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SPATIAL VARIABILITY OF NITRATE CONCENTRATIONS UNDER DIVERSE CONDITIONS IN TRIBUTARIES TO A LAKE WATERSHED[1]

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ABSTRACT: Nitrate-nitrogen (NO_3-N) concentrations in stream water often respond uniquely to changes in inter-annual conditions (e.g., biological N uptake and precipitation) in individual catchments. In this paper, we assess (1) how the spatial distribution of NO_3-N concentrations varies across a dense network of nonnested catchments and (2) how relationships between multiple landscape factors [within whole catchments and hydrologically sensitive areas (HSAs) of the catchments] and stream NO_3-N are expressed under a variety of annual conditions. Stream NO_3-N data were collected during two synoptic sampling events across >55 tributaries and two synoptic sampling periods with >11 tributaries during summer low flow periods. Sample tributaries drain mixed land cover watersheds ranging in size from 0.150 to 312 km^2 and outlet directly to Cayuga Lake, New York. Changes in NO_3-N concentration ratios between each sampling event suggest a high degree of spatial heterogeneity in catchment response across the Cayuga Lake Watershed, ranging from 0.230 to 61.4. Variations in NO_3-N concentrations within each of the large synoptic sampling events were also high, ranging from 0.040 to 8.7 mg NO_3-N/l (March) and 0.090 to 15.5 mg NO_3-N/l (October). Although Pearson correlation coefficients suggest that this variability is related to multiple landscape factors during all four sampling events, partial correlations suggest percentage of row crops in the catchments as the only similar factor in March and October and catchment area as the only factor during summer low flows. Further, the strength of the relationships is typically lower in the HSAs of catchment. Advancing current understanding of such variations and relationships to landscape factors across multiple catchments – and under a variety of biogeochemical and hydrological conditions – is important, as (1) nitrate continues to be employed as an indicator of regional aquatic ecosystem health and services and (2) a unified framework approach for understanding individual catchment processes is a rapidly evolving focus for catchment-based science and management.

(KEY TERMS: nitrate; spatial variations; multiple catchments; landscape; land cover; Cayuga Lake; New York.)

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INTRODUCTION

Nitrogen pollution has emerged as a globally recognized water quality concern, generating interest from scientific, management, and policy communities. Anthropogenic sources of reactive nitrogen (N) to the landscape have resulted in elevated loadings of N to surface waters around the world, from streams and lakes (Carpenter *et al.*, 1998; Driscoll *et al.*, 2001; Aber *et al.*, 2003; Boyer *et al.*, 2006a) to major river basins (Green *et al.*, 2004; Boyer *et al.*, 2006b; Alexander *et al.*, 2007b). The ecological effects of this surplus N delivery to surface waters can be severe, leading to acidification of streams and lakes, and over-enrichment of estuaries (Bricker *et al.*, 1999; Paerl *et al.*, 2002; Driscoll *et al.*, 2003).

In environmental settings ranging from pristine to human-modified, organic forms of N typically dominate fluxes in streams and rivers (Perakis and Hedin, 2002; Schoonover and Lockaby, 2006). However, anthropogenic impacts on the N cycle are often marked by increased contributions of NO_3^- to the total loads of N in rivers (Caraco and Cole, 1999; Seitzinger *et al.*, 2002). Nitrate frequently emerges as the dominant form of inorganic N in surface waters (Creed and Band, 1998b; Boyer *et al.*, 2006a) and is typically the primary component of the inorganic N fluxes issuing from watersheds, even in forested settings (Campbell *et al.*, 2004; Ito *et al.*, 2005) due to inputs of anthropogenic nitrogen to otherwise "pristine" locations via atmospheric deposition. Furthermore, NO_3^- is assessed as one of a suite of indicators of aquatic ecosystem health, which is often extended to the evaluation of ecosystem services.

Links between the spatial and temporal variations of the amounts of NO_3^- in surface water to landscape attributes are well established, often with a focus on surface runoff associated with a particular land use or land cover (Jordan and Weller, 1996; Jordan *et al.*, 1997; Herlihy *et al.*, 1998; Arheimer and Lidén, 2000; Boyer *et al.*, 2002; Franklin *et al.*, 2002; Strayer *et al.*, 2003; Buck *et al.*, 2004; Burns *et al.*, 2005; Cuevas *et al.*, 2006; Poor and McDonnell, 2007). Several studies have also revealed diverse contributions of NO_3^- issuing from bedrock to surface waters (Burns *et al.*, 1998b; Holloway *et al.*, 1998; Böhlke, 2003; Puckett and Hughes, 2005), particularly during drought or low flow conditions. These deep subsurface contributions of NO_3^- reflect leaching from landscape sources (Jordan *et al.*, 1997; Schilling and Zhang, 2004; Benson *et al.*, 2006) and geological sources of NO_3^- (Holloway *et al.*, 1998; Holloway and Dahlgren, 1999). For example, a host of literature demonstrate a particularly strong association between an increased proportion of row crops and NO_3^- in both ground and surface water systems across multiple scales (Jordan *et al.*, 1997; Arheimer and Lidén, 2000; McIsaac *et al.*, 2001; Benson *et al.*, 2006; Schilling and Spooner, 2006; Schoonover and Lockaby, 2006; Johnson *et al.*, 2007; Poor and McDonnell, 2007; Kang *et al.*, 2008). Few studies, however, reveal how relationships between landscape factors and NO_3^- in the stream vary throughout an annual cycle (Johnson *et al.*, 1997). Work that begins to advance our understanding of such patterns is needed.

Several detailed small-catchment studies, often conducted in relatively undisturbed forested settings [such as the United States (U.S.) Geological Survey Water, Energy, and Biogeochemical Balance and Hydrologic Benchmark watersheds and other well-instrumented sites], have advanced current understanding of the complex interactions among seasonal variations in water supply and transport, biologically available nitrogen in soils, and amounts of instream nitrate (Mitchell *et al.*, 1996, 2003; Burns, 1998; Petrone *et al.*, 2007). Studies in more diverse land use settings often focus on holding hydrological conditions relatively constant, such as investigating variations in amounts of NO_3^- in surface waters and linkages with landscape characteristics during base flow or monthly and annually averaged flows across multiple events (Herlihy *et al.*, 1998; Jones *et al.*, 2001; Wayland *et al.*, 2003; Kang *et al.*, 2008), or assessing export of NO_3^- to stream water during storm events (Jordan *et al.*, 1997; Poor and McDonnell, 2007). However, few synoptic or long-term studies specifically examine the spatial distribution of NO_3-N concentrations, with links to landscape attributes, under a variety of seasonal (biogeochemical and hydrological) conditions and across a broad gradient of catchments. Such research is highly relevant for structuring studies related to modeling and monitoring catchment processes and implementing management efforts in multiple catchments issuing to a single water body (e.g., a lake, river, or estuary) and is particularly important as the availability of NO_3^- in surface soils – the primary source of NO_3^- for hydrologic transport – fluctuates with temperature and moisture controls (Alexander *et al.*, 2007a; Knoepp and Vose, 2007), plant uptake of NO_3^- (Arheimer *et al.*, 1996), and applications of nitrogenous fertilizers (Bechtold *et al.*, 2003). Therefore, an assessment of the spatial distribution of NO_3^- concentrations in multiple catchments across varying conditions throughout the year warrants further exploration.

In this paper, we investigate (1) how the spatial distribution of NO_3-N concentrations varies across a dense network of nonnested catchments and (2) how relationships between multiple landscape factors and stream NO_3-N are expressed under different biogeochemical and hydrological conditions throughout one year. We assess NO_3-N concentrations using several synopses – or snapshots – samples at the outlets of a large, diverse subset (from $n = 11$ to 64) of catchments draining to Cayuga Lake in Central New York State. Spatial variations in stream NO_3-N concentrations, compared among four synoptic sampling events, are examined via changes in concentration ratios, Moran's *I* correlograms, and geographic mapping techniques. Pearson correlations and partial correlations are employed to investigate relationships between multiple landscape attributes and stream NO_3-N concentrations during each sampling period. The findings presented here are important for advancing the current understanding of temporal differences in the spatial variations of surface water NO_3-N concentrations across multiple unique catchments. This study is particularly relevant for national and international watershed biogeochemical research and management, as the spatial distribution of NO_3-N in surface waters continues to be linked to broader conclusions, such as the regional status of aquatic ecosystem indicators and services.

