratio ranged from 0.07 to 0.24, and wetland channel sinuosity ranged from 1.0 to 1.4. Only width was statistically different from (specifically, smaller than) a broad selection of other New England wetlands. Although study wetlands were on the small end of the range of wetlands chosen randomly from nearby watersheds in coastal New England, they were well within the observed variability, and thus believed to be geometrically representative of other wetlands in the area.

In general, velocity in the wetland channel ranged from 100 to 10,000 m/day and was quite similar to velocity upstream and downstream, which makes sense because the wetland channel was sized to pass the same flow that entered and exited the wetland. The exception was a few sites (BYF, LEE) which were affected by beaver, which reduced their velocities.

The detention time and variance of the RTDs of conservative tracer were compared to previous observations of 384 tracer releases in streams and rivers with discharge 10^{-3}–10^3 m^3/s
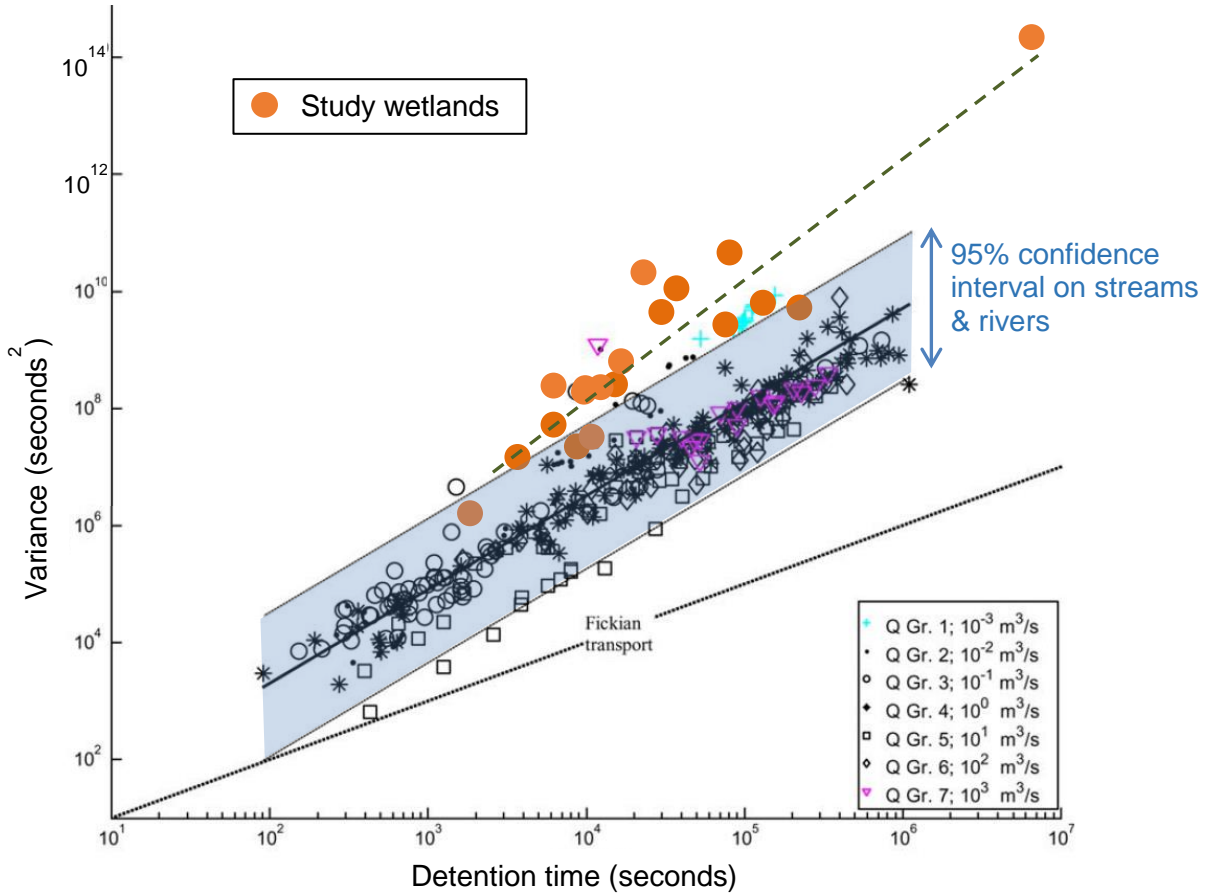
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Figure 7. Comparison of residence time distribution statistics for study wetlands to previous observations of 384 breakthrough curves from tracer releases in streams and rivers, which are divided into seven discharge (Q) classifications. Adapted from González-Pinzón et al., 2013.

