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High Frequency Monitoring and Nitrate Sourcing Reveals Baseflow and Stormflow Controls on Total Dissolved Nitrogen and Carbon Export Along a Rural-Urban Gradient

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Key Points:

- Baseflows contributed nearly as much or more of nitrogen export as stormflows across low to moderate development intensity catchments
- Stormflow NO_3^- sources were diverse and highly variable in time, while baseflows mobilized few sources with little temporal variability
- Grab sampling methods did not reliably estimate the loading observed from in situ monitoring for small catchments

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract Efforts to reduce nitrogen and carbon loading from developed watersheds typically target specific flows or sources, but across gradients in development intensity there is no consensus on the contribution of different flows to total loading or sources of nitrogen export. This information is vital to optimize management strategies leveraging source reductions, stormwater controls, and restorations. We investigate how solute loading and sources vary across flows and land-use using high frequency monitoring and stable nitrate isotope analysis from five catchments with different sanitary infrastructure, along a gradient in development intensity. High frequency monitoring allowed estimation of annual loading and attribution to storm versus baseflows. Nitrate loads were 16 kg/km^2/yr. from the forested catchment and ranged from 68 to 119 kg/km^2/yr., across developed catchments, highest for the septic served site. Across developed catchments, baseflow contributions ranged from 40% of N loading to 75% from the septic served catchment, and the contribution from high stormflows increased with development intensity. Stormflows mobilized and mixed many surface and subsurface nitrate sources while baseflow nitrate was dominated by fewer sources which varied by catchment (soil, wastewater, or fertilizer). To help inform future sampling designs, we demonstrate that grab sampling and targeted storm sampling would likely fail to accurately predict annual loadings within the study period. The dominant baseflow loads and subsurface stormflows are not treated by surface water management practices primarily targeted to surface stormflows. Using a balance of green and gray infrastructure and stream/riparian restoration may target specific flow paths and improve management.

1. Introduction

Nitrogen loading from urbanized watersheds contributes to water quality degradation and eutrophication of receiving water bodies (Bernhardt et al., 2008; Walsh et al., 2005; Wollheim et al., 2005). Urbanized watersheds can also increase or decrease dissolved organic carbon (DOC) loading to downstream waterbodies with a variety of adverse impacts (Chow et al., 2005; Prairie, 2008; Solomon et al., 2015). Mitigating the impacts of development on water quality is a major environmental management challenge. Management techniques usually focus on surface stormwater, with stormwater control methods (SCM) meant to store and slow down the transport of water while promoting infiltration, or restoration of streams and wetlands to enhance retention and removal of pollutants. SCMs, such as infiltration basins, target surface stormwater with the goal of translating it to baseflow and increasing the residence time of N and C in catchments. In contrast, stream and riparian restorations are more effective at low flows and subsequently longer residence times (Kaushal et al., 2008; Newcomer et al., 2016). Nitrogen management may also attempt to limit loading at the source by reducing watershed inputs (e.g., regulating fertilizer use) or targeting specific sources (e.g., sanitary infrastructure rehabilitation). The effectiveness of these SCMs, restorations, and nutrient reduction approaches to mediate catchment nutrient export is highly sensitive to the flow paths, timing, and magnitude of loading. Understanding how flow and hydroclimate impacts solute loading and N sources across gradients in development intensity and sanitary infrastructure use is critical to developing effective and efficient management approaches.

