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# Influence of land use and hydrologic variability on seasonal dissolved organic carbon and nitrate export: insights from a multi-year regional analysis for the northeastern USA

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**Abstract** Land use/land cover (LULC) change has significant impacts on nutrient loading to aquatic systems and has been linked to deteriorating water quality globally. While many relationships between LULC and nutrient loading have been identified, characterization of the interaction between LULC, climate (specifically variable hydrologic forcing) and solute export across seasonal and interannual time scales is needed to understand the processes that determine nutrient loading and responses to change. Recent advances in high-frequency water quality sensors provide opportunities to assess these interannual relationships with sufficiently high temporal resolution to capture the unpredictable, short-term storm events that likely drive important export mechanisms for dissolved organic carbon (DOC) and nitrate ($NO_3^-$–N). We deployed a network of in situ sensors in forested, agricultural, and urban watersheds across the northeastern United States. Using 2 years of high-frequency sensor data, we provide a regional assessment of how LULC and hydrologic variability affected the timing and magnitude of dissolved organic carbon and nitrate export, and the status of watershed fluxes as either supply or transport controlled. Analysis of annual export dynamics revealed systematic differences in the timing and magnitude of DOC and $NO_3^-$–N delivery among different LULC classes, with distinct regional similarities in the timing of DOC and $NO_3^-$–N fluxes from forested and urban watersheds. Conversely, export dynamics at agricultural sites appeared to be highly site-specific, likely driven by local agricultural practices and regulations. Furthermore, the magnitude of solute fluxes across

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watersheds responded strongly to interannual variability in rainfall, suggesting a high degree of hydrologic control over nutrient loading across the region. Thus, there is strong potential for climate-driven changes in regional hydrologic cycles to drive variation in the magnitude of downstream nutrient fluxes, particularly in watersheds where solute supply and/or transport has been modified.

**Keywords** Land use · Hydrologic variability · Dissolved organic carbon export · Nitrate export · Supply and transport control

## Introduction

Humans have altered between 30 and 50% of Earth's surface (Vitousek et al. 1997) and the scale of these alterations continues to grow (Sala et al. 2000; Motesharrei et al. 2016; Venter et al. 2016). Simultaneously, humans have also drastically altered the Earth's climate system (Karl and Trenberth 2003; Walsh et al. 2014). Together, these changes in land use and land cover (LULC) and climate have profound impacts on the ecology (Walther et al. 2002; Winder and Schindler 2004), hydrology (Barnett et al. 2005; Mitchell et al. 2006), and biogeochemistry (Davidson and Janssens 2006; Galloway et al. 2008) of watersheds. Accompanying these changes are increased runoff of nutrients (including nitrogen and phosphorus) to receiving waters, eutrophication of freshwaters and numerous cascading impacts on water quality (Smith 2003; Kaushal et al. 2011).

Anthropogenic perturbations like climate change and LULC change have altered aquatic solute fluxes (and therefore downstream water quality) by changing the magnitude and distribution of nutrient source areas within the landscape and modifying the mobilization and transport of water and solutes to from terrestrial to aquatic ecosystems. The connections between watersheds and their receiving waters can be explored effectively by using the concept of supply and transport control, which identifies the dominant controls on solute export. For example, Zarnetske et al. (2018) examined concentration-discharge relationships at 1006 stations across the United States and concluded that across all ecoregions and land uses, roughly 80% of rivers are "transport limited" for DOC; i.e., sufficient sources of DOC exist within the landscape, but the mechanism to transport DOC to receiving waters limits the amount of DOC exported from watersheds. A number of studies have documented widespread transport control and chemostatic behavior of both solute concentrations and loads, particularly in managed landscapes with legacy nutrient pools (Basu et al. 2010; Godsey et al. 2009; Thompson et al. 2011).

LULC change has numerous, interacting effects on both solute supply and transport from watersheds. Agriculture and urbanization increase the available pool of solutes (e.g. supply) but also change the way water moves through the system (e.g. transport). Conversion to agricultural or urban land cover is associated with accumulation of legacy nitrogen and phosphorus in soil and groundwater systems (Macdonald et al. 2012; Van Meter et al. 2016), as well as altered hydrological flow paths (e.g., increased overland, pipe, and ditch flow) leading to increased nutrient loading to aquatic ecosystems (Bernhardt et al. 2008). Consequently, LULC has significant biogeochemical effects on solute export to aquatic ecosystems, including changes in the timing, magnitude, and form of nutrients exported (Foley et al. 2005; Scanlon et al. 2007).

At the same time, solute export from watersheds to receiving waters will be impacted by changing climate conditions. The manifestations of global climate change are projected to vary greatly, but the northeastern US is projected to have higher temperatures (including higher winter temperatures), increased frequency of extreme precipitation events, and reduced snowpack and increased likelihood of winter rain (Horton et al. 2014). These changes to the climate will drive changes in the hydrology of watersheds, leading to increased hydrologic variability in rainfall and runoff processes (Hayhoe et al. 2007). The cascading impacts of this enhanced hydrologic variability on watershed biogeochemistry will be diverse and numerous. In particular, changes to the magnitude, intensity, and frequency of snowmelt and rainfall will have significant impacts on the magnitude of solute transport and in situ biogeochemical processing (Bernal et al. 2013; Siegert et al. 2017).

The effects of climate change and LULC change will likely interact synergistically (Kaushal et al. 2017), leading to nonlinearities in biogeochemical responses such as nutrient export. The concept of supply versus transport control is a helpful construct for evaluating how numerous anthropogenic factors may influence nutrient fluxes from watersheds to downstream receiving waters. Both land use and hydrologic variability have the potential to influence the available pool of solutes (e.g. supply) while also changing the way water moves through the system (e.g. transport). Watersheds have the capability to move between supply and transport limitation over event, seasonal, and annual timescales (Gao and Josefson 2012; Ramos et al. 2015; Vaughan et al. 2017), but anthropogenic drivers may also alter the balance of these two regimes (Basu et al. 2010). For example, while an unaltered landscape could be inherently supply limited with respect to nitrogen due to high uptake and limited available N pools, conversion to agriculture and subsequent fertilizer amendments or crop practices often shift the system to transport limitation by adding ample (and potentially labile) N to the landscape.

We utilized the framework of supply and transport control to explore the impacts of LULC and climate on export regimes, and identify the hydrologic and biogeochemical drivers that control nutrient flux from watersheds. Specifically, we propose that the temporal dynamics of annual cumulative nutrient and water yields for a given watershed contains information on the degree of supply or transport control. While water and solute export are correlated to a certain degree (because flux is a product of discharge and concentrations), the behavior of solute export relative to water export may contain information on whether export from the system is supply or transport controlled (Fig. 1a–c). For example, close correlations between cumulative water and solute export over annual time scales indicate transport control of solute export (Fig. 1b and c). We expect to observe this transport control most commonly for DOC (e.g. Zarnetske et al. 2018), but also for $NO_3^-$–N in more anthropogenically modified systems.

Watersheds with balanced supply and transport control over annual time scales will show close correlations between solute and water export, but limited seasonality and quasi-linear cumulative yield trajectories (Fig. 1b). Furthermore, systems with overall transport control but temporally (e.g. seasonally) variable supply will show close correlations between water and solute export, but will display strong seasonality in the timing of export and will deviate from quasi-linear cumulative yields (Fig. 1c). This may be particularly prevalent in agricultural landscapes, where best management practices or policy regulations may dictate the timing of nutrient amendments or fertilizer applications (e.g. nutrient supply) to the landscape. These different potential management policies and the resulting flux dynamics are indicated as different dashed lines in Fig. 1c.