STUDY AREA

Cayuga Lake Watershed (CLW) is located in the Finger Lakes Region of New York State. Cayuga Lake is the longest (61.5 km), widest (2.8 km wide), and second largest volume freshwater lake in the state outside of the Great Lakes system. Its deepest point reaches ~40.4 m. CLW is ~1,840 km^2 (Figure 1), excluding the surface area of the lake (~173 km^2) and an additional 2,018 km^2 contributing drainage area from Seneca and Keuka Lakes to Cayuga Lake's northern outlet (GFLRPC, 2004). The lake outlet flows northward to the Oswego River system emptying into Lake Ontario, one of the five Great Lakes in the U.S. A dense network of over 100 tributary subcatchments drains CLW. The study subcatchments (n = 10-64) of Cayuga Lake range from 0.15 to 312 km^2 and comprise ~77% (n = 64) of the total CLW drainage area.

The climate of the study area is humid continental, which is characterized by warm summers and long, cold winters (GFLRPC, 2004). Average annual precipitation (rain and snow) is ~89 cm and is relatively evenly distributed throughout the year (Ithaca, New York) (NEWA, 2006). The climate of the northern part of the watershed exhibits characteristics strongly influenced by the Laurentian Great Lakes, primarily Lake Ontario (GFLRPC, 2004). Land cover within CLW (minus the lake's area) is 55% agricultural (28% pasture and 27% row crops), 26% forested, 11% urban and agricultural grasses and shrub/scrub, 5% open water and wetlands, 2% developed, ~1% open water and wetlands, and less than 1% barren

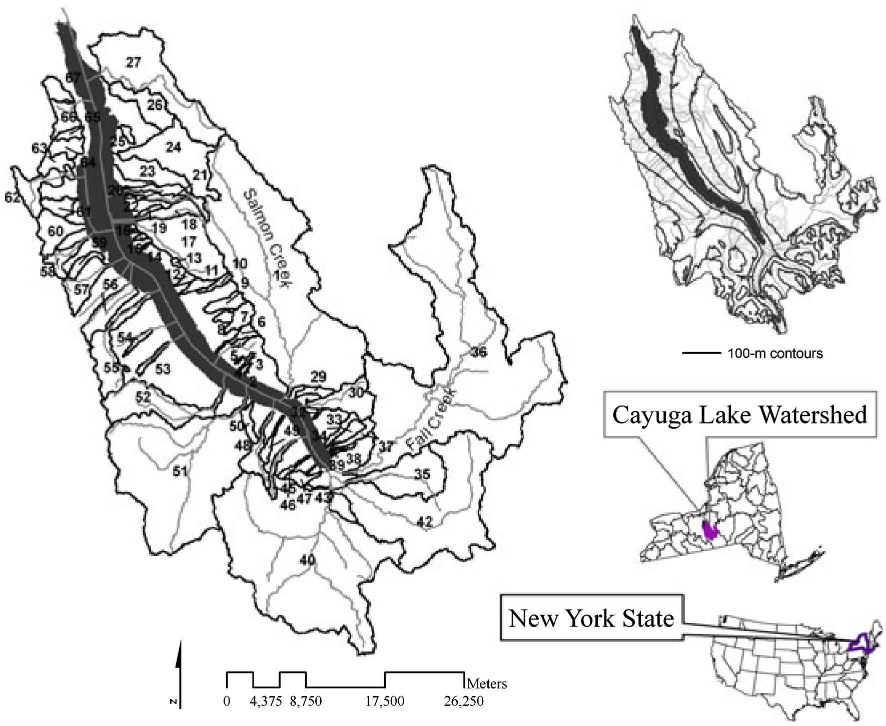

FIGURE 1. Cayuga Lake Watershed, Including the Stream Network, Sample Subcatchments, and Cayuga Lake (in black). Contours are shown in 100 meter increments.

(e.g., rocks and quarries) (MRLC, 2001). Although the land cover proportions vary across sections of the watershed, all subcatchments are predominately a mix of agriculture, forests, and developing areas (Table 1).

Elevations within CLW range from 112 to 638 m above sea level. The lake's current orientation is along a north-south gradient, with relatively low topography in the northern end trending toward a steeper gradient with deeper bedrock and sediment moving southward (Mullins and Hinchey, 1989). Glacially carved valleys in the higher elevations of the watershed create numerous steep waterfalls in the southern part of the watershed. Bedrock geology in the watershed is comprised mostly of limestone in the northern two-thirds of the watershed with Devonian and Silurian shale and sandstone in the southern portion. Surficial geology of the CLW is a variety of unsorted glacial till of varying thickness; however, the majority is comprised of poorly sorted sand-rich diamict, which is typically a coarse layer of till (GFLRPC, 2004). Till moraine is found throughout the watershed, with primarily lacustrine silt and clay of low permeability located in the northeastern portion of the watershed. Parts of the central-eastern section of the lake and southward exhibit exposed bedrock or bedrock within one meter of the surface. Soils vary in thickness and drainage patterns across the watershed are developed over glacial till, outwash terraces, kames, and sediments (GFLRPC, 2004).

TABLE 1. Characteristics of Subcatchments for the Four Synoptic Sampling Periods.

Variable	Mean	Min	Max
Area (km^2)	24.1	0.15	312
Subbasin wet areas, HSAs[1] (%)	13.2	1.64	27.1
Average annual wet N deposition (kg N/ha/yr)	7.03	6.47	7.56
Pasture, hay (%)	30.7	0.00	70.0
Row crops (%)	28.6	0.00	64.9
Forested (%)	16.5	0.00	58.3
Developed (%)	3.40	0.00	39.5
Grasses (%)	7.74	0.89	58.9
Scrub-shrub (%)	5.44	0.00	25.9
Wetlands (%)	7.27	0.00	76.4
Open water (%)	0.31	0.00	2.92
Barren land (%)	0.13	0.00	5.84
Hydric soils (%)	14.3	0.00	38.6
Topographic index (TI)	9.17	7.97	10.4
Hydrologic soil group A (%)	1.76	0.00	11.0
Hydrologic soil group B (%)	35.7	0.00	84.2
Hydrologic soil group C (%)	43.6	0.70	97.3
Hydrologic soil group D (%)	9.32	0.00	42.7
Range in elevation (m)	195	31.1	521
Average slope (%)	5.09	1.61	12.4

Notes: CLW, Cayuga Lake Watershed; HSA, hydrologically sensitive area.

[1]Percent of subbasin above mean TI for CLW + 1 SD.

Synoptic 1 (S1): March 23-24, 2005; *Synoptic* 2 (S2): August 19, 2005; *Synoptic* 3 (S3): September 3, 2005; *Synoptic* 4 (S4): October 26 and 28, 2005.

METHODS

Nitrate-N Concentrations

Synoptic sampling captures a "snapshot" of stream chemistry during a single period in time (Grayson *et al.*, 1997; Wayland *et al.*, 2003), providing a window to the spatial variability of surface water concentrations and fluxes. We collected samples at the outlet of 64 tributaries to Cayuga Lake, comprising ~77% of the CLW, during two complete synoptic sampling periods under varying hydrological and biogeochemical conditions. The sampling events included: (1) March 23-24, 2005 [*Synoptic* 1 (S1), n = 64, vegetative dormancy; early spring, prior to the final snowmelt but with minimal remaining snow (~5-10 cm)], and (2) October 26 and 28 [*Synoptic* 4 (S4), n = 55, a wet period following the growing season, autumn]. We also conducted two additional sampling rounds on major streams in CLW that continued to issue base flow during the summer to capture extreme hydrological conditions, including (1) a summer dry, low flow period [*Synoptic* 2 (S2), August 19, 2005, n = 11] and (2) a day following a land-based hurricane rainfall event, which provided a brief period of elevated flow (relative to previously dry conditions) in the tributaries [*Synoptic* 3 (S3), September 3, 2005, n = 16]. During this extremely dry summer, 75-83% of streams previously sampled during the S1 synoptic event lacked surface flow connections from their outlets to Cayuga Lake.

We sampled each tributary at its outlet to Cayuga Lake at points where mixing of lake and tributary chemistry was minimized. Samples were collected from a high velocity midsection of each stream, into a precleaned 1 l high density polyethylene (HDPE) bottle that was rinsed four times with stream water at each field site. Samples were stored at 4°C until analysis. We filtered all samples using 47 mm 0.45 μm hydrophilic polypropylene membrane filters (Pall Gelman GHP, Ann Arbor, Michigan) into 125 ml HDPE bottles (for NO_3^-), and analyzed filtered samples for NO_3^- via ion chromatography, using a Dionex DX-500 system (Dionex, Sunnyvale, California). We delineated subcatchments draining directly to our sampling points using ArcGIS 9.0 (ESRI, Redlands, California) with an Albers canonical projection, an equal area method.