(Gonzalez-Pinzon et al., 2013; Figure 7). In streams and rivers, longitudinal spreading (characterized by variance) increases predictably with detention time, though this growth is faster than the linear increase expected with Fickian transport, suggesting that the effective dispersion coefficient increases with distance traveled and with discharge (Fischer et al., 1979; Gonzalez-Pinzon et al., 2013). Nearly all of the 19 observed RTDs in this study fall outside of a 95% confidence interval based on observations in streams and rivers, indicating that transport through wetland-dominated reaches is statistically different from solute transport through channelized streams (Figure 7). Thus, this study confirms that the large off-channel storage zones in wetlands increase the residence time of solutes, especially those that enter more slowly flowing areas.

Transient storage models were successfully fit to all measured tracer breakthrough curves. For nearly all studies, the multiple-zone models better matched experimental data, especially in matching tracer concentration in the tail of the breakthrough, representing flowpaths with long residence times (Figure 8). The tail of the tracer breakthrough curve at the wetland outlet exhibits the most sensitive response to different transport pathways including exchange with transient storage zones (Wang and Jawitz 2006, Gooseff et al. 2011); the better fit of the multiple-zone models confirmed that different types of transient storage characterized by different exchange rates were present in the study wetlands. The fraction of median travel time due to transient storage (Runkel 2002) ranged from 20–80%, indicating that most solutes moving through these reaches spent half or more of their time traveling through transient storage areas that may have exhibited high biogeochemical reactivity.
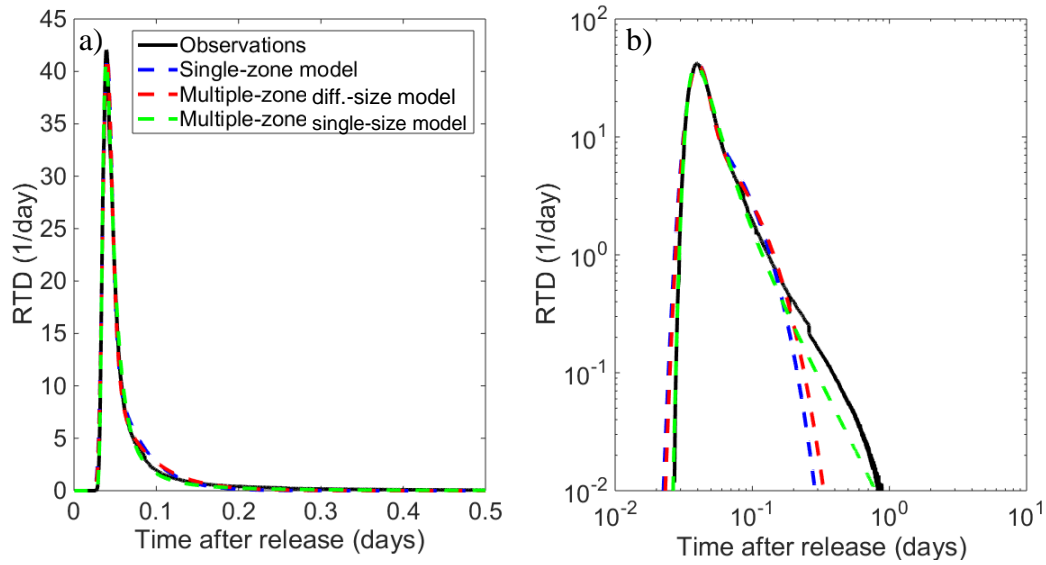
Figure 8. Measured and modeled residence time distribution (RTD) on (a) linear and (b) logarithmic axes for study REA2.

