

Land-Use Change and Stream Water Fluxes: Decadal Dynamics in Watershed Nitrate Exports

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ABSTRACT

Stream water exports of nutrients and pollutants to water bodies integrate internal and external watershed processes that vary in both space and time. In this paper, we explore nitrate (NO₃) fluxes for the 326 km² mixed-land use Fall Creek watershed in central New York for 1972–2005, and consider internal factors such as changes in land use/land cover, dynamics in agricultural production and fertilizer use, and external factors such as atmospheric deposition. Segmented regression analysis was applied independently to dormant and growing seasons for three portions of the period of record, which indicated that stream water NO₃ concentrations increased in both dormant and growing seasons from the 1970s to the early 1990s at all volumes of streamflow discharge. Dormant season NO₃ concentrations then decreased at all flow conditions between the periods 1987–1993 and 1994–2005. Results from a regression-based stream water loading model (LOADEST) normalized to mean annual concentrations showed annual modeled NO₃ concentration in stream water increased by 34% during the 1970s and 1980s (from 1.15 to 1.54 mg l⁻¹), peaked in about 1989,

and then decreased by 29% through 2005 (to 1.09 mg l⁻¹). Annual precipitation had the strongest correlation with stream water NO₃ concentrations ($r = -0.62$, $P = 0.01$). Among land use factors, corn production for grain was the variable most highly correlated to stream water NO₃ concentrations ($r = 0.53$, $P = 0.01$). The strongest associative trend determined using Chi-squared Automatic Interaction Detection (CHAID) was found between stream water NO₃ concentrations and N-equivalence of dairy production (Bonferroni adjusted P value = 0.0003). Large increases in dairy production were coincident with declining nitrate concentrations over the past decade, which suggest that dairy management practices may have improved in the watershed. However, because dairy production in the Fall Creek watershed has been fueled by large increases in feed imports, the environmental costs of feed production have likely been externalized to other watersheds.

Key words: land-use/land-cover change; agroecosystem management; CHAID; nitrogen cycle; segmented regression analysis; watershed loadings.

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INTRODUCTION

Efforts to ascertain the impact of land-use practices on downstream water quality has been an environmental concern for many years (Porter 1975;

Carpenter and others 1998; Howarth and others 2002; Petzoldt and Uhlmann 2006). More recently, environmental policies and legislation have been put into practice to establish limits for pollutant loads carried by streams and rivers (for example, total maximum daily loads or TMDLs) and to reduce point and diffuse sources of pollution. These include the 1990 Amendments to the U.S. Clean Air Act which were enacted to improve surface water chemistry (Stoddard and others 2003). Nitrogen (N) concentrations and exports are of particular concern as they are related to source water quality issues (Sandstedt 1990) and downstream ecological problems including eutrophication (Bricker and others 1999) and hypoxia (Burkart and James 1999).

Human activities have greatly augmented both N fluxes in the terrestrial biosphere (Jordan and Weller 1996) and fluxes of N cycled through aquatic systems (Vitousek and others 1997). In addition to downstream N transport by streams and rivers, watershed N losses occur on the landscape (van Breemen and others 2002) and within streams (Bernhardt and others 2005). However, our understanding of the ultimate fate of N inputs to watersheds remains incomplete (Schlesinger and others 2006).

Within the northern and eastern United States, temporal trends in stream water N dynamics vary among regions. Surface water nitrate (NO_3) concentrations declined during the 1990s in three physiographic ecoregions (the northern Appalachian Plateau, Adirondacks, and Ridge/Blue Ridge Provinces), with no statistical trend detected in New England or the Upper Midwest (Stoddard and others 2003). The direction of trends in stream water NO_3 concentration in forested catchments for earlier periods also differed between regions. In the southeast US, NO_3 concentrations increased from 1972 to 1994 (Swank and Vose 1997), whereas decreases were reported in New Hampshire for 1973–1997 (Martin and others 2000; Goodale and others 2003).

In this study, we employed a combination of approaches to detect and analyze trends in stream water NO_3 concentration and watershed NO_3 exports for a 326 km² mixed-land use catchment in central New York State. The objective of the study was to identify the driving factors in stream NO_3 dynamics considering atmospheric deposition, biological nitrogen fixation, and watershed imports of fertilizer, feed and food. We hypothesized that NO_3 export increased since the 1970s due to greater food and feed imports into the watershed.

METHODS

Study Area

The Fall Creek watershed is a 326 km² mixed land-use environment located in the Finger Lakes region of central upstate New York (42°27'12"N, 76°28'23"W). The watershed is located at the southern terminus of the Wisconsinan glaciation at elevations ranging from 270 to 600 m a.s.l. Soils in the watershed overlay the Upper Devonian Ithaca Formation of shale and siltstone (Snyder and Whipple 2003), and are generally thin and acidic except in lower landscape positions (Johnson and others 1976).

The United States Geological Survey (USGS) operates a gaging station on Fall Creek at Forest Home adjacent to the Cornell University campus at a flow control structure located 800 m upstream from Beebe Lake, 3.5 km upstream from where Fall Creek enters Cayuga Lake. Discharge data are available for the gage from 1925 to present (USGS 2007).

Land cover and population in the watershed has changed dramatically over the past 200 years. Following the end of the Revolutionary War in 1781, land in central New York was rapidly cleared by former soldiers who received tracts in exchange for military service. In each of the three counties that comprise the Fall Creek watershed (Tompkins, Cortland and Cayuga Counties, representing 58, 22 and 20% of the watershed respectively), more than 50% of land area was in agriculture by 1850 (Waisanen and Bliss 2002), compared with less than 1% in the late 1700s (Smith and others 1993). Agricultural acreage in the counties within the watershed peaked at 75% of land area in 1880 (Waisanen and Bliss 2002). Agricultural land use has since fallen to represent approximately 41% of the watershed area, with 52% of the watershed under forest cover and much of the remaining land area developed (Figure 1).

