Final Project Executive Summary

Determination of Total Nitrogen Trends and Investigation into Possible Drivers of Total Nitrogen Trends in Cannonsville Reservoir Watersheds

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Abstract

This study determined the magnitude and direction of stream total nitrogen trends and investigated the possible drivers of stream total nitrogen trends for the Catskill Mountain region of NY from 2002 to 2022. Four study sites, representing a land use gradient of higher elevation upland forests and lower elevation agricultural and residential areas, were examined to determine the magnitude and direction of TN trends and assist with the characterization of possible trend drivers. Statistical analyses, including summary statistics and Kendall trend tests, were conducted to determine trends; a literature review and land cover analysis was completed to assist in the investigation of possible trend drivers. Results indicated an overall decreasing trend in TN concentrations at all sites; trend magnitude and strength varied among the sites and statistical analysis, highlighting the importance of accounting for land cover, flow, and seasonality in long term trend analysis. Upstream and downstream sites exhibited differences in TN during summer low flow conditions, suggesting potential land use influences on stream TN. Variation in TN trends and concentrations were partially attributed to land cover, forest composition, watershed management, flow, and variations in atmospheric deposition. Challenges in quantifying the influence of specific drivers arose due to the nonlinear nature of watersheds and variations in local characteristics. The effectiveness of Best Management Practices (BMPs) and Source Water Protection Programs (SRPs) was challenging to quantify due to confounding variables, time lags, and potential for legacy N storage. This study underscored the importance of comprehensive water quality monitoring for informed source water supply management, particularly in regions with varying land uses. Characterizing nitrogen sources, fate, and export mechanisms is essential for tailoring effective watershed-specific management programs, ensuring water quality preservation for both water supplies and downstream ecosystems. This study advocates for long-term water quality monitoring, emphasizing the need to understand nitrogen dynamics in the context of both anthropogenic and natural disturbances. Maintaining multidecadal datasets and quantifying results from water quality management programs are crucial for directing future management strategies. Future research could focus on quantifying the influence of potential drivers of stream total nitrogen trends.

This study sought to determine the magnitude and direction of stream total nitrogen trends and investigate the possible drivers of stream total nitrogen trends for stream sites in the Catskill Mountain region of New York (NY) from 2002 to 2022. The Catskill Mountain region contains the source water supply for New York City, serving 9 million people 1 billion gallons of water daily. This is an unfiltered surface drinking water supply requiring watershed management to maintain water quality. Unfiltered surface water supplies are subject to impacts from storm events, land use, agriculture, and point/nonpoint source pollutants. Treatment techniques such as ultraviolet disinfection and chlorination may not suffice for disinfection, so further water quality monitoring and analysis are necessary to determine possible trends for management. Long term water quality trend analysis can assist in both short and long term watershed planning. Total nitrogen (TN) was chosen as the analyte of study for this paper as humans have altered the N cycle through land use changes, food production and energy production. Increases of N to the environment can lead to eutrophication or anoxia, posing challenges for a water supply.

The overall study region is within the Catskill Mountain region of NY; specifically targeted for this analysis were New York City Department of Environmental Protection (NYC DEP) hydrology sampling sites leading to the Cannonsville Reservoir, which has exhibited eutrophic characteristics in the past. Four study sites, representing a land use gradient of higher elevation upland forests and lower elevation agricultural and residential areas, were examined to determine the magnitude and direction of TN trends and assist with the characterization of possible trend drivers. Upstream sites were primarily forested and served as the “control” to compare to more developed downstream sites, subject to further anthropogenic impacts from land use (Wastewater Treatment Plants (WWTPs), agriculture). Since the early 1990s, this region has actively managed resources to promote water quality; program implementation has included land acquisition, watershed protection programs, wastewater treatment plant upgrades, implementation of BMPs and stream restoration projects.

