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Seasonality of nitrogen sources, cycling, and loading in a New England river discerned from nitrate isotope ratios

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S1. Isotope composition of rainwater NO_3^-

DIN concentrations in rainwater samples ranged from 2.3 to 56.4 µM (Figure S2a). Corresponding isotope ratios ranged from -6.1 to 1.7 ‰ for $\delta^{15}N_{NO3}$, from 57.8 to 75.7 ‰ for $\delta^{18}O_{NO3}$, and from 19.7 to 27.2 ‰ for $\Delta^{17}O_{NO3}$ (Figure S2b).

Both $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values in local rainwater – measured only from early September through December 2018 – scaled directly with discharge at the Stillman Bridge (Fig. S2c), implicating an increase in both as a function of mean precipitation. In order to extrapolate these precipitation isotopic end-member values to the whole observation period, we imposed best-fit logarithmic function to rainwater $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ values vs. daily river discharge measurements at the Stillman Bridge, using the latter as a proxy for precipitation. The precipitation $\delta^{18}O_{NO3}$ and $\Delta^{17}O_{NO3}$ end-member values thus derived were then used to (a) estimate the fraction of atmospheric NO_3^- in river water (Fig. 2g) and (b) account for the influence of atmospheric NO_3^- on riverine $\delta^{18}O_{NO3}$ (Fig. 2h).

Table S1. Pawcatuck River discharge and N loading statistics for the Westerly WWTF in 2018.

	Min	Max	Mean	Median
Discharge (10^4 m^3 d^{-1})	0.5	2.1	1.0	0.9
DIN flux (x 10^3 mol N d^{-1})	0.2	11.3	3.2	2.7
TON flux (x 10^3 mol N d^{-1})	<0.1	4.0	1.0	0.8
TN flux (x 10^3 mol N d^{-1})	0.9	13.2	4.1	3.7

Table S2. Summary of results from mixed-model ANOVAs testing the effects of river section (RivSect) and sampling date (Date) on multiple response variables (a-g). Sampling station was included in each model as a random effect. Numerator and denominator degrees of freedom (DF_n and DF_d, respectively) are given for each effect test and corresponding F ratio. River sections are as follows: Section 1: Stations 1 & 2; Section 2: Stations 3 & 4; Section 3: Stations 7-12; Section 4: Stations 13-15.

			Df_n	DF_d	F	p
(a)	$[NO_3^-]$	RivSect	3	9	32.1	< 0.0001
		Date	2	12	122.4	< 0.0001
		RivSect x Date	6	12	107.2	< 0.0001
(b)	$\delta^{15}N_{NO3}$	RivSect	3	9	26.2	0.0001
		Date	2	15	16.6	0.0002
(c)	$\delta^{18}O_{NO3}$	RivSect	3	9	6.2	0.0141
		Date	2	15	0.7	0.5225
(d)	$[PO_4^{3-}]$	RivSect	3	9	45.2	<0.0001
		Date	2	12	72.0	<0.0001
		RivSect x Date	6	12	32.2	<0.0001
(e)	$[NH_4^+]$	RivSect	3	9	3.2	0.0778
		Date	2	12	8.8	0.0044
		RivSect x Date	6	12	2.1	0.1238
(f)	[PN]	RivSect	3	9	0.3	0.8029
		Date	2	16	0.3	0.7378
(g)	Chl-a	RivSect	3	7	9.0	0.0085
		Date	1	7	1.4	0.2686
		RivSect x Date	3	7	1.9	0.2110