We also propose that strong deviations between cumulative solute and water export indicate shifting balance of supply and transport control for a given solute (e.g. $NO_3^-$–N). For example, periods of the year characterized by strong transport limitation would be described by normalized solute yield that outpaces water yield, such that disproportionately more solute is mobilized relative to water (Fig. 1a). This suggests that solute has accumulated in the system and the magnitude of flux is controlled by transport. As the normalized water and solute yields converge, this suggests a shift towards supply control as terrestrial pools are depleted or in situ biogeochemical uptake increases (Fig. 1a). A study by Jawitz and Mitchell (2011) identified that solute fluxes may be unequally distributed relative to water fluxes, particularly in systems with chemodynamic concentration-discharge relationships. We suggest that on an annual basis, these inequalities in the response of water and solute fluxes may be indicative of shifts between supply and transport control. Lastly, we propose that the distinct structure of cumulative export dynamics (which can be fit by different classes of functions) quantify differences in the seasonal structure of fluxes, and highlight how anthropogenic impacts have altered the flux of carbon and nitrogen into aquatic systems.

We used this conceptual framework combined with 2 years of high frequency DOC and $NO_3^-$–N time series collected from seven watersheds across the northeastern United States that differed in their LULC and regional position to address the following overarching research question: How do LULC and hydrologic variability interact to affect the controls on watershed nutrient transport (i.e., transport vs. supply control) and how does this, in turn, impact the total magnitude and timing of DOC and $NO_3$ exports. Within this overarching question, we will consider:

Q1: How does the *total magnitude* of dissolved organic carbon (DOC) and nitrate ($NO_3^-$–N) export vary as a function of (1) LULC and (2) hydrologic variability (specifically interannual variability in

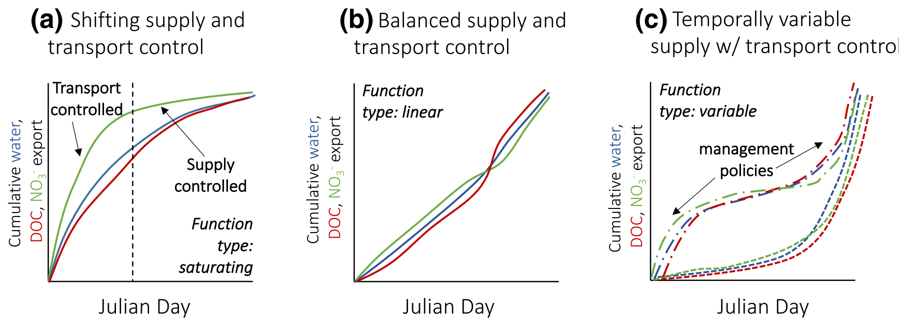



**Fig. 1** Hypothesized temporal pattern of cumulative annual water (blue), DOC (red), and $NO_3^-$ (green) export from catchments with **a** seasonally shifting supply and transport control, **b** balanced supply and transport control over time, and **c** temporally variable supply under general transport control. The hypothesized effects of different management policies on cumulative export are indicated in dotted and dashed lines in panel 1c

rainfall as a proxy for one component of climate change) across the northeastern US?

Q2: What effect does LULC have on the *timing* of DOC and $NO_3^-$–N export, and what ecohydrologic processes drive variation (or similarities) in biogeochemical response?

## Materials and Methods

### Study site description

We studied seven low-order streams across three states in the northeastern US (Delaware (DE), Rhode Island (RI), and Vermont (VT)) with varying LULC (forested, agricultural, and urban). These land uses span a gradient of anthropogenic influence from less (forested watersheds) to more intensively influenced by anthropogenic activities (urban and agricultural watersheds). These sites also span a gradient of climate defined by differences in mean annual temperatures, mean annual precipitation, and coastal versus inland influences (Table 1). The monitoring sites were operated from June 2014 through December 2016. This study will focus on 2 years of data from each of these seven sites (2015–2016) because they provided the most complete time series of DOC, $NO_3^-$–N, and discharge from each site.

We instrumented one forested stream in DE (Fair Hill Brook Table 1; Rowland et al. 2017; Johnson et al. 2018), which was the most temperate of our study sites in the northeastern US. This site is characterized by a continental climate with cold winters, warm summers, and an average annual temperature of 12.2 °C (Delaware State Climate Office 2019). Precipitation, predominantly as rainfall, is distributed throughout the year and averages approximately 1140 mm across the state, with significant interannual variability.

In RI, we studied three streams: Cork Brook (forested), Maidford Brook (agricultural), and Bailey Brook (urban, Table 1). These sites were characterized by an even distribution of precipitation throughout the year, averaging approximately 1110 mm annually. Mean annual temperatures range between 8.9 and 10.5 °C, with a great deal of variability between inland and coastal regions. Average snowfall increases from approximately 500 mm in more coastal areas up to 1100 mm in western regions, with significantly less total snowfall in mild winters (Rhode Island State Climatology Office 2019). The forested site experienced a defoliation event in 2016 as a result of gypsy moth infestation that led to the almost complete loss of canopy cover between June and July 2016 (Addy et al. 2018).

In VT, we monitored three tributaries within the Lake Champlain watershed (Table 1; Vaughan et al. 2017). Wade Brook (forested) and Hungerford Brook (agricultural) are both located in the greater Missisquoi watershed, while Potash Brook (urban) drains directly to Lake Champlain. These three streams were the northernmost sites in our study, and were the most influenced by snowpack accumulation during winter months and subsequent spring snowmelt. Mean annual temperature is between 4 and 8 °C, but varies greatly across the sites as a function of elevation and topography. Winter-time temperatures are variable and are frequently below 0 °C (Vermont State Climate

**Table 1** Summary of watershed attributes for study sites in Vermont (VT), Rhode Island (RI), and Delaware (DE)

| | Watershed area ($km^2$) | % Focal land use | Max. watershed elevation (m) | Mean watershed slope (%) | Mean annual temp (°C) | Mean annual rainfall (mm) | Latitude/longitude | 2015 Monitoring period | 2016 Monitoring period |
|---|---|---|---|---|---|---|---|---|---|
| VT | | | | | | | | | |
| Forested: *Wade Brook* | 16.7 | 95.1 | 981 | 26 | 6 | 1016 | 44° 51′N, 72° 33′W | 4/9–11/20 | 3/30–11/28 |
| Agricultural: *Hungerford Brook* | 48.1 | 44.8 | 354 | 5.6 | 6 | 1016 | 44° 54′N, 73° 30′W | 4/8–12/9 | 4/4–11/30 |
| Urban: *Potash Brook* | 18.4 | 53.5 | 143 | 5.3 | 6 | 1016 | 44° 44 N, 73° 21 W | 4/7–11/19 | 3/22–12/2 |
| RI | | | | | | | | | |
| Forested: *Cork Brook* | 4.4 | 79 | 63 | 1.3 | 9.7 | 1110 | 41° 80′N, 71° 50′W | 4/30–11/23 | 4/28–12/30 |
| Agricultural: *Maidford Brook* | 4.4 | 43 | 24.5 | 0.96 | 9.7 | 1110 | 41° 30′N, 71° 16′W | 5/21–12/31 | 5/25–12/31 |
| Urban: *Bailey Brook* | 6.6 | 67 | 24.5 | 1 | 9.7 | 1110 | 41° 30′N, 71° 17′W | 5/18–12/31 | 4/13–11/11 |
| DE | | | | | | | | | |
| Forested: *Fair Hill Brook* | 0.79 | 51 | 115 | 7.4 | 12.2 | 1140 | 39° 42′N, 75° 50′W | 3/7–12/31 | 2/26–12/28 |

Office 2019). Average annual rainfall and snowfall varies greatly as a function of topography and elevation, but averages between 965 and 1016 mm of total precipitation and ∼ 1420 mm of snowfall in most of the state (NOAA 2019).

## In-situ data collection

We used s::can spectro::lyser UV–Vis spectrophotometers (s::can Messtechnik GmbH, Vienna, Austria) to estimate DOC and $NO_3^-$–N concentrations. The spectrophotometers measured light absorbance at wavelengths from 220 to 750 nm at 2.5 nm intervals every 15–30 min. The optical path was cleaned using an automatic wiper before each measurement, in addition to manual cleaning using either dilute (3%) HCL solution and/or ethanol every 2 weeks to prevent fouling and bioaccumulation. Each spectrophotometer was co-located with a HOBO pressure transducer (Onset Computer Corporation, Bourne, MA) to monitor stage. One site in RI (Cork Brook, forested watershed) was co-located with a USGS gauging station (USGS gauge 01115280), from which we obtained discharge data. At the six remaining ungauged sites where HOBO pressure transducers were used, we developed stage-discharge rating curves to estimate continuous time series of discharge using the atmospherically-corrected stage measurements. Rating curves were developed using a combination of dilution gauging (Kilpatrick and Cobb 1985) and velocity-area calculations from stream velocity measurements (Turnipseed and Sauer 2010).