Water Sample Collections and Analysis

Water samples were collected during base flow and storm flow periods during numerous campaigns. These efforts began in 1972 in an effort to assess land-use impacts on water resources (Bouldin and others 1975). Bouldin and colleagues continued with intensive sampling throughout punctuated periods through 1994. In 1995 and 1996 the stream was sampled at high and low flows in all seasons by the New York Department of Environmental Conservation (DEC) through the Rotating Intensive Basin Studies (RIBS) program (New York State

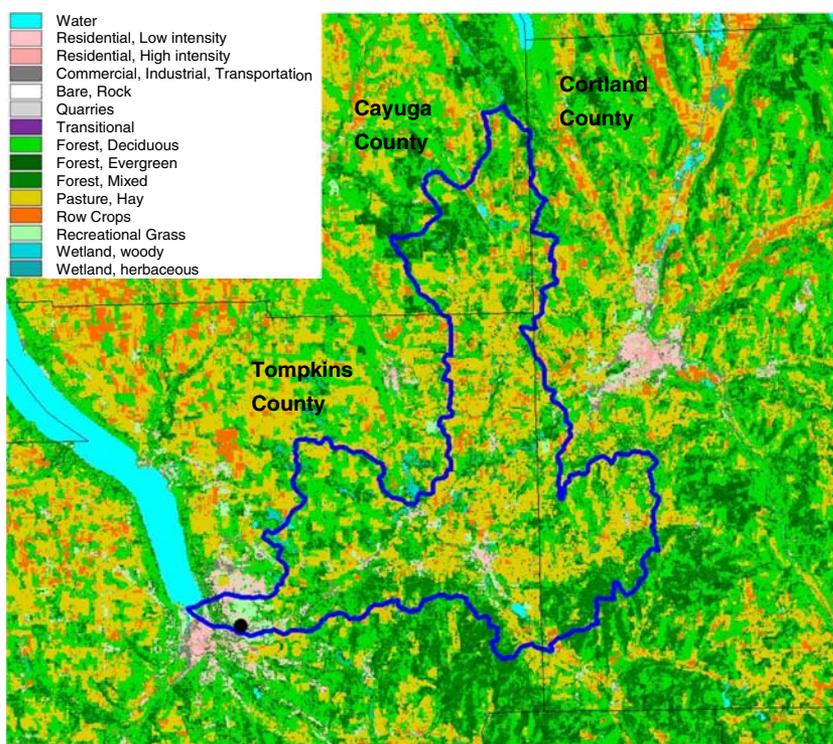


Figure 1. The Fall Creek watershed in central New York State outlined in *blue*. County boundaries are in *black*, and the USGS operated gage is indicated by the *dot* within the watershed.

Department of Environmental Conservation 1999). The Fall Creek Watershed Committee has been collecting samples at baseflow and stormflow conditions in all seasons since 2002. The sampling methodology and quality control/quality assurance of the citizen-based Fall Creek Watershed Committee initiative is coordinated by City of Ithaca and Tompkins County water quality professionals in partnership with state and federally certified laboratory personnel. As described below, nitrate analyses were performed at university and federally certified laboratories using standard procedures of the day in conjunction with quality control efforts including the use of blanks and standards.

Samples collected by the DEC were obtained 2 km downstream from the sample collection sites used in other periods. Synoptic samples collected from the upper and lower sites during the 1970s and again since 2000 show NO_3^- to be strongly correlated between the two sites ($r^2 = 0.85$ and $P < 0.05$ for the two periods analyzed separately) with relative differences that averaged less than 5% of concentrations, and were therefore appropriate for inclusion in the period of record for Fall Creek water quality.

Nitrate-N was analyzed at Cornell University by steam distillation (Bremner 1965) for samples collected between 1972 and 1975, and then using cadmium reduction coupled with continuous-flow

colorimetry (Furman 1976). The accuracy and precision of the steam distillation procedure is comparable to colorimetry (Bremner and Keeney 1965), although the procedure is quite laborious (Kellman and Hillaire-Marcel 1998). New York State DEC data were obtained using automated colorimetry following cadmium reduction (U.S. Environmental Protection Agency 1983a). Samples collected by the Fall Creek Watershed Committee were determined spectrophotometrically following manual cadmium reduction (U.S. Environmental Protection Agency 1983b) at the NY State- and EPA-certified laboratory at the Community Science Institute (CSI) in Ithaca, NY. Results for this study are based on over 1500 discrete samples for NO_3^- . These water quality data were compiled and analyzed as described below.

Time Series Analysis of Nitrate Concentrations and Watershed Exports

Segmented Regression Analysis. Segmented regression analysis (SRA) is a new statistical technique for detection of trends in water quality used to assess differences in concentration-discharge (C-Q) relationships over time (Murdoch and Shanley 2006). For SRA, a long-term data set can be subdivided into discrete segments provided that each segment results in a significant C-Q relationship,

which then allows a comparison among the segments for determining trends. We applied SRA independently to dormant (November–April) and growing seasons (May–October) for three portions of the period of record: 1972–1981, 1987–1993, and 1994–2005. The rationale for analyzing dormant and growing seasons separately is based on previous work in the watershed, which demonstrated a pronounced seasonality in NO_3 concentration in Fall Creek, as well as a strongly seasonal streamflow regime for Fall Creek, with both streamflow and stream water NO_3 concentration higher in winter than in summer (Johnson and others 1976).

For the SRA, independent regression analyses of stream discharge versus NO_3 concentration were conducted for each season for the three portions of the period of record. The significance of the C–Q relationships was determined using analysis of variance (ANOVA), and cases for which the overall regression equation as well as each individual regression term (slope and intercept) were highly significant ($P < 0.005$) were used to assess water quality trends. Flow duration curves were determined independently for each season during the three periods, and NO_3 concentrations were determined for low flow (95% flow exceedance) and high flow (5% flow exceedance) conditions independently for each season during each of the three periods.

Modeling of Annual Exports and Mean Concentrations. Watershed NO_3 exports were estimated using the mean daily stream discharge obtained from the USGS (2007) and the discrete water quality data from the various studies and monitoring campaigns using the stream water loadings estimator program LOADEST (Runkel and others 2004). LOADEST is a publicly available software program developed to estimate water quality constituent loads in streams and rivers. It was developed to calculate mass exports of sediment and chemical constituents from input files consisting of continuous discharge data and discrete streamflow concentrations using a multiple parameter regression model with bias corrections (Cohn and others 1992) incorporated into the program (Runkel and others 2004).