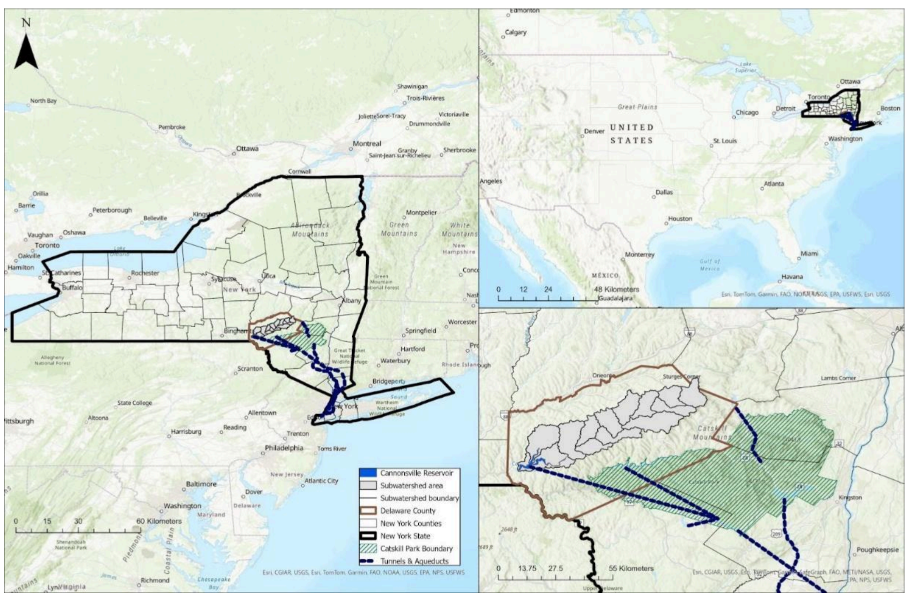


Figure 1. Overview of region of study in NY

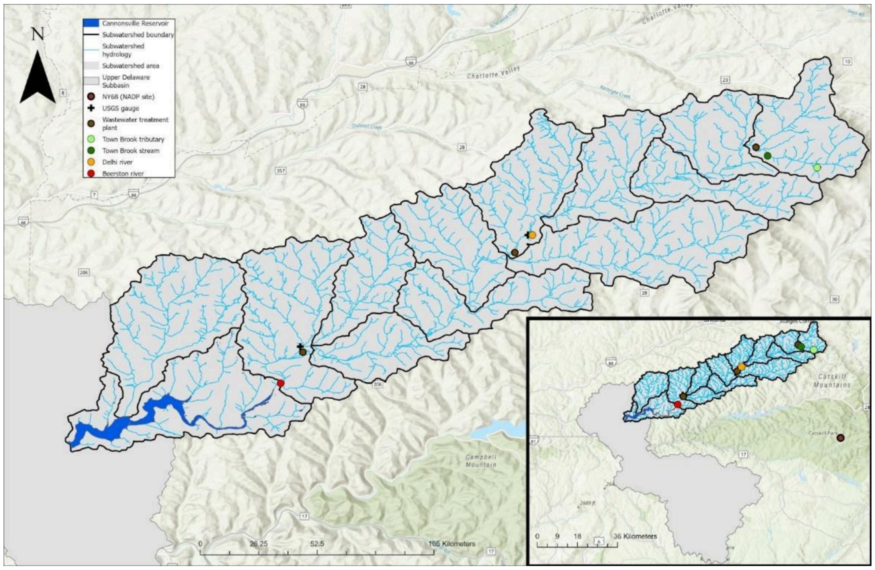


Figure 2. Upper Delaware subbasin, with thirteen Cannonsville Reservoir subwatersheds, sample sites, & relevant sites

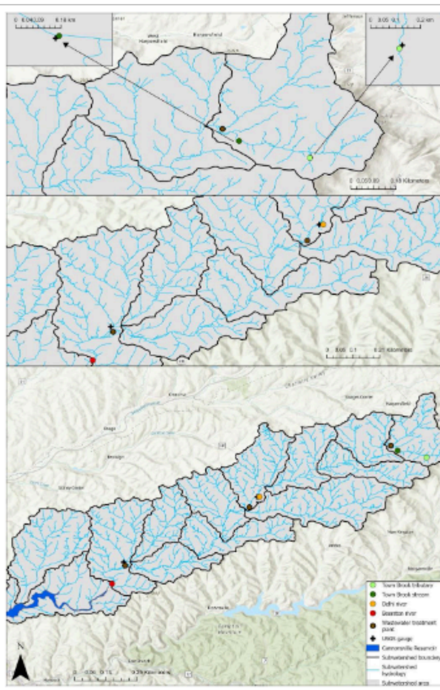


Figure 3. Overview of sample sites (bottom), Delhi river and Beerston river sites and hydrology (middle), Town Brook tributary and Town Brook stream sites and hydrology (top)

Table 1. Sample site descriptions and nearest USGS gauge station reporting flow

Sample Site Name	Latitude, Longitude	Sample Site Description	Nearest USGS gage station
Town Brook tributary	42.349116, -74.611402	Headwater tributary to Town Brook stream, upstream site	01421614
Town Brook stream	42.361196, -74.662098	Town Brook stream, southeast of Hobart, NY, upstream site	01421618
Delhi river	42.280291, -74.907690	West Branch Delaware River, upstream of Delhi, NY, downstream site	01421900
Beerston river	42.128734, -75.160193	West Branch Delaware River at Beerston, NY, downstream site	01423000

Upstream

Downstream

Grab samples were collected by NYC DEP staff on a monthly schedule and analyzed in a certified NYC DEP lab according to standard operating procedures and a quality assurance program. The majority of the missing data is from 2020-2021, coinciding with field sampling reductions due to the Covid-19 pandemic. Sample sites were chosen based on consistency in the lab method for the time period, proximity to USGS gauge stations with flow records, and to set up a land use gradient. Table 2 displays the expected vs. actual number of TN samples used for trend analysis based on the sampling schedule.

To investigate the possible drivers of TN trends within the study area, a comprehensive literature review was conducted to review prior research of nitrogen dynamics within the Catskill Mountain region. To assist in the characterization of possible TN trend drivers, summary statistics were developed for TN and discharge; additionally, land cover maps were generated in ArcGIS Pro using the National Land Cover Database 2021 dataset. Land cover percent areas were calculated and land cover patterns were identified for sample sites and adjacent subwatersheds. This study analyzed stream TN concentrations (mg/L); TN, as defined for this study, encompassed organic nitrogen, inorganic nitrogen, and ammonia. Summary statistics were generated for TN and discharge to assist in trend analysis. Statistical analysis was performed to determine the magnitude and direction of TN trends; Mann Kendall and Seasonal Kendall tests were chosen as they can account for missing data and outliers. The Seasonal Kendall test is a modified version of the Mann Kendall and accounts for seasonality effects; a period of 12 was used. All Kendall analysis was completed using Python and user generated scripts.

Figure 4 displays the overall land cover analysis for the overall region of study. The primary land cover type is forest, followed by pasture and hay production to support dairy farming. Figure 5 displays a closer view of the sample sites and their land cover analysis. Upstream site Town Brook tributary was 100% forested for contributing watershed area; upstream site Town Brook stream was primarily forested with some pasture/hay production. Both sites were not impacted by WWTPs but it is possible that Town Brook stream saw impacts from septic releases. Downstream sites Delhi River and Beerston river were impacted by residential development, WWTPs, and pasture/hay. The literature review highlighted some potential drivers of TN for this region which included land cover type and history, climate variability, variation in N inputs/sinks/export pathways, forest cover and composition, soil composition, hydrology and topography.