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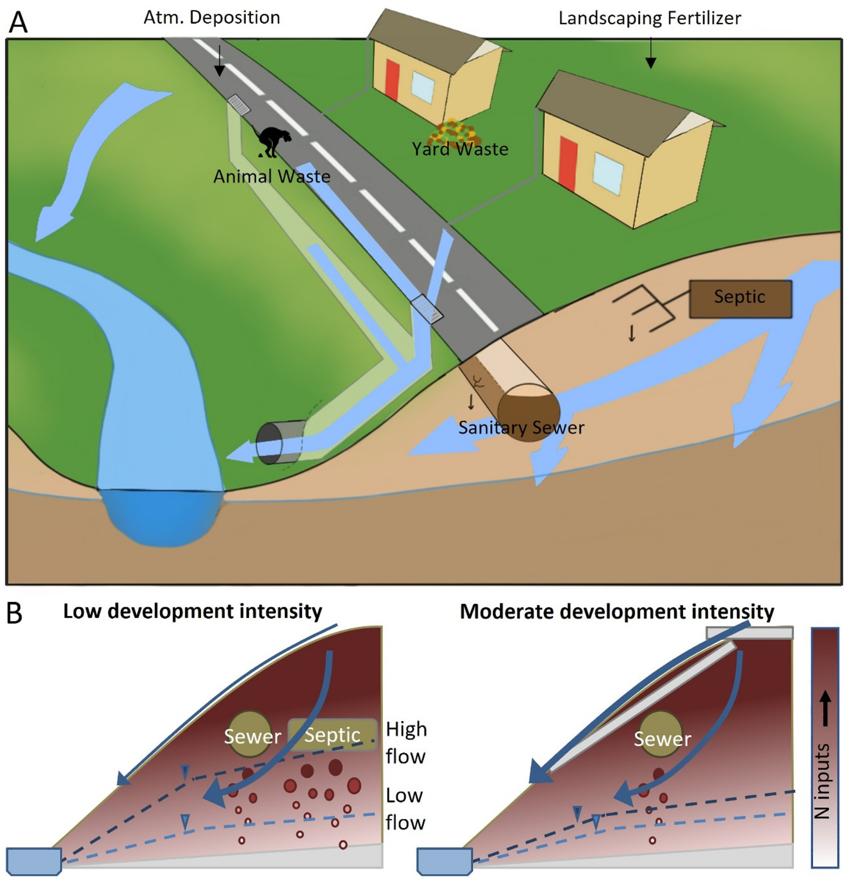

Figure 1. Conceptual model of N loading in developed catchments along the rural-urban gradient. (a) depicts sources and flow paths in 3 dimensions, while (b) depicts a hillslope cross section under different flow conditions and development intensity where the arrows indicate flow pathways of precipitation, and the color of the hillslope and circles represents the magnitude and location of N inputs. Adapted from Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al. (2022).

Roads, stormwater infrastructure, and impervious surfaces connect surface flow paths to streams and promote rapid and efficient catchment export of N and C (Bernhardt et al., 2008). However, these features vary greatly across ex-urban and urban landscapes (Delesantro et al., 2021) altering hydrologic connectivity and leading to rapid stormflows and high temporal variability in both flows (Delesantro et al., in prep) and delivery of pollutants (Blaszczak et al., 2019). Within developed landscapes, the sources of N and C are also heavily altered (Figure 1). Surface sources of N include atmospheric deposition, lawn and landscape fertilizers, landscaping waste, and pet waste (Hobbie et al., 2017). Development reduces forest cover and therefore natural DOC sources, but organic debris can collect in roof drains and stormwater infrastructure which then export pulses of DOC during stormflows (Fork et al., 2018).

Although Impervious Surface Cover (ISC) is a defining characteristic of development, it covers only a small portion of most developed watersheds. The largest area of existing and ongoing development globally is low intensity (Angel et al., 2011; Delesantro et al., 2021; Dijkstra & Poelman, 2014; Richards, 2006; Seto et al., 2012). Within these landscapes, lawns, parks, and forested patches provide opportunities for disconnection of surficial flow and promote infiltration of rainfall to subsurface flow paths. Low to moderate ISC catchments often have higher residential population density and sanitary infrastructure density than higher ISC catchments which may have more commercial land use (Delesantro et al., 2021). Wastewater is potentially the largest source of N in developed watersheds (Bernhardt et al., 2008) and is also a major source of DOC (Westerhoff and Anning, 2000). Many studies have indicated that wastewater from septic systems and leaking from sanitary sewers is the primary source of baseflow and low flow nitrate (Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022; Divers et al., 2014; Guo et al., 2021; Kaushal et al., 2011; Potter et al., 2014; Xu et al., 2021). Soils also contribute to subsurface N and C and infiltrated lawn fertilizers contribute to subsurface N (Kaushal et al., 2011). Low density development is often characterized by extensive "open development", with lower tree cover and more extensive herbaceous cover. This can have the effect of decreasing evapotranspiration, and increasing recharge, contributing to greater baseflow (Bhaskar et al., 2016) and mobilization of subsurface solute sources.