Biogeochemical and Hydrological Setting for Sampling Events

Sources and transport of nitrogen within the Fall Creek catchment (subcatchment 35) of CLW have been studied for over 30 years (Elizabeth W. Boyer, 2007, personal communication); records from this research therefore provide a context for assessing variations in the coupling of biogeochemical processes and NO_3-N concentrations in the stream within CLW. Throughout the year, precipitation is fairly evenly distributed (Figure 2, E.W. Boyer) within Fall Creek; however, seasonal controls on NO_3-N are clear, as suggested by the concomitant variations in temperate and in stream NO_3-N concentrations from 2003 to 2004. During the dormant season, plant uptake is relatively low, affording accumulation of available nitrogen in the upper soil horizons. During the summer months, plant uptake is higher, as is loss of nitrogen via denitrification, a temperature controlled process (Alexander *et al.*, 2007a).

Discharge and soil moisture was not measured within each of the 64 subcatchments; therefore, we approximate the hydrological setting throughout CLW during the year of sampling using two approaches. First, we assessed stream discharge records from a U.S. Geological Survey stream gage closest to the mouth of Cayuga Lake (Fall Creek, Station Number 04234000, subcatchment 35) in the central portion of CLW and the National Weather Service Coop Network (NCDC, 2006) Freeville 1 NE (COOP Station 303050) precipitation station within Fall Creek catchment to represent the relative daily precipitation and discharge regime during one year of sampling within CLW (Figure 3). Although unique rainfall-runoff relationships are specific to each catchment, we confirmed the relative discharge reflected by the hydrograph throughout all catchments during each of four sampling events (e.g., highest flows during October and low to zero base flow during August).

We also evaluated the spatial distribution of total precipitation during the months of each sampling event (Daly *et al.,* 2002) as an estimate of the spatial distribution of antecedent moisture conditions and hydrological setting prior to each sampling event. (Figure 4). Precipitation was estimated using the Parameter-elevations Regressions on Independent Slopes Model (Daly *et al.,* 2002) as a monthly total, which captures the spatial patterns of precipitation at a 4 km resolution. This approach works well for

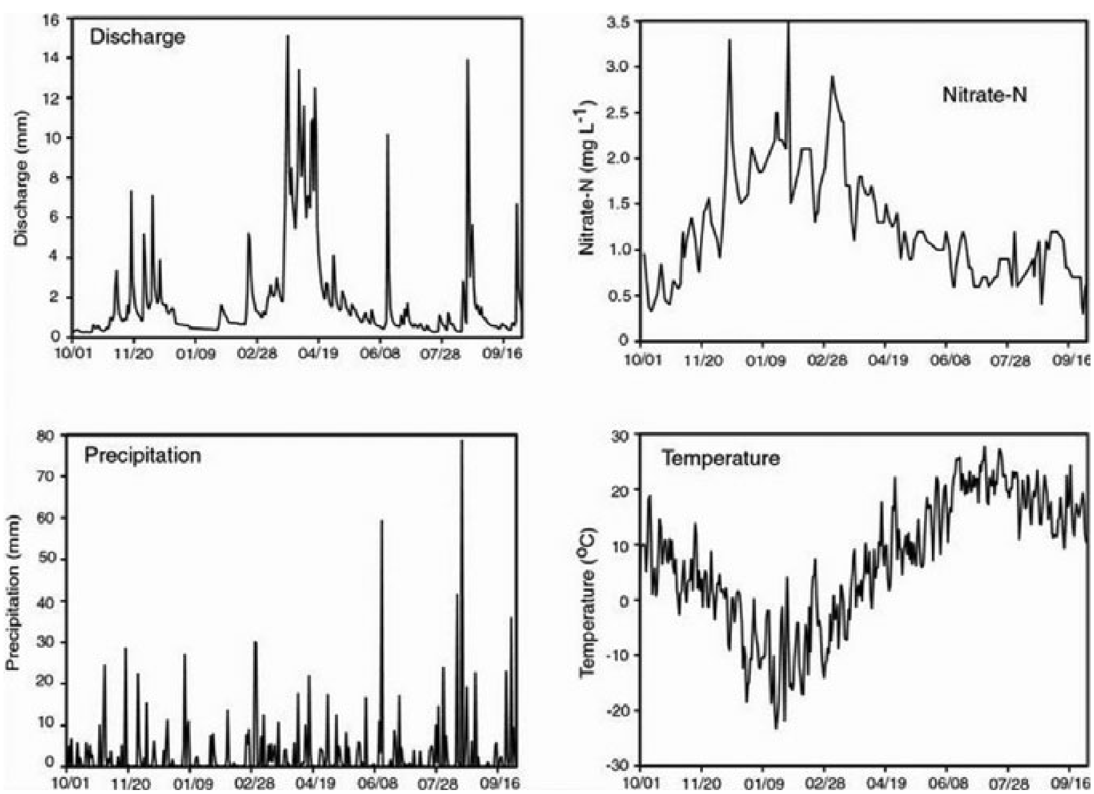

FIGURE 2. Fall Creek, New York, in Cayuga Lake Watershed: Discharge, Precipitation, Temperature, and Stream NO_3-N Measurements During 2003-2004.

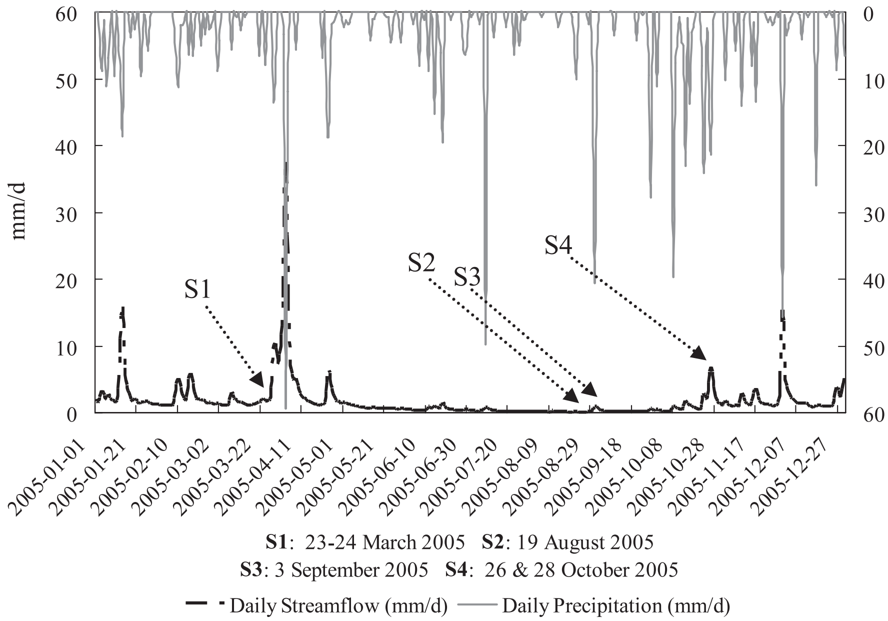

FIGURE 3. Precipitation (Freeville, New York) and Discharge (at U.S. Geological Station: Fall Creek, New York) During the 2005 Synoptic Sampling Period.

March (S1), September (S3), and October (S4) because sampling was conducted either near the end of the month (S1 and S4) or at the very beginning (S3), where the prior month's precipitation rate was assessed (i.e., August precipitation as a hydrological indicator for the September sampling). However, because sampling for S2 occurred mid-month (August 19), the spatial distribution of precipitation was unavailable. Thus, precipitation and discharge from Figure 3 served as a surrogate for hydrological setting throughout the basin during this dry period. Because March precipitation includes only snow events, precipitation rates in Figure 4 appear lower than other periods. However, qualitatively observed soil moisture conditions during stream sampling were relatively high from the remaining early March snowpack.