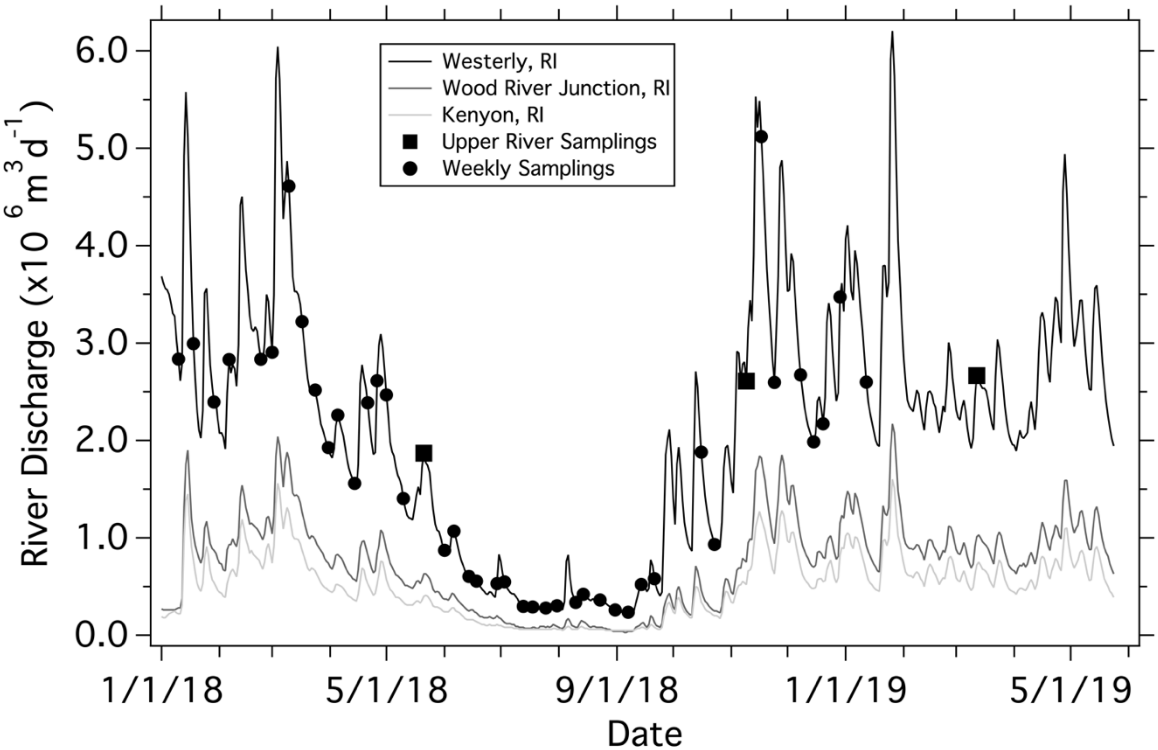


Figure S1. Mean daily river discharge at the three USGS discharge gauges along the Pawcatuck River, at Kenyon, Wood River Junction, and the Stillman Bridge in Westerly. Sampling dates indicated by symbols.

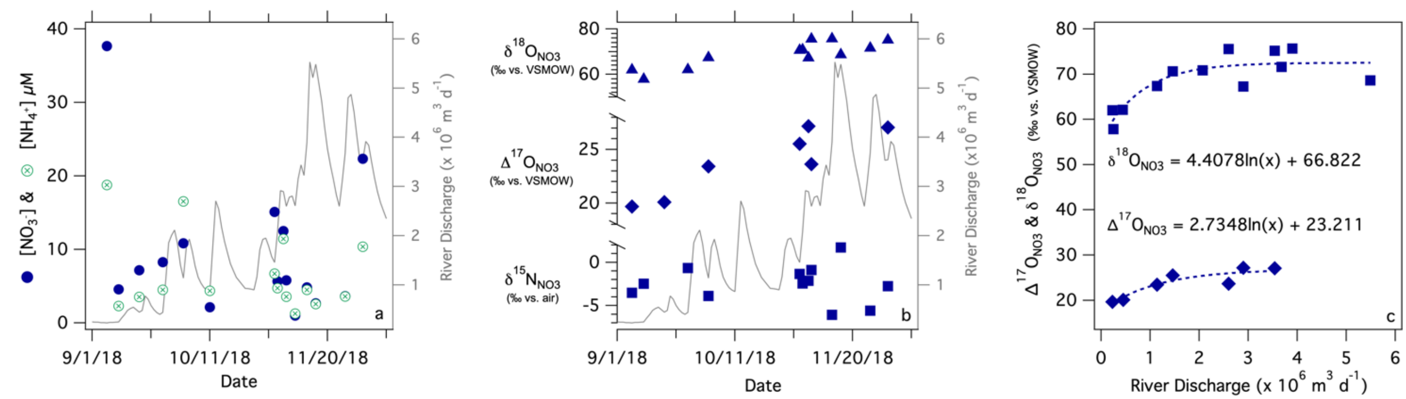


Figure S2. Solute concentrations and NO_3^- isotopologue ratios in rainwater collections at Avery Point, CT vs. sampling date: (a) [NO_3^-] & [NH_4^+]; (b) $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ & $\Delta^{17}O_{NO3}$; Grey line corresponds to the mean river discharge at the Stillman Bridge, which we use as a proxy to derive the precipitation isotopic end-members from (c) the log-linear fit of $\delta^{18}O_{NO3}$ & $\Delta^{17}O_{NO3}$ vs. river discharge.