The spectrophotometers and pressure transducers were deployed in each stream from approximately March through December of each year. In DE, the most temperate field site in the study, the sensors remained in the stream all year and were only removed for brief periods during the winter (Dec–Jan). In RI and VT, the sensors were deployed as early in the spring as possible (Mar–Apr) while still ensuring the safety of field personnel and the instruments and remained in the field until ice conditions necessitated their removal (Nov–Dec). Because sensors in RI and VT were installed only during the ice-free portion of the year, the measured "annual" flux and yield estimates reported in this study are an underestimate of total DOC and $NO_3^-$–N flux from these watersheds in a 12 month period. Comparisons of our streamflow time series with other year-round time series from nearby watersheds suggest that our sensor measurements capture the majority of water and solute flux from our watersheds (Online Resource 1).

### In-situ precipitation monitoring and historical analysis

Precipitation data for each site was monitored in situ or obtained from nearby existing precipitation monitoring networks. For the study sites in VT, precipitation was monitored in situ using a HOBO tipping-bucket rain gauge (Onset Computer Corporation, Bourne MA). For the study sites in RI, precipitation data was obtained from the NOAA Regional Climate Center CLIMOD2 database (http://climod2.nrcc.cornell.edu/, North Foster and Newport Airport data stations). Data for the DE study site was obtained from the Delaware Environmental Observation System (http://www.deos.udel.edu/data/, Fair Hill data station).

To determine whether the years in our study site were characterized by wet or dry conditions, we contextualized the current (2015–2016) precipitation records from each site with historical precipitation data. For each site, we located an existing National Weather Service station with more than 40 years of data within ~ 25 km of each site and obtained the monthly rainfall totals for the period of record (NOAA NOWData Online Weather Data; https://w2.weather.gov/climate). We used these historical data to create a distribution of annual rainfall values for each site, and then estimated the quartiles of this distribution (Online Resource 2). For the purposes of this analysis, we considered years falling in the lowest quartile (Q1) as "dry" or drier than average, whereas years falling in the upper quartile (Q4) were considered "wet" or wetter than average. Any years falling into the two median quartiles (Q2, Q3) were considered to be average in terms of total precipitation amount (Online Resource 2, Online Resource 3).

### Lab analysis of grab samples

We collected grab samples at a range of baseflow to storm flow conditions to calibrate the in situ absorbance measurements. All samples were filtered in the field using a 0.7 μm glass fiber filter into new amber HDPE bottles (Vaughan et al. 2017). Samples were kept on ice in the field and during transport. DOC samples were refrigerated until lab analysis using either an Elementar TOC analyzer (DE) or Shimadzu TOC-L analyzer (RI and VT) using the combustion catalytic oxidation method. $NO_3^-$–N samples were frozen until lab analysis using open tubular cadmium reduction method (4500-$NO_3^-$; Eaton et al. 1998) on a Latchat analyzer (VT), an Astoria Pacific Model 303A Segmented Continuous Flow Autoanalyzer (RI), or a Seal AQ2 discrete analyzer (DE).

### Calibration of spectral data to estimate DOC and nitrate concentrations

We estimated DOC and $NO_3^-$–N concentrations from the absorbance spectra using the method detailed in Etheridge et al. (2014) and Vaughan et al. (2017). This approach reduces the high-dimensionality of spectral datasets using a partial least squares regression method. This analysis was conducted using the pls package in R to generate calibration equations that were applied to the entire time series of absorbance spectra (Mevik et al. 2016). When selecting the final calibration model for each site and solute, we strove to balance parsimony and explanatory power by selecting the model that explained the greatest amount of variance and that contained the lowest number of predictors. An analysis of model fits comparing PLSR predicted and lab measured DOC and $NO_3^-$–N concentrations for each watershed are included in Online Resource 4 and 5.

### Data Analysis

We used the calibration equations (described above) to generate continuous time series of DOC and $NO_3^-$–N concentrations for each of our study sites. Across all seven sites we compared the concentration time series of DOC and $NO_3^-$–N, as well as the mass flux of DOC and $NO_3^-$–N exported (kg C or N) and the watershed-area normalized yield of DOC and $NO_3^-$–N (kg C or N $km^{-2}$). In addition to the total DOC or $NO_3^-$–N yields, we also calculated the runoff-normalized yield (kg C or N $km^{-2}$ $mm^{-1}$), which is conceptually analogous to a volume-weighted mean concentration (mass/flow volume). It represents the amount of $NO_3^-$–N or DOC mobilized per mm of runoff, and therefore allows for easier comparison of loads across years with high versus low flow.

To compare differences in the total amount of DOC and $NO_3^-$–N export across sites and years, we calculated the cumulative measured annual DOC or $NO_3^-$–N yield (kg C or N km$^{-2}$) for each site. We highlight that these are *measured* annual yields and only reflect the period of the year in which sensors were deployed and collecting data, therefore they are an underestimate of annual yields at the VT and RI sites. For simplicity we refer to these as annual yields, but highlight that they are not representative of 12 full months of data collection at all sites. To facilitate comparisons of seasonality and timing of DOC and $NO_3^-$–N export across sites and between years, we calculated a normalized cumulative yield (% of total $NO_3^-$–N or DOC yield), which divided the cumulative yield at each time point by the final cumulative yield value for that year and multiplied by 100 to obtain a percent of total annual cumulative yield at each time point. This effectively corrected for the differences in total export across years and allowed for easier analysis of the timing of export.

To facilitate comparisons between observed normalized cumulative yields patterns and hypothesized patterns of transport versus supply control (Fig. 1), we fit three classes of functions to the data to determine which function type best described observed yields:

(1) A saturating function modeled after the Michaelis–Menten kinetic function (Dodds et al. 2002) that would be reflective of a shift from transport to supply limited export (Fig. 1a). This saturating function fitted normalized cumulative export (NCE) of DOC or $NO_3^-$–N as a function of time (expressed as Julian day (T), Eq. 1). The parameters $E_{max}$ and $K_m$ represent the maximum cumulative export and the time to 50% export, respectively.

$$NCE = \frac{E_{max} \times T}{K_m + T} \quad (1)$$

(2) A quasi-linear function represented by an efficiency loss function (O'Brien et al. 2007), which would indicate balanced supply and transport limitation (Fig. 1b). Because the time series was characterized by a small degree of curvature and was not purely linear, we chose this type of function to model the quasi-linear dynamics. The quasi-linear efficiency loss function fitted NCE as a function of Julian day using the following function (Eq. 2), which is a power function where the exponent m is limited between 0.5 and 1.5 (a value of 1 would be a linear, first order function).

$$NCE = kT^m \quad (2)$$

(3) A two parameter exponential function that fitted NCE as a function of Julian day (T) and two fitted parameters (a, b; Eq. 3), which would be indicative of systems with elevated fall nutrient loading following litterfall or fall fertilizer applications (Fig. 1c).

$$NCE = ab^T \quad (3)$$

We fit each function type to each time series site by site and compared goodness of fit using a suite of three common metrics ($R^2$, root mean square error (RMSE), and corrected Akaike information criteria (AICc; Anderson and Burnham 2002). In all cases, these three metrics agreed on a single function as the best fit for a given time series (Table 2; a complete comparison of the goodness of fit metrics is shown in Online Resource 6). In a limited number of cases where none of these functions adequately fit the data, we fit piecewise functions to the normalized cumulative export time series.