Landscape Attributes

We focused on multiple indicators of landscape sources and sinks of NO_3-N and indices of hydrologi-

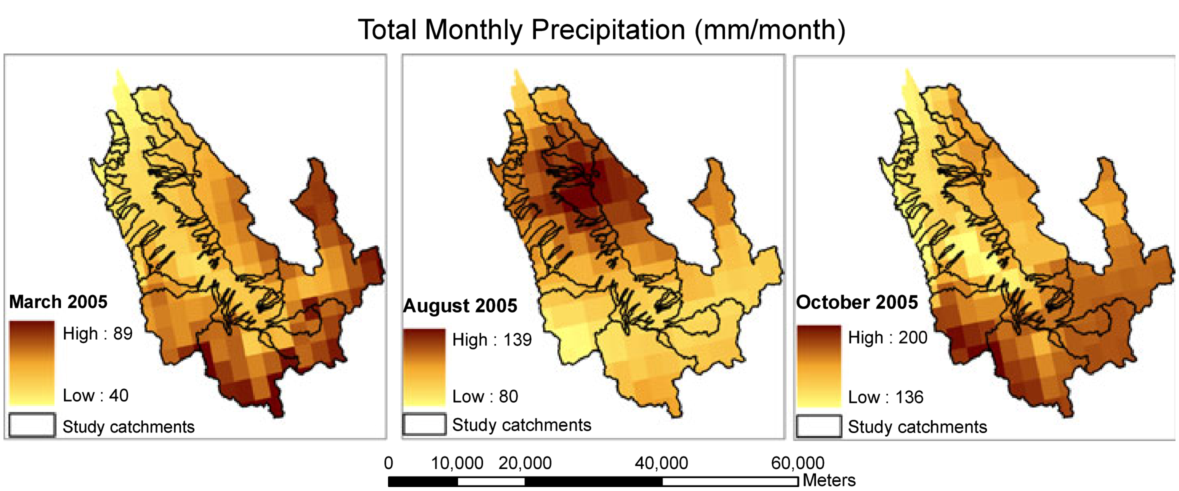

FIGURE 4. Monthly Precipitation Rates (2005) Throughout Cayuga Lake Watershed for March (S1), August (for S3 sampling), and October (S4). Precipitation is derived from modeled Parameter-elevations Regressions on Independent Slopes Model precipitation datasets at a 4 km resolution.

cal wetness and runoff to correlate with snapshots of spatially varying NO_3-N concentrations under diverse conditions. Our methods target landscape connections to stream water NO_3-N concentrations. Therefore, although NO_3^- from bedrock sources can potentially influence NO_3-N levels (Holloway *et al.*, 1998; Holloway and Dahlgren, 1999; Böhlke, 2003), particularly during the drier periods of the year, ground water analysis of NO_3-N contributions is not within the scope of this study.

We first estimated land cover data for each catchment as a proxy for sources of NO_3-N. Because most surplus N in forested land cover settings is derived from atmospheric deposition in the northeastern U.S. (Jaworski *et al.*, 1997; Boyer *et al.*, 2002), we considered leakage of NO_3-N from forested areas primarily of atmospheric origin. Other NO_3-N sources included those from fertilizer and fixation of N by crops (row crops), manure (row crops and pasture land cover), human waste sources and urban runoff (urban areas), and point sources [National Pollution Discharge Elimination System (NPDES) permits]. Land cover type for each subcatchment and for the proportion of each subcatchment in hydrologically sensitive areas (HSAs) (see Discussion below) was estimated using the 30-m resolution 2001 National Land Cover Dataset (NLCD) from the Multi-Resolution Land Cover (MRLC) Consortium (MRLC, 2001). Similar to other studies (Strayer *et al.*, 2003; Wayland *et al.*, 2003), we aggregated land cover into nine major categories, including *pasture* (NLCD 81), *row crops* (NLCD 82), *forest* (NLCD 41, 42, and 43), *developed/urban* (NLCD 22, 23, and 24), *wetlands* (NLCD 90 and 95), *grasses* (urban and rural, NLCD 21 and 71), *open water* (NLCD 11), *barren* (NLCD 31 – quarries, strip mines, etc.), and *shrub/scrub* (NLCD 52). Other input sources included estimates of contemporary annual wet N deposition for each catchment (Golden and Boyer, 2008) and sites of point source discharges throughout the basin from the U.S. Environmental Protection Agency's Pollution Compliance System, or NPDES permits (USEPA, 2006).

We investigated whether patterns of soil wetness during synoptic sampling can be correlated to nitrate loss in the landscape. Soil moisture indices have been used in multiple studies to detect areas of denitrification (see Boyer *et al.*, 2006a); therefore, we calculated the percent of hydric soil coverage within each subcatchment using data from the Soil Survey Geographic (SSURGO) database (1:15,480) (USDA-NRCS, 2006).

The mean standard topographic index (TI), which provides a metric describing the theoretical wetness potential for each point within a watershed (Beven and Kirkby, 1979) and has been applied to assess the coupling of hydrological and biogeochemical processes (Creed and Band, 1998a; Welsch *et al.*, 2001), was calculated using methods put forth by Quinn *et al.* (1995). Calculations were applied to each grid cell of a U.S. Geological Survey National Elevation Dataset (NED) (1 arc second, or ~30 m, resolution) clipped to the boundaries of CLW using the formula:

$$\mathrm{TI} = \mathrm{In}\ (a/\mathrm{Tan}\beta), \tag{1}$$

where a is the upslope contributing area per unit contour length (or grid cell resolution) and β is the steepest local slope angle among the downslope directions.

The HSAs within each subcatchment were used as an index of the extent, or proportion, of the subcatchment that responds quickly to rainfall events and to examine whether the extent and landscape characteristics, particularly row crops, in hydrologically sensitive zones in the catchments regulate NO_3-N concentrations at different points throughout the year. The HSAs were calculated by (1) adding one standard deviation to the mean TI of the entire CLW to define a "sensitive" TI value and (2) estimating the percent of each subcatchment with a TI greater than this "sensitive" value. We chose to add one standard deviation to the CLW mean TI to define a standard quantitative index value to capture both the wettest areas (i.e., greater than the mean) in each catchment and throughout CLW, and areas that have a relatively high frequency compared with the tail of the normal distribution curve (e.g., data within ~34% of the mean). The overall goal was to ensure that each unique catchment's hydrologically sensitive zone was included in the analysis, and as such was considered more "site specific" than the mean TI. The proportion of each subcatchment within HSAs ranged from ~2% to 27% (Table 1).

We calculated the percent of each hydrologic soil group (HSG) for every subcatchment (whole and HSAs) using the SSURGO soils database (USDA-NRCS, 2006). HSGs are classified into four categories (A, B, C, and D) according to a soil's infiltration rate, subsurface transmissivity, and runoff potential (USDA-NRCS, 1986). HSG A represents soils with the highest infiltration capacity and lowest runoff potential, and D approximates the inverse. Hydrologic soils group B and C soils are bounded sequentially (via infiltrate rate, transmissivity, and runoff potential) between the HSG A and HSG D soils.

We applied other topographic variables to examine influences on NO_3-N transport. Variations in topography among subcatchments were estimated using mean slope and change in elevation values calculated from NED 30-m elevation data. We calculated mean slope for each subcatchment within the whole catchment and HSA, and range in elevation within the entire subcatchments only.

Analysis: Spatial and Statistical

Analyses of the spatial variation of NO_3-N concentrations from observed synoptic data proceeded sequentially. We first analyzed the NO_3-N concentration data via spatial mapping and analysis (ArcGIS 9.1; ESRI) for each synoptic event, developing a qualitative assessment of the spatial variations in NO_3-N concentrations. To assess changes in NO_3-N concentration between sampling events, we then assessed variations in concentration ratios between each sampling event at repeated sampling sites. Prior to any statistical analyses, Shapiro-Wilk W tests were conducted on NO_3-N data and suggested that the data were nonnormally distributed. Natural log-transformed results changed all p-values from <0.05 to >0.05 ($\alpha = 0.05$); therefore, all statistical analyses were conducted on natural log-transformed concentrations (Sokal and Rohlf, 1995) using SAS 9.2 (SAS Institute, Inc., Cary, North Carolina) and R 2.6.2 (The R Foundation for Statistical Computing, Vienna, Austria).

Our statistical analysis involved multiple steps. We first calculated Pearson's product-moment correlation coefficients between landscape variables, including precipitation, within the whole catchments and HSAs and NO_3-N concentrations during each sampling event to identify important landscape-NO_3-N relationships under varying biogeochemical and hydrological conditions. Given that an increase in one land cover factor or HSG results in a decrease of others (Van Sickle, 2003), if landscape variables exhibiting significant relationships with NO_3-N concentrations were also significantly correlated with each other, we then employed a partial correlation analysis to evaluate the independent relationship of landscape factors and stream NO_3-N concentrations. We used a minimum correlation of $r \geq 0.30$ for correlations among landscape variables, a standard minimum for Pearson correlation coefficients below which even statistically significant results are considered to exhibit little – if any – linear relationship among the two variables. The partial correlation, therefore, helped clarify the relationships between landscape factors and surface water NO_3-N correlations.

