JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 114, G02002, doi:10.1029/2008JG000778, 2009

Responses of stream nitrate and DOC loadings to hydrological forcing and climate change in an upland forest of the northeastern United States

Stephen D. Sebestyen,[1] Elizabeth W. Boyer,[2] and James B. Shanley[3]

Received 6 May 2008; revised 30 October 2008; accepted 14 January 2009; published 7 April 2009.

[1] In coming decades, higher annual temperatures, increased growing season length, and increased dormant season precipitation are expected across the northeastern United States in response to anthropogenic forcing of global climate. We synthesized long-term stream hydrochemical data from the Sleepers River Research Watershed in Vermont, United States, to explore the relationship of catchment wetness to stream nitrate and DOC loadings. We modeled changes in growing season length and precipitation patterns to simulate future climate scenarios and to assess how stream nutrient loadings respond to climate change. Model results for the 2070–2099 time period suggest that stream nutrient loadings during both the dormant and growing seasons will respond to climate change. During a warmer climate, growing season stream fluxes (runoff +20%, nitrate +57%, and DOC +58%) increase as more precipitation (+28%) and quick flow (+39%) occur during a longer growing season (+43 days). During the dormant season, stream water and nutrient loadings decrease. Net annual stream runoff (+8%) and DOC loading (+9%) increases are commensurate with the magnitude of the average increase of net annual precipitation (+7%). Net annual stream water and DOC loadings are primarily affected by increased dormant season precipitation. In contrast, decreased annual loading of stream nitrate (−2%) reflects a larger effect of growing season controls on stream nitrate and the effects of lengthened growing seasons in a warmer climate. Our findings suggest that leaching of nitrate and DOC from catchment soils will be affected by anthropogenic climate forcing, thereby affecting the timing and magnitude of annual stream loadings in the northeastern United States.

Citation: Sebestyen, S. D., E. W. Boyer, and J. B. Shanley (2009), Responses of stream nitrate and DOC loadings to hydrological forcing and climate change in an upland forest of the northeastern United States, *J. Geophys. Res.*, *114*, G02002, doi:10.1029/2008JG000778.

1. Introduction

[2] Human activities alter the global cycling of nutrients, influence climate [*Watson et al.*, 2001], and affect the flow of water and solutes through landscapes [*Vitousek et al.*, 1997; *Boyer et al.*, 2002; *Milly et al.*, 2005; *Perakis and Hedin*, 2007]. Because water flow through the environment transports solutes from terrestrial source areas [*Hornberger et al.*, 1994], stream chemistry is linked to climate and the landscape processes that control the flow of solutes from riparian and upland source areas to surface waters. If the frequency and magnitude of solute fluxes from terrestrial source areas to receiving waters change due to anthropogenic forcing of climate, stream nutrient loadings may also change.

[3] With climate change, streamflow may increase in regions where precipitation is expected to increase due to the intensification of the hydrological cycle [*Labat et al.*, 2004; *Milly et al.*, 2005; *Gedney et al.*, 2006; *Huntington*, 2006; *Hayhoe et al.*, 2007; *Piao et al.*, 2007]. In a recent assessment of climate and hydrology for the northeastern United States, *Hayhoe et al.* [2007] concluded that regional climate change during the next century will lead to higher annual temperatures, earlier peak streamflow from snowmelt, increased growing season length, and increased winter precipitation. Already, streamflow patterns across the northeastern United States have changed because precipitation amount has increased in the latter half of the 1900s and snowmelt currently occurs earlier in the year relative to past decades [*McCabe and Wolock*, 2002; *Hodgkins et al.*, 2003; *Huntington*, 2003; *Hodgkins and Dudley*, 2005].

[4] During large storm events, flow path routing changes, upland and riparian source areas hydrologically connect to streams, and stream chemistry may dramatically change [*Mulholland*, 1993; *Hornberger et al.*, 1994]. Precipitation transiently saturates source areas in surficial soils that are enriched in dissolved nutrients. When hydrological connections develop, stream nitrogen and organic matter loadings

---

[1] Northern Research Station, Forest Service, U.S. Department of Agriculture, Grand Rapids, Minnesota, USA.

[2] School of Forest Resources, Pennsylvania State University, University Park, Pennsylvania, USA.

[3] U.S. Geological Survey, Montpelier, Vermont, USA.

0148-0227/09/2008JG000778$09.00

may disproportionately increase if mobile nitrogen and organic carbon are leached from surficial source areas [*Hornberger et al.*, 1994; *Boyer et al.*, 1996; *Creed et al.*, 1996]. The frequency, size, and duration of rainfall or snowmelt runoff events as well as the time between events affect the amounts of mobile nutrients that are transported from terrestrial source areas to surface waters.

[5] The amount of water flowing through the catchment and the routing of water flow among different terrestrial flow paths should directly respond to changes in precipitation amount and frequency. Although land use and land cover change may have effects, climate change does not directly affect hydraulic properties such as permeability and transmissivity of particular flow paths. With more frequent and larger storm events, larger amounts of water will be transported along surficial flow paths that preferentially route water and solutes to streams during those events. During the growing season, evapotranspiration strongly influences baseflow, but not the portion that is rapidly routed to streams as stormflow. In highly responsive catchments where streamflow rapidly returns to baseflow within several hours or days after rainfall events, the cumulative effect on seasonal and annual timescales may be a disproportionate increase in stormflow relative to baseflow and increased stream loadings of solutes that are hydrologically flushed to streams from surficial source areas in catchments.

[6] In this study, we consider the effects of climate change and hydrologic intensification on stream loadings of nitrate and dissolved organic carbon (DOC), two ecologically important solutes that are affected by human activities. We collected weekly as well as high-frequency, event-based streamwater samples to quantify how nutrient loadings vary with streamflow at an upland, forested catchment in the northeastern United States. We first quantified how the magnitude and temporal distribution of precipitation inputs affect streamflow and nutrient loadings during events, seasons, and years. We then developed regression-based hydrological models to assess how projected climate change may affect the magnitude of stream water and solute fluxes as precipitation inputs change. By altering precipitation amount and season length, we show how the direction and magnitude of stream nitrate and DOC loadings respond to hydrological forcing under projected climate change scenarios.

2. Site Description

[7] For this analysis, we use the long-term record of streamflow and meteorological data that is collected at the 40.5 ha Watershed 9 (W-9) in the Sleepers River Research Watershed of northeastern Vermont [*Shanley*, 2000]. This mountainous site represents a benchmark catchment because, like much of the northeastern United States, W-9 has a northern hardwood forest, is affected by climate change [*Huntington*, 2006; *Hayhoe et al.*, 2007], and has elevated nitrogen deposition [*Campbell et al.*, 2004]. In the 1960s, seminal studies at Sleepers River identified how source areas of stream water varied during snowmelt and rainfall events, specifically identifying preferential flow of event water via saturation overland flow and shallow subsurface flow paths to streams [*Dunne and Black*, 1970, 1971]. Streamflow recession to baseflow occurs over days to weeks after snowmelt events and over several hours to days after rainfall events. More recent studies have identified how contributions of water and solutes from surficial flow paths control the temporal variation of stream chemistry [*Kendall et al.*, 1995, 1999; *McGlynn et al.*, 1999; *Shanley et al.*, 2002a; *Ohte et al.*, 2004; *Shanley et al.*, 2005; *Sebestyen et al.*, 2008].

[8] Northeastern Vermont has a continental climate and the temperature range at W-9 is −30° to 30°C with an annual mean of 4.6°C. Twenty to 30% of the precipitation accumulates as snow from December until snow melts in March or April [*Shanley and Chalmers*, 1999; *Shanley et al.*, 2002a]. Although precipitation usually is evenly spread throughout the year, runoff and nutrient loadings are distinctly seasonal due to large snowmelt events [*Shanley et al.*, 2002a, 2002b] and low streamflow when evapotranspiration is highest during warm, humid summers.

[9] At the outlet of W-9, Pope Brook is a second-order tributary of Sleepers River which is in the Connecticut River basin. The elevation of W-9 ranges from 519 to 686 m. Calcareous granulite bedrock forms an impermeable base to a 1- to 3-m regolith of soil and glacial till [*Hall*, 1959]. On hillslopes, a dense basal till is overlain by moderately to excessively well-drained Inceptisols and Spodosols. Histosols have formed in wetlands (about 5% of the catchment area) and riparian areas.