## Results

### Hydrologic variability: interannual variability in rainfall

At six of the seven study sites, 2015 was a wetter year than 2016 (indicated by color of bars in Fig. 2, Online Resource 7). In VT, the forested and agricultural sites experienced conditions in 2015 that were wetter than average (blue bars in Fig. 2), while in 2016 the amount of precipitation was considered average (grey bars in Fig. 2). At the urban site in VT, both 2015 and 2016 were considered drier than average (red bars), although 2016 did receive less rainfall than 2015. In RI, the agricultural and urban sites received average amounts of precipitation in 2015 and lower than average precipitation in 2016, making 2016 drier than 2015 (Fig. 2, Online Resource 7). The same is true of the forested site in DE, which received average

**Table 2** Summary of best-fit functions for each watershed and solute

| | | Forested | | Agricultural | | Urban | |
|---|---|---|---|---|---|---|---|
| | | DOC | $NO_3$ | DOC | $NO_3$ | DOC | $NO_3$ |
| VT | 2015 | Sat. (0.99) | Sat. (0.99) | Sat. (0.95) | Sat. (0.92) | E.L. (0.96) | E.L.(0.99) |
| | 2016 | Sat. (0.96) | Sat. (0.99) | E.L. (0.88) | E.L. (0.79) | E.L. (0.99) | E.L. (0.98) |
| RI | 2015 | Sat. (0.93) | Sat. (0.96) | Exp. (0.98) | Exp. (0.97) | E.L. (0.98) | E.L. (0.99) |
| | 2016 | Sat. (0.98)/E.L. (0.98)* | Sat. (0.97)/E.L. (0.97)* | Exp. (0.77) | Exp. (0.56) | E.L. (0.98) | E.L. (0.90) |
| DE | 2015 | Sat. (0.97) | Sat. (0.96) | – | – | – | – |
| | 2016 | E.L. (0.99) | Sat. (0.99) | – | – | – | – |
| | | Sat. = Saturating | E.L. = Efficiency Loss | Exp. = Exponential | | | |

Entries marked with an asterisk (*) indicate time series that are fit with a piecewise function

amounts of precipitation in 2015, and lower than average amounts in 2016.

The only site that did not experience the wetter conditions in 2015 compared to 2016 was the forested site in RI. At this site, 2016 was wetter than 2015 as a result of higher than normal fall/late-season rainfall in 2016. As expected, cumulative runoff was strongly correlated with the status of the year as wet or dry (Fig. 2e, Online Resource 7).

### Effects of hydrologic variability and land use on the magnitude of $NO_3^-$–N and DOC yield

Land use had a strong influence on the magnitude of $NO_3^-$–N and DOC exported from watersheds. Broadly speaking, we observed the greatest amount of $NO_3^-$–N and DOC export from the agricultural watersheds, followed by the urban and then forested watersheds (Fig. 2a and b, Online Resource 7). Although we observed general patterns in export organized by land use, we also observed deviations from these patterns. For example, forested sites in VT exported more DOC in 2015 than did the VT agricultural watershed in either year. While we initially were interested in whether there were systematic differences between sites of the same land use in different states, we did not observe systematic or structured changes in DOC or $NO_3^-$–N export across the three states or across a northern to southern gradient.

Agricultural watersheds generally exported the greatest amount of $NO_3^-$–N and DOC, in terms of total yield (Fig. 2a and b) and runoff-normalized yields (Fig. 2c and d). When looking at total export, the urban watershed in RI was the second largest source in terms of $NO_3^-$–N and DOC yield ahead of the forested site (Fig. 2a and b). In VT, this pattern was reversed and the forested watershed had greater $NO_3^-$–N yield than the urban site (Fig. 2a).

Comparisons of runoff-normalized yields were more consistent across land use classes than total export, particularly for DOC export. In both RI and VT, the runoff-normalized DOC and $NO_3^-$–N yield was highest in agricultural sites, followed by urban and then forested sites (Fig. 2c and d). The only exception to this was the forested watershed in RI, which had the highest runoff-normalized DOC yields. The runoff-normalized yields also show less interannual variability than the total yields (Fig. 2c and d). The total yields varied by a factor of 5, but the runoff-normalized yields were quite consistent from year to year.

Across all land use classes, these changes in total export from year to year appeared to be well correlated with interannual variability in the total magnitude of precipitation and streamflow (Fig. 2e). In general, the differences in DOC and $NO_3^-$–N export between 2015 and 2016 corresponded with the status of that year as "wet" or "dry". For example, the striking decrease in cumulative DOC and $NO_3^-$–N export from the VT forested site from 2015 and 2016 corresponds with 2015 being a "wetter" year than normal, whereas 2016 was considered average in terms of precipitation (Fig. 2a and b, Online Resource 7). The forested watershed in RI was the only site that was characterized by wetter conditions in 2016, and we observed higher DOC and $NO_3^-$–N fluxes in 2016 than in 2015 at that site.

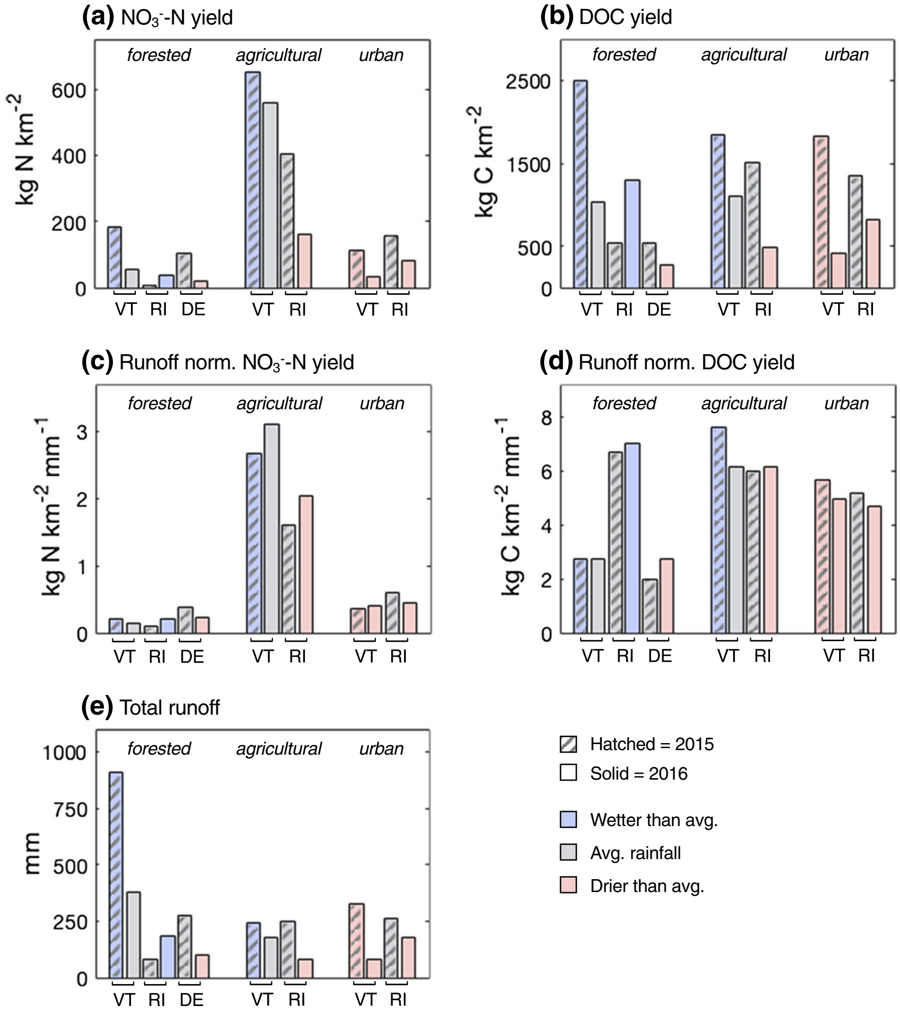



**Fig. 2** Cumulative $NO_3^-N$ **a** and DOC yields **b**, runoff normalized $NO_3^-N$ **c** and DOC yields **d**, and total runoff **e** from forested, agricultural, and urban watersheds in Vermont (VT), Rhode Island (RI), and Delaware (DE) for the monitoring periods in 2015 (hatched bars) and 2016 (solid bars). Blue bars are wetter than average years that received higher than average amounts of rainfall, while red bars are dry years that received lower than average amount of rainfall (Online Resource 3). Grey bars indicate years with average rainfall. Data used in this figure are provided in Online Resource 7 for further reference