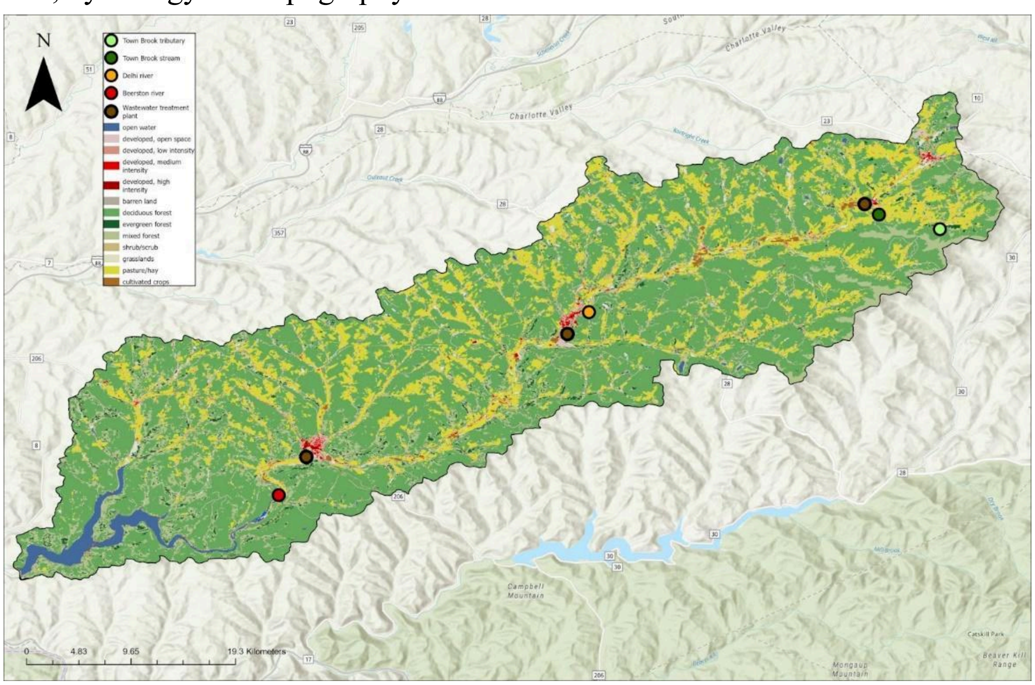


Figure 4. Land cover analysis for region of study, NCLD 2021 dataset

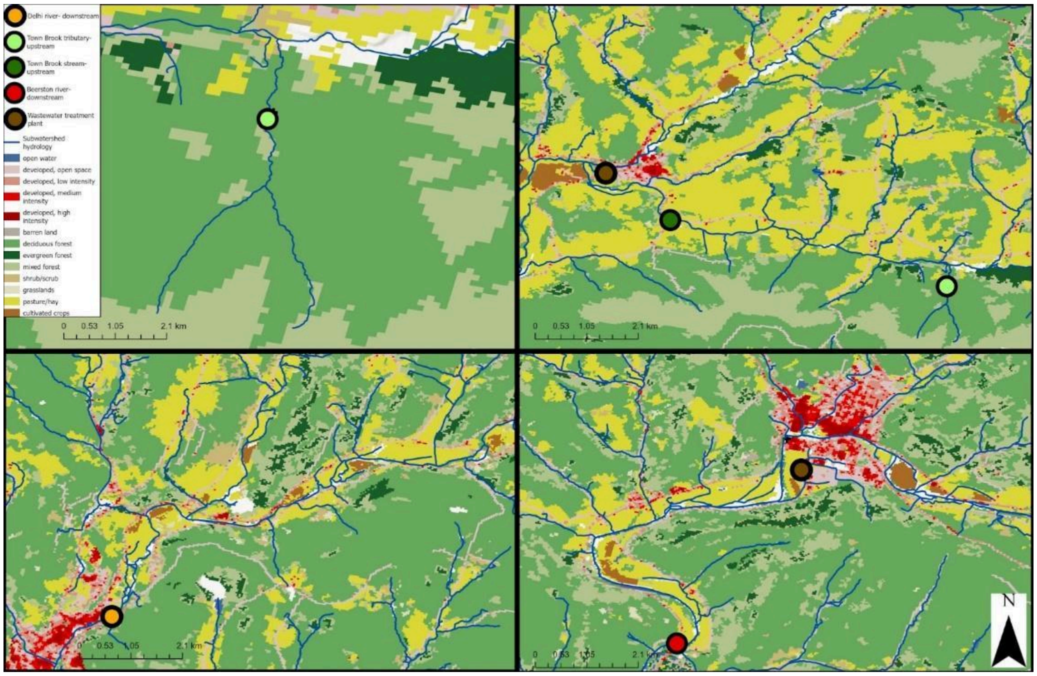


Figure 5. Land cover analysis for sample sites, NCLD 2021 dataset

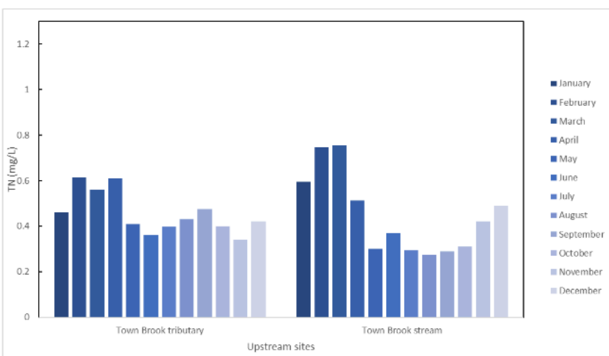


Figure 6. Upstream site TN

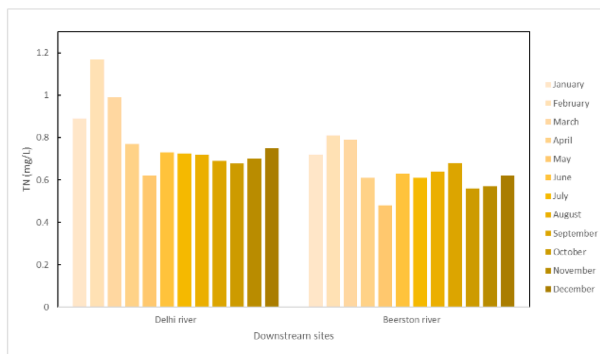


Figure 7. Downstream site TN

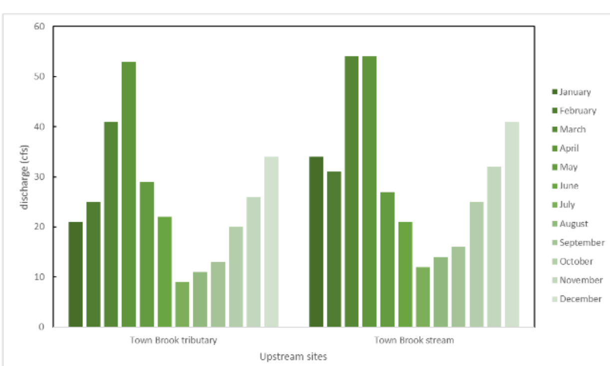


Figure 8. Upstream site discharge

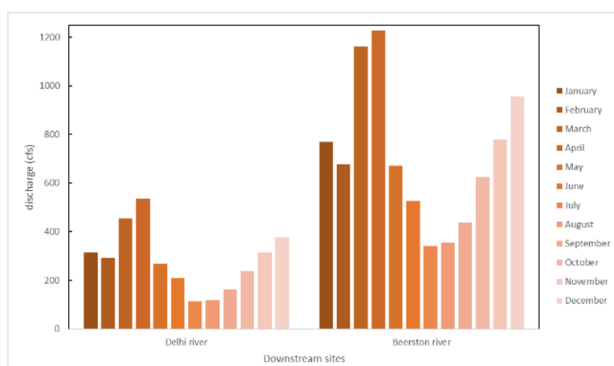


Figure 9. Downstream site discharge

Figures 6 and 7 display the TN summary statistics for upstream and downstream sites. Figures 8 and 9 display discharge summary statistics for upstream and downstream sites. For upstream sites, peak TN occurred in winter-spring and peak discharge occurred in early spring; lowest TN was observed during summer low flow conditions For downstream sites, peak TN occurred during winter and peak discharge occurred during late winter-early spring; TN remained elevated throughout the remainder of the year. Summary statistics suggested that the main difference between upstream and downstream TN occurred during summer low flow conditions, as downstream site TN remained elevated throughout the summer compared to upstream sites, suggesting a possible difference in TN drivers based on land cover.

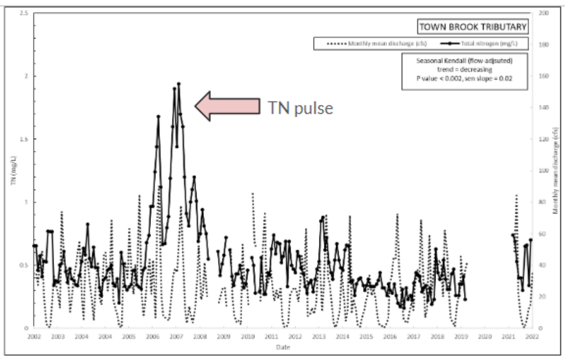
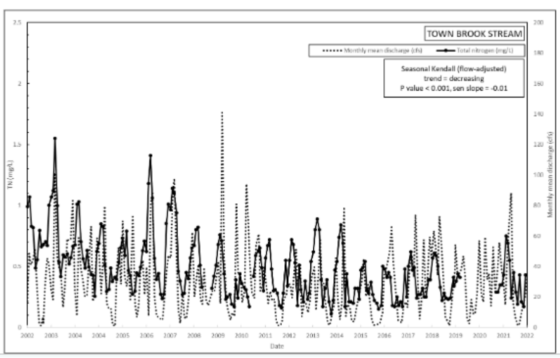


Figure 14. Town Brook tributary monthly TN concentration and monthly mean discharge (above)

Figure 15. Town Brook stream monthly TN concentration and monthly mean discharge (below)



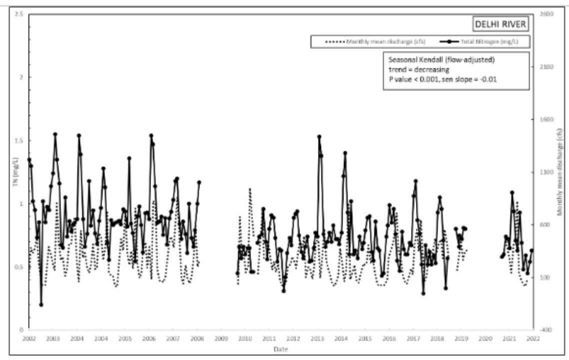
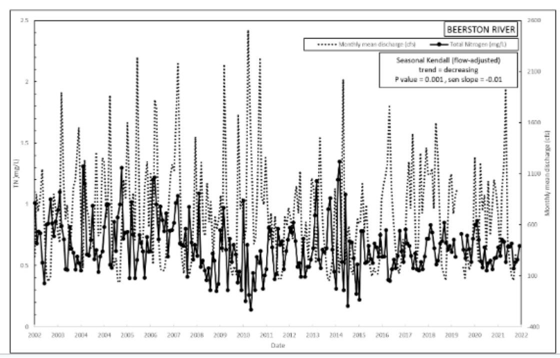


Figure 16. Delhi river monthly TN concentration and monthly mean discharge (above)

Figure 17. Beerston river monthly TN concentration and monthly mean discharge (belc