Input files of mean daily discharge and stream water concentrations were prepared for use in calculating annual watershed biogeochemical fluxes. Discharge-weighted concentrations of NO_3 were computed for days when more than one sample was collected because LOADEST requires that the number of observations (that is, samples)

per day be consistent throughout the modeled period. LOADEST was run with a daily time step for the period 1972–2005, and daily estimates were compiled by calendar year to produce annual export estimates. Flow weighted mean annual nitrate concentrations were computed for each year by dividing modeled export mass estimates by annual discharge volumes. Results were evaluated against land-use and land-cover dynamics in export flux and concentration forms.

Agricultural Production

County level agricultural production data were obtained from the National Agricultural Statistical Service (2007) and were scaled to the watershed using a GIS-based approach. We used the 1992 National Land Cover Data set (NLCD) (Vogelmann and others 2001) to compute the fraction of crop production within Tompkins, Cayuga and Cortland counties that is within the Fall Creek watershed. These values were used to scale the USDA production data for 1972–2005 to watershed-specific production estimates. This was based on the assumption that land-use practices within the Fall Creek watershed were similar to those for the areas of the counties in adjacent watersheds. The nitrogen equivalents of field crops and hay produced in the watershed were calculated from Census of Agriculture yield data (U.S. Department of Commerce 1995) using the N content in agricultural products as reported in Burkart and James (1999).

Data on alfalfa hay production began being reported only in 1983 (National Agricultural Statistical Service–New York Field Office 2007), although alfalfa is one of the two main crops grown on dairy farms in upstate New York (Fick and Cox 1995); corn is the other primary crop. Hectares planted to alfalfa were significantly related to corn acreages during the 23 years when both were reported ($r^2 = 0.67$, where: $\text{area}_{\text{alfalfa}} = 1.03 \times \text{area}_{\text{corn}} - 427$; $P < 0.01$ for the regression from analysis of variance). We used this relationship to estimate alfalfa production during the 1970s.

The dairy industry represents the largest agricultural activity in the watershed, both spatially and economically (National Agricultural Statistical Service–New York Field Office 2007). Dairy production was determined for the watershed by scaling county level milk production data from the National Agricultural Statistical Service (2007) as a function of county-specific pasture pixels in the 1992 NLCD occurring within the Fall Creek watershed. The N content of milk, 0.5% (NRC 2003), was used to determine the N-equivalence of the

annual dairy production within the watershed. Annual dairy consumption by watershed residents was computed based on US census population data and per capita consumption rates of milk, cheese and frozen dairy products (USDA Economic Research Service 2007). The N content of this consumption was estimated based on N-contents for milk, cheese (4.0%, Lynch and others 2002), and ice cream (0.8%, Dervisoglu 2006). Dairy-N watershed exports were computed annually as the difference between watershed dairy production and consumption within the watershed.

The majority of agricultural production in the watershed is used on-farm as feed for dairy cattle (Wang and others 1999). However, intensive dairy operations require substantial imports of feed in addition to grain, silage and hay produced within the watershed, which can total 60% of N imports (feed plus fertilizer) that cross watershed boundaries (Wang and others 2000). We estimated the N content of the feed grain deficit for Fall Creek watershed by multiplying dairy N-production by a conversion factor of 5 to obtain feed N requirements, and then subtracted watershed feed production (grain, silage and hay N) from the result. The conversion factor (5 units of feed-N to produce 1 unit of dairy-N) assumes farming practice efficiencies based on mean values from Dou and others (1996), and is representative for dairy farms in the study area (Tylutki and others 2004).

N Inputs and Climate Data

Nitrogenous fertilizer use data were obtained at the county level for 1972–1985 (Alexander and Smith 1990), 1985–1986 (Battaglin and Goolsby 1994), and 1987–2001 (Ruddy and others 2006). The county level data were scaled to the watershed using the ratio of row crop pixels within the watershed for each county from the 1992 NLCD data.

Nitrogen deposition was determined at two stations near the Fall Creek watershed. Wet nitrate and ammonium (NH_4^+) deposition has been collected since 1979 at the Aurora Farm, monitoring location NY08 of the National Atmospheric Deposition Program/National Trends Network (National Atmospheric Deposition Program/National Trends Network 2007), located 38 km northwest of the center of the watershed in Cayuga County. Dry and wet atmospheric N deposition have been determined since 1989 at Connecticut Hill, site CTH110 of the Clean Air Status and Trends Network

(CASTNet) (U.S. Environmental Protection Agency 2007) located 32 km southwest of the center of the watershed in Tompkins County. Wet N deposition did not differ between the two sites appreciably (annual wet N deposition was 3.35 ± 0.14 and 3.36 ± 0.14 kg N ha⁻¹ per year, mean \pm 1 SE for 1989–2005 data at Connecticut Hill and Aurora Farm, respectively), nor statistically ($P = 0.96$, Student's *T* test). We used the ratio between wet and dry N deposition at Connecticut Hill to estimate total (wet plus dry) N deposition for the longer-term Aurora farm data as the atmospheric N input for the Fall Creek watershed. The actual ratio between wet and dry N deposition at Connecticut Hill was preferred to using an empirically derived regression of the ratio between total and wet N deposition (Lovett and Lindberg 1993), which was found to overestimate total N for the Connecticut Hill site by 30%.

Climate data (daily precipitation, maximum, minimum and mean temperatures) for the Ithaca, NY climate station were obtained (National Climatic Data Center 2007) and compiled for the study period. The mean temperatures were determined for the periods January–December and January–April for each year because winter temperature dynamics have been shown to be related to stream water N fluxes (Park and others 2003).

Stream water NO_3 concentrations and exports were analyzed against parameters related to agricultural production and acreages, N imports in fertilizer, feed and atmospheric deposition, and climatic drivers including annual precipitation, winter temperatures and annual temperatures. Simple (Pearson's) correlations were computed, and data were also analyzed using the exhaustive Chi-squared Automatic Interaction Detection (CHAID) procedure for identifying clusters of data (Biggs and others 1991) and implemented using SPSS Answer Tree 3.0 (SPSS Inc., Chicago, Illinois, USA). CHAID, which has been applied to fields as varied as cancer risk assessment (Camp and Slattery 2002) and lotic habitat characteristics (Wolter and Menzel 2005), is useful for detecting and interpreting patterns in complex ecological data (De'ath and Fabricius 2000). CHAID is an algorithm that subdivides a dataset into exclusive and exhaustive segments (that is, clusters of independent variables) that differ with respect to the response variable (Diepena and Franses 2006), allowing complex interactions to be more readily considered by stratifying datasets into smaller parts (Camp and Slattery 2002).