After identifying significant relationships between landscape factors and NO_3-N concentrations, Moran's I correlograms and statistics were generated for NO_3-N concentrations during the large synoptic events (sample size was too small for summer samples) and the significant landscape factors to assess whether and where in the watershed significant landscape factors and NO_3-N concentrations exhibit similar spatial structure. Moran's I correlograms measure the degree and significance of spatial autocorrelation within different distance classes. The Moran's I statistic used for the correlograms is similar to the Pearson's correlation coefficient; the numerator measures the covariance of all pairs of points within a given distance class, while the denominator is the maximum likelihood estimator of the variance. A significance test is implemented for each distance class (Legendre and Legendre, 1998), and if the Moran's I is statistically significant, spatial autocorrelation is detected. Correlations for Moran's I typically range from 1 (positive) to -1 (negative) correlation, although it is possible to get results exceeding this range. We analyzed stream NO_3-N concentrations and significant partial correlation coefficients with distance lags of 1 km. The closer the significant Moran's I value is to the absolute value of 1, the higher the correlation between the distance and the variable (e.g., NO_3-N concentrations). While other techniques exist to analyze the spatial autocorrelation of multiple landscape variable on amounts of NO_3-N in streams (see King *et al.*, 2005), our study aims to investigate how simple relationships between landscape factors and NO_3-N vary during different parts of the year.

RESULTS

Snapshots of Nitrate Concentrations Across Sampling Periods

The upper range of NO_3-N concentrations during the March sampling event ($n = 64$) (Tables 2 and A1) approached the 10 mg/l Maximum Contaminant Level Goal (MCL) for N established by the Safe Drinking Water Act of 1974 (Phase II and IIb for NO_3-N, effective July 1992 and January 1994) (USEPA, 1994). Above this level, drinking water supplies are considered to be a threat to human health. During October sampling ($n = 55$), the mean concentration was higher than that of the other sampling periods with four small subcatchments (ranging from 2.0 to 5.9 km^2) meeting or exceeding MCL guidance levels of 10 mg/l during this period. Concentrations during the summer drought period (August: S2, $n = 11$) were the lowest, averaging 0.32 mg/l (Tables 2 and A1). During the September (S3) sampling period ($n = 16$), which followed a long drought period and was conducted one day after a hurricane-based rainfall event passed across the region resulting in a minor peak in discharge, NO_3-N concentrations

TABLE 2. Mean, Minimum, Maximum, and SD of NO_3-N Concentrations During Each Synoptic Sampling Event.

Variable	Sample Size (*n*)	NO_3-N (mg/l) Mean	Min	Max	SD
Synoptic 1 (March 23-24, 2005)	64	2.11	0.04	8.68	1.99
Synoptic 2 (August 19, 2005)	11	0.32	0.09	1.60	0.46
Synoptic 3 (September 3, 2005)	16	0.97	0.06	4.10	1.22
Synoptic 4 (October 26 and 28, 2005)	55	3.61	0.09	15.50	3.56

averaged slightly higher than the previous sampling event (0.97 mg/l). Daily base flow averaged ~0.080 mm/d (0.30 m^3/s) in Fall Creek one month prior to the event and peaked at 0.95 mm/d (3.50 m^3/s) for two days following (Figure 3).

Spatial Variations of Nitrate-N Concentrations Under Different Inter-Annual Settings

Nitrate concentrations throughout CLW respond dissimilarly to changes in antecedent moisture and seasonal availability soil NO_3-N during both the large sampling events (S1 and S4) and summer low flow events (S2 and S3). Figure 5 illustrates the magnitude of changes and the spatial distribution of NO_3-N concentrations around the lake from 30 catchments exhibiting the highest concentrations during the large synoptic events (S1 and S4), and Figure 6 shows the relative change in NO_3-N concentrations among the 11 catchments sampled during each of the four sampling events. Nine of the 11 catchments sampled during each period (Figure 6) have higher concentrations during March and October compared with summer sampling events; however, two catchments (i.e., catchments 56 and 60) in the northwest portion of CLW, exhibit relatively high concentrations during the summer low flow period (~0.070-0.090 mm/d or 0.27-0.37 m^3/s).

Among all catchments, ratios of NO_3-N concentrations from one sampling period to another (i.e., the change in measured NO_3-N at repeated sampling locations) are spatially variable (Table 3), and these variations were not correlated with the distribution of estimated monthly precipitation (see Nitrate Concentrations and Landscape Factors Under Different Inter-Annual Conditions). From March (S1) to October (S4), NO_3-N concentrations increase, on average, to approximately two times March concentrations. However, stream NO_3-N concentrations in some catchments are over seven times March concentrations during October sampling. Other catchments decrease to ~20% of their March concentrations. Concentration ratios suggest a general decrease in NO_3-N between March and August, with ratios ranging from only 0.46% March concentrations to ~85% (range: 0.010-0.85, mean = 0.23). Changes in concentration ratios between March and September (S3) are more variable. Although concentrations, on average, decrease from S1 to S3 (mean = 0.60), some catchments exhibit over two times measured March NO_3-N concentrations. Between August (S2) and September (S3), concentrations generally increased in all but one catchment. Nitrate-N concentration in all catchments (n = 11) between August (S2) and October (S4) increase (mean ratio = 61); however, ranges vary widely. While NO_3-N concentrations in some catchments during October are only approximately three times that of August, others increase over two orders of magnitude to greater than 500 times August concentrations. Changes between September (S3) and October (S4) show a similar pattern, with an average overall decrease from S3 to S4 (mean = 36) but with ranges in concentrations from 40% S3 concentrations to over 250 times that of the September sampling event.

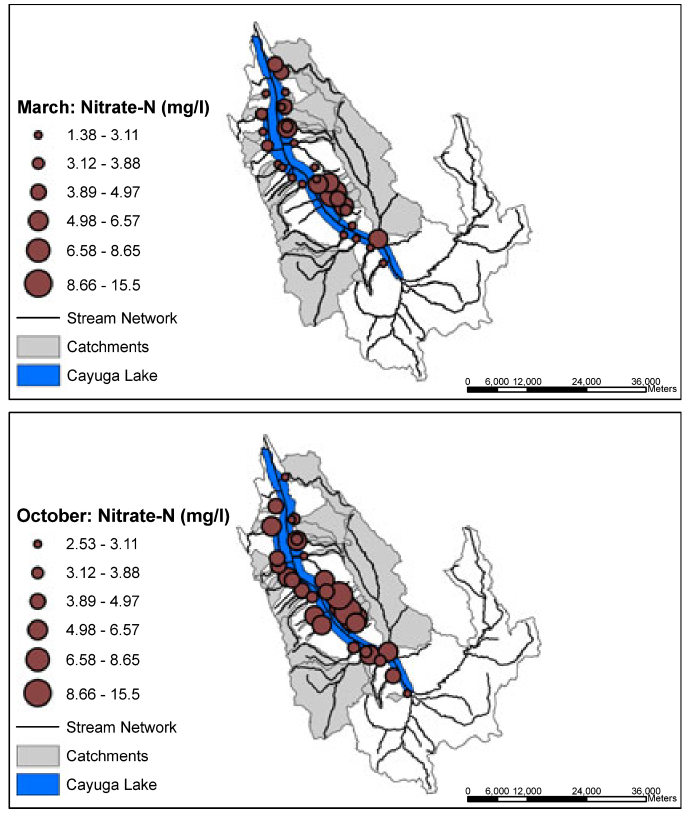

FIGURE 5. Comparison of the Changes in Magnitude and the Spatial Distribution of NO_3-N Concentrations. The map includes 30 catchments with the highest concentrations during the S1 and S4 sampling events.

Correlograms using Moran's *I* statistic further support the spatial variations in NO_3-N concentrations throughout CLW. Figures 7a and 7b depict the spatial structure for the large (S1 and S4 events); the

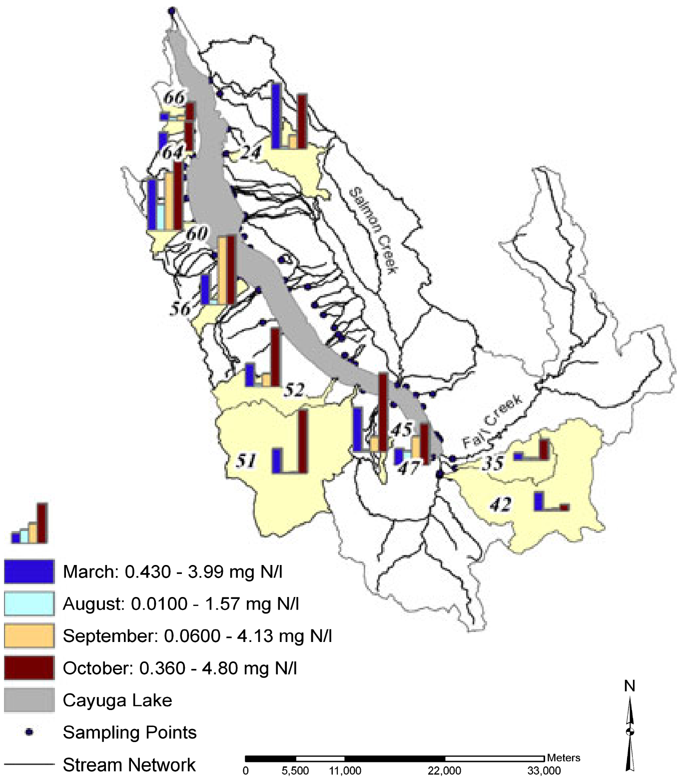

FIGURE 6. Variations in NO_3-N Concentrations Among the 11 Catchments Monitored Across All Four Sampling Events. The scale of the *y*-axis on all bar charts is zero to 4.80 mg N/l.