There is no consensus on the relative role of flows on the timing and magnitude of N or DOC loading within urban watersheds or on how sources vary across flows. Some studies have demonstrated that stormflows export more nutrients to receiving waterbodies than baseflow (Fellman et al., 2009; Inamdar et al., 2006; Wollheim et al., 2005) while others have suggested that baseflow may contribute a greater portion of nutrient loading, particularly across low and medium development intensity catchments (Janke et al., 2014; Kincaid et al., 2020; Shields et al., 2008). However, these studies have either been limited to monitoring of a single mixed-use urbanized catchment or have relied on periodic grab sampling to estimate loads, and none have attributed both loadings and sources across flows. As such these estimates do not capture the spatial heterogeneity or high temporal variability of sources and loading from urban landscapes. We found no studies which have, to date, combined monitoring of loading and N sources attribution across flows and development intensity to identify both sources and flow paths necessary for targeted watershed management. Due to difficulty of sampling at high flows, discharge-concentration regressions used to estimate loading from periodic sampling may also fail to evenly represent the full range of flows. Rare stormflows may be represented by a small percentage of the sampled discharge-concentration data set, but represent a large percentage of estimated loading, introducing considerable irreducible uncertainty.

In this study we investigated the development patterns of study catchments, the dissolved N and C export dynamics across flows and hydroclimatic conditions, and compared the sources of stormflow NO_3^- to baseflow NO_3^- across catchments to answer the following questions.

1. How do dissolved nitrogen and carbon loading change across flows and wetness conditions and what are the relative roles of baseflow and stormflow loading across a gradient of development intensity and sanitary infrastructure use?
2. What are the contributions of different nitrate sources to loading within baseflow and stormflow across a gradient of development intensity and sanitary infrastructure use?
3. How do sampling frequency impact the estimation of total dissolved nitrogen (TDN) and carbon loading across a gradient of development intensity and sanitary infrastructure use?

To answer these question, we use a novel data set of high frequency NO_3^--N, TDN, and DOC monitoring utilizing in situ spectrometry at the outlet of one largely forested catchment and three catchments along an ex-urban to urban development gradient in the North Carolina Piedmont of the United States. With this high temporal resolution data set, sometimes referred to as continuous monitoring within the discipline, we capture export across the full range of flows including rare episodic events in highly reactive and hydrologically flashy urban environments to estimate N and C stream loading. We also performed stable isotope analysis of NO_3^- to help attribute sources across flow.

2. Methods

2.1. Study Catchments

Our study catchments were selected to cover a gradient in sanitary and stormwater infrastructure use and development intensity within the North Carolina Piedmont of the U.S.A (Figure 2). All study catchments are in the Carolina Slate Belt (North Carolina Geological Survey, 1998), and are tributaries to Bolin Creek, a 40 km^2 watershed in and around Chapel Hill and Carrboro, NC. This region has undergone rapid urbanization over the past 30 years with the primary land cover transition from old fields and successional forest to urban and suburban landscapes (McDonald & Urban, 2006; Sexton et al., 2013; Taverna et al., 2005). Dissolved nitrogen makes up greater than 70% of total nitrogen in streams regionally (Munn et al., 2023; Stow et al., 2001). We selected one primarily forested catchment for reference, one septic served developed rural catchment, and two sanitary and stormwater sewer served urbanized catchments ranging in population density, infrastructure density and surface connectivity features (Table 1). Study catchments were delineated from a processed 6 m lidar derived DEM (State of North Carolina, 2018) accounting for stormwater sewers by burning them into the landscape to 1 m depth and manually inspecting boundaries. Catchments range in area from 0.95 to 1.94 km^2. The primarily forested catchment (Forested) (locally, Tally Ho—TH) is largely in Duke Forest (https://dukeforest.duke.edu). Although