## Effects of land use and hydrologic variability on the timing of $NO_3^-$–N and DOC yield

### *Forested watersheds*

Despite differences in the total amount of DOC or $NO_3^-$–N exported from forested watersheds (between states and in wet vs. dry years), there were strong similarities in the timing of export across the forested sites in all three states. Specifically, these results highlight the importance of early season fluxes to the annual cumulative flux budget in forested watersheds, particularly for $NO_3^-$–N. Even in non-snowmelt dominated sites like DE, the early season fluxes contributed up to ~ 50–75% of annual $NO_3^-$–N fluxes (Fig. 3). Wade Brook in VT, a strongly snowmelt dominated system, showed a similar trend where ~ 75% of measured $NO_3^-$–N export occurred prior to leaf-on (mid-May) in 2015 and 2016.

Regional similarities in the temporal structure of forested $NO_3^-$–N and DOC export were confirmed by the function fitting analysis (Fig. 1, Fig. 3). Across the forested sites, the cumulative DOC and $NO_3^-$–N yield time series were best fit with saturating functions that capture the importance of early spring runoff for cumulative DOC and $NO_3^-$–N fluxes (Table 2). There were three instances that were best fit by either piecewise functions or efficiency loss functions (RI 2016 DOC and NO3, DE 2016 DOC), and these exceptions to the broad trend will be discussed in more detail later.

$NO_3^-$–N and DOC export displayed different behavior relative to water export across all three forested sites. Cumulative $NO_3^-$–N$NO_3^-$–N export tended to outpace water export, whereas DOC closely tracked or lagged behind cumulative water export (Fig. 3). $NO_3^-$–N and DOC in both DE and VT were characterized by this leading/lagging behavior, which were also the sites that showed the greatest early season contributions to cumulative annual fluxes.

In DE and VT, the timing of the spring $NO_3^-$–N pulse and subsequent plateau in $NO_3^-$–N export coincided quite closely with the emergence of leaves in the forested ecosystem. In VT, the cumulative $NO_3^-$–N export time series displays a sharp break in slope in early May (Julian day 120–130) when leaves are emerging in the terrestrial ecosystem. DE is also characterized by a break in slope following the emergence of leaf out, but the transition into the mid-summer plateau is more gradual.

The temporal DOC and $NO_3^-$–N export patterns in RI were less consistent from year to year (Fig. 3). Cumulative DOC and $NO_3^-$–N yield in 2015 was driven largely by mid-season fluxes (mid-May to June) and both DOC and $NO_3^-$–N export were best represented by a saturating function (Fig. 3, Table 2). In contrast, DOC and $NO_3^-$–N fluxes in 2016 were largely driven by late-season contributions following litterfall in mid-Oct and were best fit by a piecewise combination of saturating and linear functions (Fig. 3, Table 2).

### *Urban watersheds*

The urban systems in RI and VT were characterized by a cumulative flux pattern unlike the forested or agricultural sites. These sites were characterized by low seasonal variability in DOC and $NO_3^-$–N export, which is evidenced by the quasi-linear slopes of the cumulative C, N, and Q time series (Fig. 4) and the function fitting analysis. Cumulative DOC and $NO_3^-$–N export time series from both RI and VT were best fit by quasi-linear efficiency loss functions (Table 2). Despite variability in the pattern of 2016 N export in RI, we observed low regional variability in urban DOC and $NO_3^-$–N export and found that the temporal patterns of DOC and $NO_3^-$–N export were very similar across the urban sites in RI and VT.

### *Agricultural watersheds*

In general, the agricultural cumulative export dynamics displayed the most interannual and cross-site variability (Fig. 5). Among the agricultural sites, we observed marked differences in the timing of DOC and $NO_3^-$–N export in RI and VT. In RI, autumn contributions were the dominant driver of cumulative DOC and $NO_3^-$–N export (Fig. 5), with 50-75% of DOC and $NO_3^-$–N fluxes occurring during the post-harvest period in 2015 and 2016. This temporal pattern was best fit using an exponential function that captured the late season contributions (Table 2).

In VT, late spring and early summer contributions dominated annual fluxes. DOC and $NO_3^-$–N fluxes from mid-Apr through July contributed up to of 75% of cumulative fluxes (Fig. 5). Cumulative DOC and $NO_3^-$–N fluxes from the VT agricultural system were best fit by a saturating function in 2015, but a quasi-linear function in 2016 when post-leaf off nutrient export was a greater component of annual fluxes. Unlike the forested sites, $NO_3^-$–N and DOC export from both agricultural sites closely tracked cumulative runoff, and were highly correlated with cumulative water export.

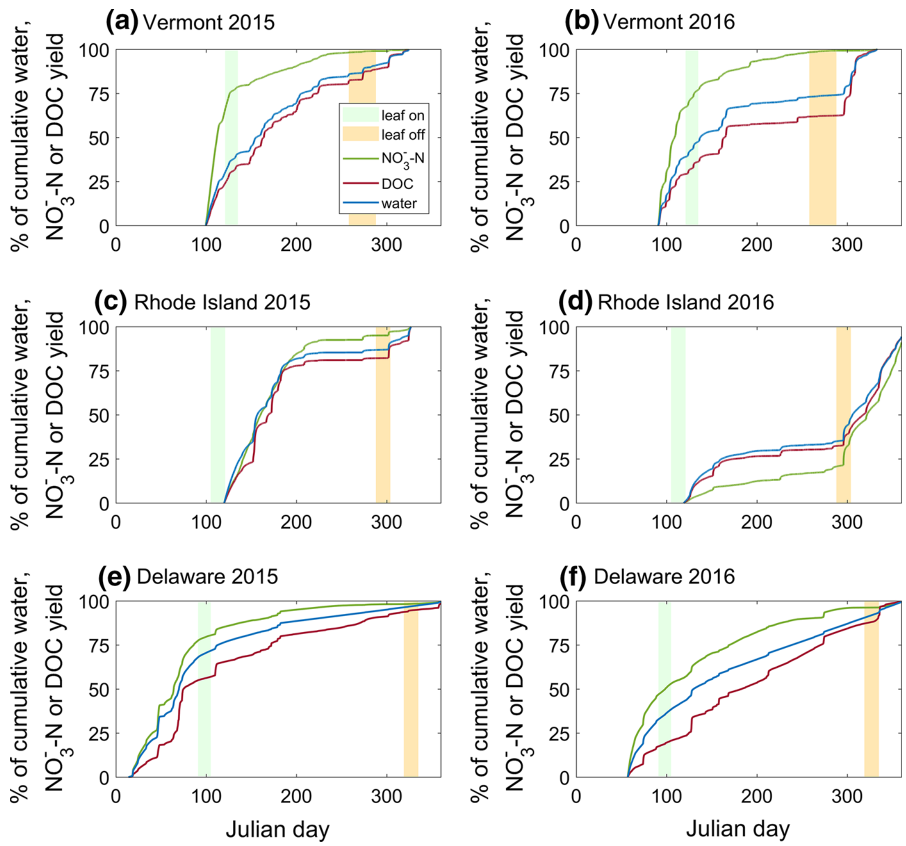
## Discussion

Our results show that both hydrologic variability and land use have strong effects on the balance of supply and transport control over nutrient export from watersheds, and that this interaction led to consistent patterns of solute export from catchments of a given land use across the northeastern US. We found that combining high-frequency biogeochemical and hydrologic time series within a supply-transport fra allowed for identification of the controls on solute export and characterized sources of temporal and regional variability. We also found this framework useful for understanding the potential impacts of climate change on DOC and $NO_3^-$–N export, and identified that changes in the distribution of precipitation across the northeastern US may lead to significant changes in the balance of supply versus transport control from catchments of all land uses.