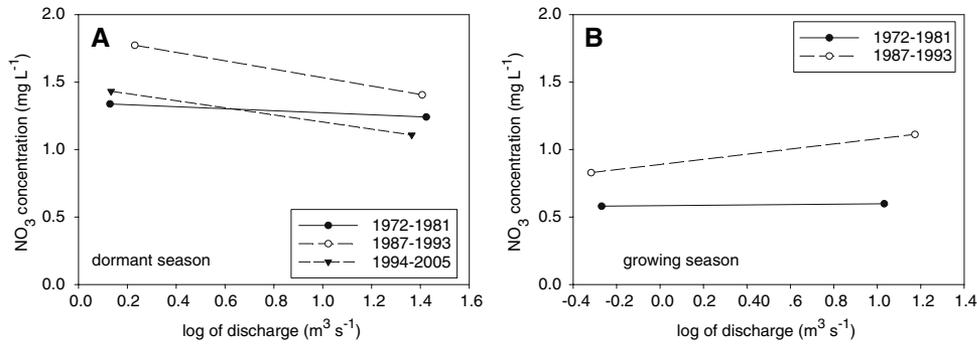


Figure 2. Concentration–discharge relationships for nitrate (NO_3) in Fall Creek, New York for the dormant season (November–April; **A**) and the growing season (May–October; **B**).

RESULTS

Annual Stream Water NO_3 Concentrations and Exports

Concentration–discharge relationships for NO_3 in Fall Creek were found to differ significantly between dormant and growing seasons for all portions of the period of record. During the dormant seasons, the C–Q relationships were negative (for example, lower NO_3 concentrations at higher flows), whereas during the growing season, the C–Q relationships were slightly to strongly positive (for example, increasing NO_3 concentration for higher discharge) (Figure 2A, dormant season and Figure 2B, growing season). Further, because dormant-season streamflow contributed $72 \pm 2\%$ (mean ± 1 SE) of annual flow in Fall Creek during 1972–2005 (USGS 2007) and NO_3 concentrations were higher during the dormant season at all flows (Figure 2), annual watershed nitrate exports are dominated by the dormant season.

Nitrate concentrations were found to be higher during the 1987–1993 period than during the 1972–1981 period for both dormant and growing seasons, and at all flow conditions (Figure 2A, B). Dormant season NO_3 concentrations then decreased at all flow conditions for the 1994–2005 period compared to the 1987–1993 period (Figure 2A). The growing season data for 1994–2005 did not show a significant C–Q relationship, precluding an SRA analysis of the trend in growing season NO_3 concentration between these two time periods.

Results of modeled mean annual NO_3 concentration in Fall Creek stream water averaged $1.37 \pm 0.03 \text{ mg l}^{-1}$ (mean ± 1 SE, $n = 34$ years) for the 1972–2005 period. The annual modeled concentrations followed a parabolic trend ($r^2 = 0.73$, $P < 0.01$), increasing during the 1970s and 1980s, decreasing beginning about 1992, and continuing to decline through 2005 (Figure 3). This parabolic pattern is consistent with the SRA results for

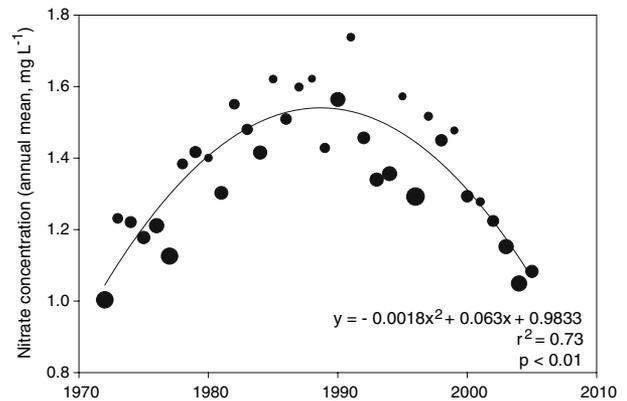


Figure 3. Mean annual NO_3 concentration in Fall Creek, New York, calculated from watershed loading model LOADEST. The diameters of the circles correspond to the annual stream discharge, which ranged from annual means of $3.5 \text{ m}^3 \text{ s}^{-1}$ (smallest circle) to $8.7 \text{ m}^3 \text{ s}^{-1}$ (largest circle).

changes in C–Q relationships for NO_3 , which showed increased NO_3 concentrations at all flows in all seasons for 1987–1993 compared to 1972–1981, and decreased NO_3 concentrations at all flows during the dormant season for 1994–2005 compared to 1987–1993 (Figure 2A, B). Although there was not a significant C–Q relationship during the 1994–2005 growing seasons, the bulk of annual nitrate export occurs during dormant seasons as previously discussed.

Trends in modeled NO_3 stream water concentrations were analyzed against landscape-scale dynamics relevant to water quality during the study period. Parameters related to agricultural production were expressed in units of kg N per hectare of watershed area, and are summarized in Table 1. Stream water nitrate (NO_3 concentrations and watershed exports) are summarized together with N import parameters (fertilizer, feed and atmospheric deposition) and land use/land cover parameters in Table 2.

Table 1. Agricultural Production of the Fall Creek Watershed, Expressed in kg N per Hectare of Watershed Area per Year (Mean \pm 1 SE)

Period	Corn (grain)	Corn (silage)	Oats	Soy	Alfalfa hay	Non-alfalfa hay	Dairy production
1972–2005	2.83 \pm 0.13	2.61 \pm 0.06	0.42 \pm 0.04	n.a.	7.49 \pm 0.35	1.45 \pm 0.06	4.47 \pm 0.06
1970s	2.79 \pm 0.25	2.67 \pm 0.11	0.74 \pm 0.05	n.a.	8.54 \pm 0.37 ¹	1.61 \pm 0.03 ¹	4.04 \pm 0.04
1980s	3.11 \pm 0.19	2.82 \pm 0.10	0.47 \pm 0.05	n.a.	9.30 \pm 0.25	1.56 \pm 0.04	4.41 \pm 0.06
1990s	2.98 \pm 0.24	2.37 \pm 0.07	0.26 \pm 0.02	n.a.	5.84 \pm 0.36	1.12 \pm 0.04	4.53 \pm 0.05
2000s	2.01 \pm 0.18	2.60 \pm 0.19	0.17 \pm 0.03	1.00 \pm 0.09	5.26 \pm 0.80	1.30 \pm 0.11	4.97 \pm 0.04