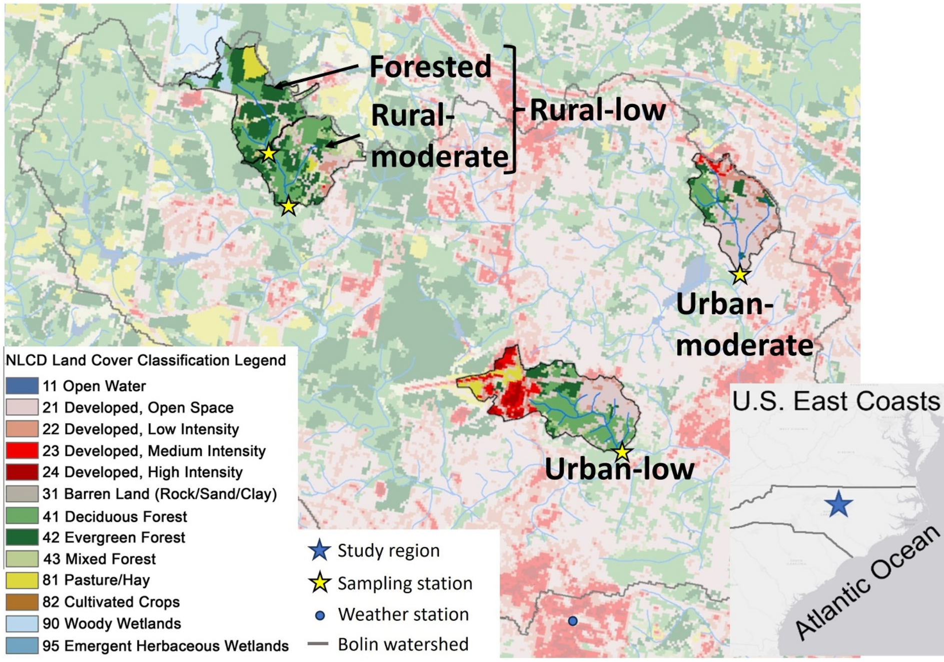

Figure 2. Map of the study catchments in the Chapel Hill region of North Carolina, USA and NLCD 2016 land cover classification.

primarily forested, the catchment contains 13 residential parcels and an experimental mowed field within Duke Forest. The forest composition of the study catchment is abandoned pine silviculture with some woody wetlands. Downstream of the Forested catchment is part of the Roger's Road neighborhood served by septic systems, referred to as Rural-moderate. The combined Forested upstream and developed Rural-moderate are designated Rural-low (locally RR). Rural-low is also largely forested and primarily composed of abandoned pine silviculture

Table 1
Table of Key Landscape Characteristics for Study Catchments, Primarily Forested (Forested), Low Development Septic Served (Rural-Low), Moderate Development Septic Served (Rural-Moderate), Low Urban Development Intensity (Urban-Low), and Moderate Development Intensity (Urban-Moderate)

		Study WS ID				
Metric	Units	Forested	Rural-low	Rural-moderate	Urban-low	Urban-moderate
Area	km^2	0.99	1.94	0.95	1.51	0.95
Agr. landcover[a]	%	7.94	5.25	2.39	5.3	0.19
Forested landcover	%	70.5	67.13	60.83	62.3	64.09
ISC (NLCD)	%	0.81	2.28	3.83	15.71	10.9
ISC (hand drawn)	%	1.57	3.77	6.9	20.03	23.22
Dev. landcover (NLCD 22–24)	%	0.81	3.86	7.08	24.64	20.4
Road density	km/km^2	2.59	3.64	4.75	5.6	7.43
Stormwater pipe density	km/km^2	0.09	0.25	0.42	1.11	2.78
Sanitary sewer density	km/km^2	0	0.43	0.88	5.13	7.36
Septic system density	Per km^2	13	94	180	3	0
Sewer TWI	–	0	0.88	1.23	0.67	1.01
Population density	Per km^2	30	259	498	313	887
Parcel density	Per km^2	13	85	161	113	276

Note. ISC, Impervious Surface Cover; NLCD, National Land Cover Data set; TWI, Topographic wetness index. [a]Agricultural landcover ("Pasture") represent mowed fields in these catchments.

but houses a population density consistent with catchments within the municipal service boundary of Chapel Hill. For annual accounting of runoff and export, Forested catchment discharge and nutrient load values were subtracted from Rural-low values to provide a conservative estimate of Rural-moderate values which assumes no losses between the Forested and Rural-low catchment sampling points. The low development intensity catchment (Urban-low) (locally, Burlage Circle—BG) was selected to approximate the regional median in population density and development features (Delesantro et al., 2021). The medium development intensity catchment (Urban-moderate) is a tributary to Booker Creek (tributary to Bolin Creek)(locally, Booker Tributary—BT). The Urban-moderate catchment has less forest cover and greater population and density of roads and sewers than Urban-low but has similar developed NLCD landcover. Stormwater and sanitary sewers are separate throughout the study area. Additional landscape metrics and methods are discussed in Delesantro et al. (2021) and Text 1 in Supporting Information S1. In figures throughout this paper, site names and their corresponding data are consistently colored to allow quick identification and comparison across figures.