3. Methods

[10] Hydrological and meteorological variables were measured for water years 1965 to 1969 and since 1992. Each water year starts 1 October and ends on 30 September of the water year. Measurements during the 1960s were made by the Agricultural Research Service of the U.S. Department of Agriculture [*USDA*, 1965] and in the 1990s and 2000s as part of the Water, Energy, and Biogeochemical Budgets (WEBB) program of the U.S. Geological Survey [*Shanley*, 2000]. Streamflow was measured at a 120° V-notch weir and discharge was calculated from a stage-discharge relationship according to standard stream gauging protocols [*Rantz*, 1982]. Snow and rainfall amount were measured with a weighing bucket gauge at a meteorological station (R29) in a forest clearing near the stream gauge. At the time of our study, precipitation data were available for water years 1992 to 2004.

[11] In 1991, routine stream chemistry sampling was initiated. For our study, weekly W-9 stream and precipitation chemistry were analyzed for the 1991 to 2005 period. Concentrations of nitrate and DOC were measured by the USDA Forest Service Northern Research Station, Durham, New Hampshire, as documented by *Campbell et al.* [2004]. Hydrochemical dynamics are rarely quantified in ecosystem studies with intensive water chemistry sampling over the entire range of streamflow conditions during hydrological events. To fully characterize hydrochemical responses over an extended time period with high-frequency data, one or more samples were collected on the rise, peak, and fall of storm and snowmelt events between January 2003 and July 2004. Event samples were collected at intervals of minutes to hours or days depending upon the magnitude of streamflow changes. In 2003 and 2004, the intensive sampling included 21 of 23 events and all major events during the 19 months. The two unsampled events were small in magnitude. Other high-frequency samples were occasionally collected before

2002 [*Kendall et al.*, 1995; *Shanley et al.*, 2002a, 2002b] and for several large storm events in 2002 and 2005. Between June 2002 and November 2005, nitrate concentrations were measured by ion chromatography with suppressed conductivity detection and DOC concentrations were measured on total organic carbon analyzers in several laboratories [*Sebestyen et al.*, 2008].

[12] To calculate nitrate and DOC mass loadings, sample concentration was multiplied by the corresponding total runoff in the interval bracketing the sample based on the time midpoint between successive samples. Loadings were linearly interpolated between the sample times and integrated to estimate daily, monthly, seasonal, and water year loadings.

[13] Two components of streamflow (quick flow and baseflow) were separated from total stream discharge using a hydrograph separation method that is based on streamflow recession analysis. We used the recursive digital filter approach that was developed by *Nathan and McMahon* [1990] to calculate quick flow (q_{QUICK}) and baseflow (q_{BASE}) with the equations:

$$q_{QUICK} = \alpha \cdot q_{QUICK-1} + \frac{1+\alpha}{2} \cdot (q_{STREAM} - q_{STREAM-1})$$
$$q_{BASE} = q_{STREAM} - q_{QUICK}$$

where q_{QUICK} is the daily quick flow amount, q_{BASE} is the daily base flow amount, $q_{QUICK-1}$ is the daily quick flow amount on the preceeding day, q_{STREAM} is the daily streamflow, and $q_{STREAM-1}$ is the daily streamflow on the preceeding day. The filter parameter α is 0.94 for W-9 and was calculated according to the *Nathan and McMahon* [1990] method. Quick flow calculated with this approach is an index that quantifies the amount of water that is contributed to a stream in response to rainfall or snowmelt [*Hornberger et al.*, 1998]. At W-9, quick flow represents water that is contributed from preferential surficial flow paths over saturated soils or through surficial soils of upland and riparian areas during stormflow [*Sebestyen et al.*, 2008]. Daily values were summed to calculate seasonal and annual quick flow amounts.

[14] Using statistical software (SPSS Inc.), multiple regression models were developed to quantify seasonal responses of stream water, nitrate, and DOC fluxes to factors that affect catchment wetness. Seasons were defined to reflect the effects of plant growth (May through September) and dormancy (October to April) on evapotranspiration, streamflow, and biogeochemical processes. The dormant season was subdivided to reflect months when rain falls (October to December is the early dormant season) versus months when precipitation accumulates in a snowpack (January to April is the late dormant season). The early and late dormant seasons were modeled separately due to the different hydrological responses between autumn rainfall and spring snowmelt. The early and late dormant season fluxes were summed to estimate total dormant season fluxes. The variables tested for inclusion in the stream runoff and quick flow models were precipitation amount, number of events per season, days since an event, and a categorical season term that distinguishes between snow inputs during the late dormant season and rain inputs during the early dormant and growing seasons. The variables tested for the solute loading models were stream runoff amount, quick flow amount, number of events per season, average days between events, number of quick flow days, and the categorical season term. Seasonal and annual wet deposition of inorganic nitrogen at the R29 meteorological station were additional variables tested for inclusion in the stream nitrate loading model. Variables were added to ($p < 0.05$) or removed from ($p > 0.10$) the regression models using the SPSS stepwise selection method. If significant, sinusoidal terms were added to model cyclical variation of stream runoff, quick flow, and nutrient fluxes [*Cohn et al.*, 1992].

[15] To assess the direction and relative magnitude of climatic change on stream runoff and nutrient loadings at W-9, precipitation inputs were adjusted from the mean of the base period (water years 1992 to 2003). Climate inputs to the model such as change in season length and precipitation amount were obtained from the northeastern United States regional assessment of *Hayhoe et al.* [2007]. To determine future growing season lengths and precipitation amounts for the northeastern United States, *Hayhoe et al.* [2007] downscaled global results from coupled atmosphere-ocean general circulation models in accordance with emissions scenarios that are fully described in the Intergovernmental Panel on Climate Change Fourth Assessment Report WG1 database [*Nakicenovic et al.*, 2000]. Of the three scenarios described by *Hayhoe et al.* [2007] for two time periods (2035 to 2064 and 2070 to 2099), we chose to model the extreme scenarios during those same time periods: B1 is a low greenhouse gas emission scenario and the A1FI is a high emission scenario. During the B1 scenario, global emissions increase until 2050 and then decrease to 1990 levels by 2100. During the A1FI scenario, global greenhouse gas emissions triple from 2000 levels by 2050 and then increase more slowly through 2100. In our model simulations, growing season precipitation patterns were shifted to reflect a longer growing season by moving the date of last frost to earlier in the year and the date of first frost to later in the year to shorten the dormant season, as summarized in Table 1. Precipitation amounts for December, January, and February (DJF) were increased to reflect projected precipitation changes (Table 1). June, July, and August (JJA) rainfall amounts were increased (A1FI 2035 to 2064 scenario), not changed (A1FI 2070 to 2099), or decreased (B1 scenarios) as appropriate for each scenario. The streamflow regression models that calculate runoff and quick flow account for differences in hydrologic responses to precipitation when days are shifted from the dormant season to the growing season when less streamflow occurs per unit precipitation due to high evapotranspiration rates. Results from the streamflow regression models were then input into the nitrate and DOC loading regression models to estimate stream solute loadings under future climate scenarios.

[16] To bracket the expected ranges of variability, we calculated lower and upper bounds in addition to mean values for the climate change scenarios. For the lower bound, precipitation inputs were adjusted from the minimum of the base period during water years 1992 to 2003 and for the upper bound were adjusted from the maximum of the base period.

[17] Seasonal volume-weighted concentrations were calculated for nitrate and DOC by dividing seasonal loadings by the seasonal runoff amount. The mean annual volume-

Table 1. Future Projections of Northeastern United States Climate Conditions for the B1 and A1FI Scenarios in the 2035–2064 and 2070–2099 Periods Relative to the 1961–1990 Base Period[a]

	2035–2064		2070–2099	
	B1	A1FI	B1	A1FI
Winter (DJF) precipitation change	+6%	+16%	+12%	+30%
Summer (JJA) precipitation change	−1%	+3%	−1%	0%
Time change of autumn first frost (days)	+1	+16[b]	+6	+20[b]
Time change in winter/spring last frost (days)	−8	−14[b]	−16	−23[b]

[a] From *Hayhoe et al.* [2007].

[b] Because no data were presented from the A1FI model, the estimates of autumn frost advance and winter/spring frost retreat were substituted from the mid high B2 emissions scenario described by *Hayhoe et al.* [2007].

weighted concentrations from the 1992 to 2003 (base period), 2035 to 2064, and 2070 to 2099 periods were calculated by dividing mean annual loadings by the mean annual runoff amount for each interval.

4. Results and Discussion

[18] Before we present model results that quantify how stream nutrient loadings respond to wetness conditions that are projected to occur with climate change, we first discuss how the relationships between hydrological processes and seasonal variation affect stream nitrate and DOC concentrations and loadings. These relationships suggest that climate change will force seasonal and annual streamflow patterns in ways that will affect future stream nutrient loadings.