TABLE 3. Changes in NO_3-N Concentration Ratios Between Sampling Events.

NO_3-N (mg/1)		Ratio of NO_3-N Concentration		
From	**To**	**Mean**	**Min**	**Max**
S1	S4	1.91	0.20	7.15
S1	S2	0.23	0.00	0.85
S1	S3	0.60	0.04	2.27
S2	S3	4.84	0.98	14.7
S2	S4	61.4	2.94	555
S3	S4	35.9	0.39	253

summer sampling events had insufficient sample size to interpret the degree of spatial correlation. The 1 km distance lags for the first 15 km are presented, and two-sided significance tests were performed for each lag to determine if the null hypothesis of no spatial correlation could be rejected. Sample sizes within each lag can vary according to how many sample pairs are separated by each lag distance range (Table 4). Sample sizes for these lags ranged from 28 to 92, and the maximum distance between two points in the dataset is 54 km. For the S1 event, five lags within the first 5 km showed significant positive spatial correlation (I = 1.1, 0.51, 0.36, 0.33, and 0.33) and for the S4 event, four of the first six distance lags

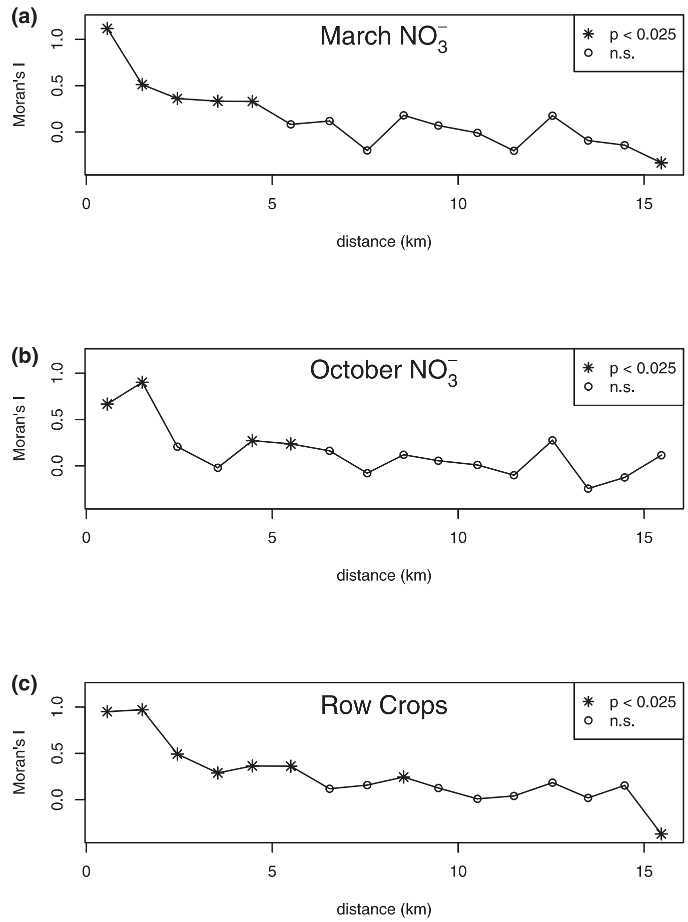

FIGURE 7. Moran's I Correlograms of Stream NO_3-N Concentrations From March (S1, panel a), October (S4, panel b) Sampling Events, and Percentage Row Crops (panel c); n.s. = Not Significant. The plots show significant positive spatial autocorrelation at lag distances up to 5-6 km for the observed NO_3-N concentrations and for the significant landscape variable – percentage row crops – from the partial correlation analysis. These plots also exhibit a similar spatial structure in terms of the decline in the degree of spatial correlation as a function of lag distance; a general decline in the amount of positive correlation is observed in the first 5-6 km, and beyond this distance significant spatial correlation trends are not observed.

showed significant positive spatial correlation (I = 0.67, 0.90, 0.21, −0.020, 0.27, and 0.24). However, two key findings are evident: (1) there is a distinct decrease in the magnitude of correlation with increasing distance and (2) beyond 5-6 km, NO_3-N concentrations throughout CLW show no detectable spatial structure, with some isolated correlations beyond 15 km, which appear to be spurious.

Nitrate Concentrations and Landscape Factors Under Different Inter-Annual Conditions

Initial Pearson correlations among landscape factors within the whole catchments and stream NO_3-N

TABLE 4. Moran's *I* Coefficients for Lags up to 15 km for March, October, and Row Crops.

Lag Distance (km)	*n*	March Moran's *I*	October Moran's *I*	Row Crop Moran's *I*
1	28	**1.12**	**0.67**	**0.95**
2	29	**0.51**	**0.90**	**0.97**
3	69	**0.36**	0.21	**0.49**
4	62	**0.33**	−0.02	**0.29**
5	73	**0.33**	**0.27**	**0.36**
6	92	0.08	**0.24**	**0.36**
7	74	0.12	0.16	0.12
8	81	−0.20	−0.08	0.16
9	57	0.18	0.12	0.24
10	62	0.07	0.06	0.13
11	69	−0.01	0.01	0.01
12	58	−0.20	−0.10	0.04
13	56	0.18	0.28	0.18
14	52	−0.09	−0.25	0.02
15	49	−0.14	−0.13	0.15

Note: Bolded values are statistically significant ($\alpha = 0.025$).

concentrations during each sample event revealed many significant relationships, particularly during S1 and S4. Eleven variables were significantly correlated with concentrations in March (all $p < 0.05$), including mean TI ($r = 0.31$), percentage HSG B ($r = 0.69$), percentage HSG C ($r = -0.69$), average slope ($r = -0.36$), percentage water ($r = -0.33$), percentage grasses ($r = -0.41$), percentage developed land ($r = -0.49$), percentage forested land ($r = -0.44$), percentage scrub-shrub land ($r = -0.35$), percentage row crops ($r = 0.72$), and percentage wetlands ($r = -0.37$). Many of the same relationships between landscape factors and NO_3-N remained during the October sampling, including Mean TI ($r = 0.010$), percentage HSG B ($r = 0.72$), percentage HSG C ($r = 0.59$), percentage water ($r = -0.52$), percentage grasses ($r = -0.45$), percentage developed land ($r = -0.44$), percentage shrub-scrub land ($r = -0.34$), and percentage row crops ($r = 0.65$), all $p < 0.05$. However, in S4, percentage HSG D becomes significant with a weak correlation ($r = -.04$), and percentage forested land and percentage wetlands become nonsignificant.

Partial correlations suggest different results, however, once independent analyses of landscape variables with NO_3-N concentrations were assessed. For S1, only percentage row crops and percentage developed land remained significant (Table 5). For S4, percentage row crops, percentage water, and percentage HSG B remained significant (Table 5). Figure 7c presents a Moran's *I* correlogram for percentage row crops, the landscape variable significant in the partial correlation analyses of both S1 and S4. It shows a similar degree and range of spatial correlation as the NO_3-N concentrations in the S1 and S4 events; the first six distance lags show a significant degree of positive spatial correlation (Table 4) ($I = 0.95$, 0.97, 0.49, 0.29, 0.36, and 0.36). Again, a general decline in the amount of positive correlation is observed in the first 5-6 km, and beyond this distance significant spatial correlation trends are not observed.

During the August and September sampling events, fewer correlations between landscape factors

TABLE 5. Partial Correlations of Stream NO_3-N Concentrations and Landscape Factors Within Whole Catchments and HSAs.

	Whole Catchments: log NO_3^- (mg N/l) Partial Correlation, *r*			
	S1: March *n* = 64	**S2: August *n* = 11**	**S3: September *n* = 16**	**S4: October *n* = 55**
Catchment area (km^2)	–	−0.816	–	–
HSG B (%)	–	–	–	0.400
Land cover: water (%)	–	–	–	−0.429
Land cover: developed (%)	−0.279	–	–	–
Land cover: row crops (%)	0.439	–	–	0.496
	HSAs: log NO_3^- (mg N/l) Partial Correlation, *r*			
	S1: March *n* = 64	**S2: August *n* = 11**	**S3: September *n* = 16**	**S4: October *n* = 55**
HSG B (%)	–	–	–	0.346
Land cover: water (%)	–	–	–	−0.398
Land cover: row crops (%)	0.274	–	–	0.521

Notes: HSA, hydrologically sensitive area; HSG, hydrologic soil group.
All correlations significant at $p < 0.05$, unless otherwise stated; – means no significant correlation.

and NO_3-N concentrations were significant within the whole catchments. For S2, only catchment area was significant, and for S3, catchment area, average slope, percentage forested land, and percentage row crops were significant (Table 5). Similar to S1 and S4, partial correlations revealed different results, eliminating all landscape factor-NO_3-N concentration correlations in S3, and maintaining catchment area as the single significant factor in August, which is partially attributed to the lack of significantly interfering variables for partial correlation analysis.