2.2. Stream Water Sampling

Grab samples were collected from all catchments every other week throughout the 2-year deployment period beginning 1 Dec 2017, and ending 1 Dec 2019. Stream water samples were taken at the outlet of the study catchments and field filtered through a 0.7 μm prefilter and 0.45 μm Whatman GF/F filter into HDPE bottles and stored on ice in the field to be frozen upon return to the lab. Samples were analyzed for NO_3^--N on a Dionex ICS-2000 ion chromatograph (Dionex Corp., Sunnyvale, CA) and total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) concentrations (mg/L) with a Shimadzu TOC-VCPH with TNM-1 module (Shimadzu Corp., Kyoto, Japan). High resolution water chemistry data was collected by in situ UV and UV-Vis absorption spectrometry (S::CAN Spectrolyser, Vienna, Austria; Sea-Bird Scientific SUNA V1 and V2, Bellevue WA, US). In situ spectrometry sensors are site calibrated to laboratory analyzed water chemistry samples as described in Section 2.3. To ensure that in situ spectrometer calibrations are robust across the full range of observed flow, ISCO 6712 autosamplers (Teledyne ISCO, Lincoln NE, USA) were used to collect stormwater chemistry samples for calibration. Keller Acculevel pressure transducers (Keller America, Newport News, VA, USA) provided real time water-level and ISCO automated samplers were triggered by program on a measurement and control datalogger (Campbell Scientific, CR1000, Logan, Utah, USA) to sample along the rising and falling limbs of selected storms across seasons. We targeted at least two storms per season. All data are publicly available (Delesantro et al., 2021, Delesantro, Duncan, Riveros-Iregui, & Band, 2022).

2.3. In Situ Sensor Deployment and Calibration

Site specific calibrations for the SUNA and S::CAN N sensors were informed by grab samples and automated collection storm samples. SUNA calibration was conducted by linear regression and S::CAN calibration was conducted using the full UV-Vis absorbance spectrum by Partial Least Squares Regression (PLSR) (Wold et al., 2001) with k-fold ($n = 10$) cross validation using the *R* package pls (Mevik & Wehrens, 2023). In our study region, the majority of TDN which is not NO_3^- is dissolved organic N (dissolved organic nitrogen (DON)) (Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022). DON is often associate with DOC and therefore the combination of DOC spectral absorbance and NO_3^- spectral absorbance allows us to estimate TDN concentrations despite there being no specific absorbance spectrum for TDN. S::CAN calibrations were conducted within overlapping temporal windows to account for seasonal variation and sensor drift. Outliers in the calibration sample data set were identified by a leave one out analysis and did not exceed 9.5% of the data set for any catchment. Calibration samples captured between 71% and 100% of the range in observed flow across study catchments. Calibrations explained between 85% and 95% of laboratory measured solute concentration (NO_3^-, TDN, and DOC) across solutes and catchments (Figure S1 in Supporting Information S1). Additional calibration details and discussion can be found in supporting information (Text S2 and S3 in Supporting Information S1).

Pressure transducers (HOBO U20, Onset, Cape Cod, Massachusetts) recorded water level and temperature every 5 min through the period of sampling and Keller Acculevel pressure transducer (Newport News, Virginia), while primarily used for triggering automated sampling, provided redundancy. Barometric pressure was measured by pressure transducers (Solinst Barologgers, Georgetown, Ontario, Canada and Vaisala PTB110/Campbell Scientific CS106, Logan, Utah, USA) deployed in dry wells open to the atmosphere to buffer temperature variation or deployed in shaded logger boxes open to the atmosphere. Barometric pressure measurements were used to offset total pressure for study catchment streams within 8 km. Gaps in flow and solute data were interpolated for

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periods of less than 40 min and gaps in solute concentration were interpolated over baseflow periods without large storms for up to 16 days or between synoptic samplings. Interpolated solute data accounted for 14.9% of data at Forested, 9.8% at Rural-low, 17.6% at Urban-low, and 15.0% at Urban-moderate and most interpolated data is during periods when water level was too low to sufficiently submerge sensor. Precipitation data from the WeatherSTEM UNC station (Figure 2) was used across for all catchments to estimate runoff percent. All study catchments were within 8 km of the precipitation gauging station.