[19] During water years 1992 to 2003 when stream chemistry was measured, the annual precipitation ranged from 983 to 1542 mm a^{-1} (mean of 1334 mm a^{-1}) and annual stream runoff ranged from 503 to 1075 mm a^{-1} (735 mm a^{-1}). The ranges were representative of wetness conditions on record since the early 1960s at W-9 (precipitation equal to 983 to 1542 mm a^{-1} and runoff equal to 452 to 1075 mm a^{-1}); see additional information included as auxiliary material (Figure S1).[1] Runoff was highest during March or April of each year when the seasonal snowpack melted. Streamflow was consistently low and least variable during the growing season when evapotranspiration was highest due to plant transpiration and warm air temperatures.

[20] Between water years 1992 and 2005, streamflow ranged from 0.00004 to 3.50 mm h^{-1}. On average, 18 ± 3 events having a minimum quick flow of 1.0 mm per event occurred per year (± standard error, ranging from 10 to 23 events per year). The highest streamflow (2.54 mm h^{-1}) corresponding to a water sample occurred on 31 August 2005 and that stream discharge value had a flow exceedance value of 0.01% (i.e., that stream discharge was exceeded less than 0.01% of the time). At least one sample was collected during six of the ten highest streamflow events on record and peak streamflow was sampled during three of the ten largest events including the second (31 August 2005), sixth (2.46 mm h^{-1} on 21 August 2005), and seventh (2.33 mm h^{-1} on 19 January 1996) highest streamflows. Peak flow was also sampled for all other events from 2002 to 2005 when high-frequency samples were collected.

[21] Baseflow nitrate concentrations typically increased from 10 to 20 μmol L^{-1} during winter and this range is considerably higher than summer baseflow concentrations that ranged from 5 to 10 μmol L^{-1} (Figure 1). Baseflow DOC concentrations were less than 100 μmol L^{-1} throughout the year and did not have a seasonal pattern like baseflow nitrate concentrations. Regardless of season, baseflow nitrate and DOC concentrations were low relative to stormflow. The high-frequency solute concentration data document the hydrological flushing of nitrate and DOC from landscape source areas during stormflow (Figure 1) and showed that the transport of solutes from the landscape was directly related to event magnitude. During events, streamflow increased up to four orders of magnitude, nitrate concentrations increased up to 25-fold, and DOC concentrations increased up to nine fold above pre-event baseflow concentrations (Figure 1). Similar flushing patterns of nitrate and DOC are observed across the northeastern United States [*McDowell*, 1985; *McHale et al.*, 2002; *Inamdar and Mitchell*, 2006; *Mitchell et al.*, 2006].

[22] At W-9, the highest nitrate concentrations were consistently measured during snowmelt runoff events [*Kendall et al.*, 1995; *Shanley et al.*, 2002b; *Ohte et al.*, 2004; *Sebestyen et al.*, 2008]. Stream nitrate concentrations during other stormflow events throughout the year increased in relation to nitrate accumulation in source areas between flushing events, atmospheric deposition during individual events, and the magnitude of peak streamflow during an event [*Sebestyen et al.*, 2008, 2009]. Unlike the highest stream nitrate concentrations that consistently occurred during snowmelt, the highest stream DOC concentrations often occurred during large magnitude, short-duration rainfall-runoff events (Figure 1). Stream DOC concentrations during events were directly proportional to streamflow.

[23] Between water years 1992 and 2003, annual precipitation, stream runoff, stream nitrate loading, and stream DOC loading in the wettest year were about double those of the driest year. The mean annual stream nitrate loading was 158 ± 48 mg m^{-2} a^{-1} (115 to 228 mg m^{-2} a^{-1}), and the mean annual DOC loading was 1309 ± 362 mg m^{-2} a^{-1} (909 to 1919 mg m^{-2} a^{-1}).

[24] Interannual differences in catchment wetness and quick flow magnitude account for the wide range of variation in stream solute loadings. Among years, nutrient loadings during quick flow were 30 to 53% of annual nitrate loadings and 44 to 64% of annual DOC loadings. During the single largest event of any particular year which corresponded to a long duration snowmelt event, 13 to 48% of the annual runoff, 6 to 42% of the annual stream nitrate loadings, and 9 to 48% of the annual stream DOC loading at W-9 occurred during quick flow. The largest stream loadings of nitrate and DOC occurred during the dormant season (Figure 2) due to snowmelt runoff events including rain-on-snow events that were larger in magnitude and longer in duration relative to rainfall runoff events. The relationships between storm events (including snowmelt events) and annual stream nutrient loadings suggest that climate change effects on the frequency and magnitude of storm events will drive future patterns of stream nutrient loadings because event-scale responses control stream runoff and solute loadings (Figure 2). In addition, streamflow responses to precipitation inputs differ among seasons (Figure 3). Because quick flow at W-9

---

[1] Auxiliary materials are available in the HTML. doi:10.1029/2008JG000778.

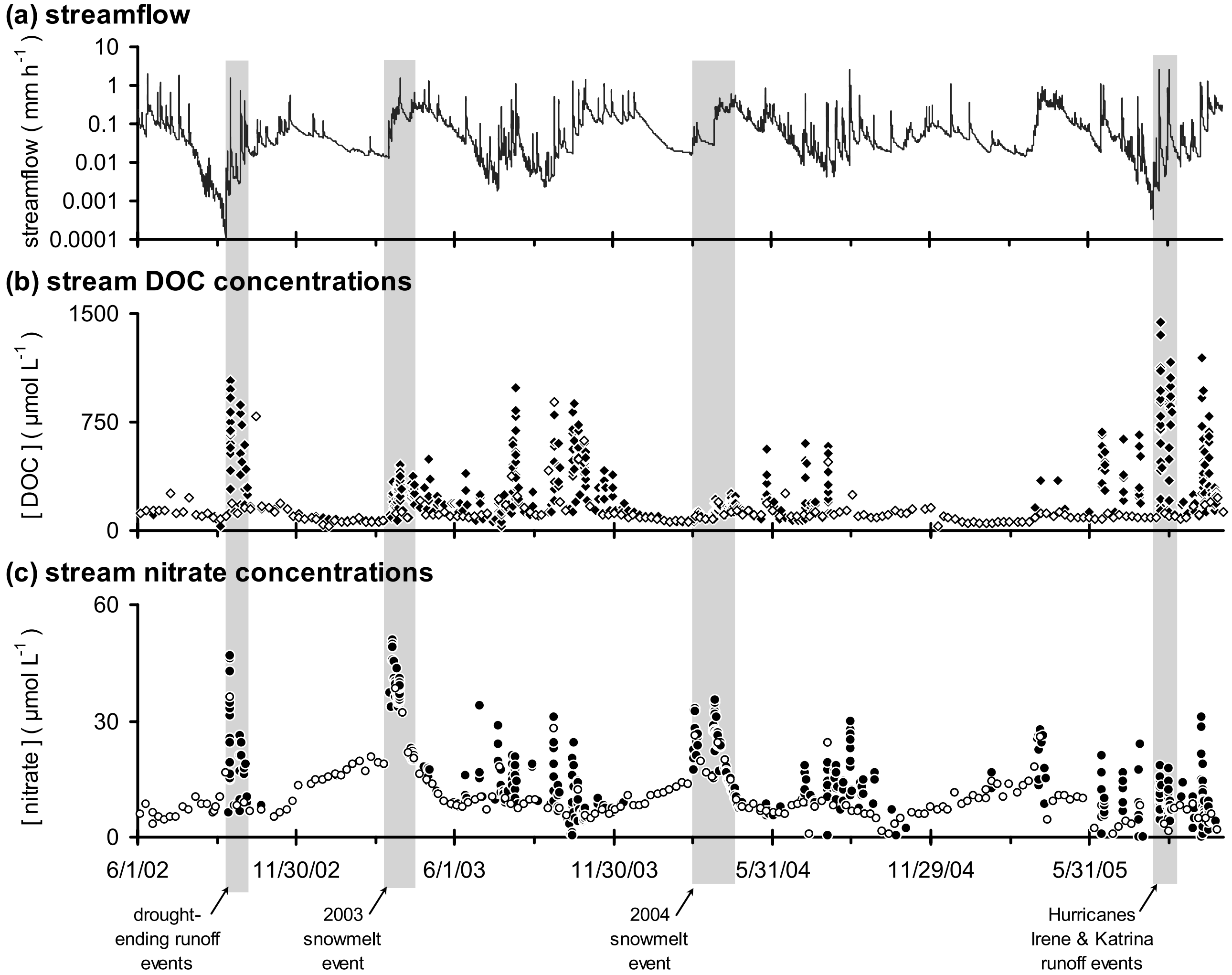


Figure 1. (a) Streamflow, (b) DOC concentrations, and (c) nitrate concentrations during the time when high-frequency samples were collected, June 2002 to November 2005. The solid symbols show samples that were collected at high frequency, and the open symbols show weekly samples. The gray shading highlights some specific hydrological events that had pronounced effects on stream nutrient concentrations.

