COUPLED HYDROLOGICAL AND BIOGEOCHEMICAL PROCESSES THAT CONTROL STREAM NITROGEN AND DISSOLVED ORGANIC CARBON AT THE SLEEPERS RIVER RESEARCH WATERSHED

by

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ABSTRACT

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COUPLED HYDROLOGICAL AND BIOGEOCHEMICAL PROCESSES THAT CONTROL STREAM NITROGEN AND DISSOLVED ORGANIC CARBON AT THE SLEEPERS RIVER RESEARCH WATERSHED.

To investigate how hydrological and biogeochemical processes control the forms and concentrations of stream nutrients in upland forests affected by elevated atmospheric nitrogen deposition, I traced sources of water, nitrogen, and dissolved organic carbon (DOC) at the Sleepers River Research Watershed (northeastern Vermont, USA). To augment long-term weekly hydrochemical data that have been collected at the site since 1991, I collected high-frequency stream water samples over multiple storm flow events from 2002 to 2005. During autumn, baseflow nitrate concentrations decreased by an order of magnitude during leaf fall and dissolved organic nitrogen briefly became the dominant form of stream nitrogen. Quantifying terrestrial to aquatic linkages revealed how coupled hydrological and biogeochemical processes affected stream nutrient variation during autumn including the “nitrate crash” and rebound. A mass balance showed that a stream reach during baseflow was a net sink for nitrate while a net source of DOC and DON. Nitrate concentrations rebounded from this “nitrate crash” during storm flow events. Isotopic signatures and end-member mixing analysis revealed when nitrate and dissolved organic nitrogen (DON) were flushed to the stream from terrestrial source areas and that up to 30% of the stream nitrate was directly contributed from atmospheric sources. Results from snowmelt studies showed when solutes entered the stream and that variable source areas were linked to the stream by preferential shallow subsurface and overland flowpaths. The highest stream nutrient concentrations occurred when nitrate originated from atmospheric sources as well as nitrified sources and terrestrial organic matter was the dominant source of DOC and DON. In the third component of my work, I examined the long-term record of stream hydrochemistry to explore the relationship between catchment wetness and stream nutrient loadings and to assess how stream nutrient loadings may respond to climate change. Model results suggest that leaching of nitrate and DOC will seasonally shift due to anthropogenic climate forcing and affect the timing and magnitude of annual stream loadings in the northeast USA during the next century. Net annual stream runoff (+8%) and DOC flux (+9%) increases

were primarily affected by increased winter precipitation. In contrast, decreased annual flux of stream nitrate (-2%) reflected a greater effect of growing season controls on stream nitrate that resulted as days shifted to the longer growing seasons. Overall, these studies identified hydrological transport processes, source variation, and biogeochemical transformations as key processes that influenced stream nutrient variation.

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CHAPTER 1

INTRODUCTION

Sources of Stream Nitrogen and Organic Carbon

The variation of surface water chemistry over time and space reflects complex biogeochemical and hydrological processes that affect solute availability and movement in upland forests. Source areas in the landscape are linked to streams by the flow of water and the biogeochemical processes that affect nutrient availability in uplands and riparian areas. Because nitrogen deposition from atmospheric sources influences biogeochemical cycles in forests and the streams that drain upland catchments (Stoddard, 1994; Aber and others, 1998; Galloway and others, 2003), there is a need to determine the effects of elevated nitrogen inputs on sources of stream nitrate and biogeochemical processes in the landscape. This information will help scientists and resource managers to address how atmospheric nitrogen pollution in upland forests contributes to impaired water quality (Carpenter and others, 1998; Alexander and others, 2000; Galloway and others, 2003), declining ecosystem health (Durka and others, 1994; Aber and others, 2003), and eutrophication of sensitive receiving waters (Bricker and others, 1999; NRC, 2000; Rabalais, 2002).

The primary forms of biologically available nitrogen in precipitation, soil, ground, and stream waters are nitrate, ammonium, and dissolved organic nitrogen (DON). Nitrogen gas (N_2) which is the most abundant element in the atmosphere is not readily available for biological uptake and is not a direct source of reactive nitrogen that cycles through forest ecosystems. Nitrate and ammonium are the two forms of dissolved inorganic nitrogen (DIN), are biologically available, and cycle in to the organic nitrogen pool via biological assimilation. Due to charge affinity and rapid biological uptake, ammonium is largely retained in surface soils whereas nitrate and DON are highly mobile and leak to groundwater when not retained by biological uptake.

Surficial soils including the organic horizons and decaying litter are the largest reservoir of nitrogen in forests (Post and others, 1985). Biological uptake from the soil nitrogen pool is a factor that regulates reactive nitrogen availability in the environment (Nadelhoffer and others, 1984; Ågren and Bosatta, 1988; Aber and others, 1989). Plants cycle reactive nitrogen back to surficial soils in the form of organic nitrogen in litterfall. In soils, microbes mineralize (break down organic nitrogen to ammonium), nitrify (convert ammonium to nitrate), denitrify (convert nitrate to nitrogen gases), and assimilate (convert DON, nitrate, and ammonium into organic matter) nitrogen.

Over the past century, human activities have doubled the amount of reactive nitrogen in the environment which affects biogeochemical cycles in terrestrial and aquatic ecosystems (Vitousek and others, 1997; Matson and others, 2002; Galloway and others, 2004). Anthropogenic nitrogen emissions affect atmospheric chemistry and elevated nitrogen deposition from atmospheric sources is linked to soil nutrient status (Lawrence and others, 1999; Aber and others, 2003), forest health (Durka and others, 1994; McNulty and others, 1996) and surface water chemistry (Boyer and others, 2002; Driscoll and others, 2003). Elevated nitrogen deposition has direct affects on forest health and tree mortality occurs in forests that receive severe, chronic nitrogen deposition (Schulze and Freer-Smith, 1991; Durka and others, 1994; McNulty and others, 1996). The effect of nitrogen deposition is regional because emitted nitrogen is scavenged by precipitation or settles out as aerosols (Johnson and Lindberg, 1992; Lovett and others, 1997). Different regions receive different amounts of nitrogen (Ollinger and others, 1993; Ito and others, 2002; Galloway and others, 2004) and some areas are minimally impacted (Hedin and others, 1995).

In undisturbed catchments that do not receive anthropogenic nitrogen, inorganic nitrogen concentrations in atmospheric deposition are low, inorganic nitrogen is tightly cycled in surficial soils, and little nitrate leaches to groundwater (Stoddard, 1994; Perakis and Hedin, 2001). Consequently, nitrate is rapidly consumed by biological uptake and the retention of inorganic nitrogen in biomass and soils is nearly complete (Hedin and others, 1995; Perakis and Hedin, 2001). In unpolluted ecosystems, stream ammonium concentrations may exceed nitrate concentrations by orders of magnitude and stream DON concentrations are much higher than DIN concentrations (Perakis and Hedin, 2002).

Across geographic regions that receive elevated atmospheric deposition such as the northeast USA (Ollinger and others, 1993), nitrogen enrichment of ecosystems affects the forms and concentrations of stream nitrogen (Boyer and Howarth, 2002; Perakis and Hedin, 2002; Galloway and others, 2004). Atmospheric DON concentrations are little affected by anthropogenic nitrogen emissions and precipitation DON concentrations are low relative to DIN (Holland and others, 1999). In response to elevated atmospheric DIN deposition to forests, stream ammonium concentrations are typically much less than nitrate or DON concentrations and stream nitrate may exceed DON concentrations by orders of magnitude (Likens and Bormann, 1995; Perakis and Hedin, 2002; Campbell and others, 2004).

In ecosystems that are affected by elevated nitrogen inputs from atmospheric deposition, nitrogen availability may exceed biological demand (Ågren and Bosatta, 1988; Aber and others, 1989). Nitrification in soils may produce a pool of mobile nitrate that may not be retained by biological uptake leading to the condition of nitrogen saturation. At the extreme of nitrogen saturation, nitrate concentrations in groundwater and stream baseflow may be chronically high because nitrate that exceeds biological uptake may be leached from a catchment (Stoddard, 1994).

In the nitrogen saturation scheme conceptualized by Stoddard (1994), patterns of stream nitrate concentations fit one of four stages. In Stage 0, baseflow nitrate concentrations are uniformly low because little nitrate leaches from soils. In Stage 1, baseflow nitrate concentrations are low during summer when biological uptake limits nitrate availability and concentrations increase during the dormant season when leached nitrate is transported to streams during storm events. In Stage 2, baseflow nitrate concentrations are high throughout the year reflecting some nitrate from atmospheric sources that leaks to and enriches groundwater. In Stage 3, stream nitrate concentrations are chronically high and severely elevated because the catchment is a net source of stream nitrate when nitrified and atmospheric sources are transported to streams.

Given the interacting factors of deposition amount (Ollinger and others, 1993; Galloway and others, 2004) and biological responses (Lovett and others, 2004), the effects of elevated nitrogen deposition on catchments and streams is heterogeneous (Lovett and others, 2002; Aber and others, 2003). Even with elevated atmospheric nitrogen deposition and evidence of early stages of nitrogen saturation, many forests retain some fraction of reactive nitrogen inputs from atmospheric deposition (Aber and others, 2003; Campbell and others, 2004). Across the northeast USA, most nitrate from atmospheric sources is assimilated into organic matter pools and may later flow to streams after remineralization and nitrification unless nitrogen gases are emitted to the atmosphere during denitrification.

When nitrogen availability increases across widespread areas due to human activities, excess nitrogen affects forest health (Durka and others, 1994), species composition (Emmett, 2007), soil nutrient status (Aber and others, 2003), and dissolved organic carbon (DOC) cycling (Pregitzer and others, 2004) which in turn is a feedback on the ecosystem processes that regulate the movement of nutrients to streams. Organic carbon is linked to nitrogen cycling in terrestrial

soils and streams by biogeochemical processing. Interactions of nitrogen and organic carbon may be important controls on stream nitrogen and DOC concentrations (McClain and others, 2003; Ollinger and others, 2003). Water, nitrogen, and carbon interact in shallow soils (Park and Matzner, 2003, 2006), riparian areas (Cirmo and McDonnell, 1997; Hedin and others, 1998), and in stream channels (Strauss and Lamberti, 2000; Bernhardt and Likens, 2002). Autotrophs (primary producers) assimilate inorganic carbon and nitrogen into organic forms, whereas heterotrophs decompose (mineralize) organic carbon and nitrogen into inorganic compounds or finer organic matter (Short and Maslin, 1977; Bott and others, 1984; Baldy and others, 1995). When no oxygen is present in saturated soils, chemolithotrophs oxidize organic carbon and use nitrate as the terminal electron acceptor in the process of denitrification (Firestone and Davidson, 1989; Hedin and others, 1998).

In streams, organic carbon is an important regulator of trace metal mobility (McKnight and others, 1992), aquatic respiration (Roberts and Mulholland, 2007), and primary production (Fisher and Likens, 1973; McDowell and Likens, 1988). Of the two forms of organic carbon, DOC fluxes typically exceed particulate organic fluxes (Bilby, 1981; Sedell and Dahm, 1990; Hope and others, 1994). Organic matter that is transported in streams originates from the biosphere, either from inputs of terrestrial organic carbon or in-stream production. Precipitation is not a major source of stream DOC because precipitation DOC concentrations are low around the globe. Except where wetlands are abundant, DOC concentrations are typically low in baseflow because DOM is adsorbed along soil flowpaths and is degraded by microbial processing (McDowell and Wood, 1984; Cronan and Aiken, 1985; McDowell, 1985).

The concentration and chemical composition of DOM may vary throughout the year due to seasonal litter inputs, decomposition, soil adsorption, and the frequency at which water flushes DOM from forest soils (Kaplan and others, 1980; McDowell and Likens, 1988; Qualls and Haines, 1992; Boyer and others, 1997; Hood and others, 2005). Although dissolved organic matter (DOM) is composed of heterogeneous organic compounds, the DOC released from fresh litter is a highly reactive substance relative to DOC that is leached from older litter and more degraded soil organic matter (Thurman, 1986; Aiken and Cotsaris, 1995; Findlay and Sinsabaugh, 2003). During autumn, DOC leached from fresh leaf litter enters soils and streams (Cummins and others, 1972; Fisher and Likens, 1973; Triska and Sedell, 1976; Dahm, 1981, 1984; McDowell and Likens,

1988; Meyer and others, 1998) and the leachate is an important energy source because the DOC is reactive and abundant (Hall and others, 2000; Qualls, 2004, 2005).

Linking nutrient sources in the landscape to stream hydrochemistry

The flow of water in landscapes varies with the magnitude, duration, and frequency of precipitation (rainfall or snowmelt) to form a continuum of hydrological connections that link source areas in the landscape with streams (Hewlett and Nutter, 1970; Dunne and Black, 1971a; Hornberger and others, 1994). Surficial soils in the unsaturated zone are chemically distinct from groundwaters because the large nutrient pool in the forest floor is affected by inputs of organic matter and solute influxes from atmospheric deposition. Once hydrological connections to surficial soils develop during storm events, water and solutes may be delivered from these source areas (Schiff and others, 1990; Hornberger and others, 1994; Boyer and others, 1996; Creed and others, 1996).

Although the variation of water chemistry with streamflow is well documented, ecosystem scientists still lack a complete understanding of the ways that ecosystem processes interact to control concentrations and fluxes of stream nutrients over events, seasons, and years. Weekly (or less frequent) stream chemistry data are extremely valuable records of long-term ecosystem responses, yet they do not represent the entire range of flow conditions. High-frequency chemical data may provide critical insight that is needed to quantify the linkages between landscapes and streams that affect stream hydrochemical variation. However, rigorous quantification of hydrochemical responses to streamflow is the exception rather than the norm because event-based sample collection is difficult given the stochastic nature of storm flow events. Sustaining high-frequency sampling for more than a few hydrological events is extemely difficult due to the required labor, supplies, time, funds, and costly laboratory analyses. Consequently, few ecosystem studies have intensively measured stream chemistry over the entire range of flow conditions and over multiple storm flow events.

For my dissertation research, I studied stream hydrochemistry to quantify the hydrological and biogeochemical processes that affect stream nutrient variation in a catchment that is affected by elevated nitrogen inputs from atmospheric deposition. At the Sleepers River Research in northeastern Vermont, USA, I measured stream hydrochemical responses with high frequency

sampling from 2002 to 2005 including an extended time period in which all high flow events in an annual cycle.

The Sleepers River Research Watershed

The Sleepers River Research Watershed is in rural northeastern Vermont (USA). Watershed 9 is a 40.5 sub-basin of the sub-basin of the 11,000 hectare Sleepers River Research Watershed and is well suited for studies of catchment hydrology and biogeochemistry. An existing instrument network was available to measure hydrology, meteorology, and chemistry. The mountainous terrain is completely forested with species that are representative of many northeast USA catchments. Nitrogen deposition is elevated at W-9 (Campbell and others, 2004). Stream nitrate concentrations increase during storm events particularly snowmelt, summer baseflow concentrations are low, and groundwater nitrate concentrations are perennially low. These conditions are consistent with Stage 1 of nitrogen saturation.

Northeastern Vermont has a humid continental climate. The temperature ranges from -30 to 30 degrees Celsius with an annual mean 4.6 degrees Celsius. The mean annual precipitation is 1334 millimeters. Precipitation is evenly spread throughout the year and twenty to thirty percent of the precipitation occurs as snow. The mean annual runoff is 735 millimeters and runoff is typically greatest in April when a seasonal snow pack melts. Stream flow is typically lowest during the hot summer months of July, August, and September when evapotranspiration is highest. In autumn, stream flow increases as transpiration decreases with plant dormancy.

Watershed 9 is a south facing catchment. The elevation ranges from 519 to 686 meter above mean sea level and the mean stream slope is 22 percent (Shanley and others, 2004). The glacial terrain was scultped by Pleistocene ice sheets and the dense glacial tills are derived from the local bedrock (Newell, 1970). Hillslopes are steep, are broken by relatively flat mid-elevation benches, and plateau at the highest elevations. The geology is Silurian and Devonian aged calcareous silicate bedrock (granulite and schists) that is interbedded with quartz-mica schists and micaceous quartzite of the Waits River Formation and the Giles Mountain formation (Hall, 1959). These carbonate-rich bedrocks buffer acidic deposition and the stream water has a calcium-bicarbonate-sulfate geochemistry (Shanley and others, 2004). A one to three meter deep dense glacial till underlies soils. On hillslopes, soils are moderately to excessively well-

drained inceptisols and spodosols that are 50 to 90 centimeters deep (Comer and Zimmermann, 1969; Shanley and others, 2003). Wetlands, riparian areas, and lowlands are poorly-drained and accumulate as much as two meters of peat (McGlynn and others, 1999; Shanley and others, 2003).

Stream flow measurements at W-9 began in 1961 (USDA-ARS, 1965) and continued intermittently through 1973. Streamflow was only measured year-round in some years. Streamflow was measured again during 1980, 1981, and 1982 (Thorne and others, 1988). Since 1991, stream water level has been measured with a float driven shaft encoder and recorded every five minutes with a Campbell datalogger. Recorded water levels were verified by reading staff gages. Stream discharge was calculated from a stage-discharge relationship, according to USGS protocols (Rantz, 1982a, b; Shanley and others, 1995)

Watershed 9 has a northern hardwood forest cover and vegetation grows from May to late-September or early October when autumn leaf fall occurs. The forest was partially logged in 1929 and selectively cut in 1960. The forest still accrues biomass. The forest is largely sugar maple (*Acer saccharum*, 73% of the basal area), yellow birch (*Betula alleghaniensis*, 11.5%), and white ash (*Fraxinus americana*, 8%). American basswood (*Tilia americana*), American beech (*Fagus grandifolia*), black cherry (*Prunus serotina*), hophornbeam (*Ostrya virginiana*), red maple (*Acer rubrum*), and striped maple (*Acer* pennsylvanicum) each comprise one percent or less of the basal area. Two conifer species, red spruce (Picea rubens) and balsam fir (Abies balsamea) are a minor amount of the total basal area (1% and 3%, respectively). Conifers are locally abundant on the well-drained soils that surround the wetlands and at a hillslope adjacent to the W-9 stream gage.

Pope Brook, the third order stream that drains W-9, flows from the Kittredge Hills and forms the headwaters of Sleepers River. Sleepers River flows eastward through the town of Danville and past the city of Saint Johnsbury before joining with the Passumpsic River which in turn is a tributary of the Connecticut River.

Upstream of the W-9 stream gage, three tributary streams from the A (16.9 hectare), B (12.9 hectare), and C (8.1 hectare) sub-basins merge to form Pope Brook. The three sub-basins have stream gages at about 521 meter elevation, 1 meter higher than the W-9 stream gage. In 1991, V-notch weirs were installed at the A, B, and C sub-basins. The weirs were constructed from plywood and sealed in dense glacial tills. Streams A and B were gaged until

2006. The stream C weir was permanently breached in 2001 and replaced with a trapezoidal flume in October 2003. At all three stream gages, stream water level was measured with float driven shaft encoders and recorded every five minutes on a Campbell datalogger.

The second order reaches of streams A and B have boulder and cobble channels. Stream flow is perennial at the stream A weir but several steep and rocky upstream reaches flow through the channel bed under baseflow conditions promoting flow of surface water along hyporheic flowpaths. At the stream B and C gaging stations, flow occasionally stops under dry summer conditions during daylight hours when evapotranspiration is maximal. If dryness persists, flow stops for up to several weeks. In contrast to streams A and B, stream C only has a distinct channel where the stream originates from a wetland and flows down a steep hillslope. At the base of the slope, surface flow is only observed during high flows because the water is largely transmitted through a subsurface network of soil pipes (up to 20 centimeters in diameter that emerge through the soil), or other diffuse preferential flowpaths through shallow soil. Surface flow resumes immediately upstream of the C flume.

The Sleepers River Watershed has a rich history of hydrological and meteorological studies (Shanley, 2000). In the 1960s, the USDA Agricultural Research Service initiated research by establishing 15 nested stream gages in the Sleepers River catchment (USDA-ARS, 1965, 1973), 17 snow courses, six groundwater wells, and 31 meteorological stations (AGU, 1965; Hendrick and Comer, 1970). In seminal studies, Dunne and Black (1971a; 1971b) documented how source areas of stream water varied during snow and rainfall events by identifying saturation overland flow and shallow subsurface flowpaths to streams. Other studies from this era quantified rainfall-runoff responses (Comer and Zimmermann, 1969; Hendrick and DeAngelis, 1976; Engman, 1981; DeAngelis and others, 1984). In the 1970s, researchers in the National Weather Service of the National Aeronautic and Oceanic Administration studied the catchments of Sleepers River to develop models and predict the timing and amount of snowmelt runoff (Anderson, 1973, 1978). In the 1980s and 1990s, scientists at the Cold Regions Research and Engineering Lab of the US Army Corps of Engineers studied energy budgets (Pangburn and others, 1992), snow properties (Albert and Hardy, 1995; Albert and Perron, 2000; Melloh and others, 2001; Melloh and others, 2002), and snowmelt (Pangburn, 1987; Calkins, 1993; Albert and Greg, 1998). Since 1991, W-9 has been a long-term study site in the Water, Energy,

and Biogeochemical Budgets program of the US Geological Survey (Shanley, 2000). Streamflow measurements resumed or continued at four of the original 15 streams and five additional gages were occasionally monitored from 1992 to 2005. Recent studies have documented riparian (McGlynn and others, 1999) and hillslope (Kendall and others, 1999; Hjerdt, 2002; Shanley and others, 2003) flowpath dynamics. Other researchers have studied sources of stream water (Shanley and others, 2002a), nitrogen (Kendall and others, 1995; Campbell and others, 2000; Campbell and others, 2004; Ohte and others, 2004), sulfur (Bailey and others, 2004; Shanley and others, 2004; Shanley and others, 2005), mercury (Shanley and others, 2002b), DOC (McGlynn and others, 1999; Shanley and others, 2002b), dissolved inorganic carbon (Wolock, 1995; Bullen and Kendall, 1998; Doctor and others, in press) and base cations (Kendall and others, 1999). In uplands, the spatial variability of nitrification rates has been studied to investigate factors that may affect why nitrate concentrations differ among sub-basins (Ross and others, 2004; Ross and others, 2006)

My research at the Sleepers River Research Watershed adds a new dimension to previous studies of stream nitrogen and DOC sources. I present results that highlight the need to quantify how the water, nitrogen, and carbon cycles interact within the landscape to affect stream solute variation. The three chapters that follow this introduction will be prepared for peer-reviewed scholarly journals. The second and third chapters detail how coupled water, nitrogen, and carbon cycles explain stream nutrient variation during two distinct seasonal events (autumn leaf fall and spring snowmelt). In conjunction with end-member mixing analysis, isotopic signatures revealed water, nitrogen, and DOC sources and pinpointed the times when solutes were contributed to the stream along surficial flowpaths. I found direct contributions of nitrate from atmospheric sources during storm flow events – an important finding that measures the amounts of atmospheric nitrogen deposition that may be exported from a catchment without being transformed or retained by biogeochemical processes that typically limit the availability and mobility of this nutrient.

In the fourth chapter, I synthesize long-term data to quantify how the timing and magnitude of streamflow affected stream nutrient fluxes in relation to climate variability and ecosystem-wide nutrient enrichment. Storm events have an overriding influence on stream nitrate and DOC loadings. Because mobilization and transport of solutes from landscape source areas was directly related to event magnitude, changes in the timing of snowmelt, rainfall, and

runoff events suggest that climate change and anthropogenic nitrogen enrichment will have direct effects on seasonal and annual patterns of stream nitrogen and DOC fluxes.

Together, findings from these three studies build upon existing conceptual models of hydrological processes that link source areas in the landscape to streams and advance the perspective that coupled water, carbon, and nitrogen cycles interact to control the temporal and spatial variation of stream nutrient concentrations.

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CHAPTER 2

CONTROL OF STREAM NITROGEN IN AN UPLAND FOREST BY COUPLED HYDROLOGICAL AND BIOGEOCHEMICAL PROCESSES DURING AUTUMN

Abstract

To study how hydrological and biogeochemical processes control the forms and concentrations of stream nitrogen in forested uplands, we collected high-frequency hydrochemical data at the Sleepers River Research Watershed in northeastern Vermont, USA. Our study focuses on streamflow and nitrogen dynamics during autumn including a week when baseflow nitrate concentrations decreased by an order of magnitude during leaf fall. Nitrate concentrations rebounded from this “nitrate crash” and increased up to 25 fold during storm flow events that followed. The decreased nitrate concentrations during the nitrate crash are explained by in-stream transformations that retained up to 72% of the nitrate entering a stream reach. During storm flow events, hydrological measurements, isotopic signatures, and end-member mixing analysis revealed that flushing of nitrate from nitrified sources in surficial soils was an important control on stream nitrate variation and that atmospheric sources contributed up to 30% of the stream nitrate. Like nitrate, dissolved organic nitrogen (DON) was hydrologically flushed to the stream during storm flow. The baseflow responses of stream nitrate and DON differed. Decomposing leaves must have slowly released DON to the stream because baseflow concentrations increased and remained high for three months. Results from the high-frequency hydrochemical and isotopic tracers suggest a conceptual model in which the interaction of transport processes, sources, and transformations explains complex processes that affect stream nitrogen variation over time.

Introduction

Via atmospheric deposition, anthropogenic nitrogen rains down across forested uplands and is linked to stream chemistry by hydrological and biogeochemical processes in the landscape. The effects of nitrogen saturation (Aber and others, 2003), ecosystem acidification (Murdoch and Stoddard, 1993; Driscoll and others, 2001), and forest decline (Durka and others, 1994; McNulty and others, 1996) may cascade through ecosystems to influence the forms and concentrations of stream nitrogen (Vitousek and others, 1997; Perakis and Hedin, 2002; Galloway and others, 2003) but ecosystem responses to atmospheric deposition are highly variable even among similar watersheds (Stoddard, 1994; Creed and others, 1996; Peterjohn and others, 1999; Lovett and others, 2000; Boyer and others, 2002; Aber and others, 2003; Campbell and others, 2004). Consequently, deciphering the impacts of atmospheric deposition on streams in nitrogen enriched ecosystems has not been straightforward.