Flow was monitored by acoustic doppler profiling (ADP) (SonTek IQ+, San Diego, California) at Rural-low and Urban-low and an additional ADP was moved between the Forested and Urban-moderate catchments. Stream cross sections were surveyed annually and after visibly erosive storm events. Deployed ADP flow measurement yielded noisy measurements and therefore periodic velocity profiling with electromagnetic velocity sensors (Marsh-McBirney Flo-Mate, Frederick, Maryland) was conducted across low flows to combine with ADP measurements and generate level-discharge rating curves for all catchments. Due to safety concerns, we did not measure high flows via manual profiling, but previous studies have used salt dilution to validate the SonTek IQ+ sensors regionally in small, urbanized streams across flows (Blaszczak et al., 2019). In situ flow monitoring allowed us to inform flow rating curves with data across the 2-year sampling period and generate new rating curves at Urban-low throughout the deployment period as necessitated by changing channel conditions due to erosive flows and sediment deposition. All level-discharge rating curves explained at least 80% of the variation in discharge and captured the full range of flow (Figures S2 and S3 in Supporting Information S1).

The final time series of flow, concentration and solute export have a 5 min time step (Figure 3). Over the 2-year deployment all four stations collected NO_3^- export data for a total overlapping 11.8 months between 1 Dec. 2017, and 1 Dec. 2019. Tropical storms, nearby construction generating debris, and sensor failure primarily contributed to data gaps. This common high frequency monitoring period is the basis for all analyses in this study. The Urban-moderate catchment was originally instrumented with a SUNA which failed in November of 2018 and was replaced by an S::CAN in January of 2019. The SUNA was not calibrated for DOC and therefore comparison of TDN and DOC export exclude the Urban-moderate catchment.

2.4. Graphical Hydrograph Separation

We have separated flow three ways representing different flow partitions to contextualize our estimates of loading across flow categories. Although we lack tracer or endmember data to establish exact definitions of flows, these three separations demonstrate commonalities irrespective of flow separation parameterization. Hydrograph separation can be conducted with streamflow data alone using graphical approaches (Eckhardt, 2005; Nathan & McMahon, 1990). We chose to use a recursive filter to estimate flow components by hydrograph separation (Nathan & McMahon, 1990). The primary flow separation is parameterized to represent slow-moving flows (slowflow) including baseflow, accounting for increased hydraulic head and saturation during events, and slow-moving storm flow likely traveling along subsurface flow paths (parameters: passes(n) = 3, filter(a) = 0.96 for Forested, a = 0.97 for Rural-low, Urban-low, Urban-moderate) (Figure 4). Based on site knowledge, we believe this separation represents a reasonable separation of flow paths between quick moving surface flow and slower moving subsurface flow. The second hydrograph separation was parameterized to capture seasonal baseflow change, but assuming little to no baseflow change across storm event timescales (parameters: $n = 3$, a = 0.992 for Forested, a = 0.997 for Rural-low, Urban-low, Urban-moderate) (Figure 4). In this scenario, quick flow represents almost all event driven flow, while baseflow is conservative, representing seasonally driven baseflow. Finally, a temporal separation, defined all flow at any datapoint as either stormflow or inter-storm baseflow (Figure 4). A datapoint is defined as stormflow when quick flow exceeds baseflow as defined by the seasonal baseflow hydrograph separation. This threshold prevents sensor noise and diel fluctuations in flow driven by ET from being identified as stormflow. The recursive filter was run in *R* (R Core Team, 2020) with code modified from the EcoHydRology package (Fuka et al., 2018).

2.5. Analysis of Solute Export Across Flows and Wetness

Nitrate, TDN, and DOC export was calculated by multiplication of sensor concentration and discharge at 5-min time steps. Uncertainty propagation in runoff and export was estimated by quadrature of the standard errors of the sensor calibrations and the water level-discharge rating curves. Partitioning of NO_3^-, TDN, and DOC export was based on the three flow separations (2.4) to estimate the flow path and timing of solute export within discrete