Figures 14-17 display monthly TN and average monthly discharge for the study sites. Town Brook tributary saw a multi year TN pulse from 2006-2008 following a selective harvest and insect defoliation event. This event highlights how land cover disturbance can impact stream TN concentrations on a multi year scale. Data gaps were due to sample analysis error, sample collection error, and sampling reductions during the Covid-19 pandemic.

Mann and Seasonal Kendall TN trend analyses were completed using observed TN data and flow-adjusted TN data, providing insights into overall patterns and trends for each site. Mann Kendall, Seasonal Kendall (observed), and Seasonal Kendall (flow-adjusted) TN trend results showed statistically significant decreasing trends. While all sites exhibited a significant decreasing trend, variations in the magnitude (sen slope) and significance levels (p values) were observed across the three tests. It was determined that the seasonal flow adjusted test was most appropriate for this analysis. Site Town Brook stream exhibited the strongest decreasing trend. Tau values, indicating the strength of correlation in time series data, were negative for all sites, confirming a strong negative correlation and the strength of the decreasing trend.

Total annual nitrogen deposition estimates from NY68 showed a decline of about 2 kg/ha, dropping from 6.35 to 4.22 kg/ha from 2002 to 2022. This suggests a potential reduction in annual wet and dry nitrogen deposition for NY68 over the study period. Further analysis was required to detect any trends in depositions data. Atmospheric deposition data from the NADP website for NY68 were gathered for annual estimates of wet and dry total nitrogen (TN) deposition (kg/ha), annual nitrate concentrations (kg/ha and mg/L), annual ammonium concentrations (kg/ha and mg/L), and precipitation (cm) for a Mann Kendall analysis. Nitrate concentration showed the strongest statistically significant decreasing trend among all variables studied; TN (kg/ha) and Nitrate (kg/ha) were found to be decreasing while ammonium (kg/ha and mg/L) and precipitation showed no trend.