Objective 2: Quantify nitrate uptake rates among different types of surface transient storage as a function of season.

During 8 out of 11 studies, the outlet concentration of nitrate was less than the inlet concentration. In addition, in 7 out of 11 studies, nitrate fluxes (concentration × discharge) entering the wetlands were smaller than fluxes out of the wetlands. Thus, nitrate was retained within most of the study reaches during the period of observation.

Within chambers, net nitrate consumption, indicated by a decrease in bulk nitrate-to-bromide concentration over time, was observed in 14 out of 20 successful chamber deployments (Table 1). Five of these concentration decreases were statistically significant at the 90% confidence level. Nitrate-to-bromide concentration was observed to remain constant or increase (suggesting nitrate production) in the remaining 6 deployments. Net zero-order nitrate consumption rates were as high as 1.02 mg/L/hr, or 61 mg/L/hr/m^2. First-order nitrate uptake rates were as high as 9 day^{-1}, and uptake velocities were as high as 2.2 m/day, which is similar to observations in other wetlands in coastal New England (Wollheim et al. 2014). First-order uptake rate constants decreased as initial (ambient + added) nitrate concentrations increased (Figure 9), supporting patterns of efficiency loss in nitrate uptake (Wollheim et al. 2014). Uptake rates were not significantly different between channel and transient storage locations within the same wetland, and were not significantly different among wetlands.
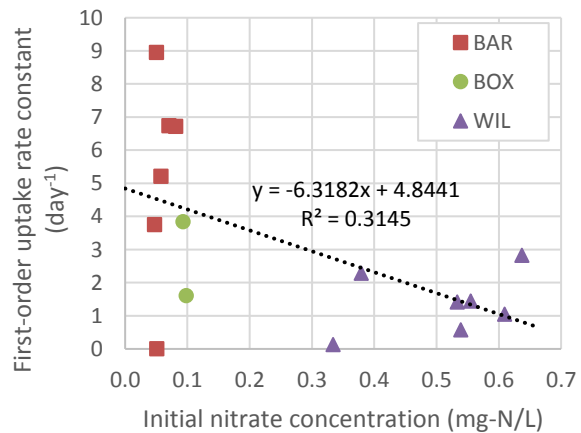

Figure 9. First-order nitrate uptake rate constants measured in chambers, compared to the initial nitrate concentration in the chamber, along with a best-fit straight line to this relationship across all sites.

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Table 1. Summary of individual chamber deployments during June 2015. Ambient concentrations represent conditions prior to nitrate release; initial concentrations reflected the added nitrate. DO depletion rates and zero-order nitrate consumptions rates are negative when DO and nitrate decrease over time. Asterisks are used to indicate rates that are significant at the 90% confidence level.