### Question 1: Interannual variability in DOC and $NO_3^-$–N yields

The first objective of our study sought to determine how the total magnitude of DOC and $NO_3^-$–N export varied in relation to (1) land use and (2) hydrologic

**Fig. 3** *Forested export*: Normalized cumulative DOC (red), $NO_3^-$–N (green), and water (blue) yield from forested watersheds in Vermont (**a**, **b**), Rhode Island (**c**, **d**) and Delaware (**e**, **f**). Periods of leaf emergence and litterfall are highlighted in green and orange boxes, respectively




variability (e.g. interannual variability in precipitation). Indeed, there were strong differences in total DOC and $NO_3^-$–N export across land use classes, and in response to variable hydrologic forcing (Fig. 2). These findings are consistent with previous studies that have shown land use is a strong determinant of DOC and $NO_3^-$–N export (Howarth 2008; Wilson and Xenopoulos 2009). As hypothesized, we observed the greatest $NO_3^-$–N export from agricultural and urban systems, consistent with studies that have shown elevated $NO_3^-$–N export from managed systems (Basu et al. 2011).

These results are made most clear by the runoff-normalized yield metrics (Fig. 2c and d). The runoff-normalized DOC or $NO_3^-$–N yield represents the relative capacity of the watershed to export constituents independent of inter-annual variability in runoff. Despite interannual variability in total runoff and total DOC and $NO_3^-$–N yield, the runoff-normalized yield values for a given watershed were consistent from year to year (Fig. 2c and d). This suggests that for a given watershed and land use class, the amount of $NO_3^-$–N and DOC exported per unit of streamflow will be relatively constant or chemostatic on an annual basis (Basu et al. 2010). We hypothesize that this is due to proportional activation of legacy nutrient source areas; as watersheds wet up, they activate greater source areas (Dunne and Black 1970; Walter et al. 2000), but the activation of new sources is proportional to the amount of runoff generated (Godsey et al. 2009). This also suggests that overall, many of these watersheds are transport limited (Zarnetske et al. 2018) as sources in the watershed are not depleted under higher rainfall/runoff conditions (which would lead to decreasing runoff-normalized yields in high flow years). These results from low-order watersheds in the northeastern US are in agreement with a growing body of work that has documented widespread biogeochemical stationarity in nutrient loads from managed catchments (Basu et al. 2010; Thompson et al. 2011).

We also saw consistent trends in runoff-normalized export across land use classes, with the greatest runoff-normalized yields from agricultural and urban

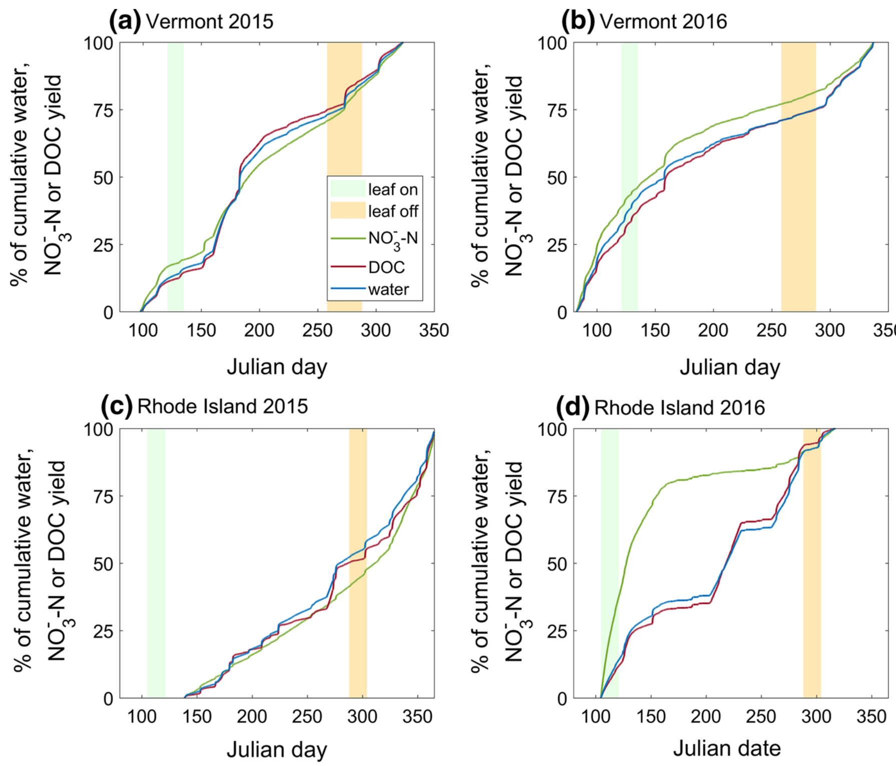



**Fig. 4** *Urban export*: Normalized cumulative DOC (red), $NO_3^-$–N (green), and water (blue) yield from urban watersheds in Vermont (**a**, **b**) and Rhode Island (**c**, **d**). Periods of leaf emergence and litterfall are highlighted in green and orange boxes, respectively. Periods of leaf emergence and litterfall are highlighted in green and orange boxes, respectively

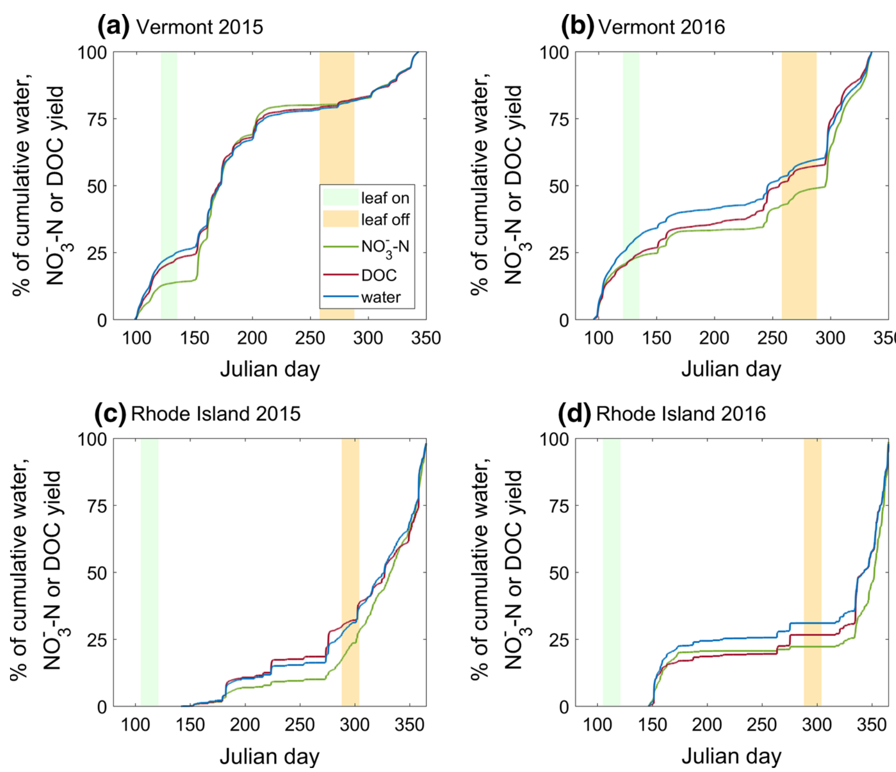



**Fig. 5** *Agricultural export*: Normalized cumulative DOC (red), $NO_3^-$–N (green), and water (blue) yield from agricultural watersheds in Vermont (**a**, **b**) and Rhode Island (**c**, **d**). Periods of leaf emergence and litterfall are highlighted in green and orange boxes, respectively

watersheds (Fig. 2c and d). This is consistent with studies that have identified anthropogenically influenced landscapes as the greatest sources of DOC and $NO_3^-$–N to downstream waters (Galloway et al. 2004; Broussard and Turner 2009). The only exception to this result was the forested RI site, which had higher runoff-normalized DOC yields than the agricultural or urban sites in RI. This site experienced a gypsy moth infestation during the summer of 2016 that led to substantial defoliation of the forest canopy and perturbations to carbon and nitrogen cycling in subsequent years (Addy et al. 2018), and we posit that this disturbance may explain the higher runoff-normalized DOC yields.