¹Estimated value.**Table 2.** Stream Water Nitrate Concentrations and Exports for the Fall Creek Watershed Together with Land Use/Land Cover and Atmospheric Deposition Parameters (Expressed in kg N per Hectare of Watershed Area per Year (Mean \pm 1 SE) Unless Otherwise Noted)

Period	NO ₃ concentration (mg l ⁻¹)	NO ₃ export	Fertilizer N imports	Feed N imports	Atmospheric deposition, total N	Atmospheric deposition, wet N	Corn (ha)	Alfalfa (ha)
1972–2005	1.37 \pm 0.03	7.31 \pm 0.25	7.56 \pm 0.25	6.29 \pm 0.72	9.04 \pm 0.29	6.06 \pm 0.20	1991 \pm 66	1595 \pm 70
1970s	1.24 \pm 0.05	7.16 \pm 0.41	8.82 \pm 0.30	2.59 \pm 0.24	n.a.	n.a.	2277 \pm 79	1817 \pm 78
1980s	1.51 \pm 0.03	7.48 \pm 0.49	7.57 \pm 0.38	4.77 \pm 0.60	9.64 \pm 0.66	6.46 \pm 0.44	2182 \pm 98	1955 \pm 46
1990s	1.45 \pm 0.04	7.55 \pm 0.59	6.67 \pm 0.36	10.02 \pm 0.78	8.71 \pm 0.34	5.84 \pm 0.22	1828 \pm 79	1312 \pm 82
2000s	1.16 \pm 0.04	6.77 \pm 0.52	5.87 \pm 0.34 ¹	12.52 \pm 1.00	8.43 \pm 0.27	5.65 \pm 0.18	1418 \pm 31	1042 \pm 108

¹Data from 2000 to 2001.

The strongest correlations found for NO₃ concentrations related to land use/land cover parameters were for N yields in corn grown for grain and in alfalfa hay (Table 3). Corn production for grain also followed a parabolic trend ($r^2 = 0.48$, Figure 4), and increased by 28% during the 1970s and 1980s (from 2.27 to 2.90 kg N ha⁻¹ per year). Corn grain production then decreased by 35% through 2005 (to 1.89 kg N ha⁻¹ per year). Climatic variables were also found to be correlated with NO₃ concentrations, with precipitation inversely related to concentration ($r = -0.62$, $P < 0.01$). Corn production for grain was evaluated against the residuals of a regression of NO₃ concentration on precipitation, which demonstrated that corn production values have a significant influence on stream water NO₃ concentration ($r = 0.53$, $P < 0.01$). The same was also found for corn production versus the residuals of NO₃ exports regressed on precipitation ($r = 0.47$, $P < 0.05$). Due to the complex interactions of internal and external factors influencing stream water NO₃ concentration and watershed NO₃ exports, the time series data were further evaluated by classification and segmentation analysis using exhaustive CHAID with results described below.

Trends in stream water NO₃ concentration were analyzed against all potential predictor variables using exhaustive CHAID (Table 4). Trends in dairy N production corresponded most strongly with those in NO₃ concentrations (Bonferroni adjusted P value = 0.0003), but in a surprising manner (Figure 5). Comparing annual data for stream water concentration and dairy production corresponding to the CHAID groupings showed that NO₃ concentration was positively related to dairy production from the 1970s through 1995 (Nodes 1 and 2, Figure 5; $r = 0.61$ from annual data), but negatively related to dairy production since 1996 (Node 3, Figure 5; $r = -0.79$ from annual data). Changes in dairy N management have taken place in the past decade, and are discussed later in the paper.

Nitrate exports from Fall Creek for the period 1972–2005 averaged 7.3 \pm 0.25 kg ha⁻¹ per year (mean \pm 1 SE, $n = 34$ years), but did not exhibit any discernable temporal trend. Results of the CHAID analysis for exports found that annual precipitation is the strongest predictor variable for watershed NO₃ exports (Table 4, Bonferroni adjusted P value = 0.0001). NO₃ exports and precipitation were positively related for CHAID groupings (Figure 6) as well as for annual data ($r = 0.75$, Table 3). Watershed NO₃ exports were also positively

Table 3. Correlation Matrix for Stream Water NO₃ Concentration and Watershed Exports, and Parameters related to Agricultural Production, Land-Use/Land-Cover Practices, Atmospheric N Deposition and Climate

	NO ₃ concentration	NO ₃ export	Corn (grain)	Corn (silage)	Oats	Alfalfa hay	Non-alfalfa hay	Corn Ha	Alfalfa Ha	Dairy prod.	Fert. import	Feed import	N Dep total	Ppt	T _{avg} 1-12
Export	-0.21														
Corn (grain)	0.53**	0.18													
Corn (silage)	0.02	0.16	0.20												
Oats	-0.05	0.00	0.41*	0.38*											
Alfalfa hay	0.32	0.11	0.56**	0.41*	0.72**										
Non-alf. hay	-0.18	0.06	0.23	0.41*	0.84**	0.73**									
Corn-Ha	0.24	0.17	0.74**	0.41*	0.82**	0.83**	0.66**								
Alfalfa-Ha	0.36*	0.10	0.59**	0.43*	0.75**	0.96**	0.72**	0.88**							
Dairy prod.	-0.20	-0.23	-0.61**	-0.18	-0.82**	-0.68**	-0.65**	-0.84**	-0.74**						
Fert. import	-0.29	-0.06	0.20	0.43*	0.72**	0.51**	0.66**	0.66**	0.52**	-0.52**					
Feed import	-0.24	-0.19	-0.69**	-0.43*	-0.86**	-0.93**	-0.79**	-0.93**	-0.94**	0.87**	-0.64**				
N-Dep. total	-0.10	0.52**	0.31	0.23	0.29	0.27	0.21	0.38*	0.27	-0.22	0.18	-0.32			
Ppt	-0.62**	0.75**	-0.18	0.23	0.07	0.02	0.22	0.01	-0.02	-0.06	0.02	-0.09	0.53**		
T _{avg} 1-12	0.04	-0.06	-0.07	-0.10	-0.21	-0.10	-0.18	-0.15	-0.13	0.22	-0.20	0.17	0.24	0.06	
T _{avg} 1-4	0.25	-0.07	0.08	-0.27	-0.20	-0.02	-0.17	-0.06	-0.04	0.17	-0.25	0.12	0.29	-0.12	0.78**

*Correlation is significant at $P < 0.05$.**Correlation is significant at $P < 0.01$.Ppt = precipitation, T_{avg} 1-12 = mean annual temperature for January-December, T_{avg} 1-4 = mean annual temperature for January-April.