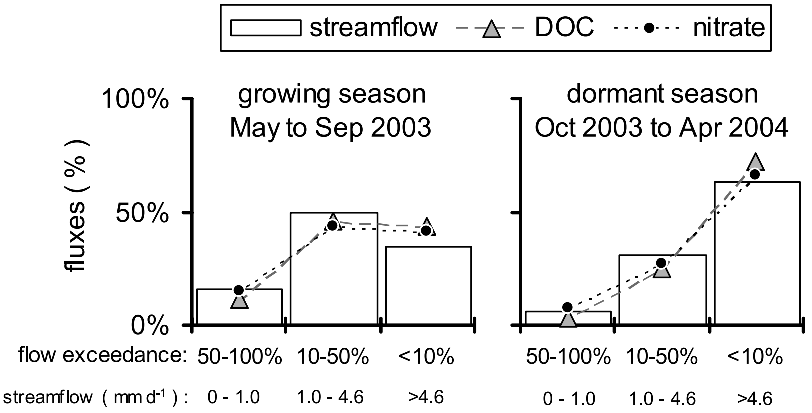


Figure 2. Most water, DOC, and nitrate were exported from the Sleepers River Watershed 9 during large magnitude events. In the dormant season, more than 50% of the water and nutrient fluxes occurred during flow conditions that occurred less than 10% of the time.

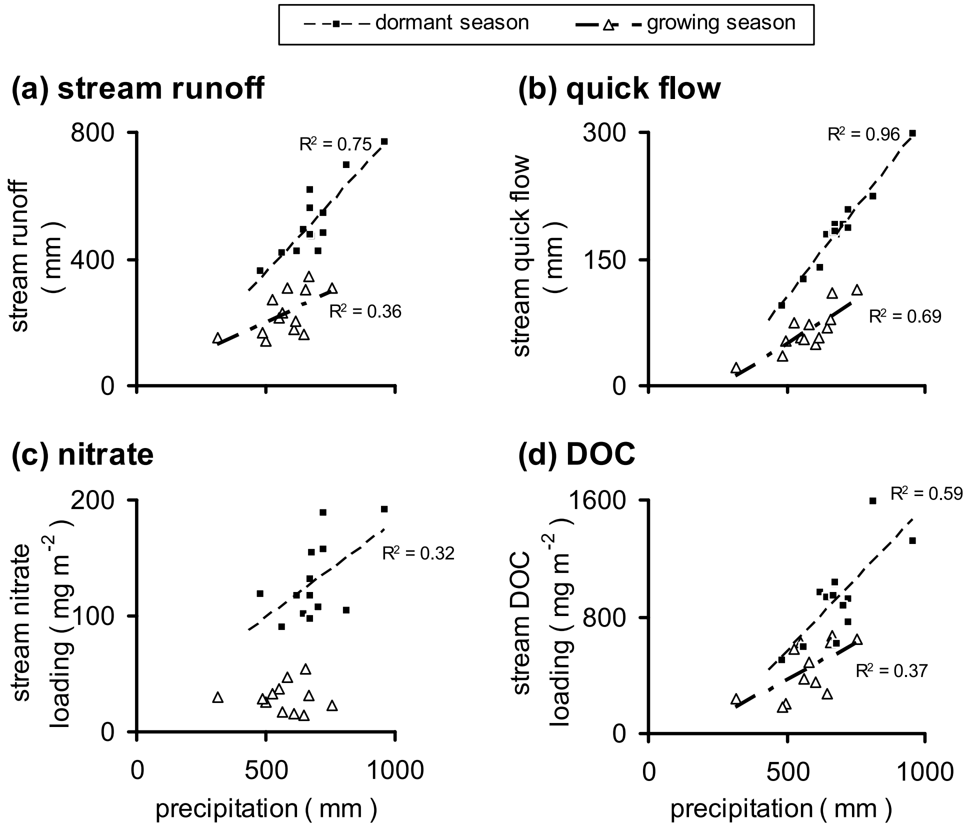


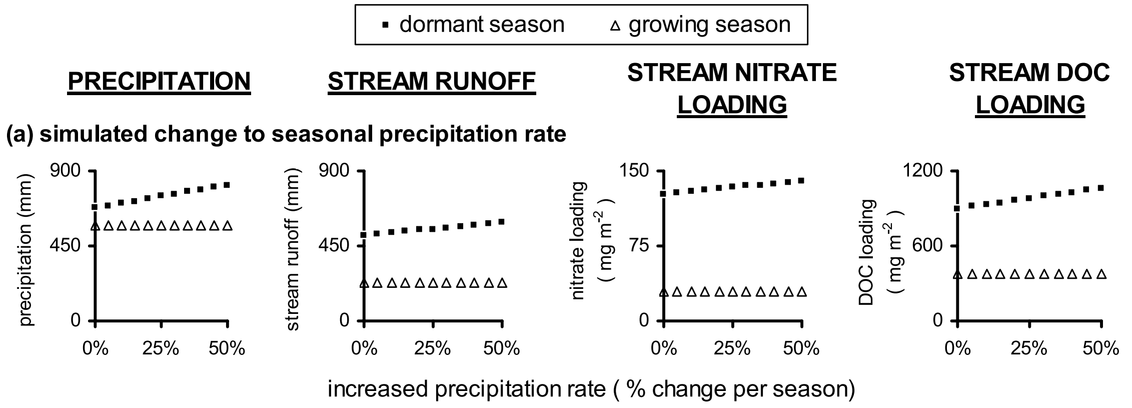
Figure 3. Seasonal stream runoff, quick flow, nitrate, and DOC fluxes versus seasonal precipitation amount for the years 1992–2003. Significant relationships ($p < 0.05$) between precipitation amount and fluxes of (a) stream runoff, (b) quick flow, (c) nitrate, and (d) DOC are shown with the trend lines.

is rapidly routed to streams by variable source area responses [*Dunne and Black*, 1970; *Kendall et al.*, 1999; *Sebestyen et al.*, 2008], evapotranspiration strongly affects baseflow during the growing season but little runoff water is evapotranspired during stormflow events. Therefore, shifts in climate that affect the amount and seasonal distribution of stormflow must be considered to quantify stream runoff and solute loadings.

4.1. Modeled Responses of Stream Nutrient Loadings to Climate Variables

[25] Regression models effectively reproduced the magnitude of seasonal water, nitrate, and DOC fluxes (Figure S2). Seasonal precipitation amount and sinusoidal terms were the only significant variables in the stream runoff ($p \ll 0.0001$) and quick flow ($p \ll 0.0001$) models. These variables explained 88% of the variation in stream runoff and 81% of the variation in quick flow. For nitrate, season (i.e., growing season, early dormant season, and late dormant season), seasonal quick flow amount, and a sinusoidal term were significant in the regression model which explained 87% of the seasonal variation of stream nitrate loading ($p \ll 0.0001$). Seasonal quick flow amount was the only significant term in the DOC model ($p \ll 0.0001$) and explained 91% of the seasonal variation of DOC loading.

[26] Stream nutrient loadings reflect the interaction of hydrological processes that leach and transport nutrients from source areas in the landscape and the biogeochemical processes that regulate nutrient mobility in upland and riparian source areas. Quick flow is a significant term in both models, indicating the importance of terrestrial to aquatic linkages in contributing solutes to surface waters during stormflow. Quick flow and stream runoff covary. Because quick flow was more significant in the nutrient loading models, stream runoff was excluded from the final models as determined using the stepwise regression model selection procedure. The relationship between quick flow and precipitation amount suggests that quick flow through surficial source areas will increase if winter precipitation increases (Figure 3). The additional variables (sine and the categorical season terms) in the nitrate models suggest different controls on solute sources and hydrological transport. These terms reflect a relationship between hydrological and seasonal biogeochemical processes. The hydrological processes encompass event magnitude, the frequency of flushing, and the seasonal effect of evapotranspiration on drying the catchment. During the growing season when high evapotranspiration is more effective at drying the catchment, the responses of stream runoff (Figure 3) and nutrient loading to precipitation are muted relative to the dormant season. For nitrate, plant growth contributes to seasonally low baseflow nitrate loading because high demand for a limited landscape supply constrains nitrogen availability during the growing season, as conceptualized by *Stoddard* [1994].