Site	Location	Rep	Date	Depth (cm)	Temp. (°C)	DO (mg/L) Start	DO (mg/L) End	DO depletion rate (mg/L/hr)	Organic carbon content	Ambient NO$_3$ (mg-N/L)	Ambient NH4 (mg-N/L)	Ambient PO$_4$ (µg-P/L)	Initial NO$_3$ (mg-N/L)	Zero-order Z	SE	r^2	p	First-order k	SE	r^2	p	Uptake velocity v$_f$ (m/day)
BAR	MC	1	6/8	25	16.45	5.81	4.01	0.47	64%				0.053	-0.05	0.18	0.02	0.81	-	3.43	0.04	0.76	-
BAR	MC	2	6/10	20	23.55	5.08	3.59	0.36	71%				0.058	0.30	0.11	0.77	0.12	5.21	1.58	0.84	0.08*	1.1
BAR	MC	3	6/10	19	24.19	5.26	5.02	0.05	65%				0.048	0.16	0.06	0.74	0.06*	3.75	1.04	0.81	0.04*	0.7
BAR	TS-up	1	6/5	14	19.4	6.33	5.83	0.12	43%				0.070	0.33	0.31	0.36	0.40	6.74	4.90	0.49	0.30	0.9
BAR	TS-up	2	6/5	19	18.54	5.50	3.20	0.54	28%	0.019	0.052	13.8	0.081	0.59	0.86	0.19	0.56	6.71	7.06	0.31	0.44	1.3
BAR	TS-up	3	6/10	20	22.89	3.67	3.37	0.08	38%				0.051	0.00	0.00	0.14	0.62	0.00	0.00	0.17	0.59	0.0
BAR	TS-down	1	6/4	20	18.26	8.27	6.63	0.47	50%				0.046	-0.04	0.09	0.16	0.74	-	2.06	0.18	0.72	-
BAR	TS-down	2	6/4	19	18.13	8.14	5.91	0.66	47%				0.051	-0.14	0.07	0.82	0.28	-	1.54	0.81	0.29	-
BAR	TS-down	3	6/8	25	15.6	4.20	3.63	0.15	43%				0.050	0.41	0.23	0.61	0.22	8.95	3.97	0.72	0.15	2.2
BOX	MC	1	6/19	17	22.61	1.46	1.38	0.02	35%				0.038	-0.03	0.09	0.06	0.76	-	1.86	0.08	0.71	-
BOX	MC	2	6/19	15	23.65	4.66	0	1.06	36%	0.053	0.050		0.101			-				-		-
BOX	MC	3	6/19	15	23.33	2.15	2.76	-0.15	38%				0.098	0.13	0.04	0.85	0.08*	1.60	0.47	0.86	0.07*	0.2
BOX	TS-up	1	6/22	15	22.75	4.86	6.08	-0.26	-				0.000			-				-		-
BOX	TS-up	2	6/24	10	23.87	2.56	6.10	-0.90	61%			17.04	0.093	0.21	0.06	0.85	0.08*	3.84	1.20	0.84	0.09	0.4
BOX	TS-up	3	6/24	14	25.63	2.15	2.98	-0.21	51%				0.058			-				-		-
BOX	TS-down	1	6/22	17	22.74	4.31	7.57	-0.69	-	0.048	0.046		0.071			-				-		-
BOX	TS-down	2	6/22	13	23.83	4.32	4.88	-0.13	-				0.092			-				-		-
BOX	TS-down	3	6/24	11	26.02	3.07	0.06	0.74	54%				0.042			-				-		-
WIL	MC	1	6/26	18	19.57	3.96	2.47	0.38	26%				0.380	0.85	0.15	0.94	0.03*	2.28	0.40	0.94	0.03*	0.4
WIL	MC	2	6/26	15	20	3.51	2.39	0.29	35%	0.470	0.165		0.534	0.58	0.30	0.65	0.19	1.41	0.71	0.66	0.18	0.2
WIL	MC	3	6/29	12	19.71	3.37	0	0.87	27%				0.666			-				-		-
WIL	TS-up	1	6/26	20	15.7	5.74	4.27	0.34	35%				0.637	1.02	0.93	0.37	0.39	2.83	3.04	0.30	0.45	0.6
WIL	TS-up	2	6/29	21	15.99	5.65	4.95	0.17	30%			8.151	0.609	0.64	0.26	0.75	0.14	1.05	0.43	0.75	0.14	0.2
WIL	TS-up	3	6/29	21	16.25	6.54	6.29	0.06	28%				0.334	0.07	0.06	0.43	0.34	0.13	0.11	0.43	0.34	0.0
WIL	TS-down	1	6/30	22	19.74	5.93	9.03	-0.88	24%				0.555	0.89	0.14	0.95	0.02*	1.44	0.22	0.95	0.02*	0.3
WIL	TS-down	2	6/30	21	20.23	3.19	3.57	-0.12	18%	0.613	0.173		0.539	0.36	0.29	0.43	0.35	0.57	0.47	0.43	0.35	0.1
WIL	TS-down	3	6/30	22	20.04	3.23	2.47	0.23	24%				0.405	-0.77	0.27	0.81	0.10	-	0.63	0.80	0.11	-

Previous research has suggested seasonal cycles in nutrient uptake and release in coastal New England (Claessens et al. 2009). Fall 2015 nutrient concentration measurements have not yet been received from the laboratory, so it is not yet possible to quantify seasonal variation in uptake rates.