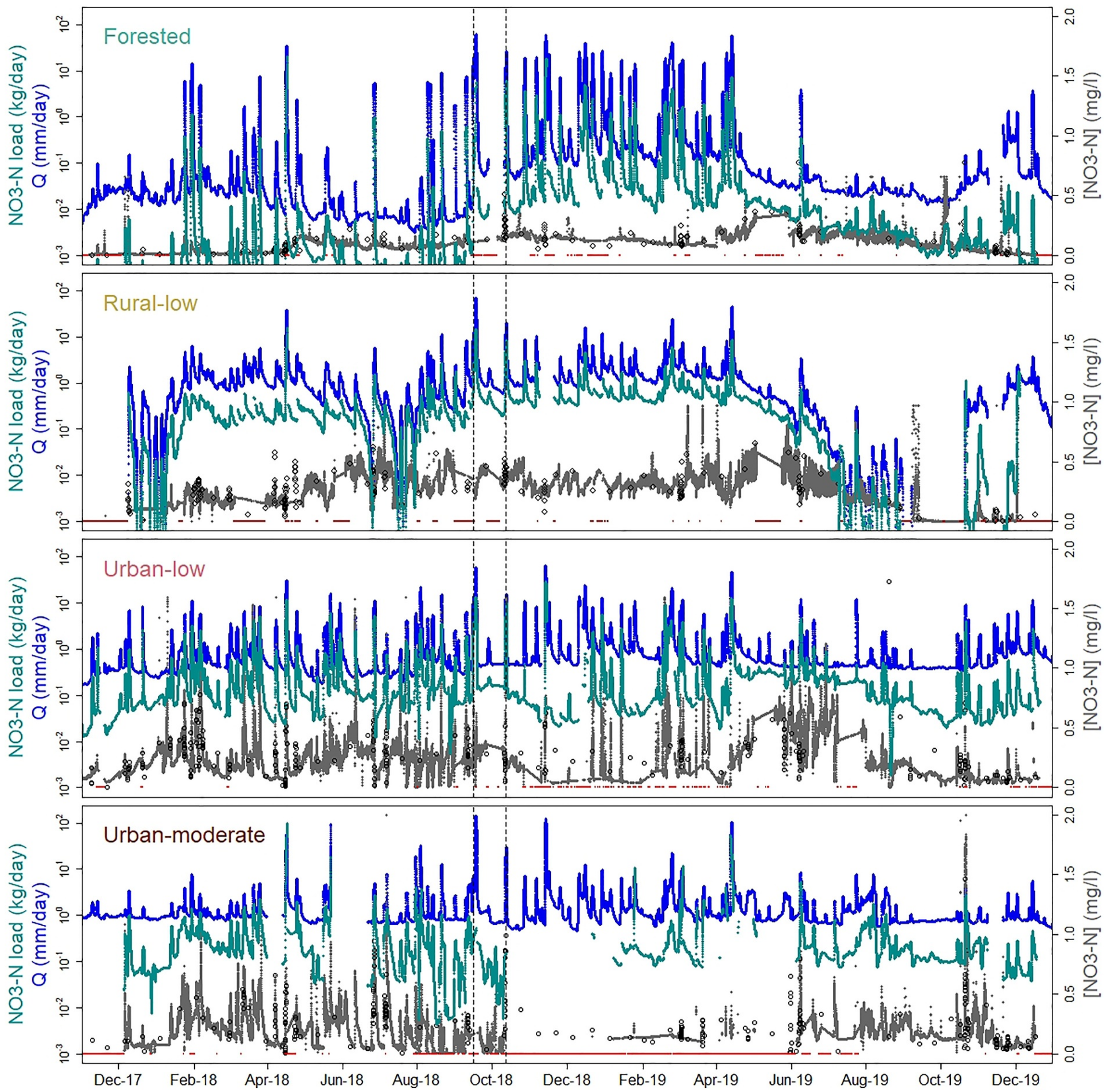

Figure 3. Time series of flow (blue points), nitrate concentration (gray points), and nitrate export (green points) for all study catchments. Black points represent grab sampled and autosampler stream chemistry measurements. Red dots along the bottom, represent intervals with incomplete data. Time series' of total dissolved nitrogen and dissolved organic carbon are in the supporting materials (Figures S4 and S5 in Supporting Information S1).

categories. To evaluate runoff and solute export over the full range of flow and wetness conditions (i.e., without discrete categories) the flow duration and cumulative percent export was analyzed as a function of flow and the 30-day antecedent flow as a metric of wetness. We used a variety of metrics to facilitate comparisons of flow and export distributions across catchments and hydrologic conditions. To characterize the contribution of high flows, we compare the flow at 75% of cumulative solute export (NO3 F75, TDN F75, DOC F75), where higher values indicate a larger percentage of export at high flows. We also calculate the duration of flows which account for the top 25% of solute export expressed as a percent and period of non-consecutive time, where smaller values indicate rare high flows are responsible for greater export. To characterize the effect wetness conditions on export, we report the percent of solute export occurring during the duration of the wettest half of the year based on 30-day antecedent flow. We present only the results of well correlated regression defined by an alpha < 0.05 and an $R^2 > 0.3$. Analysis was conducted in *R* statistical computing language (R Core Team, 2020). Bar plots of runoff and solute export were generated using ggplot in *R* (Wickham, 2016).