While there were broadly consistent differences in runoff-normalized cumulative yields and total export across land use classes, we still observed a great deal of variability from year to year in the amount of total DOC and $NO_3^-$–N export from forested, agricultural and urban watersheds (Fig. 2a and b). In some cases, the magnitude of variability observed between the two focal years of this study (e.g. 2015 vs. 2016 forested export in VT) obscured clear differences between land uses (e.g. VT forested vs. VT urban). These results confirm that hydrologic drivers are one of the dominant factors determining the magnitude of DOC and $NO_3^-$–N export. We found that the year-to-year variation in DOC or $NO_3^-$–N export within a given site was explained by whether that year was wetter or drier than the long-term average conditions (Fig. 2). This agrees with other studies conducted on event or seasonal that have documented the importance of snowmelt, rain events and other hydrologic events as a driver of nutrient mobilization and flushing from the terrestrial landscape (Boyer et al. 2000; Ågren et al. 2010; Perdrial et al. 2014). The results from our multi-year time series show that interannual variation in DOC and $NO_3^-$–N export may be explained by these same hydrologic drivers.

This has significant repercussions for the mobilization of solutes under a changing climate. The northeastern US is predicted to experience changing precipitation regimes, with warmer, wetter winters, less persistent snow cover, and greater frequency of heavy precipitation throughout the year (Horton et al. 2014). As we observed in VT, a wetter than average year in 2015 led to $NO_3^-$–N export from our forested site that exceeded $NO_3^-$–N export from our urban watershed. This suggests that changes to the precipitation regime across the northeastern US could lead to elevated export from natural systems and could even bring forested export into the range of managed systems, effectively masking the effects of land use on the magnitude of export.

These results suggest that land use and climate (specifically hydrologic variability) represent a hierarchy of controls on nutrient loading. LULC determines the magnitude of source areas (both the spatial extent and relative size of nutrient pools) and sets a range of potential DOC or $NO_3^-$–N export for a given LULC class, whereas hydrologic variability controls the degree to which these source areas are activated and the amount of transport that can occur (Basu et al. 2010). We found that runoff normalized yields for a given watershed and land use were consistent across wet and dry years during this study, but this may not be the case under a consistently wetter climate. Changes to the climate, and specifically acceleration of hydrologic drivers, have the potential to mobilize greater amounts of solutes from watersheds of all land use types in the short term, but the long-term ability of watersheds to continue functioning in a transport controlled way is unknown. It is possible that over a longer period and given stable land use, these systems could experience shifts from transport to supply controlled flux regimes. However changes to either control (LULC or hydrologic variability) will have cascading impacts on nutrient mobilization, and changes to both will lead to non-linear behavior in watershed responses.

### Q2: Effects of land use on timing of DOC and $NO_3^-$–N export

The second objective of our study was to assess the influence of land use on the timing of DOC and $NO_3^-$–N export, and where possible, understand the processes governing solute supply and transport. We found that despite variation in the amount of total export across sites, there were coherent and consistent patterns in the timing of export within forested, agricultural, and urban sites over the two monitoring years, irrespective of interannual variability in hydrologic forcing. Furthermore, there were regional similarities in solute export patterns from urban and forested watersheds across the region, suggesting that the mechanisms driving export remain consistent but are activated to varying degrees over time.

Conversely, the two agricultural sites had site-specific differences in temporal solute export dynamics, suggesting that watershed-specific processes likely control solute export in agricultural watersheds.

### Forested watersheds

In the forested watersheds, early season runoff from snowmelt and winter/spring rain was the most important driver of both DOC and $NO_3^-$–N export. The importance of the spring flush was especially critical for $NO_3^-$–N; between 50 and 75% of $NO_3^-$–N was exported from the forested watersheds in DE and VT before the emergence of leaves in early to mid May (Fig. 3). This highlights the role of snowmelt and spring runoff as an important control point (Bernhardt et al. 2017) for $NO_3^-$–N and potentially other solutes, which is consistent with previous studies in the northeastern US (Pellerin et al. 2011). The spring flush was a less dominant component of annual DOC export, but still contributed 25 and 50% of annual yield during this relatively short period of time (Fig. 3). We hypothesized that the cumulative export of $NO_3^-$–N and DOC would be best fit with a saturating function that quantified the dominance of the spring flush period for solute mobilization. With a few exceptions that we will discuss later, we found that this was broadly true in our forested watersheds (Table 2). This suggests that there is strong regional coherence in the timing of DOC and $NO_3^-$–N export (with respect to the timing of snowmelt and leaf-out dates at each site), and perhaps most interestingly that there may be similar mechanisms explaining DOC and $NO_3^-$–N mobilization in forested landscapes across the northeastern US. However, as climate change alters the timing of snowmelt or spring precipitation, we may see a regional divergence in this consistent pattern (e.g. shifts in export to earlier Julian dates) as watersheds across the northeast respond to altered hydrologic drivers.

These results are consistent with the idea that forested systems are poised in early spring for large export events (Boyer et al. 2000; Laudon et al. 2004). Over the winter, solutes like DOC and $NO_3^-$–N can accumulate in the soils (Brooks et al. 1998, 2011) and remain stored there because of low connectivity between soils and streams (due to colder temperatures and the prevalence of water stored in snow; Jencso et al. 2009). As temperatures warm, this pool of resources is available for mobilization, and during early spring the amount of export to streams and downstream waters is largely transport controlled (Fig. 1a; Andrews et al. 2011; Raymond et al. 2016). As the system moves into early summer and leaves begin to emerge, that pool of $NO_3^-$–N begins to be depleted, export declines and the system becomes supply controlled (Fig. 1a). The results of this study are notable because they suggest a high degree of regional coherence in this pattern, and indicate that this phenomenon is widespread across forested ecosystems in the northeastern US, despite differences in the form and distribution of winter precipitation and forest composition that are driven by latitudinal and elevation differences between the forested watersheds (Table 1).

The observed shift from transport into supply control at these forested sites may have an ecological dimension. In both DE and VT, this transition between potential transport and supply control of $NO_3^-$–N coincides with the emergence of leaves. This may be a sign of terrestrial plant uptake as trees and vegetation begin utilizing nitrogen to grow and photosynthesize (Zak et al. 1990). If that is the case, then the timing of this export regime transition may be sensitive to changing phenology of leaf-on dates in response to climate change. If warming temperatures allow leaves to emerge earlier, then we may see an earlier shift in the transition from transport to supply controlled. Alternately, if snowmelt occurs earlier or there is a shift towards more winter rainfall and less snowpack accumulation (but no change in the timing of leaf emergence), then we may see elevated $NO_3^-$–N export earlier in the season and a reduction in the available pool of $NO_3^-$–N for plant consumption later in the spring. These asynchronies in hydrologically driven fluxes and vegetation or soil biogeochemical responses could have cascading effects on soil N resources and ultimately forest productivity (Groffman et al. 2012).

These results are consistent with studies that suggest forested $NO_3^-$–N export will be highly sensitive to changes in the timing of snowmelt (Sebestyen et al. 2009), the partitioning of winter precipitation as rain or snow (Casson et al. 2012), and differential changes in the phenology of plant and microbial nutrient uptake (Groffman et al. 2012). Because DOC export in the forested catchments was less dominated by the spring flush signal than $NO_3^-$–

N (Fig. 3), it may be less sensitive to changes in winter precipitation and spring snowmelt, and instead be more sensitive to changes in summer precipitation (increased storminess, frequency of fall storms, etc.). This could lead to important changes in the stoichiometry of downstream DOC and $NO_3^-$–N export, as the export of these two solutes becomes decoupled and responds to changes in precipitation patterns differently. Given the findings from this study, we hypothesize that if snowmelt occurred earlier in the year, we may observe export with a reduced C:N ratio (similar DOC export and elevated $NO_3^-$–N export) early in the season but an increasing C:N as $NO_3^-$–N is depleted and DOC continues to be exported on an event scale. We compared the DOC:$NO_3^-$–N ratio of cumulative export for the forested sites in VT and DE (which differ in the degree of snowmelt influence), and found that the molar DOC:$NO_3^-$–N ratio of export in VT increased from ~ 3.5 to 14 over the monitoring period, while the ratio for DE was more consistent throughout the year (~ 2–5), lending preliminary support the idea that climate change driven changes to snowmelt might alter the stoichiometry of nutrients exported to downstream waters (Online Resource 8). Furthermore, changes in the timing and stoichiometry of nutrient export to downstream waters may have cascading implications on lake productivity (Isles et al. 2017).