(b) simulated change to season length

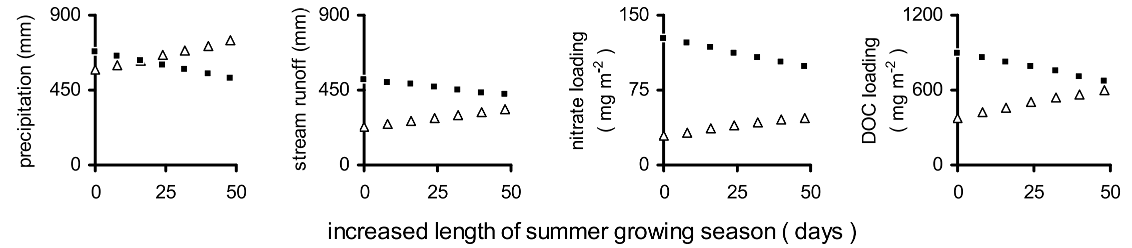


Figure 4. (a) With increased future winter precipitation (December, January, and February), dormant season precipitation and stream water and solute loadings increased. (b) With a longer growing season, model results show that precipitation amounts as well as stream water and solute loadings increase during the growing season and decrease during the dormant season.

4.2. Streamflow and Nutrient Loadings Change Under Projected Climate Change

[27] In the wetter climate scenarios for the time period 2035 to 2099, winter (DJF) average precipitation is projected to increase between 6 and 30% [*Hayhoe et al.*, 2007]. Consequently, more water will flow along surficial flow paths in upland and riparian areas linking flushing responses to stormflow chemistry and stream nutrient loadings. When only increased winter (DJF) precipitation rate is simulated in the models (Figure 4), a 12% increase of net precipitation in the dormant season is associated with increased stream runoff (+9%), quick flow (+13%), nitrate loading (+6%), and DOC loading (+11%). When net annual precipitation increased by 7%, net annual stream runoff (+6%), nitrate loading (+5%), and DOC loading (+7%) increased.

[28] When we considered only effects of season length without changing precipitation from current rates, the regression models simulated annual stream runoff and nutrient loadings that were larger in magnitude than the effect of increased winter (DJF) precipitation (Figure 4). This simulation accounts for days that shift between seasons and season-specific responses of streamflow to precipitation inputs. For the time period 2035 to 2099, growing season length is projected to increase between nine and 43 days [*Hayhoe et al.*, 2007]. When increased length of the growing season was modeled, fluxes of stream water, nitrate, and DOC changed as seasonally-varying hydrological responses were redistributed from the dormant season to the growing season (Figure 4). With a 43-day longer growing season (maximum projection), the modeled 28% increase of mean precipitation was accompanied by increased stream runoff (+39%), quick flow (+70%), nitrate loading (+58%), and DOC loading (+53%) during the growing season. As growing season length increased, the dormant season became shorter and more days shifted into the growing season when less streamflow occurs per unit rainfall (Figure 3). Decreased stream runoff (−16%), quick flow (−23%), nitrate loading (−21%), and DOC loading (−22%) occurred as net dormant season precipitation decreased by 21%. Net annual precipitation (+1%), stream runoff (+1%), and quick flow (+2%) increased. Net annual DOC loading did not change. In contrast to the minimal net effect of shifting seasonality on annual runoff and DOC loading, annual stream nitrate loading decreased by 6%.

[29] Changing regional patterns of rain, snow, and temperatures associated with anthropogenic forcing of global climate change will influence the timing and amount of water that flows through landscapes. A longer growing season was coupled with changed precipitation inputs to model the redistribution of dormant season days to the growing season during the B1 (stabilizing future emissions) and A1FI (highest projected emissions) scenarios (Figure 5). By the end of the 21st century, average increased rainfall amount (+28%) during the longer growing seasons (A1FI scenarios) drives increased mean growing season stream runoff (+39%) and increased mean loadings of stream nitrate (+57%) and DOC (+58%) at W-9. Mean rainfall during the dormant season decreases (−9%) as the precipitation increase during DJF is offset by the redistribution of rain into the 43 day longer growing season of the A1FI simulation. Stream runoff (−7%), nitrate loading (−15%), and DOC loading (−12%)

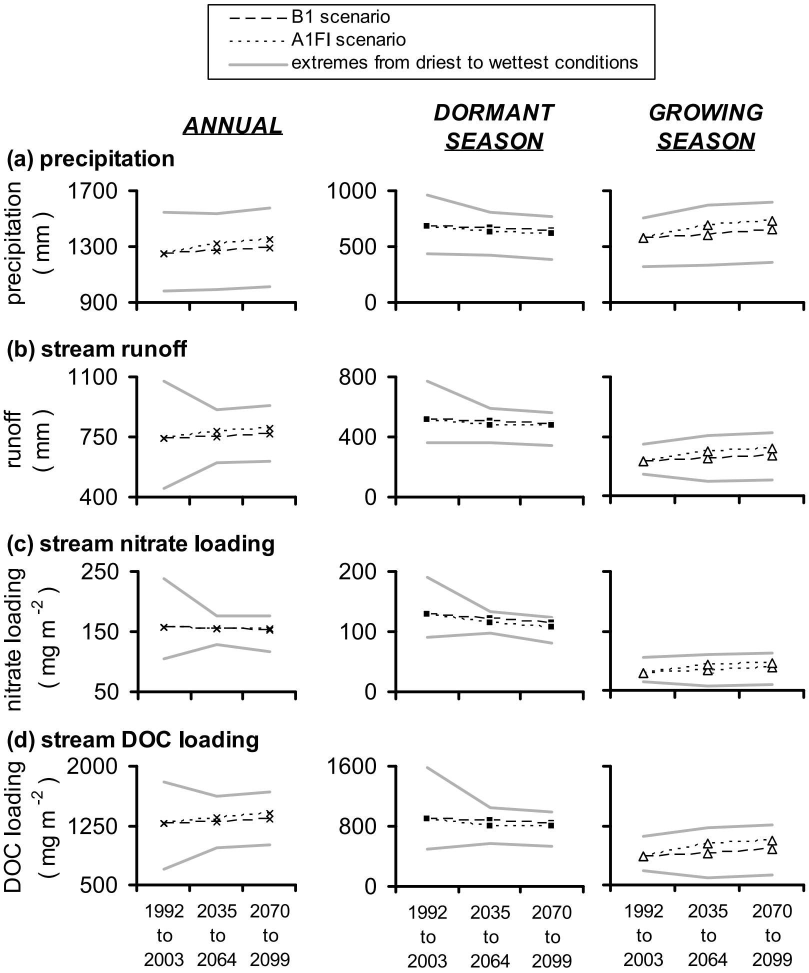


Figure 5. Projections of annual and seasonal (a) precipitation as well as stream (b) runoff, (c) nitrate, and (d) DOC loadings from the 1992–2003 (water years) base period.

all decrease in response to a reduction in the net seasonal flow of water through the landscape during the shorter dormant seasons.

[30] When the simulated seasonal fluxes were aggregated over the average water year, stream fluxes of water (+8%) and DOC (+9%) increased in response to a 7% increase of mean annual precipitation in the A1FI 2075 to 2099 simulation (Figure 5). Shifting seasonality affects annual stream runoff and DOC loading little because losses during the dormant season balanced the gains during the growing season (Figure S3). Net annual nitrate loading decreased by 2%. Changes to season length that cause fewer days of high flow of water through the landscape during the dormant season affect net annual nitrate loading more than increased dormant season precipitation.

[31] In the northeastern United States where precipitation is evenly distributed throughout a typical year, growing season baseflow is typically lower than dormant season baseflow because evapotranspiration is highest during the growing season. As days were redistributed into a longer growing season, the net annual range of runoff and nutrient loadings among the extremes of wetness conditions decreased as shown by the collapsing annual and dormant season ranges of stream runoff and nutrient loadings. For stream runoff, nitrate loading, and DOC loading, the lower bounds during the dormant season increased because additional winter (DJF) precipitation during the driest years offset losses due to shifting days to the growing season. In contrast, the upper bounds decreased because the additional winter precipitation had less effect on already large water fluxes than the lost days that were shifted to the growing season during the wettest years. The changing patterns of catchment wetness during the dormant season carried through to affect annual ranges of stream runoff and nutrient loadings. The dry years became wetter due to increased winter precipitation and the wet years became dryer due to increased days of high evapotranspiration. These results suggest that climate change will most affect runoff and nutrient fluxes during dryer or wetter than normal years. The Northeast Regional Climate Assessment [*Hayhoe et al.*, 2007] projects more extreme variability in precipitation during storm events in the future. Although we modeled changes from the driest to wettest years, more severe droughts, lower baseflow, and more intense stormflow events may lead to more variability in the latter part of the century and future conditions may reflect wider ranges than those shown in Figure 5.