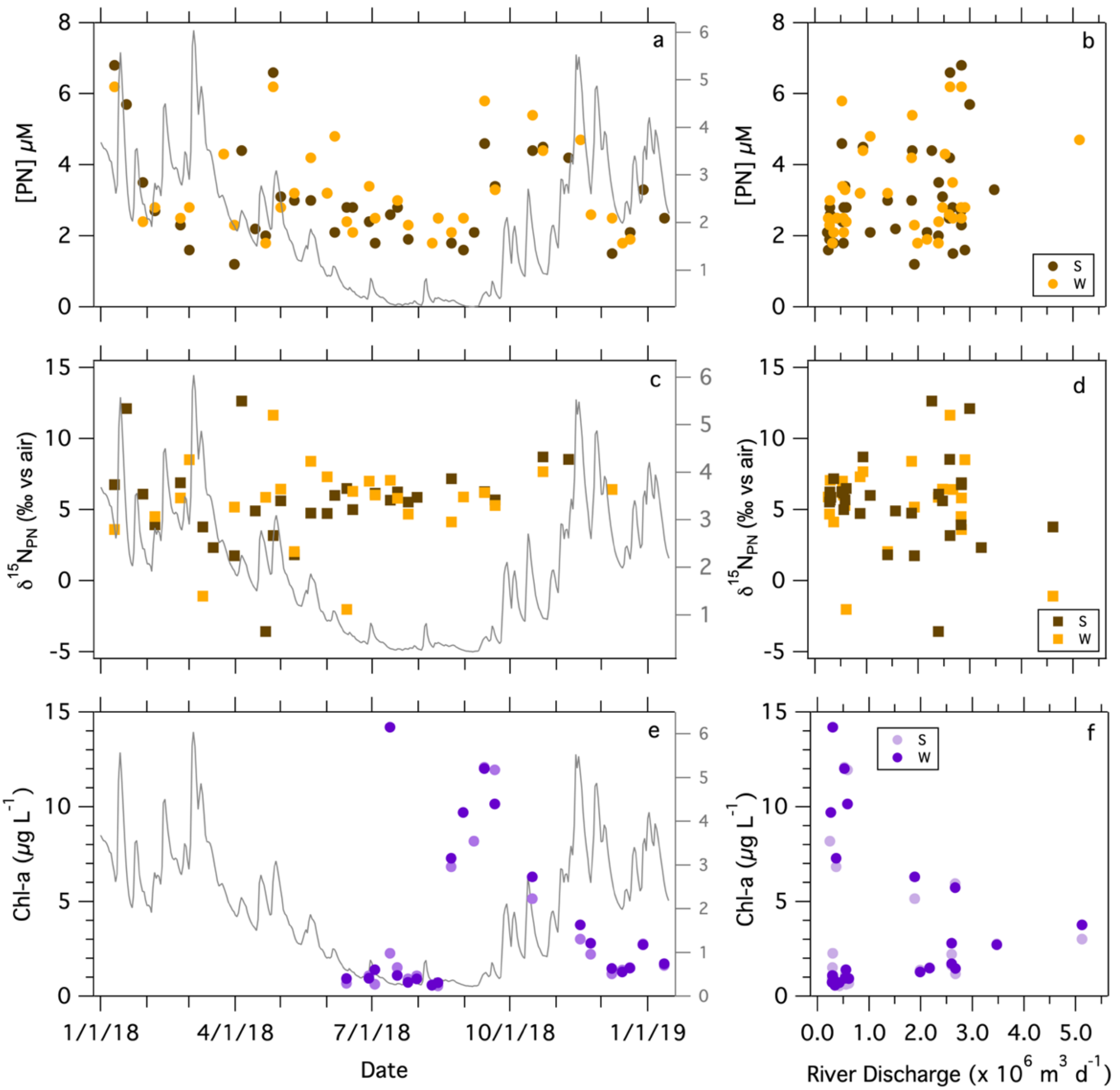
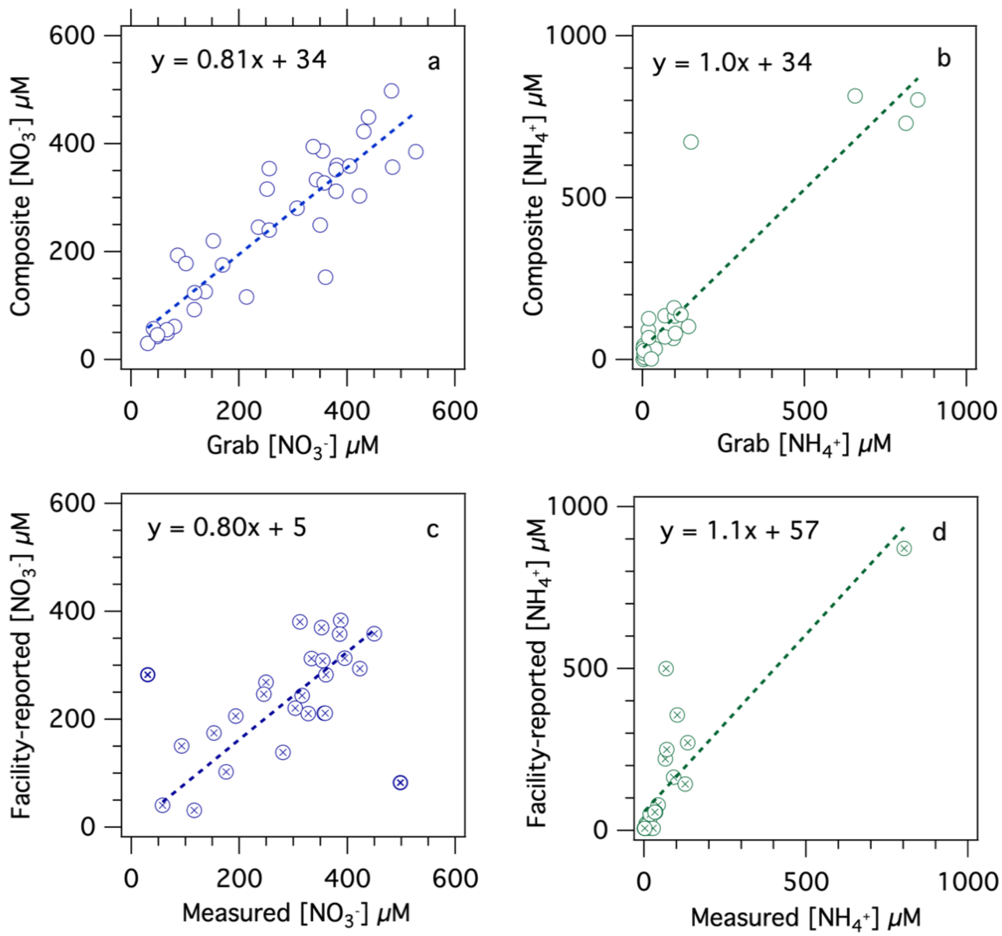