TN concentrations varied among sites, with downstream sites showing higher overall TN levels, possibly due to additional inputs from wastewater or agricultural runoff when compared to primarily forested upstream sites. Statistical analysis revealed decreasing TN trends across all sites, with upstream sites showing stronger declines. However, trend interpretation was complex due to confounding variables such as seasonality, flow, and climate which can impact water quality trend analysis. Possible drivers of TN trends for this region can include forest composition, disturbance events, land use, and atmospheric deposition. The impact of forest disturbance on TN concentrations was observed in a pulse in stream N at Town Brook tributary. Despite reductions in nitrogen emissions, legacy effects and complex interactions with climate and land use persist, affecting TN dynamics in streams. Challenges in this study included quantifying the influence of individual trend drivers and distinguishing their effects from natural variability.

Land management efforts, including source water protection programs, may have contributed to declining TN trends in the region. However, variables such as freeze-thaw cycles, and climate change effects on hydrology and nutrient cycling remain. Long-term monitoring programs are essential for understanding and mitigating the impacts of nitrogen dynamics on water quality and ecosystem health. Overall, the study underscores the importance of considering multiple drivers and temporal scales in analyzing TN trends for effective watershed management and source water preservation in the Catskill Mountain region.

The study sought to analyze trends in total nitrogen (TN) concentrations across streams in the Catskill Mountain region, focusing on understanding magnitude, direction, and potential drivers of these trends. Through statistical analysis and literature review, the study found decreasing TN trends across all sites, with variations in trend interpretation necessitating additional analyses like observed Mann Kendall and flow-adjusted Seasonal Kendall. Varied TN dynamics between upstream forested and downstream developed sites highlighted potential anthropogenic influences such as wastewater treatment plants, agriculture, and land use changes. The complexity of nutrient dynamics, influenced by factors like land cover, hydrology, and climate, underscores the challenge of disentangling the impacts of land management programs from other variables. Long-term monitoring, encompassing multidecadal datasets and diverse environmental factors, is crucial for understanding and managing water quality in the region.

Moving forward, future research could focus on quantifying the local impacts of Best Management Practices (BMPs) and Sustainable Resource Practices (SRPs) on TN concentrations, necessitating tailored study design to account for confounding variables. Additionally, monitoring N:P ratios, investigating TN dynamics during low and high flows, and developing comprehensive datasets on nitrogen storage, deposition rates, and land use variables could further enhance understanding of TN trends and their drivers in the Catskill Mountain region. Ultimately, maintaining water quality balance is essential for both the local water supply and downstream communities, necessitating a nuanced approach that considers the sources, fate, and management strategies related to nitrogen in terrestrial and aquatic ecosystems.

REFERENCES

Aber, J. D., Nadelhoffer, K. J., Steudler, P. A., & Melillo, J. M. (1989). Nitrogen saturation in northern forest ecosystems. *BioScience*, *39*(6), 378–386. https://doi.org/10.2307/1311067

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

A*pplication News No. O76 Total Organic Carbon Analysis Measurement of total nitrogen (TN) for protein estimation in pharmaceutical vaccines on the Shimadzu TOC-L with TNM-L.* (2020). Retrieved February 12, 2024, from https://www.shimadzu.com/an/sites/shimadzu.com.an/files/pim/pim_document_file/applications/application_note/10872/o76.pdf

Argerich, A., Johnson, S. L., Sebestyen, S. D., Rhoades, C. C., Greathouse, E. A., Knoepp, J. D., Mary Beth Adams, Likens, G. E., Campbell, J. L., McDowell, W. H., Scatena, F. N., & Ice, G. G. (2013). Trends in stream nitrogen concentrations for forested reference catchments across the USA. *Environmental Research Letters*, *8*(1), 014039–014039. https://doi.org/10.1088/1748-9326/8/1/014039

Baldigo, B. P., George, S. D., Winterhalter, D. R., & McHale, M. R. (2021). Biological and chemical recovery of acidified Catskill Mountain streams in response to the Clean Air Act Amendments of 1990. *Atmospheric Environment*, *249*, 118235. https://doi.org/10.1016/j.atmosenv.2021.118235

Bellmore, R. A., Compton, J. E., Brooks, J. R., Fox, E. W., Hill, R. A., Sobota, D. J., Thornbrugh, D. J., & Weber, M. H. (2018). Nitrogen inputs drive nitrogen concentrations in U.S. streams and rivers during summer low flow conditions. *Science of the Total Environment*, *639*, 1349–1359. https://doi.org/10.1016/j.scitotenv.2018.05.008

Bennett, E. M., Peterson, G. D., & Gordon, L. J. (2009). Understanding relationships among multiple ecosystem services. *Ecology Letters*, *12*(12), 1394–1404. https://doi.org/10.1111/j.1461-0248.2009.01387.x

Bishop, P., W. Dean Hively, Stedinger, J. R., Rafferty, M., Lojpersberger, J. L., & Bloomfield, J. A. (2005). Multivariate Analysis of Paired Watershed Data to Evaluate Agricultural Best Management Practice Effects on Stream Water Phosphorus. *Journal of Environmental Quality*, *34*(3), 1087–1101. https://doi.org/10.2134/jeq2004.0194

Burns, D. A., Klaus, J., & McHale, M. R. (2007). Recent climate trends and implications for water resources in the Catskill Mountain region, New York, USA. *Journal of Hydrology*, *336*(1-2), 155–170. https://doi.org/10.1016/j.jhydrol.2006.12.019

Burns, D. A., & Murdoch, P. S. (2005). Effects of a clearcut on the net rates of nitrification and N mineralization in a northern hardwood forest, Catskill Mountains, New York, USA. *Biogeochemistry*, *72*(1), 123–146. https://doi.org/10.1007/s10533-004-0355-z