Autumn leaf fall may be an opportune time to study controls on stream nitrogen dynamics in the northeast USA, a region where forests are affected by anthropogenic nitrogen. Nitrate and dissolved organic nitrogen (DON) are the dominant forms of mobile nitrogen (Campbell and others, 2000; McHale and others, 2000; Campbell and others, 2004). Although stream DON concentrations have not been shown to be strongly seasonal (Campbell and others, 2000; McHale and others, 2000), low concentrations of stream nitrate are expected during the growing season when moisture, temperatures, and plant growth favor biological uptake (Stoddard, 1994). Despite decreased vegetative demand for nitrogen with the onset of vegetation dormancy during autumn, the annual concentration minima in the eastern USA sometimes occurs during a week or two following autumn leaf fall (Murdoch and Stoddard, 1993; Likens and Bormann, 1995; Mulholland and Hill, 1997; Swank and Vose, 1997; Lovett and others, 2000; Mulholland, 2004). Autumn leaf fall from deciduous vegetation replenishes the organic matter supply during a large magnitude, pulse input that is nearly half the total annual litterfall (Fisher and Likens, 1973). Although biological nitrogen uptake increases with the input of particulate and dissolved organic carbon (Tank and others, 2000; Sobczak and others, 2003; Mulholland, 2004; Park and Matzner, 2006), the reasons for the “nitrate crash” are not fully understood and we are not aware of field studies that detail how stream DON concentrations are affected by leaf fall. Nor is it clear how hydrological and

biogeochemical processes change to bring about the nitrate crash and influence the nitrate concentration rebound during autumn.

Stream nitrate concentrations may rebound when nitrate is hydrologically flushed from uplands to streams during storm flow. Dissolved nitrogen species and organic carbon are enriched in surficial soils by biogeochemical processes that mobilize these solutes from organic matter (Hornberger and others, 1994; Boyer and others, 1996; Creed and others, 1996). During autumn, frequent storm events may occur at a time when catchment wetness increases because evapotranspiration has decreased following the growing season. In headwater streams affected by elevated nitrate deposition, high stream nitrate and DON concentrations during storm flow are associated with flowpaths through the environment that link surficial soils in upland and riparian areas to streams (Creed and others, 1996; McHale and others, 2000; Inamdar and others, 2004; Hood and others, 2005). Nitrate from nitrified sources in upland and riparian areas affect stream nitrate responses during storm flow (Creed and others, 1996; Inamdar and others, 2004). Direct transport of nitrate from atmospheric deposition to streams is another possible landscape factor that affects stream nitrate concentrations and may affect the stream nitrate rebound during autumn. Although most nitrate from atmospheric sources cycles through the soil organic pool before flowing to streams (Kendall and others, 1995; Spoelstra and others, 2001; Burns and Kendall, 2002; Pardo and others, 2004; Campbell and others, 2007), isotopic tracers of stream nitrate sources, particularly δ^{18}O-nitrate, show that nitrate from an atmospheric source may be directly contributed to streams during storm flow events (Burns and Kendall, 2002; Campbell and others, 2002; Ohte and others, 2004; Chapter 3). The nitrate isotopic approach distinguishes sources because nitrate retains an atmospherically-distinct δ^{18}O-nitrate signature (+63 to +94‰) until nitrate is immobilized (Durka and others, 1994; Kendall, 1998). The δ^{18}O-nitrate signature is reset when nitrogen is remobilized. During nitrification, the oxygen from water (δ^{18}O-H_2O ranges from -25 to +4 ‰) and air (δ^{18}O-O_2 is about +23.5‰) is assimilated into nitrate to produce δ^{18}O-nitrate that is typically in the range of -10 to +15‰ (Kendall, 1998; Mayer and others, 2001; Kendall and others, 2007; Spoelstra and others, 2007).

Leaf fall may have a secondary effect on sources of flushed nitrate and create a feedback that reduces the magnitude of nitrate concentrations during the rebound. Inputs of organic carbon leached from leaves may fuel microbial uptake of nitrate in upland soils (Park and Matzner, 2006), an effect that would

reduce mobile nitrate stores in the landscape sources areas that connect to streams during storm flow events and prolong the effects of leaf fall on nitrogen cycling.

We collected high-frequency stream water samples over baseflow and storm flow to assess hydrological and biogeochemical processes that affect stream nitrogen forms and concentrations during autumn. Because the duration of the nitrate crash, time of the nitrate concentration rebound, and the response time of DON concentrations to autumn leaf fall are not well constrained, we intensively sampled prior to, during and after autumn leaf fall (September to December 2003). With chemical and isotopic tracers, we first document how nitrogen concentrations, sources, and transport vary with streamflow conditions. We then interpret the hydrochemical signal to explain how coupled hydrological and biogeochemical processes affect stream nitrogen variation under baseflow. We use the hydrological, chemical, and isotopic data to develop a conceptual model of how source contributions of nitrogen and organic carbon, transformations, and hydrological transport affect stream nitrogen variation throughout autumn including the nitrate crash and rebound.

Site Description

The Sleepers River Research Watershed in northeastern, Vermont, USA was well suited for our study. A sub-catchment in Sleepers River, Watershed 9 (W-9), has been a part of the Water Energy and Biogeochemical Budgets program operated by the US Geological Survey since 1991 (Shanley, 2000). Routine monitoring provides a long-term record of meteorology and stream hydrochemistry at W-9 (Peters and others, 2006). The existence of a hydrological measurement network (Shanley and others, 1995; Kendall and others, 1999) was ideal for collection of high-frequency hydrochemistry data to complement the long-term data.

The site is representative of many upland landscapes of the northeast USA because W-9 is completely forested with northern hardwood species and receives chronic, elevated deposition of atmospheric nitrogen (wet deposition is 13.2 kilograms total nitrogen per hectare, Campbell and others 2004). The stream is oligotrophic with phosphate concentrations that are always below detection limits. Stream nitrate patterns are symptomatic of a stage one response of nitrogen saturation (Stoddard, 1994) in which concentrations are seasonally low in summer and increase during storm flow events, especially

snowmelt (Shanley, 2000). At W-9, groundwater nitrogen concentration is low and baseflow nitrate concentration is low.

Watershed 9 is a south facing catchment on the eastern slopes of the Kittredge Hills. Pope Brook drains W-9 and forms the headwaters of Sleepers River which in turn flows to the Passumpsic River and then the Connecticut River. The elevation across the 40.5 hectare catchment ranges from 519 to 686 meter above mean sea level. The terraced glacial topography has steep slopes that rise to plateaus where streams originate. The calcareous silicate bedrock is a granulite that is interbedded with quartz-mica schists and micaceous quartzite (Hall, 1959). Above dense glacial tills, moderately to excessively well-drained Inceptisols and Spodosols have developed to depths of 50 to 90 centimeters on hillslopes (Shanley and others, 2003). Past studies show that upland water levels in W-9 may vary over a wide range of depths in upland soils depending upon wetness conditions (Hjerdt, 2002; Shanley and others, 2003) and that hydraulic conductivities of hillslope soils increase exponentially towards the soil surface (Kendall and others, 1999). In the wetlands and riparian areas that comprise about five percent of the land area, poorly-drained Histosols are up to two meters deep (Shanley and others, 2003).

Northeastern Vermont has a humid continental climate and precipitation is evenly distributed throughout a typical year. The mean annual temperature is 4.6 degrees Celsius (Shanley and others, 2004), the mean annual precipitation is 1334 millimeters, and the mean annual runoff is 735 millimeters at W-9. Autumn leaf fall occurs from mid-September to mid-October. The forest type is mixed hardwood and the trees are predominantly sugar maple (*Acer saccharum*) with some yellow birch (*Betula alleghaniensis*), white ash (*Fraxinus Americana*), red spruce (*Picea rubens*), and balsam fir (*Abies balsamea*).

Upstream of the W-9 weir, three tributary streams from the A (16.9 ha), B (12.9 ha), and C (8.1 ha) sub-basins merge to form Pope Brook (Figure 1). In the low-gradient section of the stream between the tributary confluence and the W-9 stream gage, the pools have organic-rich, sandy bottoms and riffles have boulder and cobble beds. During the lowest flows, the stream may flow completely subsurface through the sediments of pools for several meters.

Methods

Streamflow was calculated from stage-discharge relationships in accordance with US Geological Survey protocols (Rantz, 1982). Stream stage at

W-9 was measured at a 120º V-notch weir. At the A and B sub-basins, stream stage was measured at 90º V-notch weirs. Starting 7 October 2003, stream C was gaged with a 60º trapezoidal flume.

For a year of intensive sampling in 2003, we sampled stream water at high-frequency during base and storm flow. Weekly stream water grab samples were collected at the gaging stations on Tuesdays. Additional grab samples were collected on other days, especially during October when stream waters were sampled several times a week. To sample storm flow, an ISCO automatic sampler at each stream gage collected water when threshold changes in streamflow triggered simultaneous sample collection. Samples from ISCO samplers were usually retrieved weekly in 2003 and within twelve hours in October. Throughout 2003, more than 200 stream water samples were collected at the W-9 stream gage (fewer at tributary streams). In October, at least 55 samples were collected from each stream. Water grab samples were stored in new half liter LDPE bottles that were first tripled rinsed with sample water, then filled, and refrigerated (nitrogen specie concentrations) or frozen (nitrate isotopes) until filtered.

The intensive sampling from 2003 was compared to weekly W-9 stream samples that were collected from 1991 to 2002 in collaboration with the USDA Forest Service Northern Research Station and analyzed at the Durham, NH laboratory (Supplemental Information 1).

Rain and throughfall samples were collected to quantify the amount and chemistry of water inputs to W-9 from atmospheric wet deposition. At a meteorological station in a clearing near but outside W-9, direct rainfall was measured with a weighing bucket collector and recorded every five minutes. Rainfall chemistry samples were collected weekly on Tuesdays or immediately after events (15, 21, and 28 October 2003) from a polyethylene bucket in a wet-only precipitation collector. From May to October, throughfall samples were collected weekly from three 100 m^2 deciduous or coniferous plots (Figure 1).

In the 1990s, zero-tension soil lysimeters, recording wells, sampling wells, and piezometers were installed throughout W-9 (Figure 1, Shanley and others 1995, Kendall and others, 1999). A mid-hillslope recording well (site MI) was 50 meter from and 8 meters higher than the stream. An upslope recording well (site UP) was 70 meter from and 13 meter higher than the stream. To monitor the hydrological connectivity of riparian areas, groundwater levels were measured at

the T-3 piezometer and BW-19 well. Groundwater levels were recorded every 30 minutes and were manually measured at least monthly to verify the logged data.

Samples were collected from BW-39A, a sampling well next to the UP recording well, on four dates in autumn 2003. On 12 November 2003, samples were collected at other locations (BW-40A, BW-27A, BW-37, and T-1) to evaluate the spatial variation of groundwater chemistry (Figure 1). Wells and piezometers were evacuated prior to sampling so that fresh water samples were collected for chemistry.

When soil flowpaths developed after rainfall, soil water samples from the vadose zone were collected immediately beneath the O horizon using zero-tension lysimeters. Lysimeters were next to the MI and UP wells and several samples were collected from each (four samples at MI and two samples at UP).

Sample processing and analysis (see Supplemental Information 2)

Samples for nitrate, total nitrogen, and nitrate isotope analyses were filtered through 0.45 micrometer membrane filters. Aliquots were filtered into pre-cleaned HDPE bottles and refrigerated until analyzed. Nitrate concentrations were measured using suppressed conductivity detection and a Dionex IonPac AS14 column on a Dionex DX-500 ion chromatograph. Nitrite was not quantifiable for any sample. For a subset of the samples, total nitrogen concentrations were analyzed by the alkaline persulfate oxidation technique (Solorzano and Sharp, 1980) and measured by colorimetry on a Lachat AutoAnalyzer (QuikChem FIA^{+} 8000). Dissolved organic nitrogen (DON) concentrations were calculated by subtracting nitrate from total nitrogen concentrations. Because ammonium is a small component of total stream nitrogen fluxes (over all years, mean stream ammonium was less than four percent of the total nitrogen concentration), ignoring ammonium had a minimal effect on calculated DON concentrations.

Nitrate isotopic composition was measured on a subset of the water samples. Samples were prepared using the denitrifier method (Sigman and others, 2001; Casciotti and others, 2002) and analyzed for $\delta^{15}N$ and $\delta^{18}O$ on a Micromass IsoPrime mass spectrometer at the USGS Menlo Park Stable Isotopes Laboratory (MPSIL) in California (Supplemental Information 3). Replicates of 10% of the samples were analyzed in duplicate. Due to method constraints and limited sample volumes, only samples with concentrations greater than 1.0 µmol L^{-1} were analyzed. This limitation excluded analysis of

stream samples from 13 to 14 October 2003, some soil water, and most groundwater samples.

End-member mixing analysis can be used to quantify atmospheric and nitrified sources of stream nitrate (Durka and others, 1994; Kendall, 1998). Contributions of nitrate from atmospheric (ATM) and nitrified (NIT) sources were separated using a two-component mixing model in which rain water (c_{ATM}) and average nitrified isotopic composition of soil and ground waters (c_{NIT}) were the mixing end-members used to solve the equations,

$$f_{ATM} + f_{NIT} = 1 \quad (1)$$

$$c_{stream} = f_{ATM} \times c_{ATM} + f_{NIT} \times c_{NIT} \quad (2)$$

where c is the $\delta^{18}O$-nitrate of each fraction (f) contributing nitrate to stream water as identified by the subscripts ATM or NIT.

Samples of stream, soil, and ground water for DOC measurement were filtered through 0.7 µm binder-free glass fiber filters into amber glass bottles with Teflon-lined caps and refrigerated. All DOC concentrations were measured by catalyzed persulfate wet oxidation on total organic carbon analyzers.

Stream water and solute mass balances

Stream water fluxes were calculated by integrating stream discharge for each stream gage. A concentration for a time interval was multiplied by the corresponding total runoff in that time period to calculate a solute flux. Time intervals varied with the frequency of sampling because each time interval starts at the midpoint between a sample and the preceding one. The time interval ends at the midpoint between a sample and the next one. Fluxes were linearly interpolated between the calculated values and integrated to estimate daily fluxes.

To probe the effect of data resolution, we calculated stream nitrate, DON, and DOC fluxes for October separately using the high-frequency data and using only weekly data from Tuesdays. In another exercise to discern the effect of autumn leaf fall on nitrate and DOC fluxes from September through November, the post-leaf fall effect was “removed” from the high-frequency data by substituting the mean summer baseflow nitrate and DOC concentrations for autumn baseflow chemistry.

Input/output mass balances to quantify solute losses and gains can be calculated for the study reach between the upstream gages (A, B, and C) and the W-9 gage because no other tributaries enter. From 8 October 2003 (date when

the discharge measurements resumed at stream C) to 30 November 2003, daily input/output budgets were calculated. Solute mass balance values are reported in two ways: as the mass per area per day (mg m^{-2} d^{-1}),

$$\Delta \text{mass flux}_{\text{reach}} \ (\text{mg m}^{-2}\ \text{d}^{-1}) = \text{output}_{\text{W-9}} - \sum \text{tributary inputs}, \quad (3)$$

and as the percent relative difference between the W-9 gage and the tributary inputs,

$$\Delta \text{mass flux}_{\text{reach}} \ (\%) = \frac{\text{output}_{\text{W-9}} - \sum \text{tributary inputs}}{\text{output}_{\text{W-9}}} * 100 . \quad (4)$$

The percent relative differences normalize data to show net losses or gains in the stream reach under baseflow that would otherwise be obscured by the exponentially larger fluxes that occurred with storm flow.

Results

Catchment wetness during autumn

In 2003, the annual precipitation (1578 mm) and annual runoff (900 mm) were both about 20% greater than the long-term mean. Compared to other years, stream runoff was particularly high in October (2.4 times greater than the long-term monthly average), November (2.3 times greater), and December (2.3 times greater).

The catchment was driest in September when evapotranspiration was high and little rain fell. In 2003, autumn leaf fall started in late-September and heaviest leaf fall occurred from 9 to 15 October during a week of baseflow recession. Flowpaths through the landscape changed after autumn leaf fall when catchment wetness increased in response to a series of October rainfall events. Riparian water table fluctuations were synchronous with storm flow showing that riparian areas were highly connected to the stream (Figure 2). In contrast, water levels at upland hillslope positions remained near the till and bedrock interface until rainfall recharged groundwater storage. At the midslope well, water levels began to rise in late September but fluctuations were damped and lagged relative to the stream hydrograph until the third week of October. Water levels were even more damped and lagged relative to streamflow at the upslope well.

Stream hydrochemistry during autumn

High-frequency hydrochemical measurements documented a strong response of baseflow stream nitrate concentrations during autumn leaf fall. As

leaves covered the ground and became partially or wholly submerged in stream water (see Supplemental Information 4), stream nitrate concentrations progressively decreased from 5.4 to 0.7 μmol L^{-1} as specific discharge decreased from 0.10 to 0.07 mm h^{-1} between 9 and 15 October (Figure 3). Concentrations less than 4.0 μmol L^{-1} were not observed at any other time in 2003 (Figure 4b) and nitrate concentrations during the crash were significantly different ($p << 0.0001$) than baseflow from May to August (9.03 ±1.37 μmol L^{-1}, mean ±standard error). For the long-term data (1991 to 2005), such low stream nitrate concentrations only occurred in September or October corresponding to autumn leaf fall (Figure 5a). Like the W-9 outlet stream, the nitrate crash occurred at the A, B, and C tributary streams (Figure 3).

Baseflow DON concentration slightly increased from September to December 2003 (Table 1). Unlike the rest of the year, DON was a larger component of stream total nitrogen during and after autumn leaf fall. In other years, too, the highest annual concentrations of baseflow DON followed autumn leaf fall (Figure 5a).

At the time of the nitrate crash and continuing through November, baseflow DOC concentrations were higher than baseflow samples collected in August and early September 2003. Likewise, DOC concentrations of 133 to 150 μmol L^{-1} during the nitrate crash were 20 to 36% higher than the long-term baseflow average of 111 μmol L^{-1} (Figure 4c). The annual maxima of the DOC to nitrate ratio (DOC:nitrate) occurred after autumn leaf fall (Figure 4d), consistent with other years (Figure 5b).

During storm flow events, streamflow varied over three orders of magnitude (0.002 to 1.5 mm h^{-1}) and stream chemistry dramatically changed. During storm flow, stream nitrate concentrations were up to 25 times higher than pre-event baseflow, DON was up to ten times higher, and DOC was up to seven times higher (Figure 3). In contrast to nitrate and DOC, peak DON concentrations during storm flow were higher during autumn than the rest of the year. When events were closely spaced in October, storm event nitrate, DON, and DOC concentrations increased every time that storm flow increased but concentrations did attenuate over successive events (i.e. for equal or higher streamflow, peak concentrations decreased).

The stream reach between the W-9 gage and the three tributaries was a net sink of nitrate between 7 to 14 October and a net source during storm flow (Figure 6). On 8 October, 27% more nitrate entered the stream reach than was

exported from W-9. The net losses increased every day thereafter until 14 October when 258% more nitrate entered the stream reach than was exported from W-9, a net retention of 72% (Figure 6). When nitrate concentrations rebounded, the stream reach was a net source of nitrate. Throughout much of October, the stream reach was a net source of DOC and DON during base and storm flow. From 8 to 14 October, more DOC (about 20% more per day) and DON (25 to 40% more per day) were exported from the stream reach than entered from the tributaries (Figure 6).

Nitrate concentrations of rain (6 to 36 μmol L^{-1}) and throughfall (0 to 68 μmol L^{-1}) varied over time (Figure 3). Fluxes with rainfall were also highly variable depending on the amount and chemistry of rainfall. Twenty-five percent of the nitrate input with rain from September through November occurred during one event when 0.03 g m^{-2} was deposited to the catchment on 21 October.

Despite the large input of nitrate with precipitation on 21 October, nitrate concentrations of shallow soil water were low after leaf fall (<2 μmol L^{-1}) compared to early September (12 to 15 μmol L^{-1}), see Table 1. Concentrations of DOC in shallow soil water were higher in early September (495 to 1169 μmol L^{-1}) than after leaf fall (357 μmol L^{-1}, Table 1). Likewise, DON concentrations in shallow soil water were higher (22 to 80 μmol L^{-1}) before than after leaf fall (11 to 17 μmol L^{-1}, Table 1).

Groundwater chemistry at BW-39A varied little from September to November relative to stream and soil waters (Table 1). Although spatially heterogeneous on 12 November 2003, groundwater nitrate ranged from 0 to 10.3 μmol L^{-1} at several locations and was typical of the average baseflow concentration during autumn. However, groundwater DOC (16 to 48 μmol L^{-1}) and DON (0 to 1.3 μmol L^{-1}) concentrations were significantly less ($p < 0.05$) than average baseflow concentrations.

Although the $\delta^{15}N$-nitrate values overlapped, $\delta^{18}O$-nitrate values differed among various end-members (Table 2). The $\delta^{18}O$-nitrate values of precipitation and throughfall (+70.0 to +101.3‰) were distinct from groundwater (+2.0‰) and baseflow (-0.5 to +5.8‰). During one storm event (21 October), stream $\delta^{18}O$-nitrate values increased to a peak of +32.1‰ with increased streamflow. During storm flow recession, stream $\delta^{18}O$-nitrate decreased to pre-event levels. As calculated from a two-component mixing model, a peak of 33% of the stream nitrate was directly contributed from an atmospheric source during storm flow on 21 October (Figure 8). Over the entire event, the direct contribution of

atmospheric nitrate was 16% of the total stream nitrate flux. For all other storm flow events, stream δ^{18}O-nitrate values were between -4.4 and +8.7‰.

During the nitrate crash, the stream δ^{15}N-nitrate did not change while the δ^{18}O-nitrate became more enriched when stream nitrate concentrations decreased (Figure 7). Before autumn leaf fall, the isotopic composition of baseflow nitrate differed from that of a groundwater sample (the single sample that had sufficient nitrate to measure δ^{18}O-nitrate).

Two soil water samples were collected during the 30 August storm event. The δ^{18}O-nitrate of one sample was +1.42‰, in the range of a nitrified source of nitrate. The δ^{18}O-nitrate of the other sample was +45.5‰, a value that is midway between pure nitrified and atmospheric nitrate sources. In that soil water sample, the atmospheric contribution calculated from a mixing model was 45%. On 29 September, δ^{18}O-nitrate of a soil water sample was -2.3‰ showing that the soil nitrate pool may variously be affected by atmospheric or nitrified sources. Concentrations of soil water nitrate were too low to measure the isotopic composition following leaf fall.

Discussion

Interpretation of stream hydrochemical records provides insight about processes that affect the forms, concentrations, and movement of nitrogen in the landscape. Our findings point to a conceptual model of coupled hydrological and biogeochemical processes that control stream nitrogen dynamics during autumn. We first describe a framework to link transport processes, sources, and transformations to the dynamics of stream nitrogen and organic carbon variation. We then describe biogeochemical processes that were consistent with tracer data and hydrological conditions. Finally, we discuss how source variation influenced nitrogen delivery to streams during storm flow events and show that stream nitrate concentrations rebounded when nitrified sources were flushed to streams from surficial soils.

Conceptual model to link transport, sources, and transformations in forest streams

Sources, transformations, and transport processes interact to control stream nitrogen variation. Baseflow nitrogen variation should be driven by in-stream biogeochemical processes because the groundwater that supplies water, nitrate, DON, and DOC has a chemistry that is fairly stable throughout the year

(relative to the shallow soil water and precipitation inputs). During autumn leaf fall, the magnitudes and types of biogeochemical transformations may change as inputs of fresh organic matter (particulate and dissolved forms) affect in-stream nitrogen processing (Sobczak and others, 2003; Goodale and others, in prep; Thomas and others, in prep).

In response to rainfall and increasing catchment wetness, surficial source areas in upland and riparian areas may become linked to streams during storm events (Hewlett and Nutter, 1970; Dunne, 1978). The spatial extent of connected surficial source areas varies over time because hydrological flowpaths respond to antecedent moisture and the magnitude of rainfall. As a function of both proximity and near-surface saturation, riparian areas shunt rain and throughfall to streams along surficial flowpaths that rapidly deliver water and solutes during storm flow (Hewlett and Nutter, 1970; Dunne and Black, 1971; Hornberger and others, 1994; Creed and others, 1996; Boyer and others, 1997). With sufficient rain and increasing catchment wetness, surficial soils on hillslopes may connect to streams via a number of preferential flow mechanisms that include flow above perched water tables (Mulholland, 1993), along soil macropore networks (McDonnell, 1990; Sidle and others, 2001), through highly-transmissive shallow soils (Kendall and others, 1999; Shanley and others, 2003), or as return flow (exfiltrated subsurface water that flows across saturated areas). With flow along these preferential flowpaths, stream nitrate may originate from hydrological flushing of surficial source areas (Creed and others, 1996) and the input of atmospheric nitrate (Durka and others, 1994; Ohte and others, 2004) in addition to inputs from groundwater. As landscape source areas are flushed to streams, the supply of solutes during storm flow exceeds inputs during baseflow. Furthermore, the residence times of water, particulates, and solutes in a stream during storm flow are short relative to baseflow. Corresponding to changes that occur when flowpaths change, biogeochemical transformations including net primary production (Roberts and others, 2007), net ecosystem respiration (Roberts and others, 2007), nitrification (Cooper, 1983), and nutrient uptake (Mulholland, 2004) all decrease as hydraulic gradients from hillslopes to streams increase, the mass flux of water in the stream channel increases, and hyporheic flow decreases relative to streamflow (Fisher and others, 1998; McGlynn and others, 1999; Harvey and Wagner, 2000).