[32] In contrast to modeled increases of stream DOC loading, volume-weighted stream DOC concentration decreased over the next century (Figure S4). These decreased concentrations, by 2% from the 1990 to 2003 base period to the A1FI

2075 to 2099 scenario, contrast with observations of DOC concentration increases in lakes and streams over the past several decades. Many studies have reported increased DOC concentrations over recent decades for surface waters in the northeastern United States [*Driscoll et al.*, 2003a; *Stoddard et al.*, 2003; *Findlay*, 2005], Canada [*Schindler et al.*, 1997; *Eimers et al.*, 2008], the United Kingdom [*Freeman et al.*, 2001; *Worrall et al.*, 2004; *Evans et al.*, 2006; *Worrall and Burt*, 2007; *Dawson et al.*, 2008], and northern Europe [*deWit et al.*, 2007; *Monteith et al.*, 2007]. The relatively small concentration decreases over the next century (2 to 3% per ∼100 years or 0.02 to 0.03% per year between the B1 and A1FI scenarios) are opposite in direction and much smaller in magnitude than contemporary concentration increases that exceed 5% per year [*Monteith et al.*, 2007]. Importantly, our results consider only hydrological effects on DOC fluxes. Findings from other studies suggest that direct changes in streamflow are less of a control on stream DOC concentration increases than other factors such as long-term declines in the atmospheric deposition of strong acid anions and recovery from ecosystem acidification [*Clark et al.*, 2006; *deWit et al.*, 2007; *Monteith et al.*, 2007].

[33] Shorter dormant seasons, shifts in snowmelt timing, and reduced winter runoff have the most potential to affect annual water and nutrient budgets [*Huntington et al.*, 2004]. Although we did not attempt to model the effect as precipitation changes from snow to rain with climate warming, diminished snowpack and decreased snow cover result in the loss of thermal insulation and more widespread development of impenetrable concrete frosts. Concrete frosts preclude infiltration of snowmelt waters [*Shanley and Chalmers*, 1999; *Shanley et al.*, 2002a]. If hydrological transport shifts from subsurface flow paths to flow over frozen soils during snowmelt, the rapid transport of nitrate released from the melting snowpack may substantially increase the transport of atmospherically deposited nitrate during the late dormant season [*Sebestyen et al.*, 2008]. If temperatures increase enough that precipitation falls as rain and soils do not freeze deeply, hydrological response during the late dormant season may become more like the early dormant season.

[34] Owing to the complexity of compounding uncertainty of the original IPCC climate projections, the regionally downscaled results [*Hayhoe et al.*, 2007] that served as input data to our regression models, and the error that propagates through our regression models, we have not estimated uncertainty for our model results. Although the uncertainty may be high, our hydrological approach nonetheless suggests that climate change and hydrological intensification will affect the timing and magnitude of stream nutrient loadings in the northeastern United States. Our approach also does not include feedbacks related to altered nutrient availability and the associated changes to biogeochemical cycles that may accompany climate change. Other considerations include primary production and microbial processing that will change when growing seasons are longer as well as interactions of climate with other ecological disturbances such as atmospheric deposition of pollutants. Across the northeastern United States, atmospheric deposition widely disperses anthropogenic nitrogen across forests which affects nitrogen availability, soil nutrient status, forest health, and stream chemistry [*Birdsey et al.*, 2000; *Rustad et al.*, 2000; *Boyer and Howarth*, 2002; *Aber et al.*, 2003; *Galloway et al.*, 2004; *Green et al.*, 2004]. Reactive nitrogen inputs are expected to increase in the future which may affect nutrient transformation rates, exacerbate stream nitrate export [*Driscoll et al.*, 2003b; *Galloway et al.*, 2004], and affect stream DOC loadings [*Findlay*, 2005; *Goodale et al.*, 2005]. The carbon to nitrogen ratio is an indicator of ecosystem functions that is affected by nitrogen inputs from atmospheric sources and regulates spatial and temporal patterns of nutrient availability via nitrification and denitrification [*Gundersen et al.*, 1998; *Bernhardt and Likens*, 2002; *Goodale et al.*, 2005]. Seasonal changes to the carbon to nitrogen ratio (DOC:nitrate) in our model simulations (e.g., the stream DOC to nitrate ratio increased 11% during the dormant season and decreased 13% during the growing season) suggest that aquatic nitrification may decrease in the dormant season and increase during the growing season which may affect stream nutrient export. Annually, the simulated DOC:nitrate increases 6% from the base period to 2070–2099 (A1FI scenario) due to larger changes of volume-weighted nitrate concentration (12% decrease) than DOC concentration (2% decrease). Although not the case at W-9 where the molar DOC:nitrate would only increase to 8.4 in the A1FI 2070–2099 scenario, such changes at other catchments may be enough to push the DOC:nitrate upward to surpass a critical threshold ratio of 18 to 21 which may lead to decreased leaching of nitrate from nitrogen-enriched forests [*Gundersen et al.*, 2006] and increased losses of DOC.

[35] As a net result of multiple interacting biogeochemical and hydrological processes, seasonal shifts in nutrient availability and mobility may cascade through terrestrial and aquatic nutrient cycles to affect stream nutrient loadings, downstream eutrophication, and trophic structure [*Galloway et al.*, 2003]. Although shifts in biogeochemical transformations, atmospheric deposition, and species composition will have additional effects on nutrient availability in source areas [*Emmett*, 2007], we still expect stream nutrient loadings to change as more water flows through the environment as stormflow in response to the net precipitation increases and shifting seasonality that are associated with anthropogenic climate forcing.

5. Conclusions and Implications

[36] Our hydrological approach assesses how changing the amount of water flowing through a landscape will alter nitrate and DOC transport to upland temperate forest streams. Model results suggest that runoff and stream solute loadings will shift seasonally due to hydrological changes that occur with anthropogenic climate forcing. Understanding the timing and magnitude of hydrological and hydrochemical responses is important because the effects of climate change on catchment hydrology may alter how nutrients are retained, produced (e.g., nitrified), and hydrologically flushed in headwater ecosystems with cascading implications for aquatic metabolism, nutrient export from catchments, and downstream eutrophication. Reduction of greenhouse gas emissions may be an important management option to minimize seasonal and annual changes to stream nitrate and DOC loadings because the low emission scenario (B1) has less effect than the high emission scenario at an upland forested catchment in the northeastern United States.

[37] **Acknowledgments.** This research was funded by a STAR Research Assistance Agreement (U-916154) awarded by the U.S. Environmental Protection Agency; the Horton Research Grant of the Hydrology Section of the American Geophysical Union; an Edna Bailey Sussman Fund grant; an USDA-CSREES Program award; and the USGS Water Energy and Biogeochemical Budgets program. We appreciate field, laboratory, and logistical help from G. R. Aiken, B. L. Bedford, R. D. Briggs, M. G. Brown, A. Chalmers, S. F. Clark, J. Denner, D. H. Doctor, R. Germain, C. Kendall, K. Kendall, P. J. McHale, and M. J. Mitchell. We would like to thank T. G. Huntington, D. M. McKnight, C. C. Rhoades, F. Worrall, and an anonymous reviewer for helpful comments on draft manuscripts. Archived W-9 streamflow data for the 1960s were obtained from http://hydrolab.arsusda.gov/wdc/vt.htm. This article has not been formally reviewed by the EPA. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References

Aber, J. D., C. L. Goodale, S. V. Ollinger, M.-L. Smith, A. H. Magill, M. E. Martin, R. A. Hallett, and J. L. Stoddard (2003), Is nitrogen deposition altering the nitrogen status of northeastern forests?, *BioScience*, *53*(4), 375–389, doi:10.1641/0006-3568(2003)053.

Bernhardt, E. S., and G. E. Likens (2002), Dissolved organic carbon enrichment alters nitrogen dynamics in a forest stream, *Ecology*, *83*(6), 1689–1700, doi:10.1890/0012-9658(2002)083[1689:DOCEAN]2.0.CO;2.

Birdsey, R. A., R. A. Mickler, J. Hom, and L. S. Heath (2000), Summary of prospective global change impacts on northern U.S. forest ecosystems, in *Responses of Northern U.S. Forests to Environmental Change*, edited by R. A. Mickler et al., pp. 543–568, Springer, New York.