Campbell, J., Mitchell, M. J., Groffman, P. M., Christenson, L. M., & Hardy, J. (2005). Winter in northeastern North America: a critical period for ecological processes. *Frontiers in Ecology and the Environment*, *3*(6), 314–322. https://doi.org/10.1890/1540-9295(2005)003[0314:winnaa]2.0.co;2

Chanat, J. G., & Yang, G. (2018). Exploring Drivers of Regional Water‐Quality Change Using Differential Spatially Referenced Regression—A Pilot Study in the Chesapeake Bay Watershed. *Water Resources Research*, *54*(10), 8120–8145. https://doi.org/10.1029/2017wr022403

Clow, D. W., & Mast, M. A. (1999). Long-term trends in stream water and precipitation chemistry at five headwater basins in the northeastern United States. *Water Resources Research*, *35*(2), 541–554. https://doi.org/10.1029/1998wr900050

Compton, J. E., Goodwin, K. E., Sobota, D. J., & Lin, J. (2019). Seasonal disconnect between streamflow and retention shapes riverine nitrogen export in the Willamette River Basin, Oregon. *Ecosystems*, 23(1), 1–17. https://doi.org/10.1007/s10021-019-00383-9

Crowley, K. F., & Lovett, G. M. (2017). Effects of nitrogen deposition on nitrate leaching from forests of the northeastern United States will change with tree species composition. *Canadian Journal of Forest Research*, *47*(8), 997–1009. https://doi.org/10.1139/cjfr-2016-0529

Dewitz, J. (2021). *U.S. Geological Survey*, National Land Cover Database (NLCD) 2019 Products (ver. 2.0, June 2021): U.S. Geological Survey data release, https://doi.org/10.5066/P9KZCM54

Driese, K. L., Reiners, W. A., Lovett, G. M., Simkin, S. M. (2004). A vegetation map for the Catskill Park, NY, derived from multi-temporal landsat imagery and GIS Data. *Northeastern Naturalist*, 11(4), 421–442. https://doi.org/10.1656/1092-6194(2004)011[0421:avmftc]2.0.co;2

Driscoll, C. T., Whitall, D. R., Aber, J. D., Boyer, E. W., Castro, M. S., Cronan, C. S., Goodale, C. L., Groffman, P. M., Hopkinson, C. S., Lambert, K. F., Lawrence, G. B., & Ollinger, S. V. (2003). Nitrogen pollution in the Northeastern United States: sources, effects, and management options. *BioScience*, *53*(4), 357. https://doi.org/10.1641/0006-3568(2003)053

Dubrovsky, N. M., Burow, K. R., Clark, G. M., Gronberg, J. M., Hamilton P. A., Hitt, K. J., Mueller, D. K., Munn, M. D., Nolan, B. T., Puckett, L. J., Rupert, M. G., Short, T. M., Spahr, N. E., Sprague, L. A., and Wilber, W. G. (2010). The quality of our Nation's waters—Nutrients in the Nation's streams and groundwater, 1992–2004. *U.S. Geological Survey Circular 1350*, 2010-3078

Effler, S. W., & Bader, A. P. (1998). A Limnological Analysis of Cannonsville Reservoir, NY. *Lake and Reservoir Management*, *14*(2-3), 125–139. https://doi.org/10.1080/07438149809354325

EVA Tool. (n.d.). Retrieved November 30, 2023, from https://www.mrlc.gov/eva/

Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Haworth, R. W., Cowling, E. B., Cosby, B. J. (2003). The Nitrogen Cascade. *BioScience*, 53(4), 341. https://doi.org/10.1641/0006-3568(2003)053[0341:tnc]2.0.co;2

Gilliam, F. S., Burns, D. A., Driscoll, C. T., Frey, S. D., Lovett, G. M., & Watmough, S. A. (2019). Decreased atmospheric nitrogen deposition in eastern North America: Predicted responses of forest ecosystems. *Environmental Pollution*, *244*, 560–574. https://doi.org/10.1016/j.envpol.2018.09.135

Gitau, M. W., Veith, T. L., Gburek, W. J., and Jarrett, A. R. (2006). Watershed Level Best Management Practice Selection and placement in the Town Brook watershed, New York. *Journal of the American Water Resources Association*, 42(6), 1565–1581. https://doi.org/10.1111/j.1752-1688.2006.tb06021.x

Goodale, C.L. and Aber, J.D. (2001). The long‐term effects of land‐use history on nitrogen cycling in northern hardwood forests. *Ecological Applications*, 11(1), pp.253-267. https://doi.org/10.1890/1051-0761(2001)011[0253:TLTEOL]2.0.CO;2

Golden, H. E., & Boyer, E. W. (2009). Contemporary estimates of atmospheric nitrogen deposition to the watersheds of New York State, USA. *Environmental Monitoring and Assessment*, *155*(1-4), 319–339. https://doi.org/10.1007/s10661-008-0438-8

Grieger, S., & Harrison, J. (2021). Long‐Term disconnect between nutrient inputs and riverine exports in a Semi‐Arid, agricultural watershed: Yakima River Basin 1945–2012. *Journal of Geophysical Research: Biogeosciences*, 126(9). https://doi.org/10.1029/2020jg006072

Hirsch, R. M., Slack, J. R., & Smith, R. A. (1982). Techniques of trend analysis for monthly water quality data. *Water Resources Research*, *18*(1), 107–121. https://doi.org/10.1029/wr018i001p00107

Howarth, R. W. (2022). Nitrogen. In *Elsevier eBooks* (pp. 155–162). https://doi.org/10.1016/b978-0-12-819166-8.00138-9

Hussain, Md., & Mahmud, I. (2019). pyMannKendall: a python package for non parametric Mann Kendall family of trend tests. *Journal of Open Source Software*, *4*(39), 1556. https://doi.org/10.21105/joss.01556

Isakson, R.S. (2001). Payments for Environmental Services in the Catskills: A Socio-Economic Analysis of the Agricultural Strategy in New York City's Watershed Management Plan. *Department of Economics*, University of Massachusetts. https://www.cbd.int/financial/doc/usa-pescatskills2002.pdf