Linking catchment hydrology to biogeochemistry during autumn

Leaching of DON from leaves may explain the elevated baseflow DON concentrations in the W-9 streams. In a mesocosm study, DON was released from leaf tissues within two days of immersion and the leached organic nitrogen persisted for weeks (Wetzel and Manny, 1972). Alternatively, microbes that colonize decomposing leaves may release DON to the stream (Gosz and others, 1973; Howarth and Fisher, 1976).

Data from several other studies document the occurrence of the nitrate concentration minima in autumn (Biscuit Brook, Murdoch and Stoddard 1993; Coweeta Hydrological Laboratory, Swank and Vose 1997; the Hubbard Brook Ecosystem Study, Likens and Bormann 1995; Walker Branch Watershed, Mulholland and Hill 1997, Mulholland 2004; Winnisook Brook, Lovett and others 2000). For the Walker Branch Watershed, Mulholland and Hill (1997) explain a relationship between seasonally low stream nitrate concentrations and organic carbon availability after autumn leaf fall, the time of year when in-stream transformations were highest (Mulholland, 2004).

At W-9, the release and retention of nitrate, DON, and DOC were different during baseflow and stormflow. Under baseflow, the decreased mass fluxes of nitrate through the reach (outputs relative to inputs) after autumn leaf fall indicated in-stream nitrate retention. Although we did not measure biogeochemical transformations such as assimilative uptake, nitrification, or denitrification, stream hydrochemistry suggested coupled hydrological and biogeochemical controls on stream nitrogen variation. The nitrate crash occurred when transformations during baseflow exceeded supply via transport. As indicated by nitrate concentration increases and net sources of stream nitrate during storm flow, stream nitrate concentrations rebounded because nitrate was supplied at rates that exceeded the capacity of in-stream processes to retain nitrate that was newly flushed to the stream.

Biological uptake and denitrification are the biogeochemical processes that account for nitrate retention in streams (Sobczak and others, 2003). Similar to other shaded forest streams that receive little direct light and have low nutrient concentrations (Mulholland and Hill, 1997; Bernhardt and Likens, 2004), we expected minimal autotrophic uptake of inorganic nitrogen at W-9 during autumn. Even with greater light penetration through a leafless canopy, fallen leaves shaded the W-9 streams (see Supplemental Information 4). Our expectation of negligible uptake by autotrophs during the nitrate crash at W-9 is consistent with

a study that reports light limitation of in-stream gross primary production when leaf litter covered a headwater stream in an oak-hickory forest (Roberts and others, 2007).

Assimilative nitrogen uptake by leaf colonizing bacteria and fungi (Howarth and Fisher, 1976; Webster and Benfield, 1986; Sanzone and others, 2001; Gulis and Suberkropp, 2003; Sobczak and others, 2003) may cause the low concentrations of stream nitrate that we measured. Along with assimilative uptake, in-stream nitrification and denitrification may also affect stream nitrate variation under baseflow. Along hyporheic flowpaths, in-stream nitrification affects stream nitrate concentrations over distances of tens of meters on timescales of hours (Richey and others, 1985; Mulholland and others, 2000; Tank and others, 2000; Peterson and others, 2001; McKnight and others, 2004) similar to the spatial and temporal scales of transport and transformations in the W-9 stream reach. Because in-stream nitrification is common (Strauss and Lamberti, 2000; Peterson and others, 2001), nitrification was likely a source of stream nitrate that supplemented groundwater inputs before autumn leaf fall at W-9. A number of other studies report in-stream nitrogen transformations that are coupled to organic carbon bioavailability. In contrast to other times of the year when DOC is leached from older litter and more degraded soil organic matter, fresh litter from autumn leaf fall is bioavailable organic carbon (Fisher and Likens, 1973; McDowell and Likens, 1988; Meyer and others, 1998; Sobczak and Findlay, 2002; Sobczak and others, 2003; Qualls, 2005). The measured DOC gains in the W-9 stream reach indicate an increased DOC supply after autumn leaf fall, yet stream DOC concentrations minimally increased relative to the large input of organic carbon that occurred during autumn leaf fall. This apparent paradox is explained if DOC gains in the stream led to increased heterotrophic demand for a limited baseflow nitrate supply and rapid turnover of DOC through microbial processing with the net result of a modest increase in stream DOC concentrations.

Could stream DOC cycling be linked to nitrification? Above a critical C:N of about 18 to 21, heterotrophic bacteria outcompete nitrifiers for ammonium (molar ratio) which in turn limits nitrification (Strauss and Lamberti, 2000; Bernhardt and Likens, 2002). The rise of stream water DOC:nitrate at W-9 to values of 20 to more than 100 during autumn leaf fall (Figure 4) suggested that stream nitrate was not replenished because in-stream nitrification decreased or stopped when microbial uptake drew down the stream nitrate supply. This

possible feedback on low baseflow nitrate at W-9 concentrations is consistent with low nitrification rates that have been measured at the Coweeta Hydrological Laboratory during autumn leaf fall (Tank and others, 2000).

We investigated the W-9 nitrate isotopic data as an indicator of in-stream transformations. Before autumn leaf fall, nitrate may have been nitrified in-stream causing the δ^{18}O-nitrate to reflect a signature that differed from that of groundwater. Although not definitive, the δ^{18}O-nitrate shift towards the groundwater value during the nitrate crash is consistent with a decrease of nitrification when the DOC:nitrate increased above 20.

The hyporheic zone is an important site of denitrification (Peterson and others, 2001; Mulholland, 2004; Mulholland and others, 2004). Addition of DOC along hyporheic flowpaths has stimulated denitrification (Baker and others, 1999; Sobczak and others, 2003) although low concentrations of stream nitrate may limit the nitrate supply to denitrifiers (Bernhardt and Likens, 2002). Production of DOC within the W-9 stream reach may have provided a ready supply of DOC to fuel denitrificaiton in sections of the stream that flowed subsurface during the nitrate crash when streamflow was low. If nitrate is not limiting and no other transformations change the nitrate isotopic composition, the relationship between δ^{18}O-nitrate and δ^{15}N-nitrate may be linear and have a slope between 0.5 and 1.0 during denitrification (Böttcher and others, 1990; Kendall, 1998; Groffman and others, 2006). This possible diagnostic pattern was not observed at W-9, a circumstance that does not disprove denitrification because other sources and biogeochemical processes may have affected the nitrate isotopic composition.

Quantifying nitrified and atmospheric sources of nitrate during storm flow

As noted by Ohte and others (2004), high-frequency δ^{18}O-nitrate data may be needed to quantify direct nitrate contributions from atmospheric sources. Other studies of nitrate sources using high-frequency isotope data have thus far focused on snowmelt events (Ohte and others, 2004; Chapter 3). Our high-frequency δ^{18}O-nitrate data are the first published that show and quantify direct contributions of atmospheric nitrate to streams during autumn. Along with those snowmelt studies, our data show that the soil nitrified pool of nitrate may be augmented or replaced by atmospheric sources that contribute a majority (50 to 80%) of the nitrate along flowpaths through surficial soils during specific storm events.

Stream nitrate concentrations were higher during the 15 October event than the next three events. Despite low nitrate concentrations in rain and ground water during the 15 October 2003 storm, stream nitrate concentrations increased 25 fold. Stream δ^{18}O-nitrate (<+7.7‰) at W-9 was in the range of nitrified sources. Stream nitrate must have originated from near-stream sources because deep water levels at the hillslope wells showed that highly-transmissive surficial flowpaths in uplands were not connected to streams before the last week of October (Figure 2).

Rapid transport of atmospheric nitrate partially explained high stream nitrate concentrations during the next rainfall event on 21 October. Of the possible sources, groundwater nitrate concentrations were perennially low (≤10.3 μmol L^{-1}), soil water concentrations were low (1.5 μmol L^{-1}) after the 15 October flush, and rain nitrate concentrations were high (36.2 μmol L^{-1}) during this storm event. The stream water δ^{18}O-nitrate of +32.1‰ was well above δ^{18}O-nitrate of any nitrified source that has been measured at W-9 (Figure 7, Table 2; see Kendall and others, 1995; Ohte and others, 2004; Chapter 3) and could only result from mixing of atmospheric and nitrified sources. At peak flow on 21 October, 30% of the stream nitrate was contributed from an atmospheric source while the remaining 70% originated from the flushing of a soil nitrified source. Nitrified sources must have originated from near-stream areas because surficial soils on upland hillslopes were not connected to the stream via saturated lateral flow. After 21 October, direct inputs from atmospheric sources were less than 10% during events and stream nitrate concentrations hardly increased. The terrestrial nitrate supply may have been drawn down by hydrological flushing or the low concentrations may have resulted from nitrate uptake in uplands that was stimulated by organic carbon inputs. However, dilution was not a factor that affected low soil water nitrate concentrations after leaf fall because rain concentrations were too high to dilute soil water nitrate along surficial flowpaths. If organic carbon inputs stimulated biological uptake in soils, nitrate was not completely drawn down because stream nitrate always increased when surficial sources areas were flushed. Furthermore, transport of nitrate from a nitrified source to the stream showed that some nitrate was always available in terrestrial source areas.

High-frequency data and detection of the nitrate crash

Our data expand upon long-term monitoring programs in temperate forests of the eastern USA (Murdoch and Stoddard, 1993; Likens and Bormann, 1995; Mulholland and Hill, 1997; Swank and Vose, 1997; Lovett and others, 2000; Mulholland, 2004). Although the nitrate crash is not apparent in all years of those studies, the absence of low nitrate concentrations may be an artifact of less frequent sampling. For example, a nitrate crash may not be detected if low nitrate concentrations occur between weekly samples. Likewise, a sample collected during storm flow when sources change may not reveal a nitrate crash.

When fluxes were calculated from the weekly-only data, the flux estimates differed somewhat (6% less) for nitrate reflecting stream nitrate concentrations that were sometimes high and sometimes low depending on the specific storm flow event. Stream DOC loading from the high-frequency estimate was 17% more than the weekly estimate and stream DON loading from the high-frequency estimate was 12% more than the weekly estimate. The differences of DOC and DON fluxes between weekly and high-frequency estimates reflect the weekly sampling that included low concentrations but missed high concentrations during storm events.

In September, the differences between the high-frequency and hypothetical “no leaf fall effect” flux estimates were minimal for nitrate (only 1% less before major leaf fall occurred). However, estimated nitrate fluxes for the hypothetical situation were more in October (+32 %) and November (+39%) illustrating the extent to which transformations after autumn leaf fall may have decreased stream nitrate fluxes. For each month, the “no leaf fall effect” DOC loading estimates were similar (5 to 9% less) to the observed loadings reflecting large quantities of DOC flushed during storm flow relative to the much smaller fluxes during baseflow. The “no leaf fall effect” DON loading estimate was 7% less in October and reflected the effect of increased DON production in the stream reach with leaf fall. The November “no leaf fall effect” estimate reversed and was 5% more.

Conclusions

Using a high-frequency hydrochemical approach, we identified sources of stream nitrate, the increased retention of nitrate during autumn leaf fall, and hydrological transport processes that influenced stream nitrogen variation. Two key findings are that in-stream biogeochemical processes affect baseflow

nitrogen concentrations after autumn leaf fall and quantifying nitrate responses to streamflow conditions is important for understanding nitrogen variation. After autumn leaf fall, stream DON concentrations were higher than nitrate concentrations and DON concentrations during autumn storm events were higher than any other time of the year. These insights shed light on the short-term processes ("hot moments") that occur in relatively small portions ("hotspots") of the landscape to control the forms and concentrations of stream nitrogen (Cirmo and McDonnell, 1997; McClain and others, 2003). Furthermore, apportioning sources, transformations, and transport processes in the landscape helps to explain hydrological and biogeochemical processes that affect stream nutrient variation during autumn including the nitrate crash and rebound.

A third key finding is that quantifying nitrate sources is critical to understanding stream nitrate variation during storm flow. The nitrate stable isotope data showed that direct nitrate contributions from an atmospheric source affected stream nitrate variation during certain storm flow events. Expanding upon previously identified snowmelt events (Campbell and others, 2002; Ohte and others, 2004; Chapter 3), the measured nitrate contributions from atmospheric sources identify and quantify a direct link between anthropogenic nitrogen pollution and stream nitrate concentrations fluxes in catchments of the northeast USA that are not nitrogen saturated.

As evidenced by a number of studies, the effect of autumn leaf fall on stream nitrogen cycling is important because nitrogen availability in aquatic ecosystems changes as the forms and concentrations of nitrogen change (Mulholland and Hill, 1997; Tank and others, 2000; Mulholland and others, 2004; Goodale and others, in prep; Thomas and others, in prep). Together, these studies document the occurrence and importance of changes to stream nitrogen cycling during autumn leaf fall that affect whole-ecosystem processing of nitrogen. While our study illustrates the strengths of a hydrological approach, we recommend coordinated efforts that couple high-frequency stream hydrochemical measurements with studies that quantify rates of terrestrial and in-stream transformations to definitively pinpoint how biogeochemical processes are affected by increased organic carbon availability.

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Tables

Table 1. Ranges of nitrate, DOC, and DON concentrations for stream, soil, and groundwaters prior to, during, and after the 2003 nitrate crash at the W-9 stream.

	before 7 October	nitrate crash 7 to 14 October	after 15 October
nitrate concentration (μmol L^{-1})			
W-9 stream baseflow	7.4 to 9.7	0.7 to 5.4	4.1 to 7.2
W-9 stream storm flow	7.5 to 30.9	--	4.0 to 24.4
shallow soil water	11.8 to 15.1	--	0.7 to 1.5
groundwater (BW-39A)	2.9	1.28	0
DOC concentration (μmol L^{-1})			
W-9 stream baseflow	107	133 to 150	116 to 157
W-9 stream storm flow	100 to 798	--	199 to 880
shallow soil water	495 to 1169	--	357
groundwater (BW-39A)	26	--	48
DON concentration (μmol L^{-1})			
W-9 stream baseflow	0.4 to 7.5	2.5 to 4.5	4.0 to 11.4
W-9 stream storm flow	2.5 to 23.2	--	6.1 to 25.8
shallow soil water	22.4 to 79.8	--	10.9 to 16.7
groundwater (BW-39A)	0	0.2	1.3

Table 2. Ranges of δ^{15}N-nitrate and δ^{18}O-nitrate for stream (W-9), soil, and ground waters during autumn 2003.

	δ^{15}N-nitrate (‰)	δ^{18}O-nitrate (‰)	number of samples
W-9 stream baseflow	+0.7 to +2.2	-0.5 to +5.8	9
W-9 stream storm flow	-3.3 to +6.5	-4.4 to +32.1	29
Shallow soil water	-6.8	-2.3	1
groundwater	+0.3	+2.0	1
rainfall	-4.2 to +2.0	+70.0 to +101.3	6
throughfall	+3.5	+75.9	1

Figures

Figure 1. Map of the 41 hectare forested Watershed 9 at the Sleepers River Research Watershed. The numbers identify wells and piezometers.

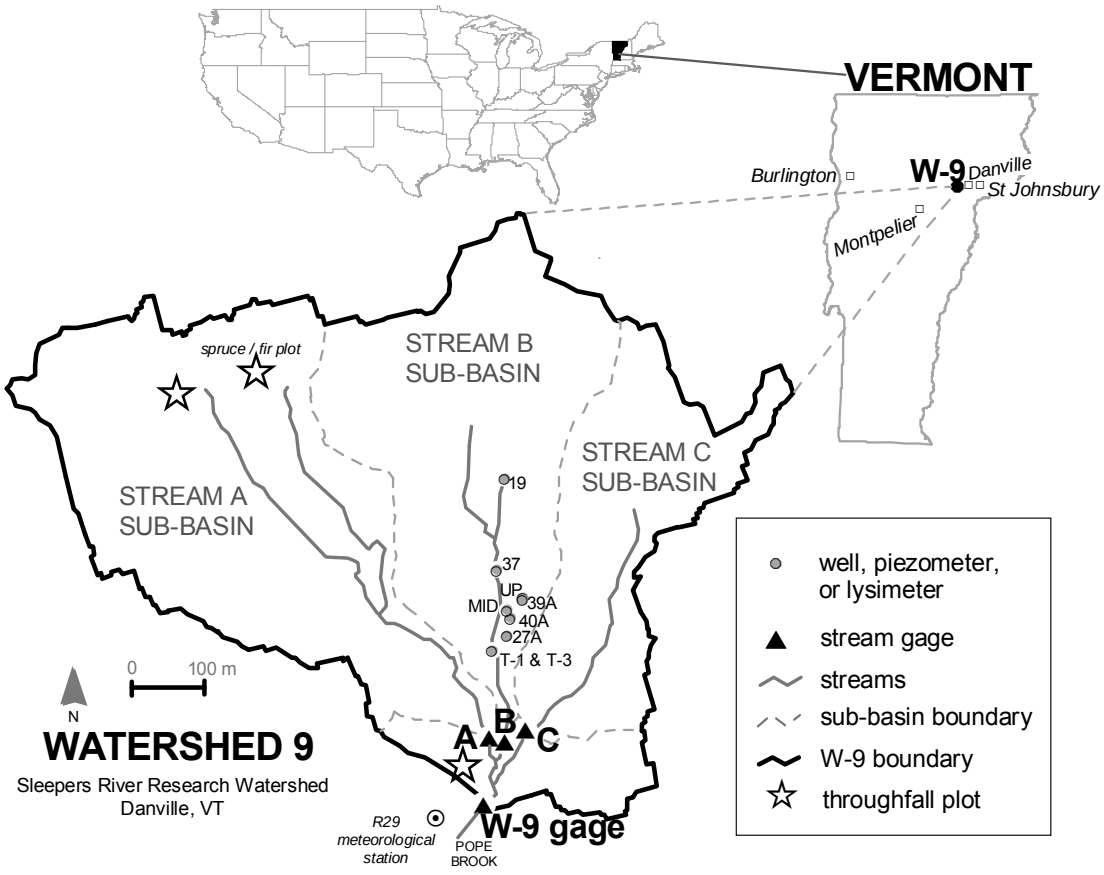


Figure 2. Hydrological responses at mid-slope and upslope sites were lagged and damped relative to near-stream areas (riparian and convergent hollow wells) that were highly connected to the stream. Data from Kendall and others (1999) show the exponential increase in hydraulic conductivity that occurs as saturation rises nearer the surface and water flows through surficial soils (b).

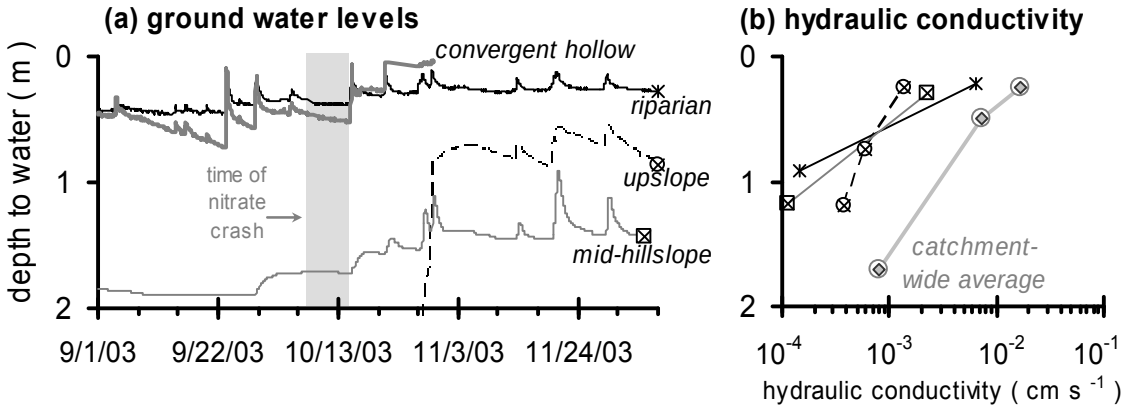


Figure 3. The amount, and distribution rain are shown along with rain and throughfall nitrate concentrations during the autumn 2003 study (a). At the W-9 stream (b) and the upstream tributaries (c), nitrate concentrations decreased from typical summer baseflow concentrations to low levels during autumn leaf fall.

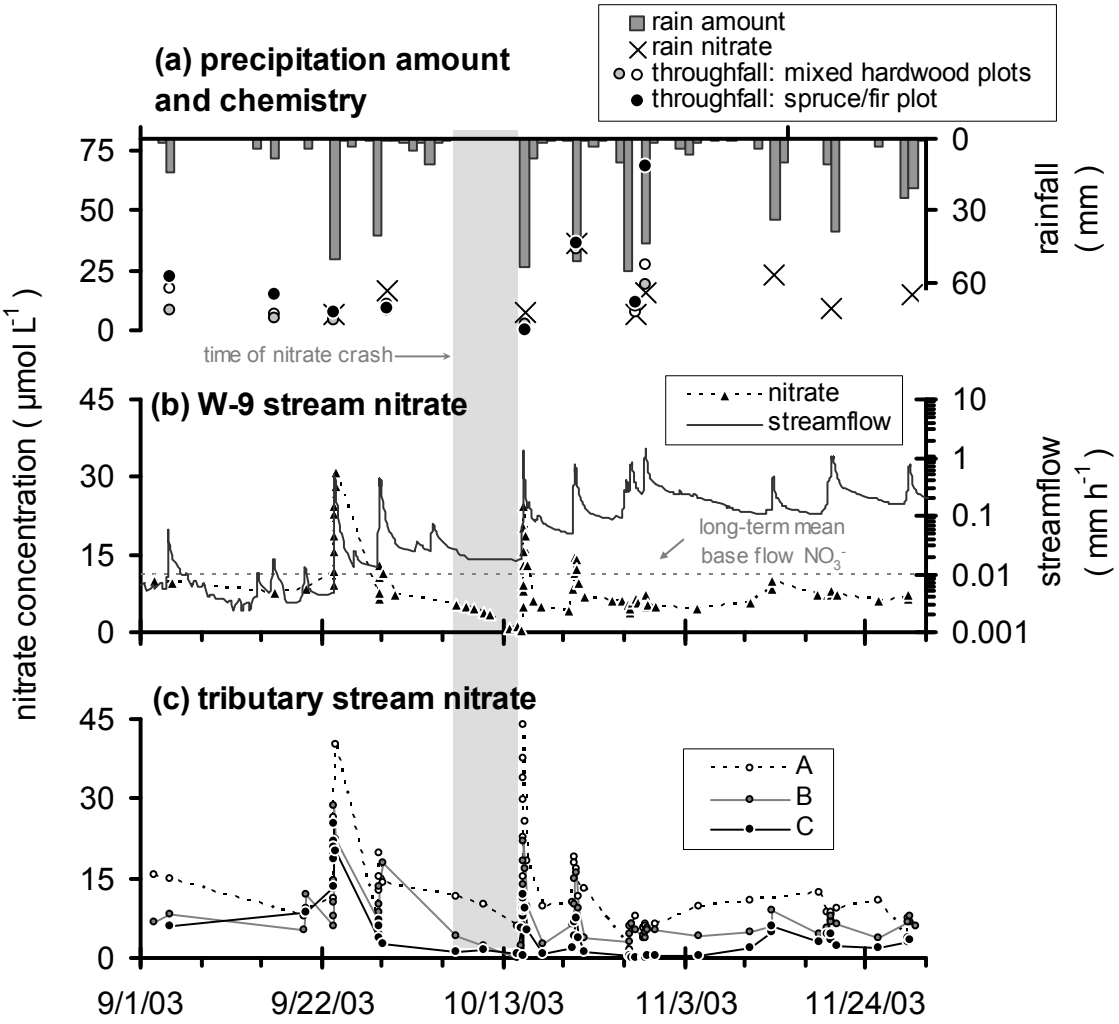


Figure 4. At W-9, streamflow varied throughout the year (a). Baseflow concentrations were fairly stable and nitrate, DON, and DOC concentrations increased under storm flow. The lowest annual nitrate concentrations occurred during leaf fall (b) when DOC (c) was more abundant relative to nitrate (d).