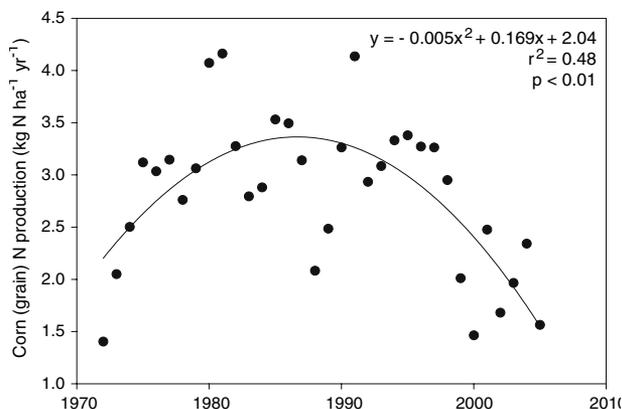


Figure 4. Nitrogen content of corn grown for grain in the Fall Creek watershed, New York. Values are kg N per hectare of watershed area per year.

related to atmospheric deposition of total N ($r = 0.52$), but no other correlations were significant (Table 3).

Watershed N Balance

The most significant changes in the N balance of the Fall Creek watershed during the study period were related to alfalfa production and feed imports (Tables 1, 2, respectively). Alfalfa production in the watershed decreased from over 9 kg N ha⁻¹ per year in the 1980s to about 5 kg N ha⁻¹ per year since 2000 (Table 1). Nitrogen fixed by the alfalfa crop, calculated from alfalfa acreage determined for the watershed at a biological nitrogen fixation (BNF) rate of 16,513 kg N km⁻² per year (average value from Heichel and others 1984), decreased from about 10 kg N ha⁻¹ per year in the 1980s to 5 kg N ha⁻¹ per year for 2000–2005.

The magnitude of the change in N input to the watershed via BNF in alfalfa cultivation is significant relative to decadal dynamics in other potential driving factors (Table 5). Annual atmospheric N deposition decreased by approximately 1 kg N ha⁻¹ during the period 1979–2005, though the decrease was almost entirely (89%) attributable to declining wet NO₃ deposition. N-fertilizer use in the watershed declined by about 1 kg N ha⁻¹ per decade between the 1970s and 2000s. Dairy production increased by 25% during the 1972–2005 period, equivalent to about 1 kg N ha⁻¹ per year for 2005 compared to 1972 (Table 1). Because crop production also decreased during this period (Table 1), the increase in dairy production would have to have been met by additional imports of feed and fodder, resulting in additional N inputs to the watershed. Using the aforementioned conversion

rate of feed-N to milk-N of 5:1 (Dou and others 1996), we calculated that during the 1980s and 1990s (the period for which data for all parameters are available), increases in imports of feed-N exceeded reductions in atmospheric N deposition, N-based fertilizer imports and BNF (Table 5).

Atmospheric deposition data for total N are not available prior to 1979, although EPA data show decadal averages for NO_x emissions to be approximately equivalent for the 1970s relative to the 1980s (U.S. Environmental Protection Agency 2000, Figure 3-3). We estimated total atmospheric N deposition to also be equivalent for the 1970s compared with the 1980s for the study area. We also estimated fertilizer inputs to decrease slightly since 2000 in concert with the decreases in crop acreage reported by the National Agricultural Statistical Service-New York Field Office (2007). Using these estimated values, we found that feed N imports to the watershed were about 2.0 kg N ha⁻¹ per year greater than the decreases in non-feed N inputs to the watershed for the 2000s compared to the 1970s.

DISCUSSION

Watershed N Exports, Inputs and Exports

Watershed NO₃ exports calculated using the LOA-DEST model for the Fall Creek watershed averaged 7.3 ± 0.25 kg NO₃-N ha⁻¹ per year. Assuming the same ratio of NO₃ to total N (NO₃/TN) in stream water exports for Fall Creek as reported by Alexander and others (2002) for the Susquehanna watershed, total N exports in Fall Creek were 9.5 kg N ha⁻¹ per year. Although this places the Fall Creek watershed in the upper 75th percentile for NO₃ and TN exports from watersheds in the northeastern US, it is comparable to the other watersheds in New York State with similar physiographic settings that were analyzed for the 1988–1993 period by Boyer and others (2002) and Alexander and others (2002): 7.4 kg NO₃-N ha⁻¹ per year for the Susquehanna basin and 6.2 kg NO₃-N ha⁻¹ per year for the Delaware.

Watershed N outputs were computed as the sum of stream water N exports and dairy N exports, with the latter calculated as dairy production in the watershed minus dairy consumption by the human population of the watershed. Food imports for human needs comprise an additional N input, and were computed at a rate of 5 kg N per capita per year (Wright and others 2004) minus per capita dairy N consumption, which was assumed to be produced within the watershed.

Table 4. Chi-Squared Automatic Interaction Detection (CHAID) Results for Stream Water NO₃ Concentrations and Watershed NO₃ Exports

Parameter	Predictor	Nodes	F	df	Adj. prob.
Stream water NO ₃ concentration	Dairy N	3	19.94	2, 31	0.0003
	Feed N	3	17.96	2, 31	0.0008
	Precipitation	2	13.00	1, 32	0.0094
	Fertilizer N	2	12.51	1, 32	0.0240
	Corn acreage	2	10.03	1, 32	0.0304
Watershed NO ₃ export	Precipitation	3	19.80	2, 31	0.0001

F = *F* statistic, used in CHAID to test differences between groups for continuous variables; *df* = degrees of freedom; *Adj. prob.* = Bonferroni adjusted *P* value.