Within the HSAs and across all events, Pearson's correlations were relatively similar – but exhibited slightly lower strength – with that of whole catchments. Differences in variables included the addition of percentage forested land and elimination of percentage scrub-shrub land during S1, the addition of percentage wetlands and deletion of average slope for S3, and addition of percentage forested land, percentage wetlands, and monthly precipitation during S4. However, as with whole catchment correlations, partial correlations factored out the influence of other significant factors. Percentage row crops in HSAs remained significant, though markedly lower than Pearson's r, for S1 (partial $r = 0.28$, $p < 0.05$) and became slightly higher for S4 (partial $r = 0.52$, $p < 0.05$) (Table 5). Only percentage HSG B and percentage water remained significant for S4. No partial correlations between landscape factors and N concentrations were evident during S2 and S3 within the HSAs.

DISCUSSION

Nitrate Variations Among Sampling Events

Nitrate concentrations were distinctly variable across each sampling event. October exhibited the highest average concentrations (3.6 mg NO_3-N/l). Ranges in October concentrations were comparable to other studies on the lower end of values (from 0.010 to 0.040 mg NO_3-N/l), and less than the median value (0.085 mg NO_3-N/l) of 85 streams draining relatively undeveloped areas of the U.S. (Clark *et al.*, 2000). Maximum concentration values were high, for example, compared with Poor and McDonnell (2007), who report the highest NO_3^- concentrations (as N) in an agricultural catchment at ~1.2 mg N/l during a storm event and Petry *et al.* (2002), who revealed NO_3^- concentrations up to 12.7 mg N/l from samples taken at regular (two weeks) intervals in agricultural catchments. Our catchment with the highest NO_3-N concentration was sampled during the October event (at 15.5 mg N/l, higher than MCL guidance levels) in a slightly smaller row crop dominated catchment compared with the other studies. These higher than average results are potentially related to: (1) elevated antecedent moisture throughout CLW relative to the other sampling periods (Figures 3 and 4), (2) consequent greater connectivity between landscape sources of NO_3-N and surface waters compared with other periods, and (3) an accumulation of NO_3-N in surface soils during dry periods from fertilizers applied during the growing season (Bechtold *et al.*, 2003). This is consistent with findings from other studies (Creed and Band, 1998b; Bechtold *et al.*, 2003), where elevated amounts of NO_3-N from surface soils are released to surface waters immediately before or during the peak in the rising limb of the hydrograph, after which concentrations can become diluted.

Concentrations in March were the second highest (mean = 2.1 NO_3-N/l); however, antecedent hydrological conditions – indicated by precipitation rates – were lower than that of September (Figure 4), suggesting that several important biogeochemical processes and sources of N in the landscape regulate NO_3-N concentrations during this period. For example, the dormant season (March) often reflects a period when soil NO_3-N availability is high in temperate climates resulting, in part, from decreased vegetative uptake of N (Arheimer *et al.*, 1996) and increased soil nitrification following a soil freezing period (Mitchell *et al.*, 1996). Further, transport from preferential elution of NO_3-N from the top of the snowpack during the initial stages of spring melt (Stoddard, 1995) and increased landscape connections with the stream during snowmelt events (Peters *et al.*, 2006) potentially provide transport mechanisms for the accumulated soil NO_3-N to surface waters during this season. Over 30 years of data in Fall Creek support this seasonal trend (Elizabeth W. Boyer, 2007, personal communication; Alexander *et al.*, 2007a), illustrated via an inverse relationship between temperature and NO_3-N concentrations in the stream (Figure 2).

Although extreme low flow conditions (~0.070-0.090 mm/d or 0.27-0.37 m^3/s) were occurring during the August sampling event, sources of NO_3-N were present and releasing from ground water supplies from landscape or bedrock sources. Further, the increase in stream NO_3-N concentrations between the August and September sampling events suggests NO_3-N exists in a flush-limited, rather than source-limited, state in the upper soil horizons during this period. This pattern is often observed following long, dry periods when accumulated NO_3-N is greater than that which is utilized by vegetation or denitrified

(Bechtold *et al.*, 2003) and is readily flushed from the soil when wetness and connectivity increase within the catchment (i.e., in response to the hurricane-based rain event the day before S3 sampling).

Spatial Variations of NO_3-N Concentrations

Changes in concentration ratios (Table 3) among the sampling periods and Moran's *I* correlograms (Table 4) clearly suggest that the response of stream NO_3-N concentrations to temporally variable biogeochemical and hydrological conditions is nonuniform across all catchments resulting in high spatial variability, similar to other studies (e.g., Peters and Donohue, 2001; Petry *et al.*, 2002). The range of differences in catchment response between the drier periods during the growing season (S2 and S3) and S4, which took place during a wet period near the end of the growing season, was the most extreme. Stream NO_3-N measured in August compared with October, for example, increased from three to over 500 times August concentrations, suggesting a wide variety of both dynamic (i.e., fate and transport processes) and relatively static (e.g., landscape cover and geomorphic setting) factors uniquely affecting each catchment (see subsequent section) with limited spatial structure to this response.

In general, we found that four of the smallest catchments exhibited the highest NO_3-N concentrations and responded most rapidly to changes in hydrological conditions, similar to that found by Peters *et al.* (2006) in multiple catchments throughout the U.S. As a result, the distribution of the smaller catchments could partially regulate the spatial variability of NO_3-N concentration across CLW. Moreover, the riparian areas in many of the smaller catchments in CLW are extremely small or have agricultural practices (i.e., row crops or pasture) extending to the stream edges. As a result, because riparian areas can exhibit higher dissolved inorganic N (primarily NO_3^-) concentrations than adjacent stream water (Lewis *et al.*, 2007), less NO_3-N could be retained at the stream edges, possibly resulting in higher NO_3-N concentrations in streams draining small, agricultural catchments.

Variations in Links Between NO_3-N and Landscape Factors

Although several relationships between landscape factors and NO_3-N concentrations were revealed with Pearson correlations, once the influence of competing factors was eliminated, only percentage of row crops shared a significant relationship among the two largest sampling events, S1 and S4, within the whole catchments and within the HSAs (Table 5). This is supported by the Moran's *I* correlograms for the S1 and S4 NO_3-N concentration sampling events (Figure 7), which demonstrate similar patterns of spatial correlation as the percentage row crop correlogram: a significant, but declining, degree of spatial correlation for the first 5-6 km with no significant correlation trends beyond this range. These patterns suggest a short-range response between the row crops percentage landscape variable and NO_3-N concentrations similar to the partial correlation analysis. This fits our conceptual model of landscape-stream NO_3-N relationships within CLW, based upon multiple studies linking row crops and stream NO_3-N (Jordan *et al.*, 1997; Arheimer and Lidén, 2000; McIsaac *et al.*, 2001; Benson *et al.*, 2006; Schilling and Spooner, 2006; Schoonover and Lockaby, 2006; Johnson *et al.*, 2007; Poor and McDonnell, 2007; Kang *et al.*, 2008). This is further supported by Johnson *et al.* (2007) who report that corn production for grain (via row crops) was most highly correlated to stream NO_3^- values in Fall Creek ($r = 0.53$, $p = 0.01$), which is the largest subcatchment in CLW. However, row crops were not a significant factor, as suggested by partial correlations, during the drier sampling periods (S2 and S3). The decomposition of the row crop NO_3-N relationship, the negative relationship between area and NO_3-N concentrations during S2, and the lack of relationships between other landscape factors and NO_3-N during the summer months could be attributed to multiple factors, including low flow conditions, lack of hydrologic connectivity between landscape sources of NO_3-N and the stream, or to small sample sizes ($n < 17$) during these sampling events.