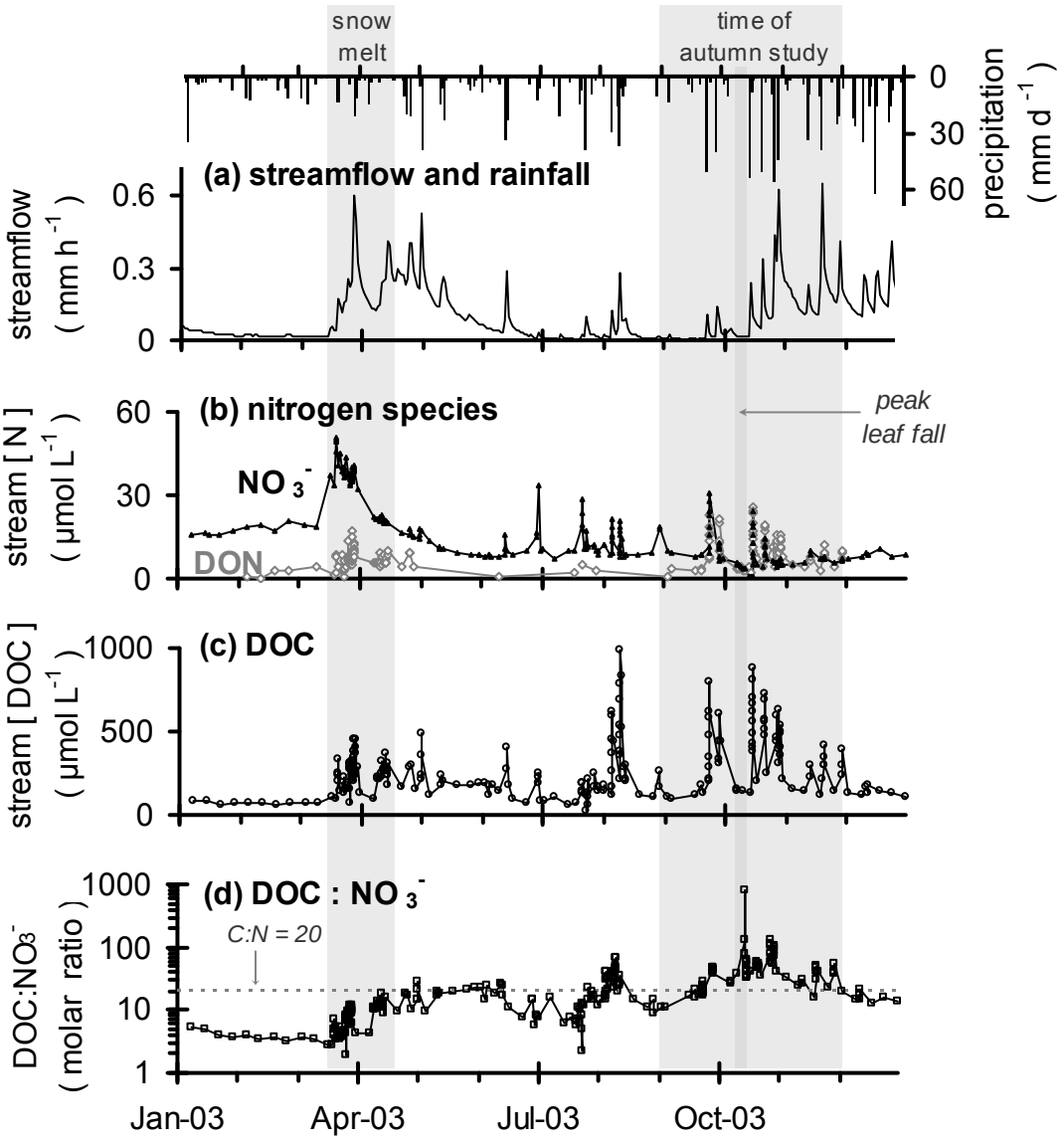


Figure 5. From 1992 to 2005, the lowest nitrate and highest DON baseflow concentrations occurred in September or October when organic carbon was more abundant relative to nitrate (b). The error bars show the standard error (upper error bar for ammonium and lower error bars for nitrate and DON in the top panel) around the average monthly concentrations.

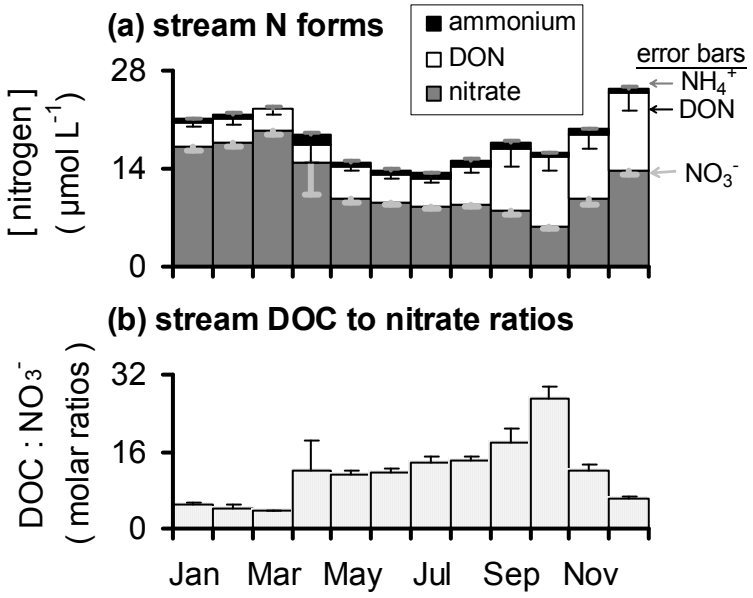


Figure 6. Nitrate mass was lost (negative flux values) in the stream reach during baseflow (8 to 14 October), but gained during storm flow (15-16 October). DON and DOC originated (positive fluxes) in the stream reach during the nitrate crash as well as storm flow.

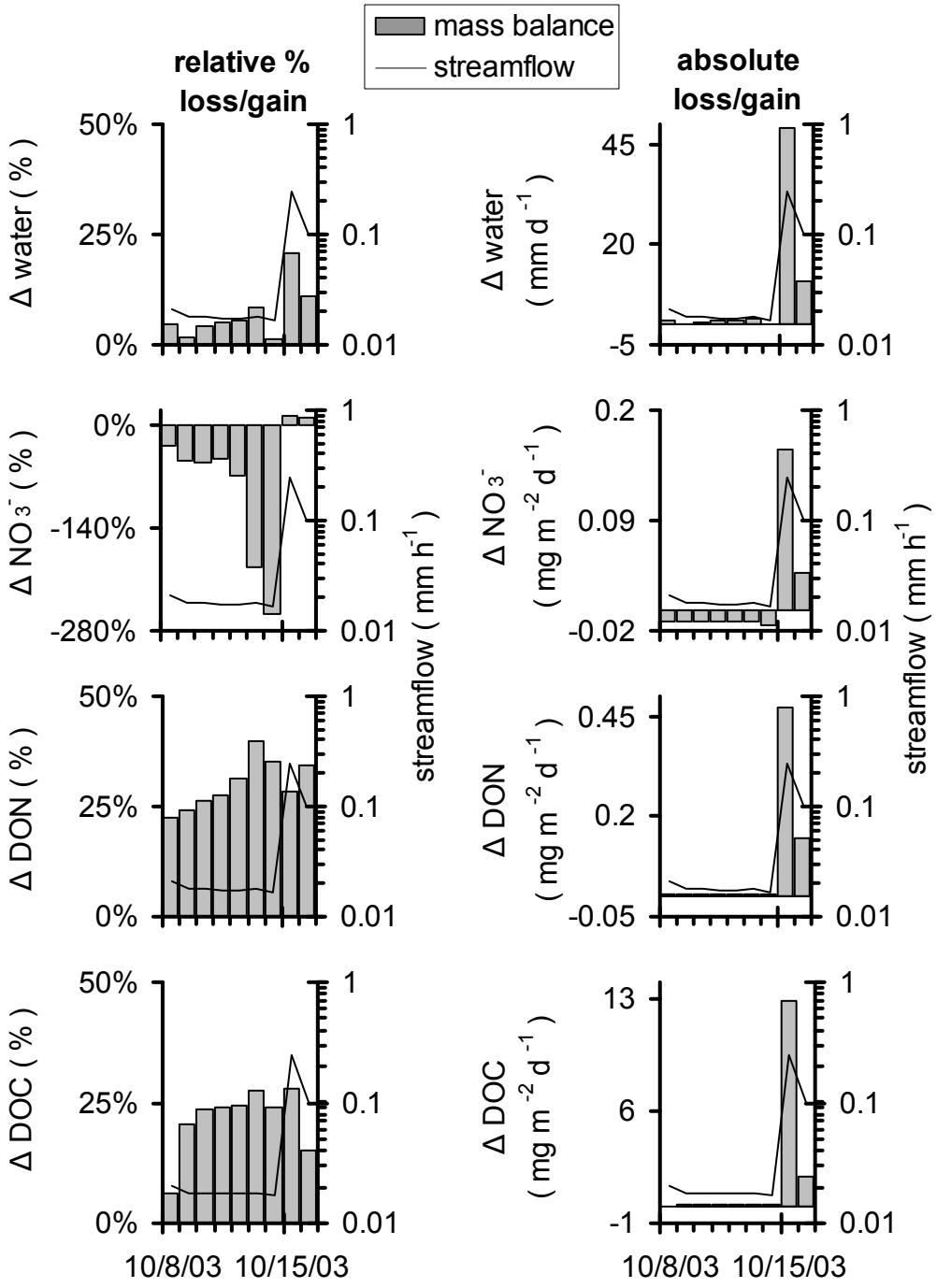


Figure 7. Baseflow $\delta^{18}O$-nitrate was different than groundwater $\delta^{18}O$-nitrate before leaf fall and shifted towards the groundwater value during the nitrate crash. The lowest nitrate concentrations during autumn leaf fall are indicated with the shaded field. The nitrate isotopic composition of water does not show a diagnostic denitrification trend, a linear relationship projected from the groundwater sample falling within bounds calculated as a Rayleigh fractionation (an enrichment factor of 8‰, the upper bound slope is 1 and the lower bound slope is 0.5, Kendall 1998; McMahon and Böhlke 2006).

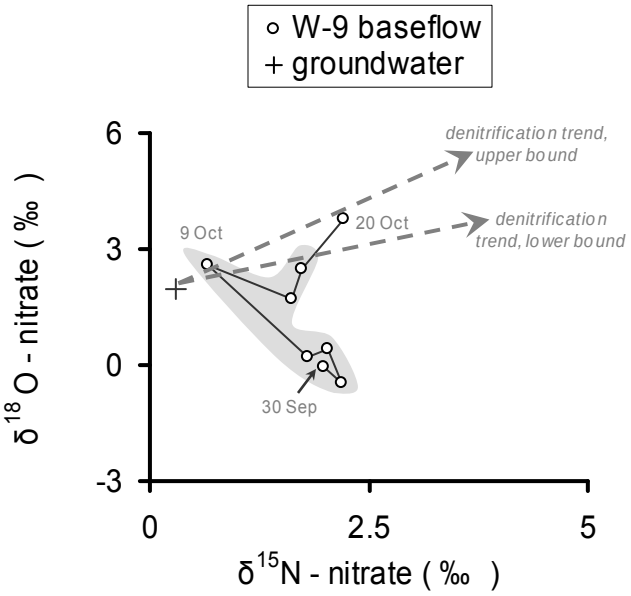
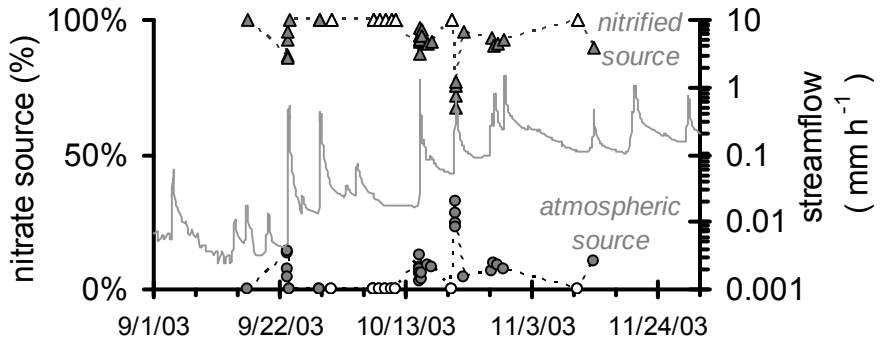


Figure 8. Two-component mixing analysis of nitrate sources reveals that stream nitrate at the W-9 gage primarily originated from nitrified sources. During the 21 October storm event, 30% of the stream nitrate was directly contributed from an atmospheric source. The shaded symbols show storm flow samples.



Supplemental Information

Supplemental Information 1.

Concentrations of nitrate and ammonium were measured by automated colorimetry (continuous flow analysis on a Technicon AutoAnalyzer), total nitrogen by catalytic oxidation combustion (Antek 720C chemiluminescent nitrogen detector coupled with a Shimadzu TOC-5000A, no measurements before 1996), and DOC concentrations by continuous flow analysis on a Technicon Autoanalyzer before 1996 (Bailey and others, 1995) and by combustion oxidation on a Shimadzu TOC-5000A thereafter.

Additional high-frequency samples were occasionally collected before and after our study (Kendall and others, 1995; Shanley and others, 1995; Shanley and others, 2002). Analysis of post-2002 samples was identical to the samples collected for the autumn 2003 study.

Supplemental Information 2.

In the lab, unfiltered grab samples were syringe filtered into lab sample bottles, HDPE bottles for nitrogen species and amber glass for DOC. All bottles were pre-rinsed and leached with deionized water (resistance exceeding 18.0 megaohms cm^{-1}).

Cellulose acetate or hydrophilic polypropylene membranes were used to filter nitrogen and nitrate isotope samples (no detectable difference between filters). Filters were first flushed with sample and then storage bottles were rinsed with filtered sample. In October when possible, some stream nitrogen samples were syringe-filtered in the field with Pall GH Polypro hydrophilic polypropylene disposable in-line filters. Nitrate concentrations were measured at the EW Boyer Water Chemistry Lab. Paired grab and field-filtered samples were collected to test for differences of filters and the effects of holding time on nitrate concentrations. Analysis of sample pairs showed no detectable difference between field and laboratory filtering and no effect of storage time on nitrate concentrations. Total nitrogen was measured in the WL Silver Ecosystem Laboratory at the University of California, Berkeley.

Whatman GF/F filters used for lab filtering and glass bottles for DOC samples were pre-baked for six hours at 450˚ Celsius. For field filtered samples, PURA-DISC GF/F disposable in-line syringe filters were used although these filters could not be baked. Because the 2003 samples spanned the duration of several different studies of DOC, concentrations were measured at several

laboratories: MPSIL on a OI Analytical 1010 TIC/TOC analyzer; USGS New York District Water-Analysis Laboratory, Troy, NY on a Dohrman DC 80 TOC analyzer (Lawrence and others, 1995; Lincoln and others, 2005); USGS, Boulder, CO on an OI Analytical 700 TOC Analyzer (Aiken, 1992); and the MJ Mitchell Biogeochemistry Lab, SUNY-ESF, Syracuse, NY on a Tekmar-Dohrmann Phoenix 8000 TOC analyzer.

For every ten to twenty samples, blanks of deionized water were processed the same as other samples for nitrate and DOC analyses. No contamination of samples from collection, storage, or processing was detected from blanks.

Supplemental Information 3

All samples were corrected and adjusted for exchange and fractionation against blanks and international nitrate isotopic standards USGS 34 and USGS 35 (Böhlke and others, 2003). Analytical precision (1σ) was 0.2‰ for δ^{15}N-nitrate and 0.7‰ for δ^{18}O-nitrate.

Isotopic composition is reported in standard delta (δ) notation as the relative abundance on a permil (‰) basis,

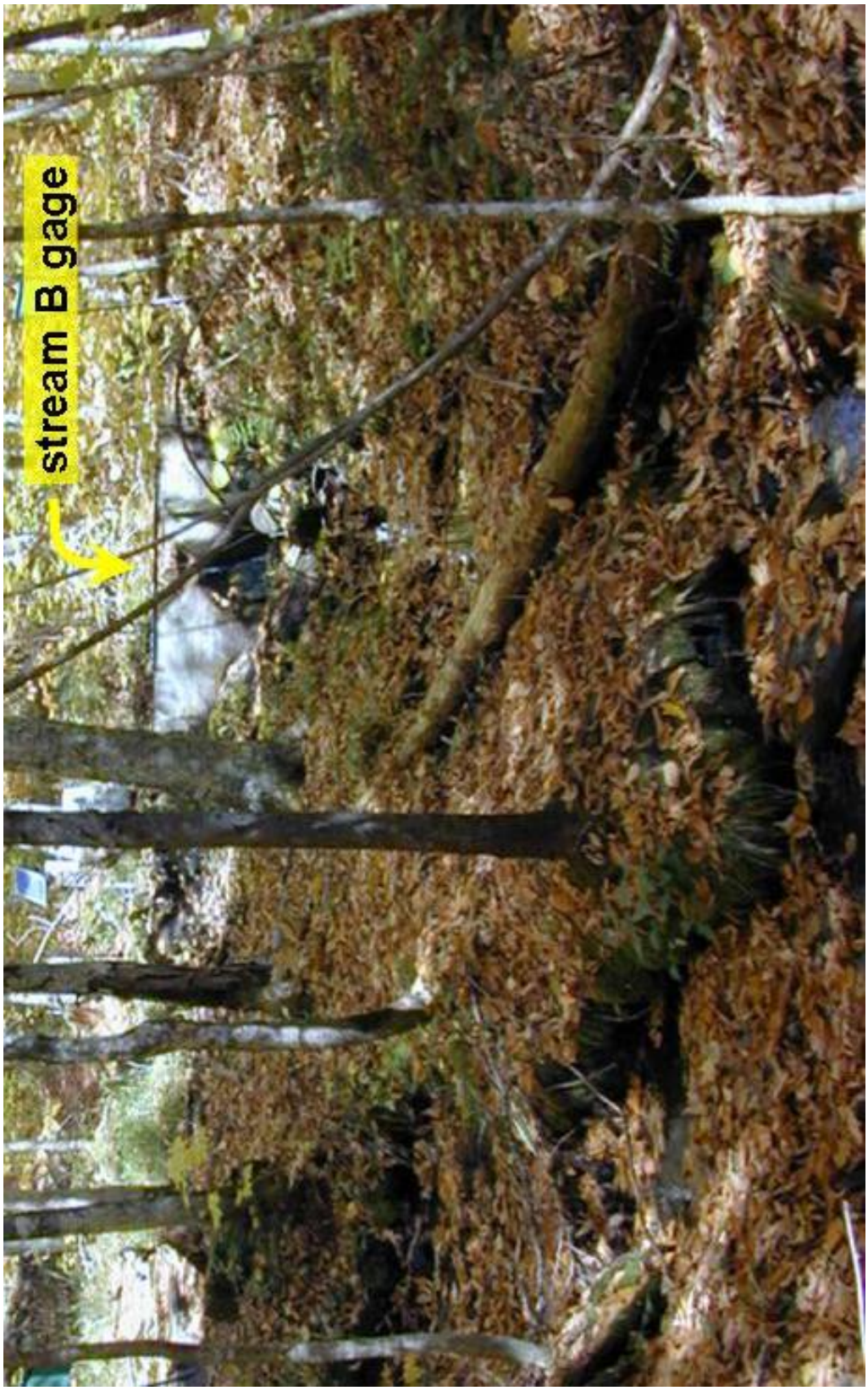
$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) * 1000 \quad (5)$$

where Rsample is the sample isotope ratio and Rstandard is the isotope ratio of a recognized standard, Vienna Standard Mean Ocean Water for oxygen isotope values (δ18O) and atmospheric nitrogen gas (N2) for δ15N (Coplen, 1996).

Supplemental Information 4.

Three photos (following pages) of the A and B stream confluence. Photo (a) was taken 7 October 2003 after the onset of leaf fall. Photo (b) from 11 October 2003 shows the channel covered with leaves during the time of peak leaf accumulation in the stream prior to high flows. Photo (c) from 26 October 2003 shows the channel after high flows when leaf litter had moved downstream or to the bottom of the channel.

(a) 7 October 2003



(b) 11 October 2003

(c) 26 October 2003

CHAPTER 3

STREAM NITRATE AND DISSOLVED ORGANIC MATTER DURING SNOWMELT AT AN UPLAND FOREST ARE CONTROLLED BY SOURCE VARIATION AND HYDROLOGICAL PROCESSES

Abstract

We explored factors that control the temporal variation of nitrogen and organic carbon in surface waters of an upland, forested catchment in northeastern Vermont, USA. Using high-frequency stream water samples collected during snowmelt runoff events, we traced sources of water, nitrate, and dissolved organic matter (DOM). Hydrochemical characterization with isotopic signatures of water and end-member mixing analysis revealed when solutes entered the stream and that variable source areas were linked to the stream by preferential shallow subsurface and overland flowpaths. Freshly-leached, terrestrial organic matter was the dominant source of high dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations in stream water. In contrast, in this region where atmospheric nitrogen deposition is chronically elevated, high concentrations of stream water nitrate originated from atmospheric sources as well as nitrified sources. Although hydrological flushing from shallow soil sources also contributed to stream nitrate variation, the presence of isotopically distinct atmospheric nitrate in streams during spring snowmelt indicated that atmospheric sources may move through the landscape to streams quickly, short-circuiting biogeochemical processes that typically retain nitrogen in the landscape. Overall, results from the high-frequency hydrochemical sampling identified hydrological transport processes and source variation as key processes that influenced stream nutrient variation during snowmelt.

Introduction

Nitrogen deposition from atmospheric sources affects soil nutrient status and stream nutrient loadings in upland forests of the northeastern USA (Stoddard, 1994; Boyer and others, 2002; Aber and others, 2003). In the landscape and stream water, nitrogen and dissolved organic matter (DOM) are abundant in a variety of actively cycled forms that influence ecological dynamics. The effects of anthropogenic nitrogen sources on stream chemistry are a particularly concern because this excess nitrogen is linked to ecosystem acidification, forest decline, aquatic eutrophication, and shifts in ecosystem function (Murdoch and Stoddard, 1992; Lawrence and others, 2000; Driscoll and others, 2003; Galloway and others, 2003; Emmett, 2007). In contrast to minimally polluted forested catchments, stream nitrate concentrations typically exceed dissolved organic nitrogen (DON) concentrations and may exceed ammonium concentrations by orders of magnitude in forests that are affected by nitrogen pollution from atmospheric deposition (Perakis and Hedin, 2002; Vanderbilt and others, 2003). Despite well-documented global effects of elevated nitrogen inputs, the ecosystem processes that control the variation of stream nitrate and DOM concentrations in upland forests are poorly understood. Furthermore, the reported increase of stream dissolved organic carbon (DOC) concentrations over past decades (Stoddard and others, 2003; Worrall and Burt, 2007), the need to understand how bioavailable DOC affects aquatic metabolism (Aiken and Cotsaris, 1995; Findlay and Sinsabaugh, 2003), and interactions of the carbon and nitrogen cycles in catchments (McClain and others, 2003; Goodale and others, 2005; Chapter 2) highlight a need to understand the landscape processes that affect the movement of dissolved inorganic and organic nutrients to streams.

During storm flow, high concentrations of stream water nitrate and DOM indicate the importance of hydrological processes in regulating the nutrient chemistry of surface waters (Peters and others, 1995). Although groundwater is a perennial source of water and solutes to streams, groundwater concentrations are often too low to account for high nitrate and DOM concentrations during storm flow. Studies have identified that solutes are flushed to streams from chemically distinct source areas in the landscape as water flows along shallow subsurface and overland flowpaths during storm events (Schiff and others, 1990; Mulholland, 1993; Hornberger and others, 1994; Boyer and others, 1996; Creed and others, 1996). These findings illustrate the direct link of hydrological

processes to solute inputs from atmospheric deposition and biogeochemical cycles that affect nutrient sources in surficial soils.

The direct and immediate effects of atmospheric nitrogen deposition on stream chemistry have been difficult to evaluate because most nitrogen from atmospheric sources is assimilated into terrestrial organic matter pools (Campbell and others, 2004) where the nitrogen remains sequestered for weeks on up to decades or longer. After organically bound nitrogen is mobilized through mineralization and nitrification, the nitrate may be leached and transported to streams as water flows through forest soils or as overland flow interacts with the forest floor (Rascher and others, 1987; Kendall and others, 1995). Stream nitrate may also originate directly from atmospheric sources if hydrological flowpaths directly transport atmospheric nitrate to streams and bypass the microbial and abiotic processes that retain nitrate in the terrestrial environment. Although some studies that evaluate sources of stream nitrate using chemical and isotopic tracers have found that most of the stream nitrate during snowmelt originates from nitrification in soils (Burns and Kendall, 2002; Piatek and others, 2005; Campbell and others, 2006), other studies have found that substantial amounts of stream nitrate may originate from atmospheric deposition that accumulates over weeks or months in a snowpack (Campbell and others, 2002; Ohte and others, 2004). To bridge the gap between these different findings, Ohte and others (2004) suggest that direct input of nitrate from atmospheric sources may not be distinguishable from nitrified sources without high-frequency isotope data. Similar to tracers of nitrate sources, characterization of DOM chemical composition may indicate the sources of high stream DON and DOC concentrations during storm flow (Aiken and Cotsaris, 1995; McKnight and others, 1997; Hood and others, 2005).

We use a hydrological approach in which stream water samples were collected at high frequency to identify the sources of stream nitrate, DON, and DOC at an upland forest. We focus on snowmelt runoff events because these large hydrological events have an overriding influence on the annual flux of nutrients from catchments; the melt of a seasonal snowpack releases water and solutes during large magnitude and extended duration runoff events (Shanley and others, 2002a; Shanley and others, 2002b). We used end-member mixing analysis to quantify the relative water and solute contributions of the dominant end-members (precipitation, soil, and ground waters) to stream water to

determine how the flow of water through different landscape source areas controls variations of stream nitrogen and DOM.

Site Description

We studied catchment processes at watershed 9 (W-9), a 40.5 hectare forested sub-basin of the Sleepers River Research Watershed and a site in the Water Energy and Biogeochemical Budgets program of the US Geological Survey (Shanley, 2000). The mountainous W-9 is near Saint Johnsbury, VT, USA, and is typical of many upland forests of the northeast USA. Nitrogen inputs from atmospheric deposition to W-9 (13.2 kilograms total nitrogen per hectare as wet deposition, Campbell and others, 2004) are chronically elevated. A seasonal snowpack starts accumulating in December and typically melts between mid-March and mid-April. Twenty to 30% of the mean annual precipitation (1323 millimeters) falls as snow and runoff is typically highest during spring snowmelt (Shanley and others, 2002a; Shanley and others, 2002b).

Hydrological processes have been intensively studied at the Sleepers River Watershed. In the late 1960s, Dunne and Black (1971a, b) first quantified the contributions of dynamic subsurface and surface flow processes in variable source areas that controlled the movement of water from the landscape to a stream. Subsequent studies have found that storm flow chemistry is influenced by preferential flowpaths that route storm runoff through surficial soils that have high hydraulic conductivities (Kendall and others, 1999; McGlynn and others, 1999; Shanley and others, 2003).