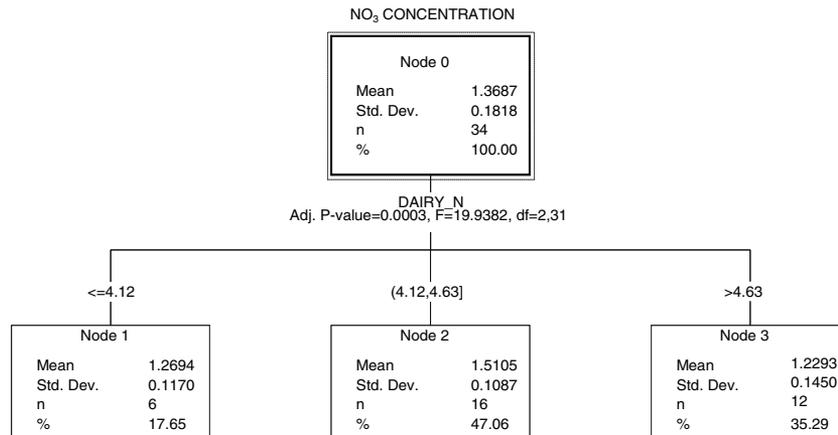


Figure 5. CHAID results for predictor variables related to mean annual NO₃ concentration in stream water, Fall Creek, New York for 1972–2005. *Node 0* gives mean and standard deviation of entire time series. *Nodes 1, 2 and 3* are segregated by dairy production values (kg N per hectare of watershed area per year), with dairy production cutoff values given above the node boxes for *Nodes 1, 2 and 3*. The mean annual stream water NO₃ concentration for each node is presented together with the standard deviation of NO₃ concentration for the data that comprise the node, and the percentage of the total dataset included in each node.

Total N inputs to the watershed averaged about 33 kg N ha⁻¹ per year, of which stream water exports of total N accounted for 28%. This ratio was close to the mean found by Boyer and others (2002) for mixed land use watersheds in the northeastern US (25%), and within the range of other watersheds in New York State with similar physiographic settings: 23% for the Susquehanna basin and 32% for the Delaware basin. Summing the N content of dairy exports to watershed N exports in stream water increased the fraction of input N accounted for to 40%. In an analysis of nitrogen fate in northeastern US watersheds, van Breemen and others (2002) demonstrated that most of the nitrogen not exported by streams or via agricultural products was lost from watersheds in gaseous forms, with lesser amounts retained in soils and vegetation.

NO₃ Concentration Trends

Hydrologic processes and nutrient dynamics (for example, fertilizer application and plant uptake) differ markedly between winter and summer periods in the study area, which is reflected in the differences between C–Q relationships for dormant versus growing seasons that were pervasive during the period of study. Precipitation in the Fall Creek watershed is evenly distributed over the year (Johnson and others 1976), with evapotranspiration during the growing season responsible for reduced summer stream flow. Evapotranspiration also limits NO₃ leaching, although summer storm events do mobilize NO₃ from the landscape to streams. This feature coupled with fertilizer applications to crops contribute to the positive C–Q relationship during the growing season, whereas

Table 5. Nitrogen Balance for Fall Creek Watershed

	1970s	1980s	1990s	2000s		Changes 1980s–1990s	Changes 1970s–2000s
N inputs							
BNF	9.09	9.78	6.57	5.22		–3.22	–3.88
Fertilizer	8.82	7.57	6.67	5.87 ¹		–0.89	–2.95
Atmos. dep.	9.64 ²	9.64	8.71	8.43		–0.93	–1.21
					Non-feed-N	–5.04	–8.04
Feed	2.59	4.77	10.02	12.52	Feed-N	5.25	9.93
Food imports ³	1.54	1.65	1.78	1.80		0.13	0.26
Total inputs	31.68	33.41	33.74	33.83		0.34	2.15
N outputs							
Dairy exports ⁴	3.58	3.85	3.89	4.24		0.03	0.66
Total N exports, stream water ⁵	9.31	9.72	9.82	8.79		0.10	–0.52
Total outputs	12.89	13.57	13.71	13.03		0.13	0.14

All values given in kg N per hectare of watershed area per year. BNF = biological nitrogen fixation.

Atmos. dep. = Atmospheric deposition.

¹Data for 2000–2001.

²Estimated values.

³N imports in food at 5 kg N per person per year (Wright and others 2004) less dairy N consumption.

⁴Dairy production minus consumption by population of watershed.

⁵Calculated as Total N export = 1.30 × NO₃ export based on TN:NO₃ ratio from adjacent Susquehanna watershed (Alexander and others 2002).

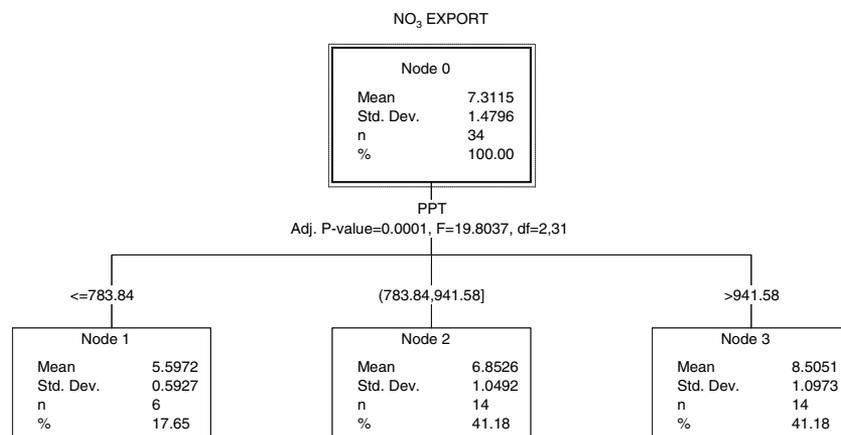


Figure 6. CHAID results for predictor variables related to watershed NO₃ exports for the Fall Creek (New York) watershed, 1972–2005. *Node 0* gives mean and standard deviation of entire time series. *Nodes 1, 2 and 3* are segregated by precipitation (mm per year), with precipitation cutoff values given above the node boxes for *Nodes 1, 2 and 3*. The mean stream water NO₃ export (kg N per hectare of watershed area per year) for each node is presented together with the standard deviation of NO₃ export for the data that comprise the node, and the percentage of the total dataset included in each node.

higher winter flows tend to become more dilute in NO₃ as discharge increases.