Other than percentage of row crops, the influence of landscape factors varied across sampling periods, and among catchments, to the extent that no correlations were present during S3. For example, in August, during an extremely dry period, only catchment area exhibited a significant (and strong) negative relationship with NO_3-N. This is consistent with smaller catchments typically exhibiting "flashier" hydrological and flushing behavior compared with larger catchments in response to rain events (Peters *et al.*, 2006), and with studies suggesting that upstream land cover is more influential on NO_3-N concentrations in lower order streams (i.e., with a larger contributing area) than smaller, higher order streams (Buck *et al.*, 2004). However, we observed no relationships between landscape factors and NO_3-N in the HSAs during the two dry sampling periods after controlling for other significant relationships between explanatory variables, suggesting additional explanations for this relationship. In addition to low flow conditions and lack of hydrologic connectivity between the landscape and stream during the summer, sample sizes during both summer events were substantially lower than the March and October sampling periods, which could also partially contribute to the lack of landscape variable-stream NO_3-N concentrations relationship.

Partial correlation coefficients between NO_3-N and HSG B are also significant during October in both the whole catchment and HSAs (Table 5), potentially suggesting higher connectivity between these typically moderately well-drained to well-drained soils and the tributaries during this wet period. For example, modeled N export coefficients suggest that under "normal" wetness conditions, a lower ratio of atmospherically deposited N is typically delivered to surface water systems in cultivated catchments under HSG B soils compared with those with HSG C or HSG D soils (e.g., see Sheeder *et al.*, 2002). However, this ratio increases under wetter soil conditions, potentially elevating NO_3-N transport from HSG B soils.

Although we used publically available spatial datasets as indicators of the transport and fate of NO_3-N throughout the catchments (e.g., HSGs, estimated monthly precipitation), similar to other studies (Sheeder *et al.*, 2002), only direct measurements would elucidate the actual extent of influence of soil moisture properties on denitrification and delivery of NO_3-N to surface waters. The application of indicator factors, in addition to the use of snapshots of stream data, introduces multiple layers of complexity into estimates of relationships between landscape factors associated with catchment fate and transport of NO_3-N to streams. Further, potential landscape linkages between actual soil wetness and stream NO_3-N concentrations as a result of denitrification, for example, are also highly spatially and temporally variable (Arheimer and Lidén, 2000; Buck *et al.*, 2004). Regardless of the potential limitations of this approach, it is clear that across the four snapshots of stream chemistry within CLW, landscape relationships with NO_3-N vary spatially and among synoptic sampling events, with the exception of row crops during the larger sampling periods.

Implications for Future Watershed Research and Management

While we know that unique catchment characteristics result in complex interactions and highly individual changes in stream NO_3-N concentrations, assessing this spatial heterogeneity in catchment response across multiple catchments within a single basin and under a variety of seasonal conditions is important on several fronts. First, spatial variations in stream NO_3-N concentrations and links to landscape characteristics are often evaluated as indicators of regional aquatic ecosystem health and ecosystem services. Understanding variations in catchment response to annual changes in hydrological and biogeochemical conditions is imperative to draw these broader conclusions. Further, most of our knowledge concerning variable hydrological and biogeochemical catchment responses to seasonal changes derives from small-catchment studies in relatively undisturbed forested settings (e.g., Burns *et al.*, 1998a; McHale *et al.*, 2000; Band *et al.*, 2001; Mitchell *et al.*, 2006; Christopher *et al.*, 2008). While these studies are imperative for understanding processes regulating sources, fate, and hydrological transport of solutes through a catchment, details gained from this research are also unique to the catchment from which they originate, further advancing the call for a unifying framework for hydrological (McDonnell *et al.*, 2007) and biogeochemical catchment-based science and supporting the need for conceptualizing a set of principles underpinning this complexity (McDonnell *et al.*, 2007).

A unifying approach to research focusing on multiple catchments is particularly useful for allocating resources more efficiently to assess biogeochemical and hydrological regulators of NO_3-N at the catchment scale to clarify decisions on modeling and monitoring approaches (Mitchell, 2001). This unifying framework could also extend to the watershed management community, decreasing the complexity of each individual management case.

CONCLUSIONS

Nitrate-N concentrations are highly variable across >55 unique mixed land cover catchments of the CLW, ranging from 0.040 to 8.68 mg NO_3-N/l and 0.090 to 15.5 mg NO_3-N/l during the March and October sampling events, respectively. Summer low flows also exhibited such variability, though the sample size (n = 11) and concentration values are considerably lower. Spatial variations across the catchments of CLW exhibit extensive heterogeneity of stream NO_3-N response to diverse seasonal biogeochemical and hydrological settings and unique catchment characteristics, as indicated by changes in NO_3-N concentration ratios and spatial mapping. However, NO_3-N concentrations are generally higher during wetter periods and when available NO_3-N in the soil is elevated (i.e., the dormant season or after extended dry periods with potentially elevated NO_3-N accumulation in the upper soil horizons). This is consistent with multiple other small-catchment studies.

When competing landscape variables are factored out, row crops exhibit the strongest landscape-NO_3-N relationship, but only during the larger sampling events, which take place during wetter periods of the year. Further, only one landscape factor – catchment area – is significant during the August summer sampling event after other competing factors are eliminated. However, during the September sampling period, minimal landscape-nitrate relationships exist within whole catchments and within HSAs. Additional research would clarify these low flow-NO_3-N source relationships.

It is well known that individual catchments respond uniquely to changes in hydrological and biogeochemical conditions. However, research assessing spatial variations of NO_3-N in surface waters throughout multiple catchments and estimating relationships of NO_3-N to landscape attributes under seasonal settings that affect both biogeochemical processes (e.g., biological uptake of N) and hydrological conditions is particularly important. For example, stream NO_3-N concentrations – and often land cover factors affecting NO_3-N – continue to be employed as indicators of regional aquatic ecosystem health and ecosystem services. Further, the unique response of NO_3-N across multiple catchments in CLW advances the call for a unifying framework for hydrological and biogeochemical catchment-based science and management.

APPENDIX

TABLE A1. Nitrate-N (mg/l) Concentrations for Each Catchment During the Sampling Events. UNT = unnamed tributary.

Catchment	Catchment Name	Mar-05	Aug-05	Sep-05	Oct-05
1	Salmon Creek	5.83			6.57
2	UNT	0.48			0.34
3	UNT	1.84			1.64
4	UTN	1.70			
5	Morrow Creek	6.71			
6	UNT	3.81			5.62
7	UNT	5.62			15.44
8	UNT	4.53			14.92
9	UNT	8.68			15.53
10	UNT	6.37			9.93
11	UNT	6.18			1.23
12	UNT	1.84			4.96

TABLE A1 (Continued)

Catchment	Catchment Name	Mar-05	Aug-05	Sep-05	Oct-05
13	UNT	1.62			5.43
14	UNT	0.16			0.09
15	UNT	0.04			
16	UNT	1.07			
17	Fames Creek	4.18			
18	Little Creek	2.13			2.99
19	UNT	3.23			
20	UNT	0.60			0.65
21	Dean Creek	6.23			5.05
22	Glen Creek	3.77			3.73
23	UNT	2.61			3.08
24	Great Gully	3.99	0.14	0.82	3.31
25	UNT	2.50			2.39
26	UNT	4.77			1.98
27	Yawger Creek	4.20			3.11
28	Seneca River inlet	0.94	0.03		1.21
29	Minnegar Creek	0.68		0.23	1.89
30	Gulf Creek	0.49			0.87
31	Headwaters of Gulf Creek	0.40			1.18
32	UNT	0.99			
33	UNT	0.21			0.49
34	UNT	0.10			0.18
35	Cascadilla Creek	0.43	0.12	0.12	1.26
36	UNT	0.76		0.11	0.75
37	UNT	0.10			
38	UNT	0.16			
39	UNT				0.54
40	Inlet across from Six Mile Creek in Ithaca	0.44			0.38
42	Six Mile Creek	1.12	0.06	0.11	0.36
43	UNT	0.35			
44	UNT	0.12			
45	Glenwood Creek	2.69	0.11	0.93	4.80
46	Indian Creek	0.50			0.66
47	Williams Brook	0.97	0.83	1.74	2.53
48	Willow Creek	2.36		1.23	3.69
49	UNT	1.41			
50	UNT	0.78		0.13	5.54
51	Taughannock Creek	1.49	0.01	0.06	3.88
52	Trumansburg Creek	1.38	0.15	0.78	3.59
53	Bergen Creek	1.18		0.89	5.34
54	Lively Run	0.98			5.53
55	Sheldrake Creek	1.47			3.43
56	Groves Creek	1.82	0.28	4.13	4.23
57	Mack Creek	1.78			4.23
58	Big Hollow Creek	1.36			4.65
59	UNT	1.81			5.05
60	Hicks Gully	3.12	1.57	3.52	4.63
61	UNT	2.10			1.75
62	Red Creek	0.97			1.14
63	Schuyler Creek	3.19			5.13
64	UNT	1.13	0.31	0.43	1.78
65	UNT	1.99			4.75
66	Canoga Creek	0.45	0.19	0.28	1.09
67	UNT	0.35			0.31

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