Pope Brook drains W-9 and is a headwater tributary of the Sleepers River drainage which in turn flows to the Passumpsic River, the Connecticut River, and the Atlantic Ocean. The forest that completely covers W-9 is predominantly sugar maple (*Acer saccharum*) with other northern hardwood species, namely yellow birch (*Betula alleghaniensis*), white ash (*Fraxinus americana*), red spruce (*Picea rubens*), and balsam fir (*Abies balsamea*). Watershed 9, with elevations between 519 and 686 meters, is a south-facing catchment on the eastern flanks of the Kittredge Hills. The terraced glacial topography is characterized by steep slopes with relatively flat mid-elevation benches. The bedrock is calcareous granulite interbedded with quartz mica phyllite (Hall, 1959). The one to three meter deep soil profile has a base layer of dense glacial till that is overlain by moderately to excessively well-drained Spodosols. Poorly-drained Histosols have formed in wetlands (about 5% of the catchment area) and riparian areas

(Shanley and others, 2003). Soil patches in W-9 may freeze to shallow depths (tens of centimeters) but widespread impermeable frost layers have not historically developed (Shanley and Chalmers, 1999).

Methods

In the 2003 and 2004 snowmelts, hydrology and chemistry were intensively measured. Streamflow was calculated from a stage-discharge relationship according to US Geological Survey protocols (Rantz, 1982). Since 1991, stream stage has been measured every five minutes at a 120º V-notch weir instrumented with a float-driven shaft encoder. The recorded water levels were verified with weekly and more frequent manual readings of stream stage when the weir pool was ice free.

Precipitation amount was measured with a Belfort weighing bucket gage at a meteorological station (R29) in a forest clearing near the stream gage but outside of W-9 and 519 m above mean sea level. Precipitation samples for chemistry were collected weekly or more frequently from a polyethylene bucket. Snow samples were melted off-site and transferred into sample bottles.

Snow water equivalent was measured weekly to quantify the accumulation and melt of the snowpack in 2003 and 2004. Snow depth and density were measured with an Adirondack-type snow tube at the R1-A meteorological station, a site higher in elevation (636 meters above mean sea level) and about one kilometer west of the W-9 stream gage.

In 2004, snowmelt amount, chemistry, and isotopic composition were measured on samples collected from the base of the snowpack with snowmelt lysimeters (1.0 square meter surface area). Snowmelt collectors were placed on three hillslopes at sites SM-11, SM-12, and SM-13. Snowmelt drained into buried PVC reservoirs and samples were collected at least daily after substantial melt (greater than 1 millimeter).

Weekly W-9 stream samples were collected on Tuesdays and additional grab samples were collected on other days during site visits, especially after the onset of snowmelt when samples were collected daily or more frequently. To augment grab sampling, an ISCO automatic sampler collected stream water when threshold changes in streamflow triggered sample collection (intervals ranging from minutes to hours).

Groundwater chemistry was measured at wells located throughout the catchment to characterize groundwater sources (Figure 9). Installation of PVC

wells and piezometers in the early 1990s is described elsewhere (Kendall and others, 1999). At least one casing volume of groundwater was evacuated prior to sampling. A nested pair of shallow (T-6, 0.3 m deep) and deep (T-4, 2.1 m deep) piezometers in the riparian zone near the W-9 gaging station was sampled repeatedly (22 times) from 25 March through 5 May 2004. Other wells were sampled monthly from January through March or several times in April to characterize the spatial variation of groundwater chemistry in 2004. In 2003, to characterize when shallow soils became saturated and hydrologically connected to the stream, groundwater levels were measured every 10 to 30 minutes in the riparian zone (T-3 piezometer), mid-hillslope (MI recording well), and upslope (UP recording well) on a transect extending from the stream up a planar hillslope.

On three dates in 2003 and 2004, shallow soil water samples from the vadose zone were collected from zero-tension lysimeters at midslope (0.10 meter depth) and upslope (0.13 meter depth) sites after melt pulses or rain-on-snow events.

Sample processing and analysis

Although briefly described herein, the collection, processing, storage, and analysis of samples from 2003 and 2004 are detailed elsewhere (Chapter 2). Water grab samples were collected in new LDPE bottles that were first triple rinsed with sample, then filled, and refrigerated until filtered within three months. When possible, some samples were syringe-filtered in the field directly into laboratory cleaned high-density polyethylene (ions and total nitrogen) and amber glass (DOC) lab sample bottles. Syringes were first rinsed and then filters were flushed with sample water. Pre-cleaned lab sample bottles (Chapter 2) were rinsed with filtered sample water. Analysis of several sample pairs showed no detectable difference between field and laboratory filtering and no effect of storage time on sample ion chemistry.

Stream, soil, ground, snow, rain, and snowmelt water samples for ion concentrations, total nitrogen concentrations, and nitrate isotopic analyses were filtered through 0.45 millimeter membrane filters; cellulose acetate or hydrophilic polyproylene filters for lab filtering and hydrophilic polypropylene disposable in-line filters for field filtering. Aliquots for ion and total nitrogen analyses were filtered into rinsed Nalgene HDPE sample bottles and refrigerated until analyzed. Nitrate concentrations were measured using ion suppressed conductivity detection and a Dionex IonPac AS14 column on a Dionex DX-500 ion

chromatograph at the EW Boyer Water Chemistry Lab at the State University of New York College of Environmental Science and Forestry in Syracuse. For a subset of the samples, total nitrogen concentrations were analyzed by the alkaline persulfate oxidation technique (Solorzano and Sharp, 1980) and measured by flow injection analysis on a Lachat AutoAnalyzer (QuikChem FIA^{+} 8000) at the WL Silver Ecosystem Laboratory at the University of California, Berkeley. Dissolved organic nitrogen concentrations were calculated as the difference between nitrate and total nitrogen concentrations. Nitrite was not quantifiable in any sample. Ammonium is a small component of the stream nitrogen budget and ignoring ammonium had a minimal effect on calculated DON concentrations (Chapter 2). Cation (calcium, magnesium, and strontium) and silica concentrations were measured by inductively coupled plasma optical emission spectrometry (Perkin-Elmer Optima 330 DV) at the Analytical and Technical Services Laboratory of the State University of New York College of Environmental Science and Forestry in Syracuse.

To trace sources of stream water and nitrate, isotope ratios were measured on a subset of the water samples. In forested catchments, nitrate isotopic signatures differentiate nitrate from atmospheric (rain or snow) and nitrified sources (Kendall, 1998). Although δ^{15}N-nitrate of sources may overlap, δ^{18}O-nitrate is distinct between atmospheric (+60 to +100‰) and nitrified sources (-10 to +15‰) because nitrate loses the atmospheric δ^{18}O signal when subjected to microbial processing (Kendall, 1998). Nitrate isotope samples were stored frozen. Samples were processed using the bacterial denitrifier method (Sigman and others, 2001; Casciotti and others, 2002). The oxygen (δ^{18}O-nitrate) and nitrogen (δ^{15}N-nitrate) isotopic compositions were measured on a Micromass IsoPrime mass spectrometer at the USGS Menlo Park Stable Isotopes Laboratory (MPSIL) in California. Isotopic composition was corrected and adjusted for exchange and fractionation against blanks and international nitrate isotopic standards USGS 34 and USGS 35 (Böhlke and others, 2003). Ten percent of the samples were analyzed in duplicate. Analytical precision (1σ) was 0.2‰ for δ^{15}N-nitrate and 0.7‰ for δ^{18}O-nitrate.

The oxygen isotopic composition of water (δ^{18}O-water) was prepared by the carbon dioxide equilibration method (Epstein and Mayeda, 1953; Horita and Kendall, 2004) and analyzed at the MPSIL on a Finnigan MAT 251 mass spectrometer. Analytical precision (1δ) was 0.1‰ for δ^{18}O-water.

Isotopic composition is expressed as the relative abundance on a permil basis (‰) using standard delta (δ) notation.

$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) * 1000 \quad (6)$$

where R_{sample} was the sample isotope ratio and $R_{standard}$ was the isotope ratio of a recognized standard: Vienna Standard Mean Ocean Water for oxygen ($\delta^{18}O$) and atmospheric nitrogen gas ($\delta^{15}N$).

Stream, soil, and ground water DOC samples were filtered through 0.7 µm binder-free glass fibre filters into amber glass bottles and refrigerated. For field filtration, PURA-DISC GF/F disposable in-line syringe filters were used. Concentrations were measured on total organic C analyzers at several laboratories: USGS MPSIL on a OI Analytical 1010 TIC/TOC analyzer; USGS New York District Water-Analysis Laboratory, Troy, NY on a Dohrman DC 80 TOC analyzer (Lawrence and others, 1995); USGS, Boulder, CO on an OI Analytical 700 TOC Analyzer (Aiken, 1992); and the MJ Mitchell Biogeochemistry Lab, SUNY-ESF, Syracuse, NY on a Tekmar-Dohrmann Phoenix 8000 TOC analyzer.

Indices of DOC composition were measured for some stream water samples. The carbon isotopic composition of DOC ($\delta^{13}C$-DOC) was measured for nine of the 2004 samples at the MPSIL on a total organic carbon analyzer that was interfaced with a Micromass IsoPrime continuous flow mass spectrometer (St-Jean, 2003; Doctor and others, in press). In 2004, the hydrophobic organic acid (humic) fraction of DOC was isolated from eleven 3-liter samples using Amberlite XAD8 resin (analytical absorption chromatography) at the USGS Laboratory in Boulder, CO (Aiken and others, 1992).

Flux calculation and mixing analysis

To calculate stream solute fluxes, a concentration was multiplied by the corresponding total runoff in a time period to calculate the flux per interval spanning the mid-point between samples. With hydrochemical data from past studies (Shanley and others, 2002a), we calculated fluxes of water and nutrients from W-9 for the years 1992, 1993, and 1994 as well as 2003 and 2004. The center of mass for the period from 1 January to 30 April was computed as the date and flux amount when the cumulative stream export of water, nitrate, DON,

or DOC mass from W-9 exceeded fifty percent (similar to Hodgkins and others, 2003).

In 2004 when snowmelt and groundwater end-members of stream water were adequately characterized with frequent samples, three-component end-member mixing analysis (EMMA) was used to calculate the amount of stream water that originated from groundwater, shallow soil water, and precipitation (Christophersen and others, 1990). A principle components analysis of standardized conservative chemical (calcium, magnesium, strontium, and silica concentrations) and isotopic (δ^{18}O-water) tracer data was used to develop the EMMA model (Burns and others, 2001; Hooper, 2003). The fractions (f) of groundwater (GW), soil water (SW), and precipitation (PPT) were calculated by solving the following simultaneous equations:

$$f_{GW} + f_{SW} + f_{PPT} = 1 \quad (7)$$

$$U_{1_{stream}} = f_{GW} \times U_{1_{GW}} + f_{SW} \times U_{1_{SW}} + f_{PPT} \times U_{1_{PPT}} \quad (8)$$

$$U_{2_{stream}} = f_{GW} \times U_{2_{GW}} + f_{SW} \times U_{2_{SW}} + f_{PPT} \times U_{2_{PPT}} \quad (9)$$

where U_1 and U_2 are the first and second principle components from the PCA. The *U* space of end-members (see Hooper 2003) was varied by date according to input data from precipitation (melt data from lysimeters and rain data) and soil water. Groundwater concentrations varied more over space than time and the groundwater end-member was defined by averaging data from synoptically sampled well locations (eight sites). Because contributions from shallow soil water and precipitation represent quick flow via shallow subsurface and overland flowpaths, these two components were summed to calculate quick flow.

$$f_{quick\ flow} = f_{SW} + f_{PPT} \quad (10)$$

The uncertainty ($W_{3\text{-comp}}$) was calculated for each EMMA component (GW, SW, or PPT) according to the approach described by Burns and others (2001).

$$W_{3-comp} = \left(\left[V_{Ca} \times W_{Ca} \right]^2 + \left[V_{Mg} \times W_{Mg} \right]^2 + \left[V_{Sr} \times W_{Sr} \right]^2 + \left[V_{si} \times W_{Si} \right]^2 + \left[V_{\delta^{18}O} \times W_{\delta^{18}O} \right]^2 \right)^{0.5} \quad (11)$$

where V_c was the eigenvector and W for each constituent (Ca, Mg, Sr, Si, or δ^{18}O-water) was the analytical uncertainty.

Nitrate sources during the 2003 and 2004 snowmelt runoff events were separated into two fractions (f), atmospheric (ATM) and nitrified (NIT), using a two-component mixing model in which snowmelt or rain water (c_{ATM}) and groundwater from hillslope wells (c_{NIT}) were used as mixing end-members to solve the equations,

$$f_{ATM} + f_{NIT} = 1 \quad (12)$$

$$c_{stream} = f_{ATM} \times c_{ATM} + f_{NIT} \times c_{NIT} \quad (13)$$

where c is the $\delta^{18}O$-nitrate of each component contributing nitrate to stream water as identified by the subscripts ATM or NIT.

Uncertainty ($W_{2\text{-}comp}$) of the two-component mixing analysis was calculated according to the approach of Genereux (1998).

$$W_{2-comp} = \left(\left[\frac{c_{NIT} - c_{stream}}{(c_{NIT} - c_{ATM})^2} \times W \right]^2 + \left[\frac{c_{stream} - c_{ATM}}{(c_{NIT} - c_{ATM})^2} \times W \right]^2 + \left[\frac{-1}{(c_{NIT} - c_{ATM})^2} \times W \right]^2 \right)^{0.5} \quad (14)$$

where c_{ATM} is the $\delta^{18}O$ of atmospheric nitrate (snowmelt and rainfall samples) and c_{NIT} is the $\delta^{18}O$ of nitrate from a groundwater nitrified source. The absolute error (W) was assigned as the analytical precision for $\delta^{18}O$-nitrate (0.7‰).

The amount of stream water nitrate originating from atmospheric sources was calculated by multiplying stream water nitrate concentrations by the atmospheric fraction (f_{ATM}) and the corresponding total runoff. Concentrations and fractions were linearly interpolated between samples.

Results

Although we include data from other snowmelt events at W-9, we highlight the 2004 snowmelt when multiple tracers of stream water and solute sources were simultaneously measured at high-frequency along with snowmelt input, groundwater, and soil water chemistry.

Snow started to accumulate in December 2003 and snowmelt occurred during March and April 2004 (Figure 10). Before a first, early melt period, a maximum snow water equivalent (SWE) of 222 mm was measured 24 February. During a brief period of snowmelt in response to warm air temperatures and rainfall, ten percent of the SWE (28 millimeters) was lost from the snowpack in the first week of March 2004 and a maximum streamflow of 0.1 mm h^{-1} was measured on 6 March. With this first snowmelt pulse, snow that covered the stream channel from January through early March 2004 melted into the stream and areas of saturation overland flow were observed near the stream.

Streamflow recession occurred from 7 to 24 March when temperatures were freezing. Over these two weeks, 22 more millimeters of SWE accumulated in the snowpack and the stream channel again became covered with snow. A second SWE peak of 216 mm was measured 23 March.

During a second period of snowmelt that started 25 March 2004, streamflow again increased and thereafter remained above winter baseflow for

the duration of snowmelt. The stream was snow-covered until the end of the first week of April. In the second week of April, snow melted from near-stream areas and exposed these variable source areas to rain that fell later in April. During a rain-on-snowmelt event on 13 April, the peak streamflow of 0.6 mm h^{-1} was measured. Although quick flow fluctuations generally tracked streamflow (Figure 11), the largest quick flow amount of 0.23 (±0.02) mm h^{-1} occurred 18 April. Melt progressed until SWE was not measurable after 20 April (Figure 10). In total, eight weeks elapsed from the start of snowmelt in 2004 until the snowpack melted.

Stream hydrochemistry

Under winter baseflow conditions, stream nitrate concentrations increased steadily from 8.5 to 13.9 µmol L^{-1} while streamflow decreased from 0.15 mm h^{-1} on 1 January to 0.02 mm h^{-1} on 24 February (Figure 11). Stream nitrate concentration responses to streamflow and snowmelt are grouped into three distinct phases (pulse 1 of early melt, pulse 2 of early melt, and late melt). With a first snowmelt pulse, stream nitrate concentrations rapidly increased to a high of 33.3 µmol L^{-1} on 3 March when streamflow was 0.08 mm h^{-1}. From 7 to 24 March during streamflow recession, stream water nitrate concentrations declined to pre-melt baseflow levels. As snowmelt resumed, a second pulse of nitrate occurred. The highest stream nitrate concentration of 35.2 µmol L^{-1} was measured on 27 March when streamflow was 0.27 mm h^{-1}. After 27 March in late melt, nitrate concentrations did slightly increase as streamflow increased with fluctuations from day to day. However the magnitudes of the concentration increases dampened as snowmelt progressed (i.e. the response of nitrate concentrations to storm flow attenuated with time). For example, when the highest streamflow of snowmelt 2004 occurred just before midnight on 13 April, the high nitrate concentration of 14.9 µmol L^{-1} was nearly identical to the pre-melt nitrate concentration and was considerably less than the early peak concentration of 35.2 µmol L^{-1}. Stream nitrate concentration was positively correlated with quick flow (calculated from EMMA) during the first (before 5 March, $p << 0.0001$, $R^2 = 1.00$) and second (before 27 March, $p << 0.0001$, $R^2 = 0.99$) pulses early in snowmelt (Figure 12). After 27 March in late snowmelt, stream nitrate concentrations were no longer positively correlated with quick flow.

Under winter baseflow, stream DOC concentration decreased from January to February (Figure 11). The minimum concentration of stream water

DOC, 55 μmol L^{-1}, occurred on 10 February under winter baseflow (0.02 mm h^{-1}) and the highest DOC concentration (258 μmol L^{-1}) during snowmelt occurred with the highest streamflow (0.58 mm h^{-1}) on 13 April 2004. Stream DOC concentrations were positively correlated with streamflow ($p << 0.0001$, R^2 = 0.55) and quick flow amount ($p << 0.0001$, $R^2 = 0.67$, Figure 12). Unlike nitrate, DOC concentrations consistently increased with increased streamflow and increased quick flow throughout snowmelt.

Under winter baseflow, stream DON concentration decreased from 2.7 μmol L^{-1} on 1 January to 2.1 μmol L^{-1} on 24 February (Figure 11). During snowmelt, stream DON concentration increased as flow increased during snowmelt and was positively correlated with streamflow ($p << 0.0001$, $R^2 = 0.64$, Figure 11 and Figure 13). Stream DON concentration peaked at 8.53 μmol L^{-1} during early March and a second time on 14 April 2004 (8.44 μmol L^{-1}) with a sample that was collected about 30 minutes after highest streamflow. In stream water, DON concentrations attenuated somewhat through the snowmelt runoff event. Stream DON concentration was positively correlated with quick flow amount during the first melt pulse ($p = 0.004$, $R^2 = 0.58$), during the second pulse prior to the highest streamflow ($p << 0.0001$, $R^2 = 0.80$), and after the highest streamflow ($p << 0.0001$, $R^2 = 0.48$, Figure 12).

Snowmelt 2003 was four weeks shorter than snowmelt 2004 and the maximum streamflow of 1.5 mm h^{-1} in 2003 was 2.5 times greater than that of the 2004 snowmelt (0.6 mm h^{-1}). Stream nitrate concentrations in 2003 peaked early and nitrate responses to storm flow subsequently attenuated (see Ohte and others, 2004) like 2004. In 2003, stream DOC and DON concentrations peaked with peak streamflow (Figure 13). Relative to 2003, stream nitrate concentration was 44% higher, DOC was 19% lower, and DON was 103% higher in 2004 (Figure 11 and Figure 13).

The nitrate center of mass typically occurred before the water center of mass in all years and the water center of mass occurred before both DON and DOC centers of mass (Figure 14). In 2004, the nitrate center of mass occurred three days before the water center of mass (5 April). The DON and DOC centers of mass both occurred three days after the water center of mass in 2004.

Stream water and nutrient sources

Although melt water nitrate concentrations from the snow lysimeters in 2004 were high as snowmelt began (59 μmol L^{-1} with the first ionic pulse and 98

μmol L^{-1} with the second snowmelt ionic pulse), concentrations rapidly diminished and continued to decline to a low of 3 μmol L^{-1} in mid April (Figure 15). Nitrate concentrations of melt water were higher than shallow groundwater and shallow soil water concentrations until 1 April 2004. Among individual rainfall events, the amounts (6 to 23 mm, Figure 10) and nitrate concentrations (5 to 92 μmol L^{-1}, Figure 15) of rainfall were highly variable. The combined nitrate input to the catchment from melting snow and rainfall was 97 mg m^{-2}.

In 2004, δ^{18}O-nitrate of pre-melt stream water (-5.0 to -0.8‰) and groundwater (-2.3 to +2.2‰, Table 3) were in the range of a nitrified source (values falling between -10 and +15‰, Kendall, 1998). The pure atmospheric nitrate end-member of snow, snowmelt, and rain ranged from +76 to +101‰ (Table 3). The maximum stream δ^{18}O-nitrate of +42‰ occurred when the nitrate concentration was highest on 27 March (Figure 15). In contrast to δ^{18}O-nitrate, δ^{15}N-nitrate values of end-member waters overlapped within a range (-12 to +7‰) too narrow to distinguish nitrate sources (Table 3).

In 2003, nitrate inputs from atmospheric sources were highest (up to 26%) early in melt and 1 to 15% after an early high concentration pulse of nitrate (Figure 16). Again in 2004, atmospheric contributions were highest (up to 49%) early in melt and 1 to 14% in late melt. The uncertainty of nitrate source estimates was 7.3 to 8.1% in 2003 and 1.0 to 1.3% in 2004. Between 1 January and 30 April, the total stream nitrate fluxes from both nitrified and atmospheric sources were higher in 2003 (160% of 2004). Similarly, the amount of atmospheric nitrate was 6.5 ±0.5 mg m^{-2} in 2003 and 4.7 ±0.07 mg m^{-2} in 2004. In 2004, the total stream outflow of 63.9 mg NO_3^- m^{-2} was 66% of total precipitation inputs and the outflow of 4.7 mg NO_3^- m^{-2} from atmospheric sources was 7.3% of the total precipitation inputs. Similar to the center of mass for total nitrate, we determined the center of mass for each nitrate source. The center of mass for stream nitrate from direct atmospheric sources occurred five days before the water center of mass and nitrate from nitrified sources occurred eight days after.

On 27 March 2004, soil water δ^{18}O-nitrate values (+69.7‰) were intermediate between atmospheric (+87.4‰) and nitrified end-members (-2.3‰). Mixing analysis of nitrate sources revealed 80% atmospheric and 20% nitrified nitrate in soil waters. In 2003, δ^{18}O-nitrate of shallow soil water decreased from +71‰ on 1 April to +14‰ on 15 April 2003.

Groundwater nitrate concentrations were heterogeneous among the synoptically sampled wells on 8 and 19 April 2004. Although groundwater wells sampled the entire screened interval that extended from the soil surface to bedrock, the shallow (T-6) and deep (T-4) piezometers in the riparian zone sampled specific-depth groundwaters and characterized depth-stratified flowpath chemistry. Groundwater from the deep piezometer consistently had low nitrate concentrations (<1.0 μmol L^{-1}) and nitrate concentrations of shallow riparian groundwater were low under baseflow and increased with snowmelt. Shallow groundwater nitrate peaked at 36.4 μmol L^{-1} on 26 March 2004, the same day as stream water nitrate and the δ^{18}O-nitrate (Figure 15).

The indices of DOC composition (percent humic fraction and δ^{13}C-DOC) shifted towards values of freshly-leached terrestrially-derived organic carbon sources with highest streamflow. The humic fraction of stream water DOC increased as snowmelt progressed (Figure 11). A negative log-linear relationship between streamflow and δ^{13}C-DOC was significant ($p = 0.021$, $R^2 = 0.70$).

Discussion

To relate landscape sources to catchment processes, we present a conceptual model of the hydrological processes that affect stream flow and chemistry during snowmelt. In the context of this framework, we discuss catchment processes that influence stream nutrient variation during snowmelt.

Antecedent moisture is low as snowmelt begins and surface saturation is limited to near-stream areas. During the initial wet-up of a catchment, overland flow across saturated surfaces may rapidly connect snowpack sources to streams (Dunne and Black, 1971b; McGlynn and others, 1999). As snowmelt and rainfall recharge subsurface storage, the water table rises to saturate the land surface across an increasing area of the landscape as controlled by topographic gradients. Although flowpaths hydrologically connect to uplands later than down-slope areas that are closer to the stream (Hjerdt, 2002; Bishop and others, 2004), preferential subsurface flowpaths in highly transmissive shallow soils may rapidly transmit water and leached solutes from these source areas when saturation expands into surficial hillslope soils (Schiff and others, 1990; Hornberger and others, 1994; Kendall and others, 1999; McGlynn and others, 1999; Hjerdt, 2002; Shanley and others, 2003).

As catchment wetness increases, stream chemical variation reflects the sequence in which hydrological flowpaths link source areas to streams, the

solute sources that are available, and amount of water that flows through the landscape. When a solute is contributed from a source that originates along a preferential flowpath during storm flow, stream concentrations will be high until the source is exhausted or flow subsides. The early increase and subsequent attenuation of stream nitrate concentrations at W-9 was consistent with transport from landscape sources that were depleted during snowmelt. As shown by isotopic tracers, contributions from atmospheric sources from the melting snowpack were highest early in melt when stream nitrate concentrations peaked. Due to the nitrate inputs from atmospheric sources, outflux of nitrate from the catchment (i.e. center of mass) occurred early relative to water and DOM.

The direct transport of highly concentrated nitrate from an atmospheric source explains the early peak of stream nitrate concentrations during snowmelt. Nitrate was eluted from the snowpack and concentrations rapidly declined as snowmelt progressed. In early snowmelt, nitrate contributions from both atmospheric and nitrified sources to the stream must have originated from near-stream areas. Direct input of high concentration melt water from snow that covered the channel contributed nitrate having an atmospheric isotopic signature until this source melted away. Melt waters may also have been routed to the stream via saturation overland flow across variable source areas. Riparian areas were hydrologically connected to the stream at all times as shown by near-surface water levels and water table fluctuations that were synchronous with streamflow. In contrast, groundwater levels rose to saturate upland soil profiles only after snowmelt, shallow subsurface, and stream nitrate concentrations had decreased (Figure 13).