Figure S3. (a) Chlorophyll-a at the Stillman and Westerly bridges vs. sampling date (b) Chlorophyll-a vs. mean daily river discharge recorded at the Stillman Bridge (c) [PN] at the bridges vs. sampling date, (d) [PN] vs. mean daily river discharge. (e) $\delta^{15}N_{PN}$ at the bridges vs. sampling date, (f) $\delta^{15}N_{PN}$ vs. mean daily river discharge.



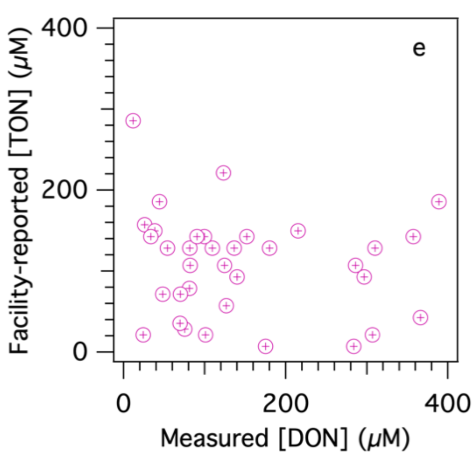


Figure S4: (a) [NO_3^-] in composite vs. grab samples from the Westerly WWTF, measured at UConn; (b) [NH_4^+] in composite vs. grab samples measured by UConn (c) Plant-reported [NO_3^-] in composite effluent vs. [NO_3^-] measured at UConn; (d) Plant-reported [NH_4^+] in composite effluent vs. [NH_4^+] measured at UConn; (e) Facility-reported [TON], measured as Total Kjeldahl Nitrogen minus NH_4^+, vs. [DON] in grab and composite samples, measured at UConn.