The greatest deviation in the forested response was observed in RI in 2016. This year was best fit with a piecewise function that captured the distinct transition in cumulative export that occurred in mid-October (Fig. 3). In 2016, this site experienced a drought-induced gypsy moth infestation that defoliated the canopy in July (Addy et al. 2018), and may have allowed nutrients to accumulate in soils in the absence of tree uptake. Following this very dry summer, the site received significant amounts of fall precipitation that likely resulted in flushing of terrestrial DOC and $NO_3^-$–N, which drove the cumulative yield pattern for that year (Fig. 3). This again highlights the important role of hydrologic and ecological forcing (or the lack thereof) in determining nutrient export. Increased storminess or increased droughts punctuated by rainy periods will also have a significant impact and will lead to shifts in the timing of export, highlighting the vulnerability of forested ecosystems to these changes (Loecke et al. 2017).

### Urban and agricultural watersheds

In contrast to forested sites, the urban watersheds were characterized by a different temporal pattern in annual loading. The two urban sites monitored in this study had quasi-linear DOC and $NO_3^-$–N export over the monitoring period and were best fit with quasi-linear efficiency loss functions (Fig. 1b, Fig. 4). We propose that these unique export dynamics are driven by balanced degrees of solute supply and transport throughout the year. Urban watersheds are highly engineered systems that are designed to move water and solutes off the landscape quickly and efficiently. Rainfall/runoff moving through the system will have more limited interaction with reactive soil zones and biota (e.g. vegetation) and faster transport through the system (Bernhardt et al. 2008), and greater interaction with anthropogenic N and C sources in the built environment (Paul and Meyer 2001). Numerous studies have shown urban system to be “flashy” and highly responsive to rain events (Walsh et al. 2005). We suggest that over the time scale of a water year, this short-term responsiveness or flashiness leads to a balanced supply of solutes and rapid transport out of the system (Fig. 1b). Unlike forested systems that temporally disaggregate solute accumulation and export (e.g. accumulation of solutes and water during the winter that flush out in the spring/summer), urban systems do this consistently throughout the year. We propose that this temporal “evening out” of the biogeochemical and hydrologic cycles in urban systems represent an additional facet of urban homogenization (Kaye et al. 2006; Groffman et al. 2014), where natural seasonality in biogeochemical cycling can be overwritten by the engineered dynamics of urban systems.

Unlike the regional similarities we observed in forested and urban export (Figs. 3 and 4), the agricultural systems in VT and RI were characterized by separate, unique patterns of DOC and $NO_3^-$–N export (Fig. 5). Cumulative DOC and $NO_3^-$–N export from the watersheds in RI were consistently characterized by an exponential function, which capture the importance of late season contributions to annual yields in this system. This is consistent with studies that shown greater carbon and nutrient release from agricultural soils following fall harvest and tillage practices (McLauchlan 2006). The VT watersheds were best fit with different classes of functions in 2015 and 2016.

In 2015 (a wetter than average year), cumulative DOC and $NO_3^-$–N yields were best fit with saturating functions, but in 2016 (an average precipitation year) they were best described with a quasi-linear efficiency loss model. This highlights that the timing of export varied significantly from year to year in response to variable precipitation inputs, which are likely to impact solute supply via decisions about the timing of nutrient amendment and harvest (which are often mediated by antecedent and forecast weather and soil moisture regimes). It is not surprising that the cumulative yield dynamics are quite different between the agricultural sites, where Hungerford Brook (VT) is dominated by a few relatively large dairy, hay and corn operations, while Maidford Brook (RI) in a mixture of vineyards, row crops and nurseries.

We propose that the complexity in the temporal patterns of export from site to site and between years is a function of the complexity of these managed landscapes (Fig. 1c). Within a given landscape, nutrient export is a function of recent nutrient additions (if applicable) and historical/legacy nutrient additions. This means that export may be responsive over short time scales as mobile fractions (e.g. recently applied manure) are mobilized and transported, but can also reflect the signature of legacy solute pools in the landscape (e.g. legacy GW or soil N). In both cases, the extent to which those contemporary or legacy pools are activated is in part controlled by the magnitude of precipitation and runoff generated on the landscape. Thus, export dynamics will be a function of the land use legacies and unique management, governance and farming practice–specific conditions that are present in any watershed where agricultural practices are the dominant land use and driver of nutrient export. It is therefore likely that there are numerous temporal solute export dynamics that could be observed in agricultural watersheds that will depend on the dominant agricultural practices governing the watershed and the legacies of nutrient accumulation in these landscapes (Van Meter et al. 2018).

One similarity across the two agricultural sites and the urban sites was a strong coupling between water and solute export. In both the agricultural and urban sites, DOC and $NO_3^-$–N export was tightly correlated with runoff (Figs. 4 and 5), suggesting that this synchronization of the hydrologic and biogeochemical fluxes through these systems is a characteristic of engineered landscapes (Basu et al. 2011). In agricultural systems as well as urban systems, the landscape is modified to accelerate the movement of water through surface and subsurface flowpaths. This suggests that the opportunity for soils and riparian areas to modulate the magnitude of export (by acting as a solute sink or dampening export) is more limited. As such, the timing and form of solute export becomes tightly coupled to runoff, as the retention capacity of the watershed is effectively short-circuited.

## Conclusions

This study used a unique 2 year, regional data set to identify the important interactions between LULC and hydrologic variability that control the timing and magnitude of DOC and $NO_3^-$–N export across broad regional scales. Specifically, we found that:

- Leveraging high-frequency biogeochemical and hydrologic time series of cumulative solute export dynamics in a supply-transport framework is an effective approach for understanding linkages between climate and land-use as drivers of temporal variability in solute export. The temporal export patterns presented in this paper are not an exhaustive typology of export regimes, and we propose that these may vary across land uses and climate regimes. But we posit that the approach presented here provides a method for quantifying differences and deviations in controls across sites and between solutes.
- DOC and $NO_3^-$–N export varied systematically as a function of land use type, with the greatest export from managed watersheds (urban and agricultural). Hydrologic drivers (e.g. the magnitude of precipitation and streamflow) were critical variables that co-varied with interannual variability in DOC and $NO_3^-$–N export across all land use types.
- The timing of DOC and $NO_3^-$–N export varied systematically across the three focal land use classes; forested export was characterized by a strong "spring flush" signal and transition from transport to supply control as trees leaf out, suggesting that these systems may be highly sensitive to climate change. In contrast, export from urban systems was "homogenized" throughout the year and represented rapid but balanced

solute supply and transport. Agricultural DOC and $NO_3^-$–N export was not characterized by a single temporal pattern, likely as a result of the numerous management decisions that may vary from watershed to watershed. We also observed that the highly managed systems like agricultural and urban watersheds showed a synchronization of hydrologic and biogeochemical fluxes as a function of draining the landscape and short-circuiting the terrestrial system.

- Watershed DOC and $NO_3^-$–N export from all land uses is likely to be highly sensitive to changes in climate, especially the amount and timing of rainfall and snowmelt. Climate-driven changes to the distribution of precipitation have the potential to alter both the total amount of export (e.g. mask differences in total export across watersheds of different land uses), and the timing and synchronicity of DOC versus $NO_3^-$–N export to downstream ecosystems.

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