Both SRA and LOADEST modeling approaches indicated changes in mean NO₃ concentration in Fall Creek that increased and then decreased on a decadal time scale. Stoddard and others (2003) analyzed trends in stream water NO₃ concentrations during the 1990s throughout the United States and found that declines were greatest for streams of the Northern Appalachian Plateau ecoregion, which the Fall Creek watershed straddles.

These same streams also exhibited increasing trends in NO₃ concentrations during the 1980s (Stoddard and others 2003). The change in NO₃ concentrations during the 1990s for Northern Appalachian Plateau streams averaged –1.37 µeq l⁻¹ per year (–0.02 mg l⁻¹ per year) (Stoddard and others 2003). This regional decline is equivalent to the decline in NO₃ concentrations in Fall Creek during the same period (Figure 3).

Forested catchments in cooler regions of New England seem to exhibit different trends in stream

water NO_3 concentrations. Goodale and others (2003) found declines in NO_3 concentration between the 1970s and 1990s to be highest in New England watersheds with regenerating forest cover, as forest recovery results in increased N uptake by secondary forests. In addition, watersheds with larger percentages of forest cover have lower rates of total N inputs related to agricultural activities (Boyer and others 2002). Forest cover increased in Fall Creek throughout the twentieth century in response to agricultural abandonment (Flinn and others 2005). Fall Creek NO_3 concentration trends, however, did not track changes in land cover. Cropped hectares increased in the 1970s and decreased in the 1980s, whereas mean annual NO_3 concentration in Fall Creek increased during both decades (Figure 3). The within-decade trends in cropped area are significant: corn plus alfalfa hectares grew linearly ($r^2 = 0.67$) by 60% between 1972 and 1981, then decreased linearly ($r^2 = 0.78$) by 25% between 1981 and 1991, although these trends are not apparent in the decadal means of Table 2.

We did not find a significant correlation between the modeled results for annual stream NO_3 concentrations and N deposition. Although an association has been shown for New England streams in forested catchments (Aber and others 2003), other studies have suggested that stream NO_3 concentrations are difficult to correlate with N depositional trends (Murdoch and Shanley 2006). Nor did we find a substantial correlation between stream water NO_3 concentrations and annual temperature metrics, which were found to be inversely related for a forested watershed in the Adirondack ecoregion (Park and others 2003). Stoddard and others (2003) argue that regional differences in decadal trends in NO_3 concentration between New England and the Northern Appalachian Plateau are due to lower ambient NO_3 concentrations in New England streams. It is also difficult to draw parallels between watersheds with differing land cover and between watersheds with different spatial scales. For example, NO_3 fluxes from the meso-scale and mixed land use Fall Creek watershed were 20 times higher compared to forested 1st order catchments in the study region, which averaged $0.3 \text{ kg NO}_3\text{-N ha}^{-1}$ per year for 2005 (Goodale 2006).

We were interested to determine if external factors such as temperature and N deposition were significant drivers of the Fall Creek stream water NO_3 trend (Figure 3). However, the CHAID analysis and the correlation analysis were consistent and suggested a lack of associations between NO_3 concentration and both temperature and N depo-

sition. That is, trends in NO_3 concentration are significantly correlated with trends in precipitation, but not with temperature or N deposition trends (Table 3), and neither temperature nor N deposition was found to be a significant predictor of NO_3 concentration using exhaustive CHAID (Table 4). Because dairy production continued to increase despite decreases in cropped areas in the watershed, it is possible that changes in land-use management practices could account for the stream water NO_3 trends. We consider this in the next section.

Land-Use Practices and Dairy N Management

During the study period, dairy production increased significantly, requiring large increases in feed imports to the Fall Creek watershed. These increased imports were associated with increasing stream water NO_3 concentration, but only until about 1994. Feed imports continued to increase after 1994, which we estimated to double between 1995 and 2005. Feed imports became the largest term of the N budget, and were approximately equivalent to the sum of N deposition and fertilizer imports for 1995–2005. Yet stream water NO_3 concentration declined during this period, suggesting possible improvements in dairy N management.

We considered manure N returns as a proxy for dairy N management. Ruddy and others (2006) estimated manure N returns to agricultural land at county levels for the 1980s and 1990s. We allocated these data to the Fall Creek watershed based on 1992 NLCD pasture pixels as we did with other dairy and agricultural parameters. Manure N returns decreased by 19% during the 1990s compared to the 1980s, from about $17 \text{ kg N per hectare}$ of watershed area per year for the 1980s, to about 14 kg N ha^{-1} per year during the 1990s. This decrease in returns of manure N is not incompatible with increased dairy production during the same period. Improvements in the conversion rate from feed N to dairy N are able to improve N use at the farm level by nearly 50% (Kohn and others 1997), reducing the 5:1 feed N to dairy N ratio to less than 4:1. In a farm-level trial of the Cornell Net Carbohydrate and Protein System (Fox and others 2004), Klausner and others (1998) demonstrated a 9% increase in milk production while manure N excretion concurrently decreased by a third.

Significant investment has been made in improving agricultural environmental management in the Cayuga Lake basin, which includes the

Fall Creek watershed (New York State Department of Agriculture and Markets 2000). The guidance documents of the New York State Comprehensive Nutrient Management Plan detail a range of best management practices that have been implemented, including manure management approaches that consider hydrologically sensitive areas (*sensu* Walter and others 2000). No-till farming, which has been shown to reduce NO₃ losses from fertilized fields by 12–20% (Trewavas 2004), has also been widely adopted in the last decade. Currently, agricultural environmental management activities are in place on 9,000 farms in New York, including 600 farms in the counties that comprise the Fall Creek watershed (New York State Soil and Water Conservation Committee 2005).

It is not possible to quantify the water quality impact of dairy N management practices for the Fall Creek watershed from available data. Nevertheless, results of the present study suggest that reductions in the ratio of dairy N production to stream water NO₃ concentrations for the 1995–2005 period relative to previous decades (Figure 5, node 3) are associated with improved land-use management practices in the Fall Creek watershed. Further research would be required to determine if dairy management improvements are in fact a causal mechanism for improved water quality. The hypothesis that NO₃ export increased over the past three decades due to greater food and feed imports into the watershed was not found to be supported by the data, which demonstrated a decreasing trend in NO₃ concentration since 1990 which coincided with changes in dairy production and management. Additionally, since dairy production in the Fall Creek watershed has been fueled by large increases in feed imports, the environmental costs of feed production have likely been externalized to other watersheds.

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