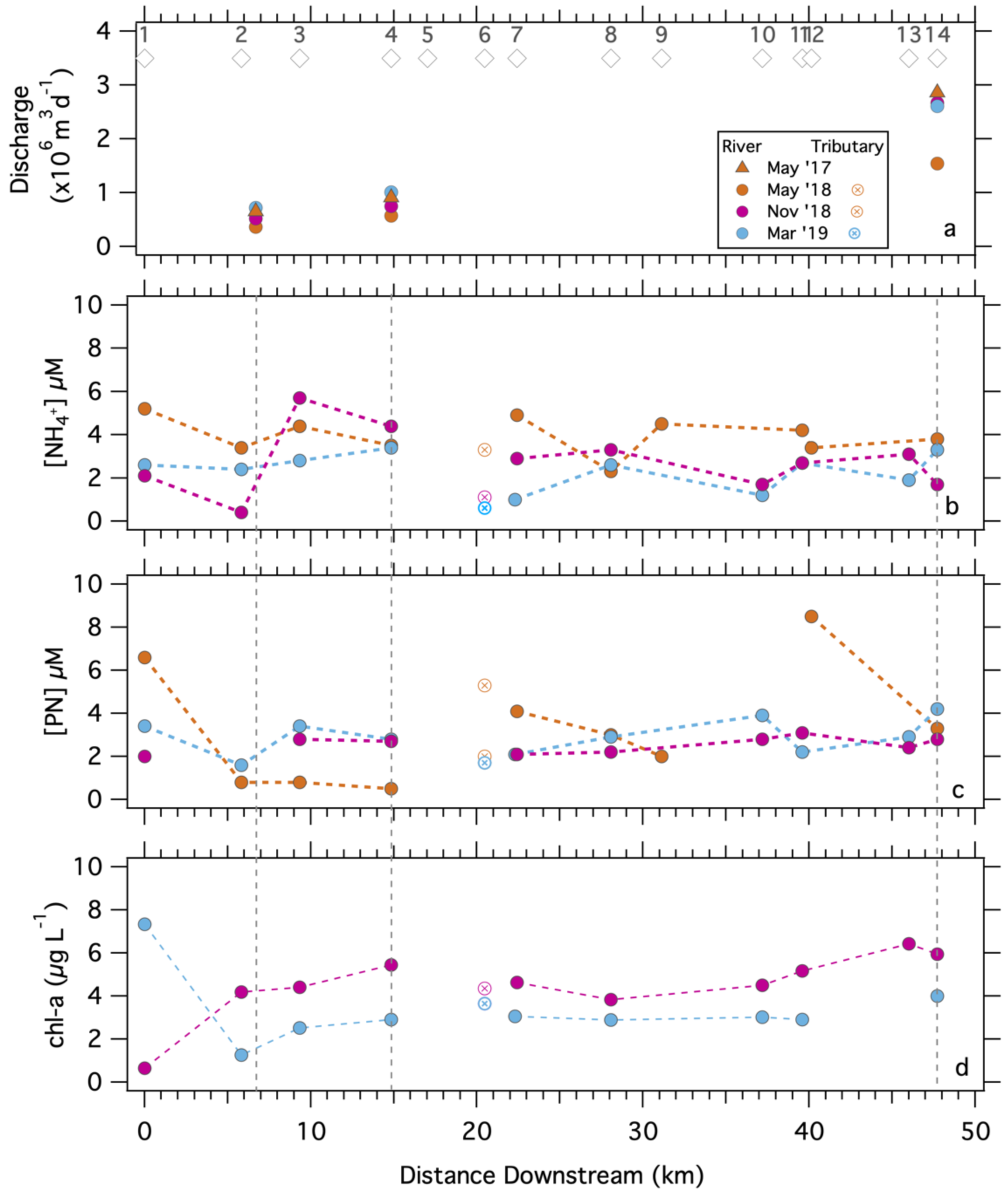


Figure S5: Solute concentrations observed at discrete locations along the Pawcatuck River from its origin at Worden Pond to the Westerly Bridge during discrete along-river sampling campaigns. (a) Mean daily river discharge recorded at three flow gauges along the Pawcatuck River during the sampling campaigns; (b) [NH_4^+]; (c) [PN]; and (d) chlorophyll-a.