In surficial hillslope soil, precipitation inputs, leaching, and perhaps transformations contributed to the variation of nitrate concentrations in soil water. Nitrate from snowmelt having an atmospheric $\delta^{18}O$-nitrate signature infiltrated shallow soils early in melt and dominated shallow soil water nitrate but did not affect deep groundwater nitrate concentrations. The atmospheric source affected nitrate concentrations along shallow groundwater flowpaths as shown for the T-6 piezometer. The change in isotopic composition of soil water nitrate from a predominantly atmospheric source (83%) to a predominantly nitrified source (81%) later in snowmelt may indicate nitrification in shallow soils. This interpretation is consistent with another study that measured nitrification in surficial soils during snowmelt in the Adirondack mountains of New York (Campbell and others, 2006).

As excess nitrogen from anthropogenic sources cascades through terrestrial biogeochemical cycles, nitrified nitrate may enrich groundwaters that feed streams (Stoddard, 1994; Galloway and others, 2003). Stoddard (1994) described a hydrochemical framework to assess nitrogen saturation of ecosystems in which acutely elevated stream nitrate concentrations during events indicate stage one nitrogen saturation. As our work shows, high stream nitrate concentrations at W-9 during snowmelt reflected direct inputs of high concentration, isotopically distinct atmospheric deposition that was routed to streams via rapid transport along preferential flowpaths. In this respect, our findings highlight a need to identify hydrological processes and nitrate sources in addition to patterns of nitrate concentrations that are related to seasonal biological uptake to determine the nitrogen saturation status of catchments and to quantify the direct linkages of atmospheric deposition to stream nitrate patterns.

Sulfate from atmospheric deposition is an analog to snowmelt nitrate dynamics. Sulfate concentration is chronically elevated in atmospheric deposition across the northeast USA (Driscoll and others, 2001; Likens and others, 2001) and most sulfate released from the snowpack is assimilated by microbes into the soil organic pool (Mitchell and others, 2001; Shanley and others, 2005; Campbell and others, 2006). A small amount of stream sulfate was directly contributed from an atmospheric source during snowmelt 2000 at Sleepers River (Shanley and others, 2005). Compared to nitrate, less sulfate (always less than 7%) was directly contributed to the stream from an atmospheric source because background concentrations from soil and bedrock sources are high (Bailey and others, 2004; Shanley and others, 2005).

The late DON and DOC centers of mass relative to nitrate are attributable to the different sources that supply these solutes to the stream. Atmospheric deposition is not a major source of DOM. Because DOM concentration attenuates with depth in soils (Cronan and Aiken, 1985; McDowell and Likens, 1988; Aiken and Cotsaris, 1995) and is low in the groundwater of W-9 (McGlynn and others, 1999; Shanley and others, 2003), groundwater was not the source of high storm concentrations. As shown by shallow soil water and shallow riparian groundwater concentrations, DOC concentration was high in surficial soil layers. Soluble organic matter in surficial soils is leached by transient flow through these soils or as overland flow interacts with the forest floor (Thurman, 1986; Kaplan and Newbold, 1993; McHale and others, 2000).

In stream water, DOC concentration increased with increased flow and peaked during highest storm flow, a response that suggested that the amount of water flowing through the environment was insufficient to leach all the soluble organic matter from forest soils. Different source areas of the landscape hydrologically connected to the stream as catchment wetness increased during snowmelt. In early snowmelt, source areas of stream water DOM originated from near-stream areas. As saturated areas expanded, groundwater levels rose into shallow hillslope soils to hydrologically link sources of DOM to the stream. When catchment wetness in a snowmelt event is highest, surficial flowpaths through the landscape are most extensive. As variable source areas expanded farther from streams into the landscape, greater amounts of less-degraded (by microbial activity), highly aromatic allochthonous DOC in the humic fraction were transported from shallow soil flowpaths where water flowed through litter in the forest floor. Similarly, less-degraded, freshly-derived terrestrial DOC having low δ^{13}C-DOC was flushed to the stream from shallow soil source areas during highest streamflows. The relationship between quick flow and concentrations of DOM, increased inputs of humic substances, and low δ^{13}C-DOC were all indicative of DOM that was leached when shallow hillslope soils became hydrologically connected to the stream.

Differentiating sources allows us to assess residence times of nitrate and DOM in catchments. Inputs from surficial flowpaths indicate that DOM was freshly leached from soluble organic matter and rapidly transported to the stream via preferential flowpaths through the landscape. The direct contribution of nitrate from atmospheric sources to stream water indicates that some nitrate is unaltered by terrestrial biogeochemical processes such as microbial transformations that retain nitrogen. When nitrate from atmospheric sources bypasses catchment retention processes, that nitrate only remains in a catchment as long as the snowpack persists (weeks to months). At the shortest time scales, stream nitrate that originates from rain may pass through the catchment in less than a day.

Conclusions

By deciphering sources and source areas of stream solutes, our research at the Sleepers River Research Watershed identified controls on nitrate, DON, and DOC concentration and flux patterns during snowmelt. Stream nitrate concentrations peaked early in melt and decreased later in melt because the

snowpack nitrate supply and shallow soil water pools that were the source of high stream concentrations became depleted as melt progressed. Our study highlights the need to collect samples early in a snowmelt event, at high-frequency, and over the entire range of streamflow conditions. Using high-frequency sampling, multiple environmental tracers, and end-member mixing analysis, we quantified how anthropogenic nitrogen enrichment directly affected nitrate concentrations at W-9. Nitrate inputs from atmospheric sources were a factor that contributed to the early nitrate center of mass. In contrast, stream DOM concentrations and chemical composition changed when catchment wetness increased and water that flowed along surficial flowpaths interacted with soluble organic carbon sources in the forest floor and shallow soils.

With high-frequency sampling, isotopic tracers, and mixing analysis, our study highlights a hydrological approach to provide a window into complex catchment processes that influence stream chemical variation during storm flow. These concepts may be applied across diverse ecosystems to understand how sources and transport processes interact to control stream solute loadings. Our study also highlights how a hydrological approach can be used to detect and quantify the effects of atmospheric nitrogen pollution on upland catchments. As the only source of anthropogenic nitrogen to many forested catchments, it is important to quantify the direct links between elevated atmospheric deposition of nitrogen and high stream nitrate concentrations. Although the direct flux of nitrate from atmospheric sources (7% of the nitrate outflow from the catchment) between January and April may be a small quantity, the amounts are quantifiable. Our study provides data to assess future impacts of inputs from atmospheric nitrogen pollution that affect upland catchments. Overall, these findings improve our understanding of stream nutrient sources and dynamics to provide a basis for land managers and environmental regulators who oversee land stewardship.

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Tables

Table 3. Ranges of δ^{15}N-nitrate and δ^{18}O-nitrate for stream, soil, and groundwaters during the 2003 and 2004 snowmelts.

	number of samples	δ^{15}N-nitrate (‰)	δ^{18}O-nitrate (‰)
2003 (Ohte and others, 2004)			
pre-melt W-9 stream	1	+3.0	-7.7
snowmelt W-9 stream	75	-0.3 to +7.4	-2.5 to +19.8
shallow soil water	5	-11.7 to +7.2	+5.07 to +71.1
groundwater (wells)	14	-10.6 to +21.1	+1.7 to +5.9
groundwater (shallow riparian)	0	--	--
rainfall	3	-1.8 to -3.8	+77.6 to +88.4
snow	0	--	--
melt water	0	--	--
2004			
pre-melt W-9 stream	4	+1.2 to + +1.9	-5.0 to -0.8
snowmelt W-9 stream	32	-0.1 to +1.8	-0.4 to +42.6
shallow soil water	1	-0.3	+69.7
groundwater (wells)	3	+1.9 to +4.7	-2.3 to +2.2
groundwater (shallow riparian)	6	-0.1 to +7.1	+4.5 to +57.7
rainfall	7	-2.6 to +2.3	+75.7 to +100.8
snow	4	-0.8 to +1.1	+83.9 to +89.2
melt water	4	-1.0 to +1.4	+82.0 to +86.8

Figures

Figure 9. Map of the 41 hectare forested Watershed 9 at the Sleepers River Research Watershed shows streams, the stream gage, subsurface water sampling points, and snow lysimeters.

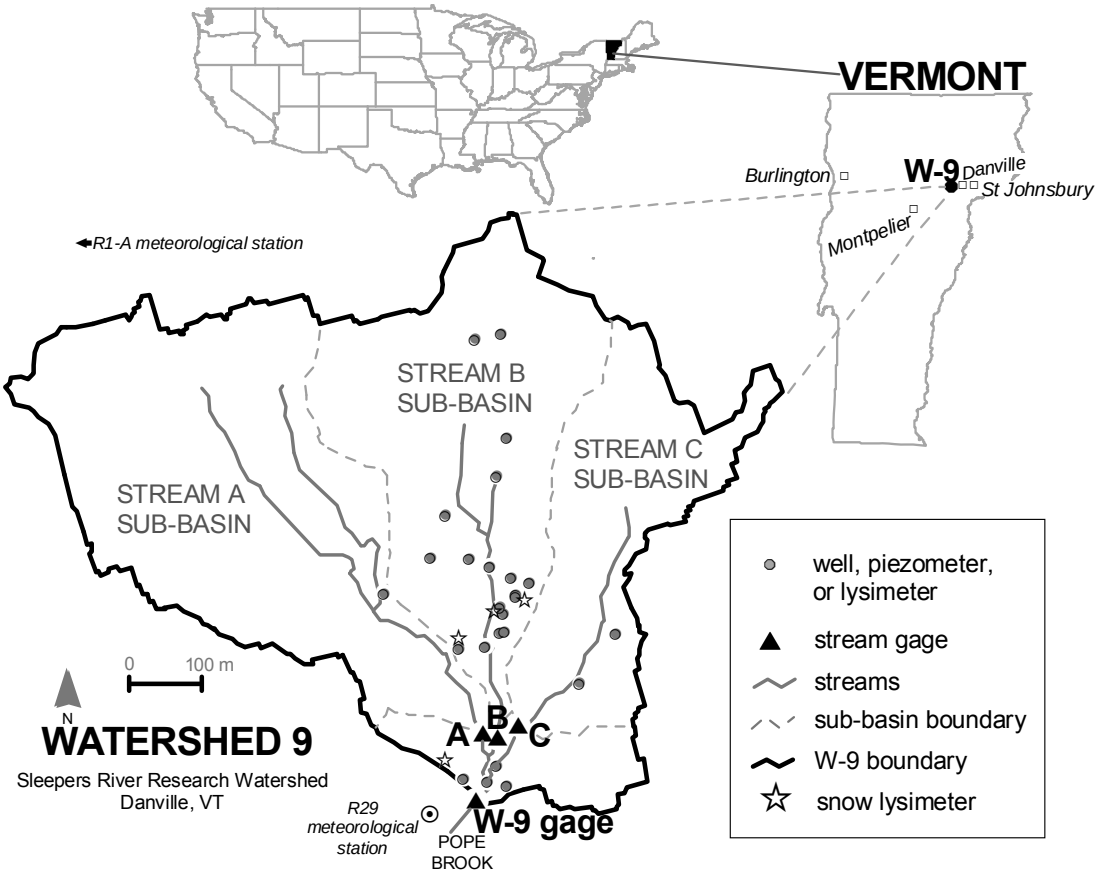


Figure 10. Weekly snow water equivalent (SWE) measurements show the accumulation and melt of the snowpack (a). Streamflow (b) varied with snowmelt when air temperatures were above freezing and several small rainfall events (a).

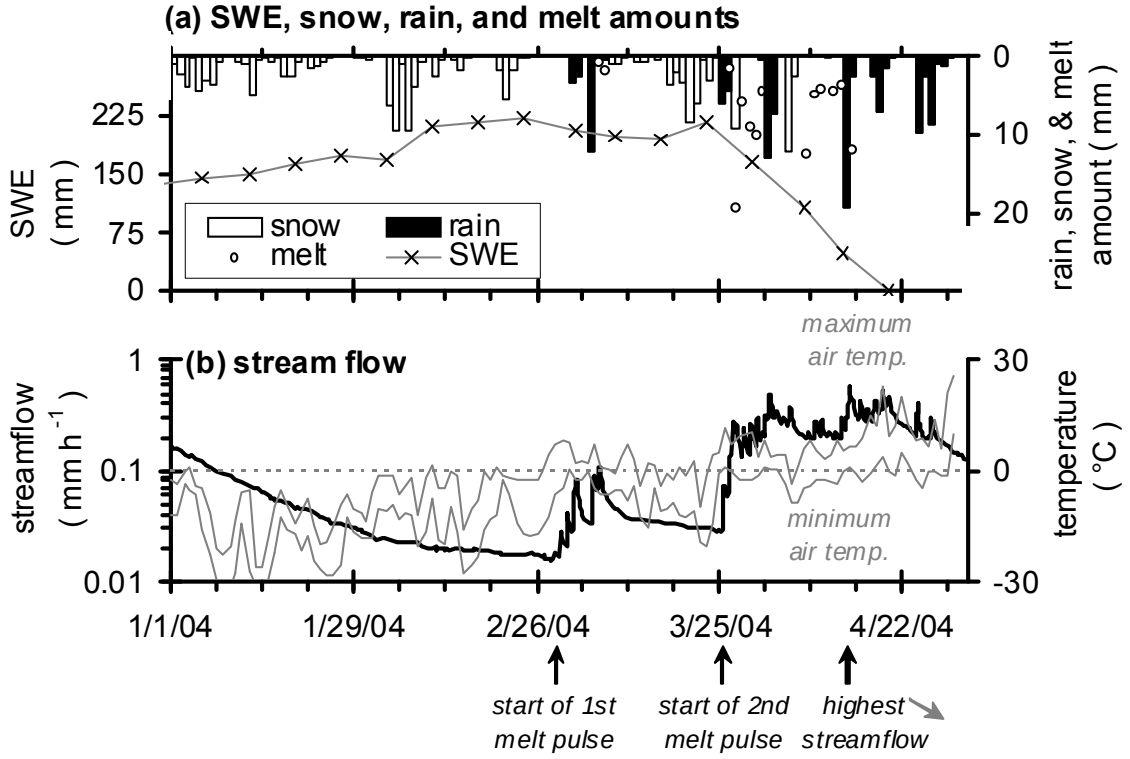


Figure 11. Quick flow during the 2004 snowmelt tracked streamflow (a). The highest nitrate concentration occurred early during snowmelt (b). In contrast, DON concentration (c), DOC concentration (d), and inputs of freshly-leached DOM as indicated by the higher humic fraction and more negative δ^{13}C-DOC (e) were highest at the time of highest streamflow.

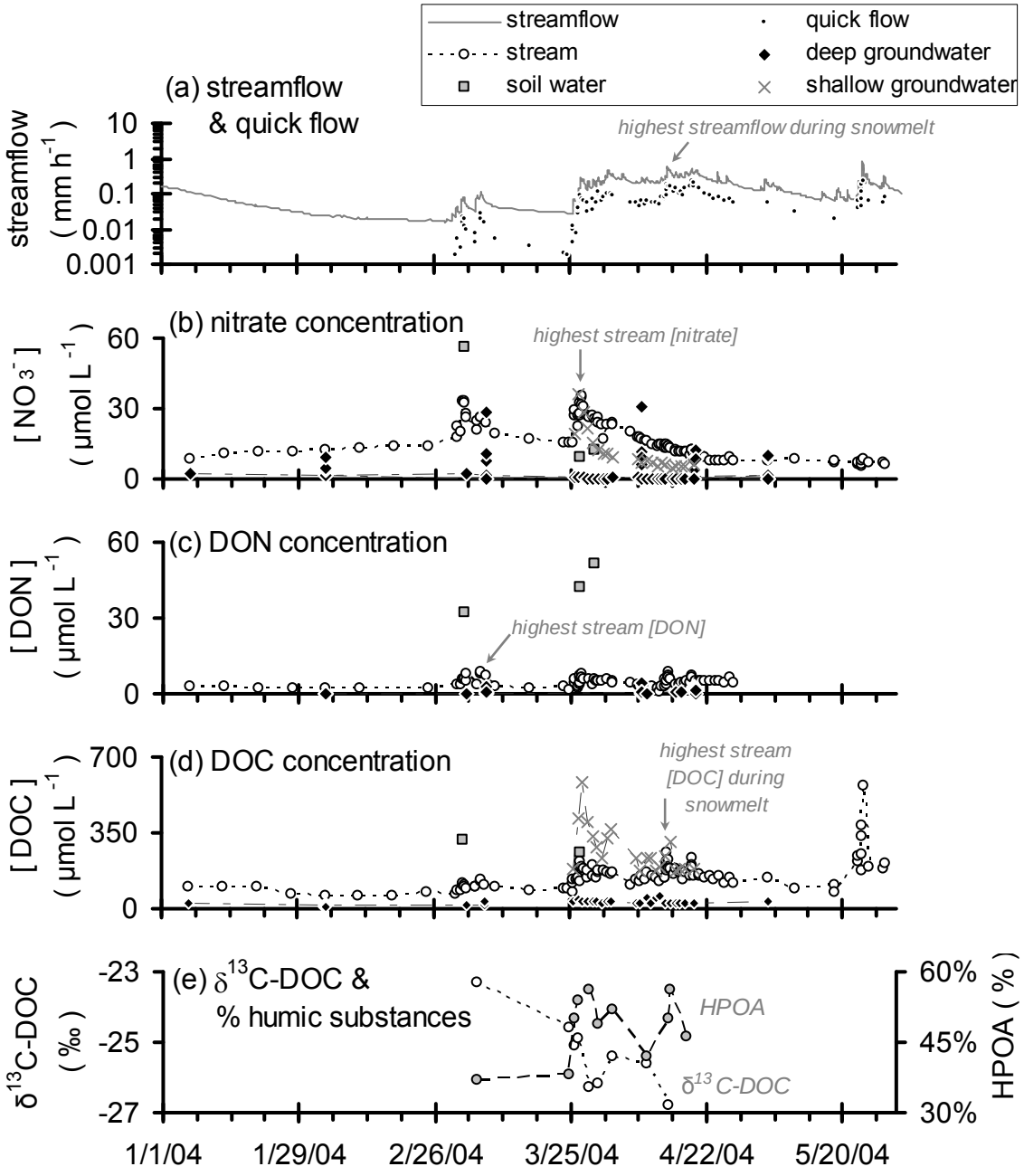


Figure 12. In 2004, nitrate, DOC, and DON concentrations increased with the quick flow contribution to streamflow.

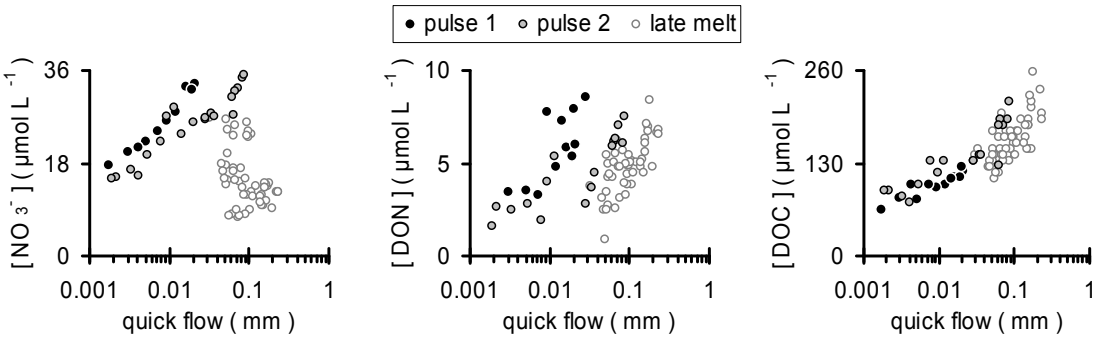


Figure 13. The highest nitrate (b) concentration occurred early in the 2003 snowmelt while DON (c) and DOC (d) concentrations were highest with the highest streamflow. Water levels show the depth to saturation in the soil profile (d).

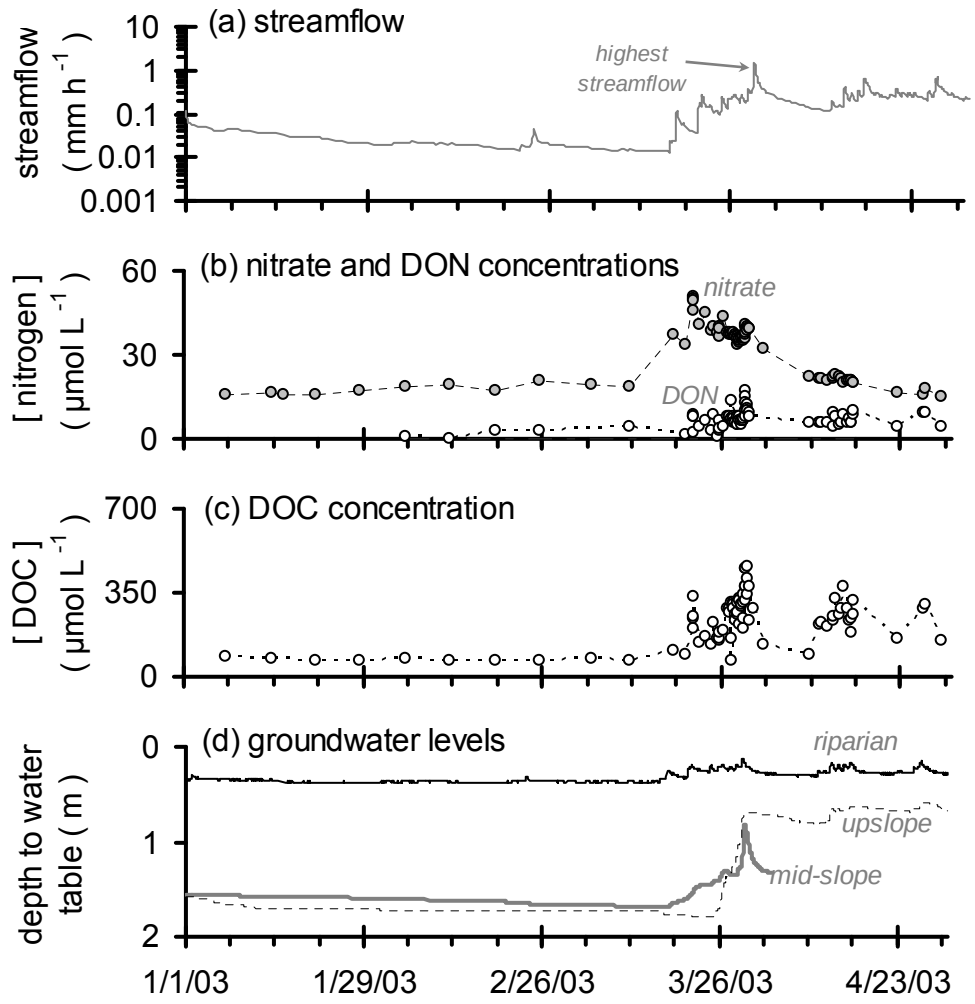


Figure 14. Among years, the early nitrate center of mass (up to six days, a) and the late DON (b) and DOC (c) centers of mass (relative to water) documented how nutrient fluxes varied among solutes.

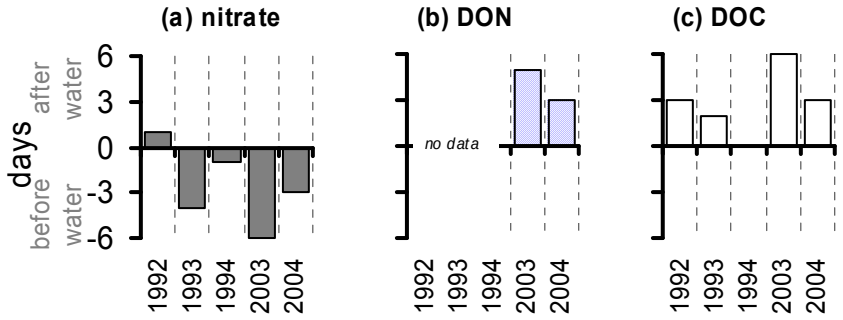


Figure 15. The highest nitrate concentrations of melt water (the ionic pulse of nitrate, a) and in stream water (b) occurred during two pulses early in snowmelt. Nitrate concentrations in shallow riparian ground water also peaked with stream water nitrate. During storm flow, the stream δ^{18}O-nitrate shifted towards an atmospheric end-member and indicated a mix of atmospheric and nitrified sources. Maximum atmospheric contributions coincided with the ionic pulses (d). The uncertainty estimates of quick flow magnitude are shown with the error bars. For nitrate sources, the uncertainties (less than 1.3%) are not shown.