Johnson, C. E. (2013). Chemical properties of upland forest soils in the Catskills region. *Annals of the New York Academy of Sciences*, n/a-n/a. https://doi.org/10.1111/nyas.12259

LaPierre, S., & Germain, R. H. (2005). Forestland Parcelization in the New York City Watershed. *Journal of Forestry*, 103(3), 139–145. https://doi.org/10.1093/jof/103.3.139

Latty, E.F., Canham, C.D. and Marks, P.L. (2004) The effects of land-use history on soil properties and nutrient dynamics in northern hardwood forests of the Adirondack Mountains. *Ecosystems*, 7, pp.193-207. http://dx.doi.org/10.1007/s10021-003-0157-5

Lawrence, G. B., Lovett, G. M., & Baevsky, Y. H. (2000). Atmospheric deposition and watershed nitrogen export along an elevational gradient in the Catskill Mountains, New York. *Biogeochemistry*, *50*(1), 21–43. https://doi.org/10.1023/a:1006332230890

Lin, J., Compton, J. E., Sabo, R. D., Herlihy, A. T., Hill, R. A., Weber, M. H., Brooks, J. R., Paulsen, S. G., & Stoddard, J. L. (2023). The changing nitrogen landscape of United States streams: Declining deposition and increasing organic nitrogen. *PNAS Nexus,* 3(1). https://doi.org/10.1093/pnasnexus/pgad362

Louisiana Department of Environmental Quality (LDEQ). (2015). Nitrogen and Phosphorus Trends of Long-Term Ambient Water Quality Monitoring Sites in Louisiana. *Office of Environmental Services*, Louisiana Department of Environmental Quality, Baton Rouge, LA.

Lovett, G. M., Weathers, K. C., & Sobczak, W. V. (2000). Nitrogen saturation and retention in forested watersheds of the Catskill Mountains, New York. *Ecological Applications*, *10*(1), 73–84. https://doi.org/10.1890/1051-0761(2000)010

Matonse, A. H., Pierson, D. C., Frei, A., Zion, M. S., Anandhi, A., Schneiderman, E., & Wright, B. (2012). Investigating the impact of climate change on New York City's primary water supply. *Climatic Change*, *116*(3-4), 437–456. https://doi.org/10.1007/s10584-012-0515-4

McHale, M. R., Ludtke, A. S., Wetherbee, G. A., Burns, D. A., Nilles, M. A., & Finkelstein, J. S. (2021). Trends in precipitation chemistry across the U.S. 1985–2017: Quantifying the benefits from 30 years of Clean Air Act Amendment Regulation. *Atmospheric Environment*, 247, 118219. https://doi.org/10.1016/j.atmosenv.2021.118219

McHale, M.R., Murdoch, P.S., Burns, D.A., and Baldigo, B.P. (2008). Effects of forest harvesting on ecosystem health in the headwaters of the New York City water supply, Catskill Mountains, New York. *U.S. Geological Survey,* Scientific Investigations Report 2008–5057, 22 p.

McHale, M. R., & Phillips, P. J. (2001). Stream-water chemistry, nutrients, and pesticides in Town Brook, a headwater stream of the Cannonsville Reservoir Watershed, Delaware County, New York, 1999. *Hathi Trust Digital Library (the HathiTrust Research Center)*. https://doi.org/10.3133/wri014050

McHale, M. R. & Siemion, J. (2014). Turbidity and Suspended Sediment in the Upper Esopus Creek Watershed, Ulster County, New York. *U.S. Geological Survey*. Accessed 8 August 2023. https://pubs.usgs.gov/sir/2014/5200/pdf/sir2014-5200.pdf

McHale, M. R., Siemion, J., & Murdoch, P. S. (2021). The water quality of selected streams in the Catskill and Delaware water-supply watersheds in New York, 1999–2009. *Scientific Investigations Report*. https://doi.org/10.3133/sir20205049

Medalie, L., Hirsch, R. M., & Archfield, S. A. (2012). Use of flow-normalization to evaluate nutrient concentration and flux changes in Lake Champlain tributaries, 1990–2009. *Journal of Great Lakes Research*, *38*, 58–67. https://doi.org/10.1016/j.jglr.2011.10.002

Mehaffey, M. H., Nash, M. S., Wade, T. G., Ebert, D. W., Jones, K. B., & Rager, A. (2005). Linking Land Cover and Water Quality in New York City'S Water Supply Watersheds. *Environmental Monitoring and Assessment*, *107*(1-3), 29–44. https://doi.org/10.1007/s10661-005-2018-5

Mitchell, M. J., Driscoll, C. T., Kahl, J. S., Likens, G. E., Murdoch, P. S., & Pardo, L. H. (1996). *Climatic Control of Nitrate Loss from Forested Watersheds in the Northeast United States*. *30*(8), 2609–2612. https://doi.org/10.1021/es9600237

Mukundan, R., Hoang, L., Gelda, R. K., Yeo, M.-H., & Owens, E. M. (2020). Climate change impact on nutrient loading in a water supply watershed. *Journal of Hydrology*, *586*, 124868. https://doi.org/10.1016/j.jhydrol.2020.124868

Murdoch, P. S., Burns, D. A., & Lawrence, G. B. (1998). Relation of Climate Change to the Acidification of Surface Waters by Nitrogen Deposition. *Environmental Science & Technology*, *32*(11), 1642–1647. https://doi.org/10.1021/es9708631

Murdoch, P. S., & Shanley, J. B. (2006). Detection of water quality trends at high, median, and low flow in a Catskill Mountain stream, New York, through a new statistical method. *Water Resources Research*, *42*(8). https://doi.org/10.1029/2004wr003892

Nadelhoffer, K.J. (2007). Atmospheric Nitrogen Deposition: Implications for Terrestrial Ecosystem Structure and Functioning. In: Visgilio, G.R., Whitelaw, D.M. (eds) *Acid in the Environment*. Springer, Boston, MA. https://doi.org/10.1007/978-0-387-37562-5_5

National Academies of Sciences, Engineering, and Medicine. 2020. *Review of the New York City Watershed Protection Program*. Washington, DC: The National Academies Press. https://doi.org/10.17226/25851

National Atmospheric Deposition Program (NRSP-3). 2022. *NADP Program Office*, Wisconsin State Laboratory of Hygiene, 465 Henry Mall, Madison, WI 53706.