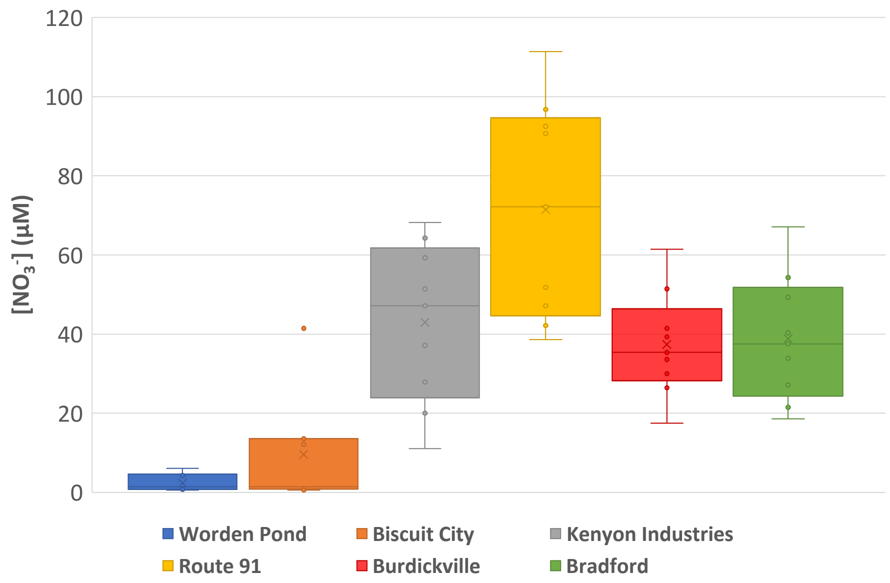


Figure S6. Box and whisker plot of median $[NO_3^-]$ in samples collected in the month of October from 2007 to 2016 at locations along the upper Pawcatuck River by the Wood-Pawcatuck Watershed Association (WPWA, 2020). The top and bottom of each box are the 25th and 75th percentiles, distances between reflect the interquartile ranges, and the line inside each box is the sample median. Whiskers extending above and below capture population minima and maxima. Single data points outside of whiskers correspond to outliers

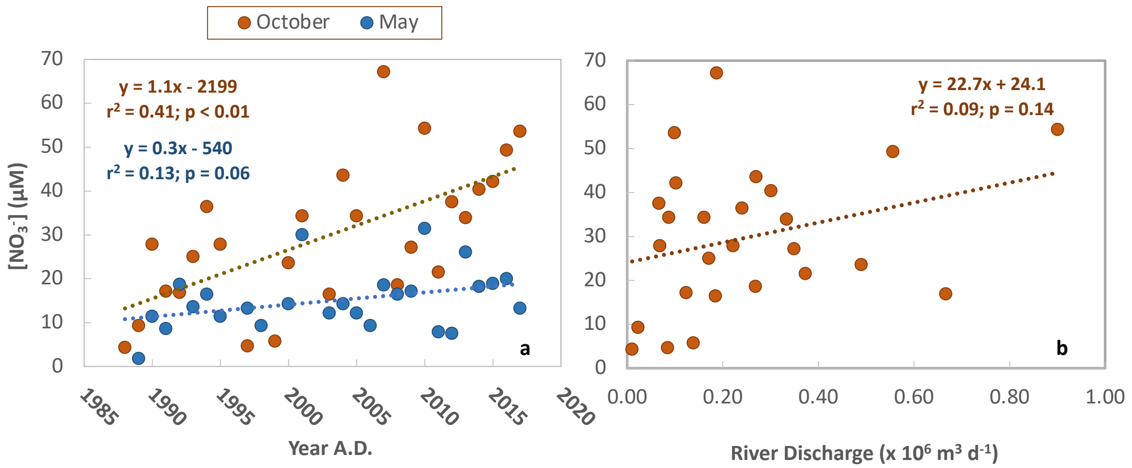


Figure S7. (a) [NO_3^-] in samples collected at Bradford (Station 8) on the Pawcatuck River, recorded from monthly samplings in May and in October from 1989 to 2016 by the Wood-Pawcatuck Watershed Association (WPWA, 2020). (b) [NO_3^-] in October vs. the monthly-averaged river discharge at Wood River Junction in the corresponding year. Regression lines are the least-squares linear fits, with corresponding r^2 and probability statistics.