Boyer, E. W., and R. W. Howarth (2002), *The Nitrogen Cycle at Regional to Global Scales*, 519 pp., Kluwer, Boston, Mass.

Boyer, E. W., G. M. Hornberger, K. E. Bencala, and D. M. McKnight (1996), Overview of a simple model describing variation of dissolved organic carbon in an upland catchment, *Ecol. Model.*, *86*(2–3), 183–188, doi:10.1016/0304-3800(95)00049-6.

Boyer, E. W., C. L. Goodale, N. A. Jaworski, and R. W. Howarth (2002), Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA, *Biogeochemistry*, *57*(1), 137–169, doi:10.1023/A:1015709302073.

Campbell, J. L., et al. (2004), Input-output budgets of inorganic nitrogen for 24 forest watersheds in the northeastern United States: A review, *Water Air Soil Pollut.*, *151*(1–4), 373–396, doi:10.1023/B:WATE.0000009908.94219.04.

Clark, J. M., P. J. Chapman, A. L. Heathwaite, and J. K. Adamson (2006), Suppression of dissolved organic carbon by sulfate induced acidification during simulated droughts, *Environ. Sci. Technol.*, *40*(6), 1776–1783, doi:10.1021/es051488c.

Cohn, T. A., D. I. Caulder, E. J. Gilroy, L. D. Zynjuk, and R. M. Summers (1992), The validity of a simple statistical model for estimating fluvial constituent loads: An empirical study involving nutrient loads entering Chesapeake Bay, *Water Resour. Res.*, *28*(9), 2353–2363.

Creed, I. F., L. E. Band, N. W. Foster, I. K. Morrison, J. A. Nicolson, R. G. Semkin, and D. S. Jeffries (1996), Regulation of nitrate-N release from temperate forests: A test of the N flushing hypothesis, *Water Resour. Res.*, *32*(11), 3337–3354.

Dawson, J. J. C., C. Soulsby, D. Tetzlaff, M. Hrachowitz, S. M. Dunn, and I. A. Malcolm (2008), Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments, *Biogeochemistry*, *90*(1), 93–113, doi:10.1007/s10533-008-9234-3.

deWit, H., J. Mulder, A. Hindar, and L. Hole (2007), Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition, *Environ. Sci. Technol.*, *41*(22), 7706–7713, doi:10.1021/es070557f.

Driscoll, C. T., K. M. Driscoll, K. M. Roy, and M. J. Mitchell (2003a), Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition, *Environ. Sci. Technol.*, *37*(10), 2036–2042, doi:10.1021/es020924h.

Driscoll, C. T., et al. (2003b), Nitrogen pollution in the northeastern United States: Sources, effects, and management options, *BioScience*, *53*(4), 357–374.

Dunne, T., and R. D. Black (1970), Partial area contributions to storm runoff in a small New England watershed, *Water Resour. Res.*, *6*(5), 1296–1311.

Dunne, T., and R. D. Black (1971), Runoff processes during snowmelt, *Water Resour. Res.*, *7*(5), 1160–1172.

Eimers, M. C., S. A. Watmough, and J. M. Buttle (2008), Long-term trends in dissolved organic carbon concentration: A cautionary note, *Biogeochemistry*, *87*(1), 71–81, doi:10.1007/s10533-007-9168-1.

Emmett, B. A. (2007), Nitrogen saturation of terrestrial ecosystems: Some recent findings and their implications for our conceptual framework, *Water Air Soil Pollut. Focus*, *7*(1), 99–109, doi:10.1007/s11267-006-9103-9.

Evans, C. D., P. J. Chapman, J. M. Clark, D. T. Monteith, and M. S. Cresser (2006), Alternative explanations for rising dissolved organic carbon export from organic soils, *Global Change Biol.*, *12*(11), 2044–2053, doi:10.1111/j.1365-2486.2006.01241.x.

Findlay, S. E. G. (2005), Increased carbon transport in the Hudson River: Unexpected consequence of nitrogen deposition?, *Front. Ecol. Environ.*, *3*(3), 133–137.

Freeman, C. D., C. D. Evans, D. T. Monteith, B. Reynolds, and N. Fenner (2001), Export of organic carbon from peat soils, *Nature*, *412*, 785, doi:10.1038/35090628.

Galloway, J. N., J. D. Aber, J. W. Erisman, S. P. Seitzinger, R. W. Howarth, E. B. Cowling, and B. J. Cosby (2003), The nitrogen cascade, *BioScience*, *53*(4), 341–356.

Galloway, J. N., et al. (2004), Nitrogen cycles: Past, present and future, *Biogeochemistry*, *70*, 153–226, doi:10.1007/s10533-004-0370-0.

Gedney, N., P. M. Cox, R. A. Betts, O. Boucher, C. Huntingford, and P. A. Stott (2006), Detection of a direct carbon dioxide effect in continental river runoff records, *Nature*, *439*(7078), 835–838, doi:10.1038/nature04504.

Goodale, C. L., J. D. Aber, P. M. Vitousek, and W. H. McDowell (2005), Long-term decreases in stream nitrate: Successional causes unlikely; possible links to DOC?, *Ecosystems*, *8*(3), 334–337, doi:10.1007/s10021-003-0162-8.

Green, P. A., C. J. Vörösmarty, J. N. Galloway, B. J. Peterson, and E. W. Boyer (2004), Pre-industrial and contemporary fluxes of nitrogen through rivers: A global assessment based on typology, *Biogeochemistry*, *68*(1), 71–105, doi:10.1023/B:BIOG.0000025742.82155.92.

Gundersen, P., I. Callesen, and W. de Vries (1998), Nitrate leaching in forest ecosystems is related to forest floor C/N ratios, *Environ. Pollut.*, *102*(1), 403–407.

Gundersen, P., I. K. Schmidt, and K. Rauland-Rasmussen (2006), Leaching of nitrate from temperate forests—Effects of air pollution and forest management, *Environ. Rev.*, *14*(1), 1–57, doi:10.1139/A05-015.

Hall, L. M. (1959), The geology of the St Johnsbury quadrangle, Vermont and New Hampshire, *Bull.*, 13, 105 pp., Vermont Geol. Surv., Montpelier.

Hayhoe, K., et al. (2007), Past and future changes in climate and hydrological indicators in the US Northeast, *Clim. Dyn.*, *28*(4), 381–407, doi:10.1007/s00382-006-0187-8c.

Hodgkins, G. A., and R. W. Dudley (2005), Changes in streamflow timing in New England during the 20th century, *Fact Sheet 2005-3019*, 4 pp., U.S. Geol. Surv., Washington, D. C.

Hodgkins, G. A., R. W. Dudley, and T. G. Huntington (2003), Changes in the timing of high river flows in New England over the 20th century, *J. Hydrol.*, *278*(1–4), 244–252, doi:10.1016/S0022-1694(03)00155-0.

Hornberger, G. M., K. E. Bencala, and D. M. McKnight (1994), Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado, *Biogeochemistry*, *25*(3), 147–165, doi:10.1007/BF00024390.

Hornberger, G. M., J. P. Raffensperger, P. L. Wiberg, and K. N. Eshleman (1998), Catchment hydrology: The hillslope-stream continuum, in *Elements of Physical Hydrology*, pp. 199–221, John Hopkins Univ. Press, Baltimore, Md.

Huntington, T. G. (2003), Climate warming could reduce runoff significantly in New England, USA, *Agric. For. Meteorol.*, *117*(3–4), 193–201, doi:10.1016/S0168-1923(03)00063-7.

Huntington, T. G. (2006), Evidence for intensification of the global water cycle: Review and synthesis, *J. Hydrol.*, *319*(1–4), 83–95, doi:10.1016/j.jhydrol.2005.07.003.

Huntington, T. G., G. A. Hodgkins, B. D. Keim, and R. W. Dudley (2004), Changes in the proportion of precipitation occurring as snow in New England (1949–2000), *J. Clim.*, *17*(13), 2626–2636, doi:10.1175/1520-0442.

Inamdar, S. P., and M. J. Mitchell (2006), Hydrologic and topographic controls on storm-event exports of dissolved organic carbon (DOC) and nitrate across catchment scales, *Water Resour. Res.*, *42*, W03421, doi:10.1029/2005WR004212.

Kendall, C., D. H. Campbell, D. A. Burns, J. B. Shanley, S. R. Silva, and C. C. Y. Chang (1995), Tracing sources of nitrate in snowmelt runoff using the oxygen and nitrogen isotopic compositions of nitrate, in *Biogeochemistry of Seasonally Snow-Covered Catchments*, edited by K. A. Tonnessen et al., pp. 339–347, Int. Assoc. of Hydrol. Sci., Great Yarmouth, U. K.