National Primary Drinking Water Regulations | US EPA. (2023, January 9). US EPA. Retrieved November 30, 2023, from https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#Organic

Pennino, M. J., Compton, J. E., Leibowitz, S. G. (2017). Trends in Drinking Water Nitrate Violations Across the United States. *Environ. Sci. Technol., 51*, 13450-13460. http://dx.doi.org/10.1021/acs.est.7b04269

Redder, B. W., Kennedy, C. D., Buda, A. R., Folmar, G. J., & Boyer, E. W. (2021). Groundwater contributions of flow and nitrogen in a headwater agricultural watershed. *Hydrological Processes*, *35*(5). https://doi.org/10.1002/hyp.14179

Renwick, W. H., Vanni, M. J., Fisher, T. J., & Morris, E. L. (2018). Stream Nitrogen, Phosphorus, and Sediment Concentrations Show Contrasting Long-term Trends Associated with Agricultural Change. *Journal of Environmental Quality*, *47*(6), 1513–1521. https://doi.org/10.2134/jeq2018.04.0162

Rowland, F. E., Stow, C. A., Johnson, L. T., & Hirsch, R. M. Lake Erie tributary nutrient trend evaluation: Normalizing concentrations and loads to reduce flow variability. (2021). *Ecological Indicators*, *125*, 107601. https://doi.org/10.1016/j.ecolind.2021.107601

Runting, R. K., Bryan, B. A., Dee, L. E., Maseyk, F. J. F., Mandle, L., Hamel, P., Wilson, K. A., Yetka, K., Possingham, H. P., & Rhodes, J. R. (2016). Incorporating climate change into ecosystem service assessments and decisions: a review. *Global Change Biology*, *23*(1), 28–41. https://doi.org/10.1111/gcb.13457

Sagoff, M. (2002). On the value of natural ecosystems: The Catskills parable. *Politics and the Life Sciences*, *21*(1), 19–25. https://doi.org/10.1017/s0730938400005724

Siemion, J., McHale, M. R., Lawrence, G. B., Burns, D. A., & Antidormi, M. (2018). Long-term Changes in Soil and Stream Chemistry across an Acid Deposition Gradient in the Northeastern United States. *Journal of Environmental Quality*, *47*(3), 410–418. https://doi.org/10.2134/jeq2017.08.0335

TNM-L. (n.d.). Www.ssi.shimadzu.com. Retrieved August 28, 2023, from https://www.ssi.shimadzu.com/products/total-organic-carbon-analysis/toc-analysis-accessories-and-add-ons/tnm-l/index.html

Seitzinger, S. P., Styles, R. V., Boyer, E. W., Alexander, R. B., Billen, G., Howarth, R. W., Mayer, B., & N. van Breemen. (2002). Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. *Springer EBooks*, 199–237. https://doi.org/10.1007/978-94-017-3405-9_6

Smith, A. J., Duffy, B. T., Onion, A., Heitzman, D. L., Lojpersberger, J. L., Mosher, E. A., & Novak, M. A. (2018). Long-term trends in biological indicators and water quality in rivers and streams of New York State (1972-2012). *River Research and Applications*, *34*(5), 442–450. https://doi.org/10.1002/rra.3272

Tetzlaff, D., Seibert, J., McGuire, K. J., Laudon, H., Burns, D. A., Dunn, S. M., & Soulsby, C. (2009). How does landscape structure influence catchment transit time across different geomorphic provinces? *Hydrological Processes*, *23*(6), 945–953. https://doi.org/10.1002/hyp.7240

U.S. Census Bureau QuickFacts: Delaware County, New York. (n.d.). Www.census.gov. Retrieved August 28, 2023, from https://www.census.gov/quickfacts/delawarecountynewyork

U.S. Geological Survey. (2019). 3D Elevation Program 1-Meter Resolution Digital Elevation Model (published 20200606), accessed February 25, 2024 at URL https://www.usgs.gov/the-national-map-data-delivery

U.S. Geological Survey. (2023). *National Hydrography Dataset (NHD)* - USGS National Map Downloadable Data Collection: USGS - National Geospatial Technical Operations Center (NGTOC)

USGS | National Water Dashboard. (n.d.). Dashboard.waterdata.usgs.gov.f https://dashboard.waterdata.usgs.gov/app/nwd/en/?aoi=default

Wang, K., Davis, D., and Steinschneider, S. (2021). Evaluating suspended sediment and turbidity reduction projects in a glacially conditioned catchment through dynamic regression and fluvial process‐based modelling. *Hydrological Processes*, 35(9). https://doi.org/10.1002/hyp.14351

Wang, K., Mukundan, R., & Gelda, R. K. (2023). Modeling source water disinfection byproducts formation potential using environmental variables. *Journal of the American Water Resources Association*. https://doi.org/10.1111/1752-1688.13172

Watershed Water Quality - Hydrology | NYC Open Data. (n.d.). Data.cityofnewyork.us. Retrieved August 28, 2023, from https://data.cityofnewyork.us/Environment/Watershed-Water-Quality-Hydrology/e3xf-jwmj

Welsch, D. L., Kroll, C. N., McDonnell, J. J., & Burns, D. A. (2001). Topographic controls on the chemistry of subsurface stormflow. *Hydrological Processes*, *15*(10), 1925–1938. https://doi.org/10.1002/hyp.247

Zion, M. S., Pradhanang, S. M., Pierson, D. C., Anandhi, A., Lounsbury, D. G., Matonse, A. H., and Schneiderman, E. M. (2011). Investigation and modeling of winter streamflow timing and magnitude under changing climate conditions for the Catskill Mountain Region, New York, USA. *Hydrological Processes*, 25(21), 3289–3301. https://doi.org/10.1002/hyp.8174

Van Meter, K. J., Byrnes, D., & Basu, N. B. (2023). Memory and Management: Competing Controls on Long‐Term Nitrate Trajectories in U.S. rivers. *Global Biogeochemical Cycles*, *37*(4). https://doi.org/10.1029/2022gb007651