Objective 3: Scale biogeochemical and hydrologic insights to wetland-dominated reaches throughout New England watersheds.

Reach-scale nitrate uptake rate constants calculated for study sites exhibiting retention were within the range of previous results from flow-through wetlands in Massachusetts (Wollheim et al. 2014) and Wisconsin (Powers et al. 2012) and, with the exception of study LEE, are higher than uptake rate constants for streams (Wollheim et al. 2014), confirming that small wetlands play a large role in providing the important ecosystem service of nitrate retention. In general, nitrate uptake rate constants were similar between sites. There were few significant relationships between nitrate uptake rate constants and wetland geometry, suggesting that all studied wetlands contributed similarly to nutrient retention and processing. All three instances of nitrate production occurred in fall, when uptake rates tended to be low as well.

When retention was assumed spatially constant throughout the wetland channel and storage zones, different storage zone models resulted in similar reach-scale nitrate uptake rate constants. However, when increased uptake in off-channel transient storage areas (cf. Wollheim et al. 2014) was considered, different storage zone connectivity resulted in different effective reach-scale uptake rates: a small or poorly connected storage zone with rapid uptake to result in the same observed reach-scale retention. Thus, both spatial variations in uptake and connectivity are both important in understanding reach-scale processing, and wetland-dominated stream reaches may serve as hot spots for nutrient retention because uptake rates are higher and/or residence times are longer. These reach-averaged removal rates will be suitable for direct incorporation into existing watershed models of the system (Wollheim et al. 2008; Stewart et al. 2011).

Objective 4: Share results with local and regional policy makers

We have shared results with local and regional policy makers to assist in on-going efforts to manage and mitigate nitrate loading in coastal New England rivers. Methods and results have been presented to members of the public, local policy makers, and scientists, at the Lamprey River Watershed Association at the Lamprey River Symposium, the Northeast Section Meeting of the Geological Society of America, the New England Association of Environmental Biologists annual meeting, the New Hampshire Waters and Watershed Conference, and the American Geophysical Union Fall Meeting. In addition, motivation for the project has been discussed with students and members of the public through school groups, the KEEPERS summer program, and UNH Ocean Discovery Day.

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Woodward, J., A. Moskal, L. Kalnejais, and A. Lightbody. Sediment oxygen consumpion in New England wetlands. UNH Undergraduate Research Conference. April 23, 2016.

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Lightbody, A., Wilderotter, S., Rosengarten, D., Lawrence, K. Contribution of fluvial wetlands to nitrogen retention in urbanizing coastal watersheds. Lamprey River Research Symposium, NH Water Resources Research Center. January 9, 2015.

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Outreach

Presentation of watershed hydrology and water quality to 80 elementary school students as part of the UNH Leitzel Center, Kids Eager for Engineering Program with Elementary Research-based Science (KEEPERS) program, July 2014 and 2015. Unit featured on KEEPERS promotional materials: http://www.leitzelcenter.unh.edu/pdf/carmelina_cestrone.pdf

Hydrology and water quality presentations to over 300 elementary and middle students and the public through UNH Ocean Discovery Day, Oyster River Girls' STEM Club, Hampstead Middle School, Moharimet Elementary School Science Friday, etc.

Participation in the Lamprey River Advisory Committee, and discussion with volunteers/staff from the Ipswich River Watershed Association and Oyster River Watershed Association

Initiation of collaboration with Peter Steckler at the Nature Conservancy, who is currently updating the Land Use Plan for New Hampshire's Coastal Watersheds to account for differences in wetland ability to retain nitrogen

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