Kendall, K. A., J. B. Shanley, and J. J. McDonnell (1999), A hydrometric and geochemical approach to test the transmissivity feedback hypothesis during snowmelt, *J. Hydrol.*, *219*, 188–205, doi:10.1016/S0022-1694(99)00059-1.

Labat, D., Y. Godderis, J. L. Probst, and J. L. Guyot (2004), Evidence for global runoff increase related to climate warming, *Adv. Water Resour.*, *27*(6), 631–642, doi:10.1016/j.advwatres.2004.02.020.

McCabe, G. J., and D. M. Wolock (2002), A step increase in streamflow in the conterminous United States, *Geophys. Res. Lett.*, *29*(24), 2185, doi:10.1029/2002GL015999.

McDowell, W. H. (1985), Kinetics and mechanisms of dissolved organic carbon retention in a headwater stream, *Biogeochemistry*, *1*, 329–352, doi:10.1007/BF02187376.

McGlynn, B. L., J. J. McDonnell, J. B. Shanley, and C. Kendall (1999), Riparian zone flowpath dynamics during snowmelt in a small headwater catchment, *J. Hydrol.*, *222*(1–4), 75–92, doi:10.1016/S0022-1694(99)00102-X.

McHale, M. R., J. J. McDonnell, M. J. Mitchell, and C. P. Cirmo (2002), A field-based study of soil water and groundwater nitrate release in an Adirondack forested watershed, *Water Resour. Res.*, *38*(4), 1031, doi:10.1029/2000WR000102.

Milly, P. C. D., K. A. Dunne, and A. V. Vecchia (2005), Global pattern of trends in streamflow and water availability in a changing climate, *Nature*, *438*(7066), 347–350, doi:10.1038/nature04312.

Mitchell, M. J., K. B. Piatek, S. F. Christopher, B. Mayer, C. Kendall, and P. J. McHale (2006), Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: A combined hydrological, chemical and isotopic approach, *Biogeochemistry*, *78*(2), 217–246, doi:10.1007/s10533-005-4277-1.

Monteith, D. T., et al. (2007), Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry, *Nature*, *450*(7169), 537–539, doi:10.1038/nature06316.

Mulholland, P. J. (1993), Hydrometric and stream chemistry evidence of three storm flowpaths in Walker Branch Watershed, *J. Hydrol.*, *151*(2–4), 291–316, doi:10.1016/0022-1694(93)90240-A.

Nakicenovic, N., et al. (2000), *IPCC Special Report on Emissions Scenarios*, 570 pp., Cambridge Univ. Press, New York.

Nathan, R. J., and T. A. McMahon (1990), Evaluation of automated techniques for base flow and recession analyses, *Water Resour. Res.*, *26*(7), 1465–1473.

Ohte, N., S. D. Sebestyen, C. Kendall, J. B. Shanley, S. D. Wankel, D. H. Doctor, and E. W. Boyer (2004), Tracing sources of nitrate in snowmelt runoff using a high-resolution isotopic technique, *Geophys. Res. Lett.*, *31*, L21506, doi:10.1029/2004GL020908.

Perakis, S. S., and L. O. Hedin (2007), State factor relationships of dissolved organic carbon and nitrogen losses from unpolluted temperate forest watersheds, *J. Geophys. Res.*, *112*, G02010, doi:10.1029/2006JG000276.

Piao, S., P. Friedlingstein, P. Ciais, N. de Noblet-Ducoudre, D. Labat, and S. Zaehle (2007), Changes in climate and land use have a larger direct impact than rising CO_2 on global river runoff trends, *Proc. Natl. Acad. Sci.*, *104*(39), 15,242–15,247, doi:10.1073/pnas.0707213104.

Rantz, S. E. (1982), Measurement and computation of streamflow, vol. 1, Measurement of stage and discharge, *U.S. Geol. Surv. Water Supply Pap.*, *2175*, 284 pp.

Rustad, L. E., J. M. Melillo, M. J. Mitchell, I. J. Fernandez, P. A. Steudler, and P. J. McHale (2000), Effects of soil warming on carbon and nitrogen cycling, in *Responses of Northern U.S. Forests to Environmental Change*, edited by R. A. Mickler et al., pp. 357–382, Springer, New York.

Schindler, D. W., P. J. Curtis, S. E. Bayley, B. R. Parker, K. G. Beaty, and M. P. Stainton (1997), Climate-induced changes in the dissolved organic carbon budgets of boreal lakes, *Biogeochemistry*, *36*(1), 9–28, doi:10.1023/A:1005792014547.

Sebestyen, S. D., E. W. Boyer, J. B. Shanley, C. Kendall, D. H. Doctor, G. R. Aiken, and N. Ohte (2008), Sources, transformations, and hydrological processes that control stream nitrate and dissolved organic matter concentrations during snowmelt in an upland forest, *Water Resour. Res.*, *44*, W12410, doi:10.1029/2008WR006983.

Sebestyen, S. D., J. B. Shanley, and E. W. Boyer (2009), Using high-frequency sampling to detect effects of atmospheric pollutants on stream chemistry, in *Proceedings of the Third Interagency Conference on Research in the Watersheds, 9–11 September 2008, Estes Park, CO*, edited by R. M. T. Webb and D. J. Semmens, U.S. Geol. Surv., Washington, D. C., in press.

Shanley, J. B. (2000), Sleepers River, Vermont: A water, energy, and biogeochemical budgets program site, *Fact Sheet 166-99*, 4 pp., U.S. Geol. Surv., Washington, D. C.

Shanley, J. B., and A. Chalmers (1999), The effect of frozen soil on snowmelt runoff at Sleepers River, Vermont, *Hydrol. Process.*, *13*, 1843–1857.

Shanley, J. B., C. Kendall, T. E. Smith, D. M. Wolock, and J. J. McDonnell (2002a), Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA, *Hydrol. Process.*, *16*(3), 589–609, doi:10.1002/hyp.312.

Shanley, J. B., P. F. Schuster, M. M. Reddy, D. A. Roth, H. E. Taylor, and G. R. Aiken (2002b), Mercury on the move during snowmelt in Vermont, *Eos Trans. AGU*, *83*(5), 45,47–48.

Shanley, J. B., B. Mayer, M. J. Mitchell, R. L. Michel, S. W. Bailey, and C. Kendall (2005), Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and ^{35}S activity, *Biogeochemistry*, *76*(1), 161–185, doi:10.1007/s10533-005-2856-9.

Stoddard, J. L. (1994), Long-term changes in watershed retention of nitrogen, its causes and aquatic consequences, in *Environmental Chemistry of Lakes and Reservoirs*, edited by L. A. Baker, pp. 223–284, Am. Chem. Soc., Washington, D. C.

Stoddard, J. L., J. S. Kahl, F. A. Deviney, D. R. DeWalle, C. T. Driscoll, A. T. Herlihy, J. H. Kellogg, P. S. Murdoch, J. R. Webb, and K. E. Webster (2003), Response of surface water chemistry to the clean air act amendments of 1990, *Rep. EPA/620/R-03/001*, U.S. Environ. Prot. Agency, Washington, D. C. (Available as PB2003-102732 from http://www.ntis.gov)

U.S. Department of Agriculture (USDA) (1965), Hydrologic data for experimental agricultural watersheds in the United States, 1960–61, *Misc. Publ. 994*, 496 pp., Agric. Res. Serv., Washington, D. C.

Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, and D. G. Tilman (1997), Human alteration of the global nitrogen cycle: Sources and consequences, *Ecol. Appl.*, *7*(3), 737–750.

Watson, R. T., et al. (2001), *Climate change 2001: Synthesis report*, 34 pp., Intergov. Panel on Clim. Change., Geneva.

Worrall, F., and T. P. Burt (2007), Flux of dissolved organic carbon from U.K. rivers, *Global Biogeochem. Cycles*, *21*, GB1013, doi:10.1029/2006GB002709.

Worrall, F., et al. (2004), Trends in dissolved organic carbon in UK rivers and lakes, *Biogeochemistry*, *70*(3), 369–402, doi:10.1007/s10533-004-8131-7.

E. W. Boyer, School of Forest Resources, Pennsylvania State University, University Park, PA 16802, USA. (ewb100@psu.edu)

S. D. Sebestyen, Northern Research Station, Forest Service, U.S. Department of Agriculture, 1831 Highway 169 East, Grand Rapids, MN 55744-3399, USA. (ssebestyen@fs.fed.us)

J. B. Shanley, U.S. Geological Survey, Montpelier, VT 05602, USA. (jshanley@usgs.gov)