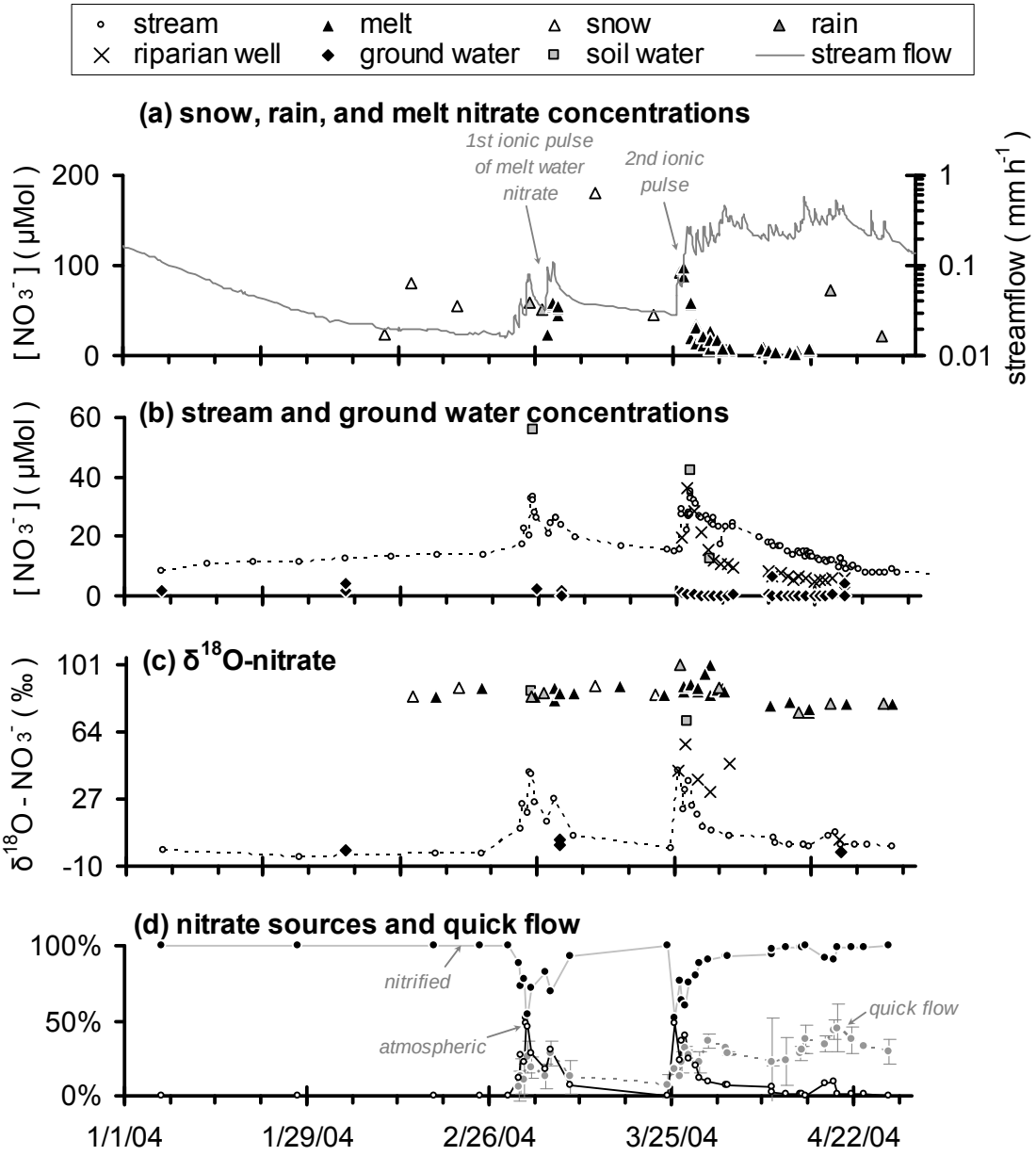
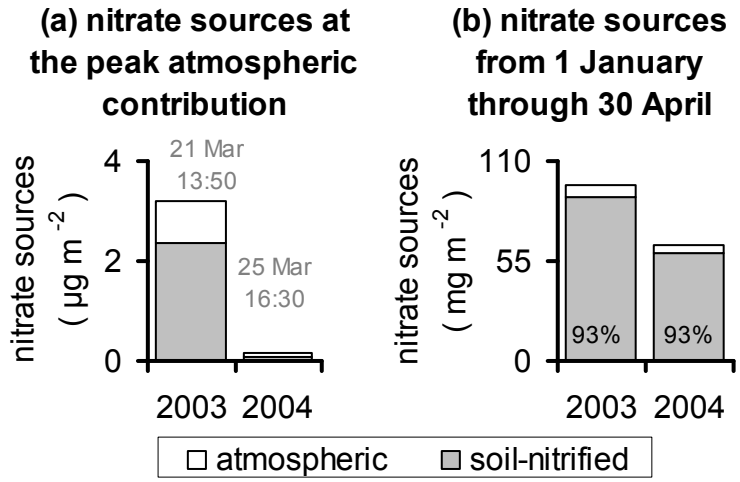


Figure 16. The amount of atmospheric nitrate at the time of peak atmospheric contribution was 26% in 2003 and 49% in 2004 (a). Over the snowmelt runoff event (January to April), atmospheric sources were 7% in 2003 and 2004 (b).



CHAPTER 4

RESPONSES OF STREAM NITRATE AND DISSOLVED ORGANIC CARBON LOADINGS TO HYDROLOGICAL FORCING AND CLIMATE CHANGE IN AN UPLAND FOREST OF THE NORTHEAST USA

Abstract

In the next century, higher annual temperatures, increased growing season length, and increased winter precipitation are expected across the northeast USA in response to anthropogenic forcing of global climate. We synthesized long-term stream hydrochemical data from the Sleepers River Research Watershed in Vermont, USA to explore the relationship of catchment wetness to stream nitrate and DOC loadings. We modeled changes to 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 to 2099 time period show that nutrient flux responses to climate change were highly variable between the dormant and growing seasons. In a warmer climate, growing season fluxes (runoff +20%, nitrate +57%, and DOC +58%) increased as more precipitation (+28%) and storm flow (+39%) occurred during a longer growing season (+43 days). Decreased stream water and nutrient fluxes occurred in the dormant season despite an increased winter precipitation rate. Net annual stream runoff (+8%) and DOC flux (+9%) increases are commensurate with the magnitude of the average increase of net annual precipitation (+7%). Net annual stream water and DOC fluxes were primarily affected by increased winter precipitation. In contrast, decreased annual flux of stream nitrate (-2%) reflected a greater effect of growing season controls on stream nitrate that resulted as days shifted to the longer growing seasons. Our findings suggest that leaching of nitrate and DOC will seasonally shift due to anthropogenic climate forcing and affect the timing and magnitude of annual stream loadings in the northeast USA.

Introduction

Human activities alter the global cycling of nutrients (NRC, 2001; Austin and others, 2003; Hungate and others, 2003), influence climate (Watson and others, 2001), and affect the flow of water and solutes through landscapes (Hope and others, 1994; Vitousek and others, 1997; Boyer and others, 2002; Milly and others, 2005; Perakis and Hedin, 2007). Because water flow through the environment transports solutes from terrestrial source areas (Hornberger and others, 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.

During large storm events, upland and riparian source areas may hydrologically connect to streams (Mulholland, 1993; Hornberger and others, 1994; Fisher and others, 1998). Precipitation transiently saturates source areas in surficial soils that are enriched in dissolved nutrients. When hydrological connections develop, stream nitrogen and organic matter loadings may disproportionately increase if mobile nitrogen and organic carbon are leached from surficial source areas (Hornberger and others, 1994; Boyer and others, 1996; Creed and others, 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 (Hornberger and others, 1994; Boyer and others, 1996; Creed and others, 1996). Despite dramatic changes in flowpath routing and stream chemistry, hydrochemical dynamics during storm flow are rarely quantified in ecosystem studies with intensive water chemistry sampling over the entire range of streamflow conditions during hydrological events.

With anthropogenic climate forcing, streamflow may regionally increase as precipitation increases due to the intensification of the hydrological cycle (Labat and others, 2004; Milly and others, 2005; Gedney and others, 2006; Huntington, 2006; Hayhoe and others, 2007; Piao and others, 2007). In a recent assessment of climate and hydrology for the northeast USA, Hayhoe and others (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 northeast 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 and others, 2003; Huntington, 2003; Hodgkins and Dudley, 2005).

We collected high-frequency, event-based water samples in addition to weekly stream water samples to quantify how nutrient loadings vary with streamflow at an upland, forested catchment of the Sleepers River Research Watershed (Vermont, USA). Our study focuses on the catchment-wide hydrological responses that control nitrate and dissolved organic carbon (DOC) in surface waters to consider two ecologically important solutes that are affected by human activities. We first quantify how the magnitude and temporal distribution of precipitation inputs affect streamflow and nutrient fluxes during events, seasons, and years. We then develop regression-based hydrological models to assess how projected climate change may affect streamflow and nutrient fluxes. Because climate change does not affect the terrestrial flowpaths along which nutrients are transported as long as land use and land cover do not change, the amount of water flowing through the catchment should be a direct response to changes in precipitation amount. By altering precipitation amount and season length in models, we show how the direction and magnitude of stream nitrate and DOC loadings respond to hydrological forcing under projected season length and precipitation changes for the northeast USA.

Site Description

We studied stream hydrochemical responses to catchment wetness and climate change at the Sleepers River Research Watershed in northeastern Vermont. In the 1960s, seminal studies here 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 flowpaths to streams (Dunne and Black, 1971a, b). With a long-term record of streamflow and meteorological data, the 40.5 hectare Watershed 9 (W-9) in the Sleepers River Research Watershed reflects a benchmark catchment for the northeast USA. Like much of the northeast region, W-9 is affected by climate change (Huntington, 2006; Hayhoe and others, 2007) and elevated nitrogen deposition (Campbell and others, 2004).

Northeastern Vermont has a continental climate and the temperature range at W-9 is -30 to 30 degrees Celsius with an annual mean of 4.6 degrees Celsius. Twenty to 30% of the precipitation accumulates as snow from December until snow melts in April (Shanley and Chalmers, 1999; Shanley and

others, 2002a). Although precipitation usually is evenly spread throughout the year, runoff and nutrient fluxes are distinctly seasonal due to large winter snowmelt events (Shanley and others, 2002a; Shanley and others, 2002b) and low streamflow when evapotranspiration is highest during warm, humid summers.

The mountainous W-9 catchment is in the Kittredge Hills. Pope Brook, which drains W-9, is a third-order tributary of Sleepers River which is in the Connecticut River basin. The forest is predominantly sugar maple (Acer saccharum) with other northern hardwood (deciduous) and conifer species. The elevation of W-9 ranges from 519 to 686 meters. A calcareous granulite bedrock forms an impermeable base to a one to three meter deep soil and glacial till profile (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.

Methods

Hydrological and meteorological variables were measured for water years 1965 to 1969 and 1992 to present (each water year starts 1 October and ends on 30 September of the water year). Streamflow was measured at a 120º V-notch weir and discharge was calculated from a stage-discharge relationship according to US Geological Survey protocols (Rantz, 1982). Snow and rainfall amount were measured with a weighing gage at a meteorological station (R29) that is in a forest clearing near the stream gage. Prior to the USGS WEBB era, measurements in the 1960s were made by the USDA Agricultural Research Service (USDA-ARS, 1965).

In 1991, routine stream chemistry sampling was initiated as part of the Water, Energy, and Biogeochemical Budgets (WEBB) program of the US Geological Survey (Shanley, 2000). 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 every storm event 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 over 19 months. Other high-frequency samples were occasionally collected before 2002 (Kendall and others, 1995; Shanley and others, 2002a; Shanley and others, 2002b) and for several large storm events in 2002 and 2005.

Although briefly described herein, the collection, processing, and analysis of samples from 2003 and 2004 are detailed elsewhere (Chapter 2). Weekly W-9 stream and precipitation samples were collected from 1991 to 2002 and concentrations of nitrate and DOC were measured by the USDA Forest Service Northern Research Station, Durham, NH (Campbell and others, 2004). Samples collected between June 2002 and November 2005 were filtered through 0.45 micrometer membrane filters for nitrate and 0.7 micrometer binder-free glass-fiber filters for DOC. Filtered samples were transferred into pre-cleaned high-density polyethylene lab sample bottles for nitrate and amber glass bottles for DOC. Nitrate concentrations were measured by suppressed conductivity detection on an ion chromatograph. Concentrations of DOC were measured on total organic carbon analyzers in several laboratories as described in Chapter 2.

To calculate nitrate and DOC mass fluxes, a concentration was multiplied by the corresponding total runoff in a time interval surrounding the sample. Time intervals varied with the frequency of sampling because each time interval starts midway between a sample and the preceding one. The time interval ends at the midpoint to the next sample. Fluxes were linearly interpolated between the calculated values and integrated to estimate daily, monthly, seasonal, and water year fluxes.

The quick flow component of streamflow was separated from total stream discharge using a hydrograph separation method that is based on streamflow recession analysis (Nathan and McMahon, 1990). 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. At W-9, quick flow represents water that is contributed from preferential flowpaths that pass through surficial soils of upland and riparian areas during storm flow.

Using statistical software (SPSS), multiple regression models were developed to quantify seasonal responses of stream water, nitrate, and DOC fluxes to factors that affect catchment wetness. At W-9, the seasons can be broadly 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 precipitation fell as rain (October to December = early dormant season) or accumulated as snow (January to April = late dormant season). The early and late dormant season were modeled separately due to the different hydrological responses between autumn rainfall and winter snowmelt. The early

and late dormant season fluxes were added to estimate total dormant season fluxes. Precipitation, the number of events per season, the days since an event, and season (early dormant, late dormant, and growing) are the variables that were tested for inclusion in the stream runoff and quick flow models. The variables tested for the solute flux models were stream runoff amount, quick flow amount, the number of events per season, average days between events, number of quick flow days, and season. Seasonal and annual inorganic nitrogen deposition were additional variables tested for inclusion in the stream nitrate flux models. Variables were added to ($p < 0.05$) or removed ($p > 0.10$) from 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 and others, 1992).

To assess the direction and relative magnitude of climatic change on stream water and nutrient fluxes at W-9, precipitation inputs were adjusted from the mean of the 1992 to 2003 base period. As summarized in Table 4 , climate predictions were obtained from the northeast USA regional assessment of Hayhoe and others (2007) for a high carbon dioxide emission scenario (A1FI) and a low emission scenario (B1). To determine growing season length and precipitation amount for the northeast USA, Hayhoe and others (2007) downscaled global results from coupled atmosphere-ocean general circulation models that are fully described in the Intergovernmental Panel on Climate Change Fourth Assessment Report Working Group One database (Nakicenovic and others, 2000). In the B1 scenario, carbon dioxide emissions increase until 2050 and then decrease to 1990 levels by 2100. In the A1FI high emission scenario, global carbon dioxide emissions double by 2050 and then slightly decrease 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 earlier in the year and the date of first frost later in the year to shorten the dormant season. Precipitation amounts for December, January, and February (DJF) were increased to reflect projected winter precipitation changes (Table 4). 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.

Results and Discussion

Before we present model results that quantify how stream nutrient fluxes respond to wetness conditions that are projected to occur with climate change, we first explain how hydrological processes and seasonal variation affect stream nitrate and DOC concentrations and fluxes.

Hydrology and solute dynamics

The mean annual precipitation of 1334 mm y^{-1} (983 to 1542 mm y^{-1}) and annual stream runoff 735 mm y^{-1} (503 to 1075 mm y^{-1}) from 1992 to 2003 were representative of the range of wetness conditions on record since the early 1960s (precipitation = 983 to 1542 mm y^{-1} and runoff = 452 to 1075 mm y^{-1}), see Supplemental Information 5. Runoff was always highest when high streamflow was sustained for several weeks as a seasonal snow pack melted in March or April of each year. Streamflow was consistently low and least variable because evapotranspiration was highest due to plant growth and warmest air temperatures (Figure 17).

Between 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 $year^{-1}$). At the highest sampled streamflow (2.54 mm h^{-1} on 31 August 2005), the stream discharge was exceeded less than 0.2% 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.

Baseflow nitrate concentrations were low during the growing season. During the dormant season, baseflow nitrate concentrations were higher during winter than summer. Baseflow DOC concentrations were less than 100 µmol L^{-1} throughout the year and were less variable than baseflow nitrate concentrations. Regardless of season, baseflow nitrate and DOC concentrations were low relative to storm flow.

The high-frequency concentration and streamflow data documented the hydrological flushing of nitrate and DOC from landscape source areas during storm flow (Figure 18) and that the transport of solutes from the landscape was directly related to event magnitude (Figure 19). During events, streamflow increased up to four orders of magnitude, nitrate concentrations increased up to

twenty-five fold, and DOC concentrations increased up to nine fold above pre-event baseflow concentrations (Figure 18). Similar flushing patterns of nitrate and DOC are observed across the northeast USA (McDowell, 1985; McHale and others, 2002; Inamdar and Mitchell, 2006; Mitchell and others, 2006).

At W-9, the highest nitrate concentrations were consistently measured during snowmelt runoff events (Kendall and others, 1995; Shanley and others, 2002b; Ohte and others, 2004; Chapter 3). Nitrate concentrations may be high during other storm flow events throughout the year depending upon the relationship between nitrate accumulation in source areas, atmospheric deposition during individual events, and the frequency of storm flow events (Chapter 2). Unlike the highest nitrate concentrations that consistently occurred during snowmelt, the highest DOC concentrations often occurred during large magnitude, short-duration rainfall-runoff events (Figure 18).

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

Significant power law relationships ($p << 0.0001$) of nitrate and DOC fluxes to event magnitude highlight links between solute sources in the landscape and stream nutrient fluxes during storm flow (Figure 19). Among years, nutrient fluxes with the quick flow component of runoff were 30 to 53% of annual nitrate fluxes and 44 to 64% of annual DOC fluxes. Quick flow during the single largest event of any particular year contributed from 13 to 48% of the annual runoff, 6 to 42% of the annual stream nitrate flux, and 9 to 48% of the annual stream DOC flux at W-9. The largest stream water fluxes of nitrate and DOC occurred during the winter due to large magnitude and extended-duration snowmelt runoff events (Figure 20). The relationships between storm events and annual stream nutrient loadings suggest that climate change that affects the frequency and magnitude of storm events will force future patterns of stream nutrient fluxes.

Modeled responses of stream nutrient loadings to climate variables

Regression models effectively reproduced the magnitude of seasonal water, nitrate, and DOC fluxes (Supplemental Information 6). Seasonal precipitation amount and sinusoidal terms were significant factors in the stream

runoff ($p << 0.0001$) and quick flow ($p << 0.0001$) models. These variables explained 88% of the variation for stream runoff and 81% of quick flow variation. 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 nitrate fluxes ($p << 0.0001$). Seasonal quick flow amount was the only significant term in the DOC model ($p << 0.0001$) which explained 91% of the seasonal variation of DOC fluxes.

Stream nutrient fluxes reflect the interaction of hydrological processes that leach and transport nutrient 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 storm flow. The differences between the nitrate and DOC models reflected different controls on solute sources and hydrological transport. The seasonal term in the nitrate model is associated with physical processes due to the dynamic relationship between hydrological and seasonal biogeochemical processes. The hydrological processes encompass both event magnitude and the frequency of flushing. During the growing season, stream nitrate and DOC fluxes were lower relative to precipitation amount in part due to the smaller magnitude of streamflow in summer when high evapotranspiration has a greater affect of drying the catchment (Figure 17). For nitrate, plant growth contributes to seasonally low stream nitrate fluxes because high demand for a limited landscape supply constrains nitrogen availability during the growing season, as conceptualized by Stoddard (1994).

Water and nutrient responses change under projected climate change

In the wetter climate scenarios for the time period 2035 to 2099, winter (DJ F) average precipitation was projected to increase between 6% and 30% (Hayhoe and others, 2007). Consequently, more water will flow along surficial flowpaths in upland and riparian areas linking flushing responses to storm flow chemistry and stream nutrient loadings. When only increased winter precipitation is simulated in the models (Figure 21), a 12% increase of net precipitation in the dormant season is associated with increased stream runoff (+9%), quick flow (+13%), nitrate flux (+6%), and DOC flux (+11%). In the dormant season, increased stream runoff (+10%), nitrate flux (+10%), and DOC flux (+14%)

occurred when net precipitation increased (+9%) with the increased rate of winter precipitation. Net annual stream runoff (+6%), nitrate flux (+5%), and DOC flux (+7%) increased when net annual precipitation increased by 7%.

When we considered only effects of a longer growing season, our regression models simulated annual stream water and nutrient fluxes that were larger in magnitude than the effect of increased winter precipitation (Figure 21). For the time period 2035 to 2099, growing season length is projected to increase between nine and forty-three days (Hayhoe and others, 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 21). 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 flux (+58%), and DOC flux (+53%) in the growing season. As growing season length increased, the dormant season became shorter. Decreased stream runoff (-16%), quick flow (-23%), nitrate flux (-21%), and DOC flux (-22%) occurred as net dormant season precipitation decreased by 21%. Net annual precipitation (+1%), stream runoff (+1%), quick flow (+2%), and DOC flux (0%) increased. In contrast to the minimal net effect of shifting seasonality on annual runoff and DOC fluxes, annual stream nitrate flux decreased by 6%.

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 B1 and A1FI scenarios (Figure 22) due to redistribution of dormant season days to the growing season. By the end of the 21st century, average increased rainfall amount (+28%) during the longer growing seasons (A1FI scenarios) may drive increased mean growing season stream runoff (+39%) and increased mean fluxes of stream nitrate (+57%) and DOC (+58%). Mean rainfall during the dormant season decreased (-9%) as the December, January, and February precipitation increases were offset by the loss of rain in days that were redistributed into the 43 day longer growing season. Stream runoff (-7%), nitrate flux (-15%), and DOC flux (-12%) all decreased as less water flowed through the landscape in the dormant season.

When the seasonal fluxes were aggregated over the water year, a 7% increase of mean annual precipitation in the A1FI (2075 to 2099) simulation occurred as stream fluxes of water (+8%) and DOC (+9%) increased (Figure 22).

Shifting seasonality affects annual stream runoff and DOC fluxes little because losses during one season balanced the gains during the other season. In contrast, net annual nitrate flux decreased by 2%. Changes to season length and fewer days of high fluxes during winter affect net annual nitrate fluxes more than increased winter precipitation.

Growing season baseflow is typically lower than dormant season baseflow because potential evapotranspiration is greatest in the growing season. As days were redistributed into a longer growing season, the net annual range of water and nutrient fluxes among the extremes of wetness conditions decreased as shown by the collapsing annual and dormant season ranges of stream runoff and nutrient fluxes. The lower bound during the dormant season increases because additional winter precipitation in the driest years offsets losses due to shifting days to the growing season. In contrast, the upper bound decreases because the additional winter precipitation has 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 carry through to affect annual ranges of stream runoff and nutrient fluxes. The Northeast Regional Climate Assessment projects more extreme variability in precipitation during storm events in the future (Hayhoe and others, 2007). Although we modeled changes from the driest to wettest years, more severe droughts, lower baseflow, and more intense storm flow events may lead to more variability in the latter part of the century and future conditions may reflect wider ranges than that shown in Figure 22.

Many studies have reported increased DOC concentrations over recent decades for surface waters in northeast USA (Driscoll and others, 2003a; Stoddard and others, 2003; Findlay, 2005), Canada (Schindler and others, 1997), and the United Kingdom (Freeman and others, 2001; Worrall and others, 2004; Evans and others, 2006; Worrall and Burt, 2007). Although few studies quantify stream DOC fluxes, Worrall and others (2004) report that DOC fluxes in UK rivers are currently increasing by 2.3% per year and that increased discharge may partially explain the increased DOC fluxes. Similar to the wetter winters and increased growing season fluxes in our simulations, Worrall and others (2004) reported that the observed increased DOC fluxes of UK rivers have occurred as winters became wetter, highlighting how seasonal hydrological dynamics may influence DOC fluxes.

Stream nutrient export varies with hydrological processes as well as inputs from external sources and seasonal patterns of biological uptake and microbial processing (Mulholland, 1993; Hornberger and others, 1994; Creed and others, 1996; Boyer and others, 1997). Recent changes to catchment hydrology coincide with other ecosystem perturbations such as increased inputs of reactive nitrogen from atmospheric deposition that have altered nitrogen availability and soil nutrient status in forested uplands (Birdsey and others, 2000; Rustad and others, 2000; Aber and others, 2003; Galloway and others, 2004; Pregitzer and others, 2004). Because atmospheric deposition disperses anthropogenic nitrogen across widespread areas, atmospheric deposition has affected stream chemistry and forest health across the northeast USA (Boyer and Howarth, 2002; Aber and others, 2003; Galloway and others, 2004; Green and others, 2004). Reactive nitrogen inputs are expected to increase in the future and continued elevated atmospheric nitrogen deposition may exacerbate stream nitrate export (Driscoll and others, 2003b; Galloway and others, 2004). Nitrogen enrichment leads to the condition of ecosystem nitrogen saturation if nitrogen availability exceeds biological nutritional requirements (Aber and others, 1989; Stoddard, 1994). Between 1992 and 2005, event and seasonal patterns of stream nitrate concentrations at W-9 (Figure 18) were consistent with stage one of nitrogen saturation wherein stream nitrate concentrations increase during large storm flow events and are seasonally low during summer baseflow (Stoddard, 1994). On average, 74% of the annual atmospheric input of dissolved inorganic nitrogen is retained at W-9 (Campbell and others, 2004). For each year, we calculated nitrogen retention as the difference between inorganic nitrogen deposition with precipitation and the stream nitrate loading. Among years, inputs and retention have a positive linear relationship ($p = 0.0005$, Figure 24). This relationship suggests that large proportions of the total inputs are currently retained in the catchment across years. Such a trend suggests that W-9 has not advanced towards stage 2 (elevated dormant season stream nitrate concentrations) or 3 (chronically elevated stream nitrate concentrations) of nitrogen saturation (Stoddard, 1994). However, if chronic nitrogen inputs from elevated atmospheric deposition continue, the capacity to retain nitrogen may change and stream nitrate export may increase due to the effects of ecosystem nitrogen saturation in addition to increases that occur as more water flows through the landscape.

Because nitrate and DOC fluxes typically are highest during the dormant season due to snowmelt (Figure 22), further decreases to net precipitation and

streamflow in the winter have the potential to most affect annual budgets. Although we did not attempt to model the effect as precipitation changes form 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 and others, 2002a). If hydrological transport shifts from subsurface flowpaths to flow over frozen soils during snowmelt (Shanley and Chalmers, 1999; Shanley and others, 2002a), the rapid transport of nitrate released from the melting snowpack may substantially increase the transport of atmospherically-deposited nitrate during the late dormant season. If temperatures increase enough that precipitation falls as rain and soils do not severely freeze, hydrological response during the late dormant season may become more like the early dormant season.

Our hydrological approach assesses how changing the amount of water flowing through the landscape will alter the flow of water and solutes to streams. The effects of climate change on catchment hydrology may alter how nutrients are retained, produced (e.g. nitrified), and leached in ecosystems with cascading implications for aquatic metabolism, nutrient export from catchments, and downstream eutrophication. Efforts to reduce greenhouse gas emissions may be an important management option to minimize seasonal and annual changes to stream nitrate and DOC fluxes because the low emission scenario (B1) has less effect than the high emission scenario.

For reactive nutrients such as nitrogen and organic carbon, our approach does not address feedbacks related to altered nutrient availability and the associated changes to biogeochemical cycles. In our model simulations of future climate change scenarios, the relative abundance of nitrate and DOC changed seasonally. These seasonal shifts may affect stream nutrient fluxes because the nitrogen and carbon cycles interact in ecosystems in ways that affect nutrient availability (McClain and others, 2003; Findlay, 2005; Goodale and others, 2005; Chapter 2). In particular, the model results suggest that the stream DOC to nitrate ratio may increase 11% during the dormant season and decrease 13% during the growing season. The carbon to nitrogen ratio is an indicator of ecosystem functions that regulate nutrient availability such as spatial and temporal patterns of nitrification and denitrification (Gundersen and others, 1998; Bernhardt and Likens, 2002; Ollinger and others, 2003; Goodale and others, 2005). Consequently, nutrient transformations may change. For example,

nitrification may increase during the growing season and decrease in the dormant season. With higher net primary productivity and microbial activity over the growing season, seasonal shifts in nutrient availability and mobility may cascade through terrestrial and aquatic nutrient cycles to affect stream nutrient fluxes, downstream eutrophication (Boyer and others, 2002; Driscoll and others, 2003b), and species composition (Emmett, 2007). Despite species shifts and continued atmospheric deposition that will affect biogeochemical processes and source availability in upland and riparian areas, we still expect stream nutrient loadings to change as more water flows through the environment in response to precipitation increases and shifting seasonality.

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Tables

Table 4. Future projections of northeast USA climate conditions for the B1 and A1FI scenarios in the 2035 to 2064 and 2070 to 2099 relative to the 1961 to 1990 base period, from Hayhoe and others (2007).

	2035 to 2064		2070 to 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 *	+6	+20 *
Time change in winter/spring last frost (days)	-8	-14 *	-16	-23 *

* Since 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 in Hayhoe and others (2007).

Figures

Figure 17. From 1992 to 2003, seasonal fluxes of stream runoff (a) and quick flow (b) were correlated with precipitation amount ($p < 0.05$).

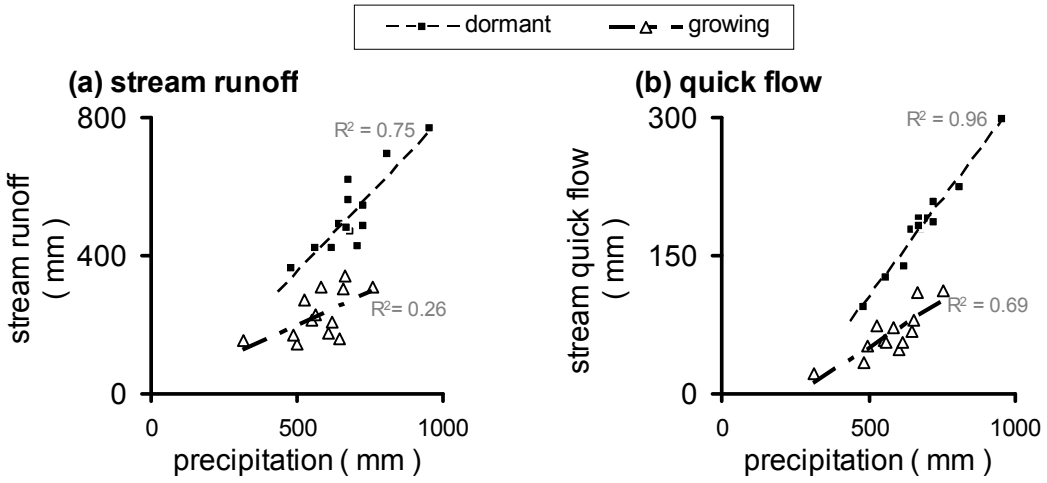


Figure 18. Concentrations of nitrate and DOC plotted on hydrographs from the high frequency data that collected June 2002 to November 2005. The solid symbols show samples collected at high-frequency and the open symbols show weekly samples. The shading highlights specific hydrological events that affected stream nutrient concentrations.

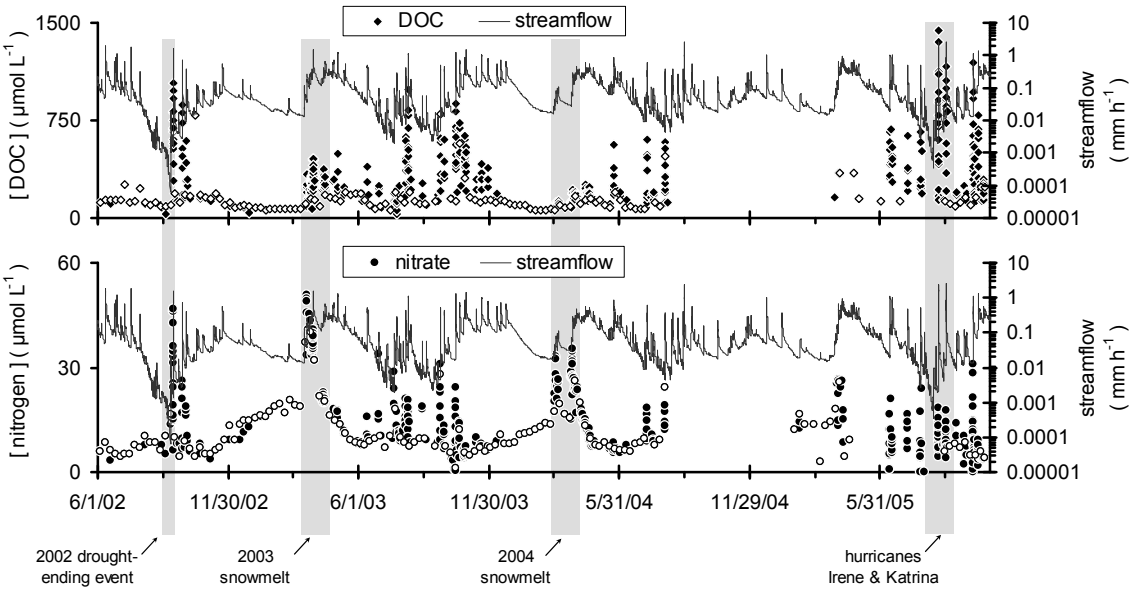


Figure 19. Nitrate (a) and DOC (b) fluxes were strongly correlated with quick flow magnitude. All events that were sampled at high-frequency are shown.

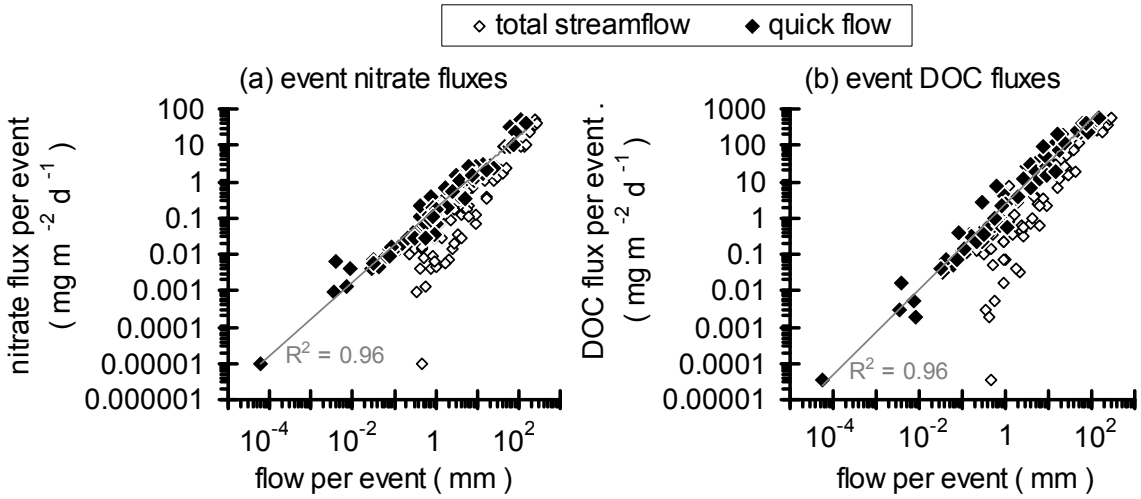


Figure 20. Fluxes during large magnitude events contributed most to stream nutrient loadings. In the dormant season, more than 50% of the water and nutrient fluxes occurred during flow conditions that occurred less than 10% of the time.

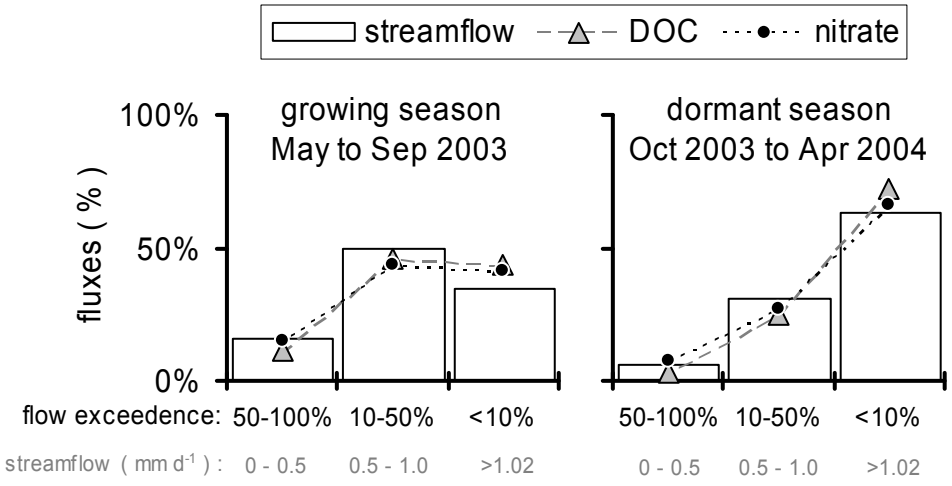


Figure 21. With a longer growing season, model results show precipitation and stream fluxes that increase over the growing season and decrease in the dormant season (a). With increased future winter precipitation (December, January, and February), dormant season precipitation and stream fluxes increased (b).

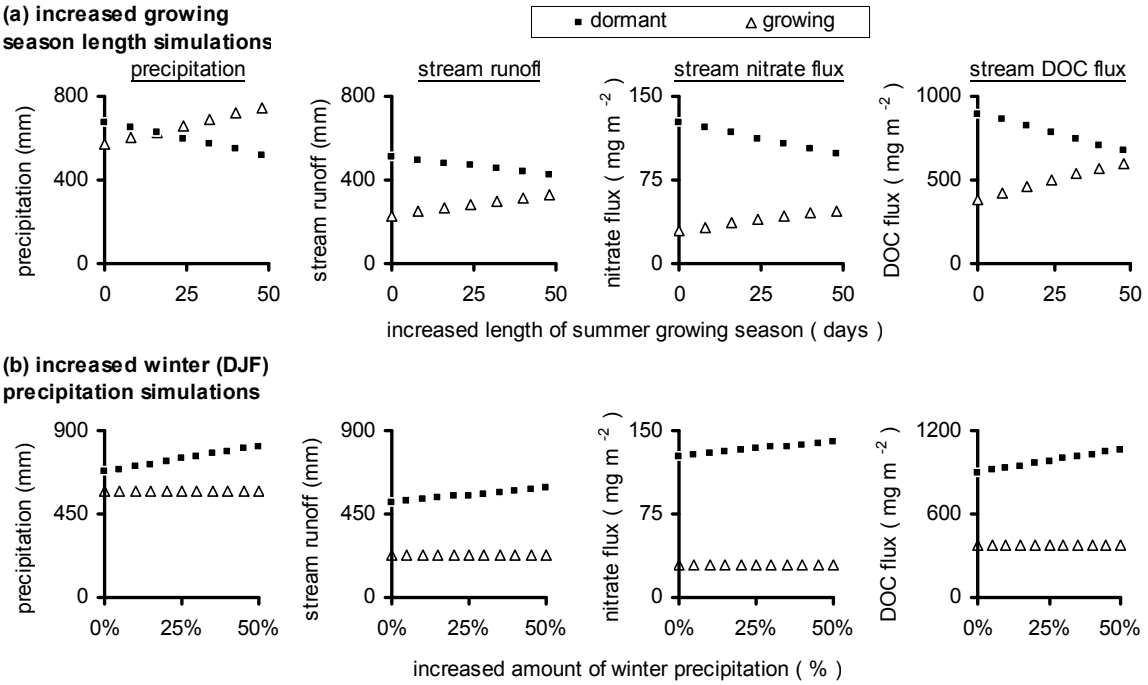


Figure 22. Projections of annual and seasonal water, nitrate, and DOC fluxes from the 1992 to 2003 base period. The bounds show the range from the driest to wettest conditions and are calculated from the extremes of wetness conditions that were measured in the 1993 to 2003 base period.

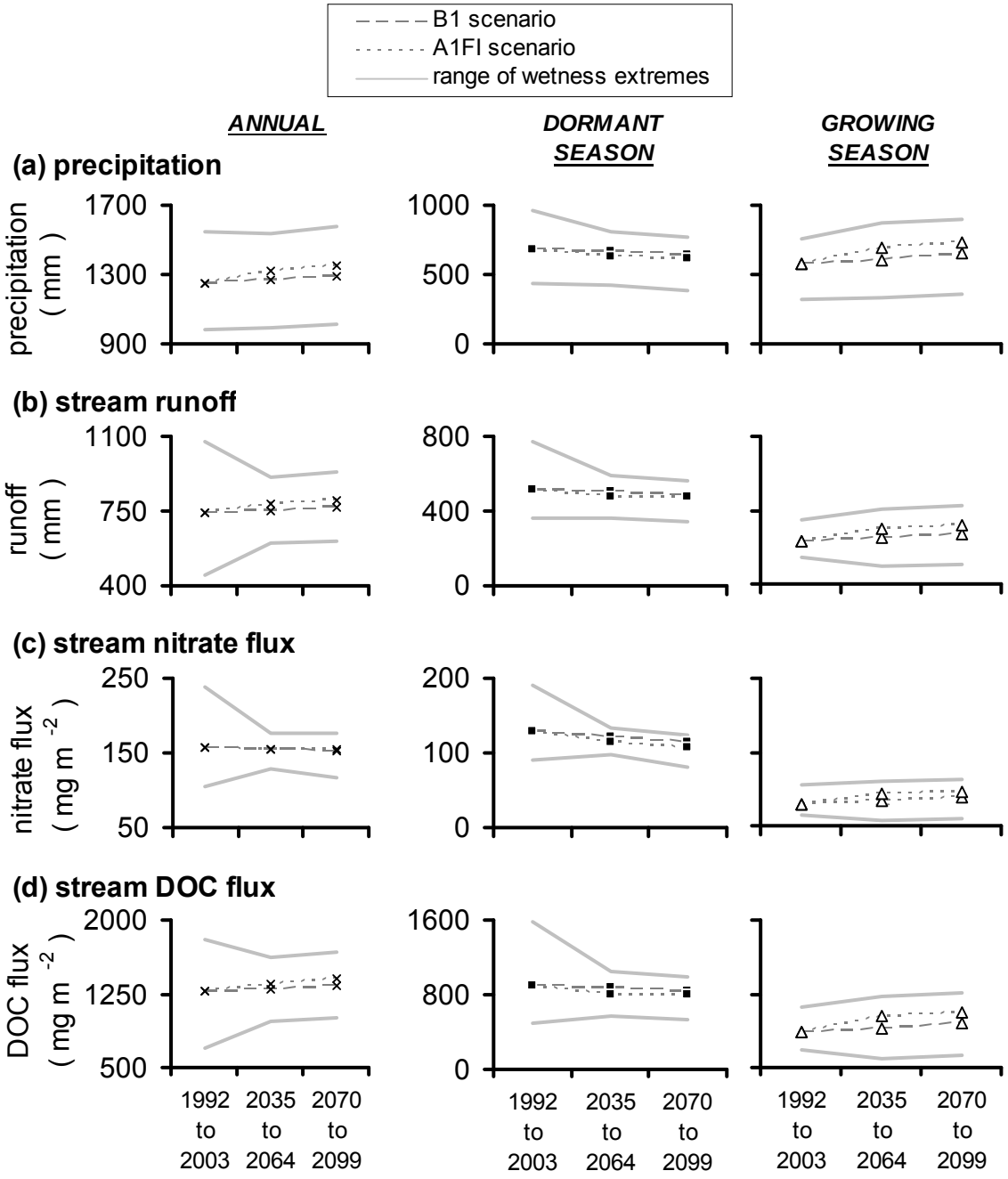


Figure 23. Contributions from shifting seasonality and changing precipitation inputs for the A1FI scenario (2070-2099). Shifting seasonality affects annual stream runoff and DOC fluxes little because the losses/gains between seasons balance each other. Changes to season length and fewer days of high fluxes during winter affect net annual nitrate fluxes more than increased winter precipitation.

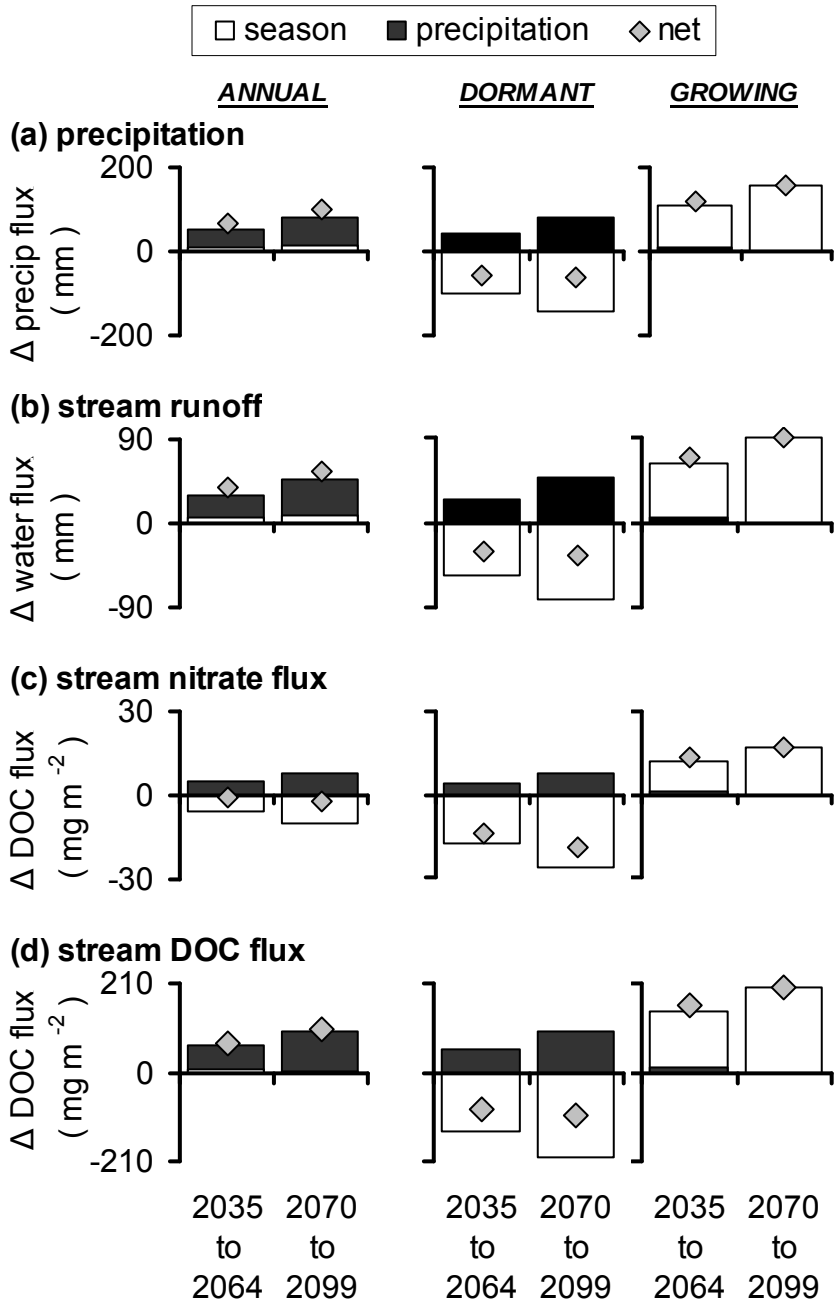
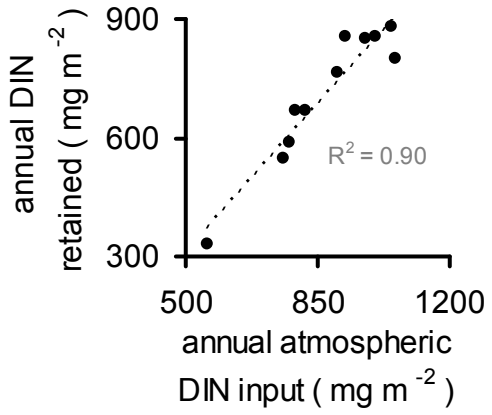
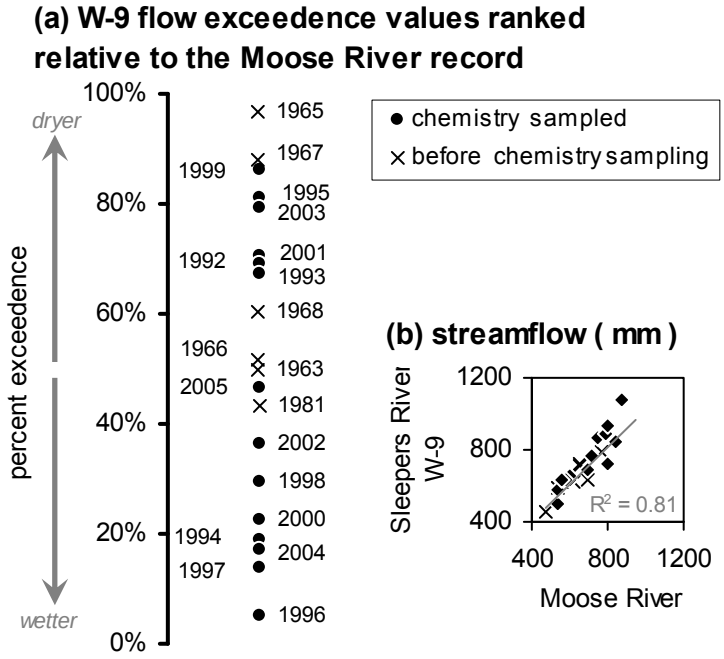


Figure 24. From 1992 to 2003, the amount of nitrogen retained at W-9 increased as dissolved inorganic nitrogen inputs with precipitation increased (p = 0.000009).

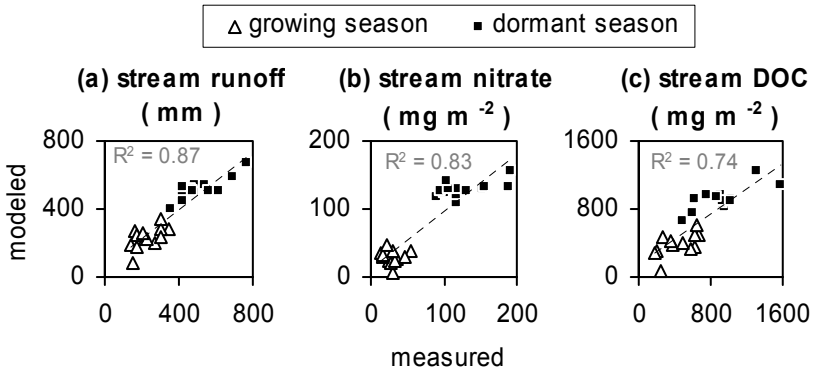


Supplemental Information

Supplemental Information 5. The discontinuous streamflow record at W-9 was compared to a nearby continuous record of streamflow (1960 to 2005). The Moose River at Victory, VT (US Geological Survey National Streamflow Information Program site number 01134500, about 25 km away) had a continuous record of flow from 1960 to present (archived data for the 1960s are available at http://hydrolab.arsusda.gov/wdc/vt.htm). During the time that chemical samples were collected at W-9 from 1992 to 2005, annual runoff spanned nearly the entire range on record since the early 1960s.



Supplemental Information 6. Regression models effectively reproduced the magnitude of seasonal water ($p << 0.0001$), nitrate ($p << 0.0001$), and DOC ($p << 0.0001$) fluxes during seasons from 1992 to 2003.



VITA

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Education

Institution	Location	Dates	Degree
State University of New York College of Environmental Science and Forestry	Syracuse, NY, USA	2001 - 2007	PhD
Cornell University	Ithaca, NY, USA	1997 - 2000	MS
Susquehanna University	Selinsgrove, PA, USA	1993 - 1997	BS

Employment History

Employer	Position	Dates
USDA Forest Service	research hydrologist	2007 - present
University of California	graduate researcher	2005 - 2007
Cornell University	research assistant	2000
State University of New York at Cortland	hydrologic tech	2000
Cornell University	graduate research / teaching assistant	1997 - 2000
Susquehanna University	undergraduate research assistant	1996