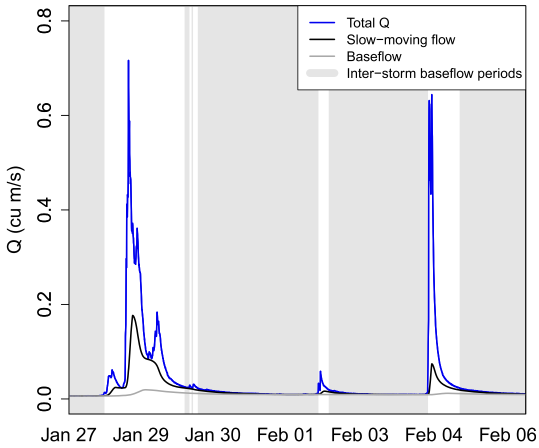

Figure 4. Example plot of a 5 min time interval with estimated slowflow, baseflow, and inter-storm baseflow. The black line shows estimated slowflow parameterized to separate quick event surface flows from slower flows likely transported via subsurface pathways. The gray line shows estimated baseflow parameterized to capture seasonal baseflow and has very little event scale variation. The gray shaded area depicts the temporal flow separation creating a binary separation between stormflow and inter-storm baseflow.

2.6. Nitrate Isotope Sampling and Analysis

Stable isotopic analysis of NO_3^- was conducted for baseflow samples and stormflow samples for five common storms across all four catchments. Selected baseflow samples were distributed across baseflows and antecedent flow. Selected storm samples were distributed across the range in event flow, and samples were selected on both rising and falling limbs. However, due to differences in event response between catchments, that is, the magnitude and rate of flow change on rising and falling limbs, selected storm samples do not necessarily represent the same conditions across catchments and storm events may be represented by different number of samples across catchments. A total of 233 samples were defined as baseflow or stormflow for analysis by the previously mentioned inter-storm baseflow separation. The primarily forested catchment was represented with only 35 samples due to low NO_3^- concentrations (less than approximately 0.05 mg/l) that could not be reliably analyzed for isotopic N. All other catchments were represented by 61–73 samples. Frozen samples were analyzed using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) for δ15N- NO_3^- and δ18O- NO_3^- at the University of Pittsburg Regional Stable Isotope Laboratory for Earth and Environmental Science Research. All samples were analyzed in duplicate, and values averaged. Samples with greater than 0.5 deviation in the delta values between duplicates were re-run or removed as erroneous. Isotopic end members of NO_3^- sources were established from the literature and existing data sets. Ammonium nitrification endmember values from lawn fertilizer and rainfall were estimated from the Baltimore LTER lawn lysimeter study; δ15N- NO_3^- = 0.92‰ (SD = 1.91), δ18O- NO_3^- = −1.44‰ (SD = 2.53) (Cary Institute, Kaushal, 2016). Synthetic nitrate fertilizer endmember values were estimated from the literature, δ15N- NO_3^- = −0.00‰ (SD = 2), δ18O- NO_3^- = 23.50‰ (SD = 1.3) (Amberger & Schmidt, 1987; Kendall et al., 2008). Atmospheric deposition endmember values were estimated from NADP sampling near Raleigh, NC; δ15N- NO_3^- = −2.40‰ (SD = 1.00), δ18O- NO_3^- = 76.30‰ (SD = 2.40) (Kendall et al., 2008). Soil NO_3^- isotopic endmember values were estimated as the mean of the primarily forested catchment stream sample values; δ15N- NO_3^- = 4.56‰ (SD = 1.64), δ18O- NO_3^- = 3.04‰ (SD = 1.93) (Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022). Wastewater endmember δ15N- NO_3^- and δ18O- NO_3^- values were estimated to be 10.69‰ (SD = 1.32) and 6.13‰ (SD = 1.53) respectively (Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022; Xue et al., 2009).

A stable isotope mixing model using a Bayesian framework was used to solve standard mixing equations (Parnell et al., 2013) (Text S4 in Supporting Information S1) and estimate the probable proportion of nitrate from each source during stormflow and inter-storm baseflow periods. Stable isotope measurement of stream nitrate was represented as a linear combination of the source endmembers where the coefficients represent the proportion of each source. The Bayesian implementation of this model produces a probability distribution for the proportion of nitrate load for each sample or set of samples from each source and has been widely applied for nitrate source attribution (e.g., Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022; Diver et al., 2014; Xue et al., 2012). The model was run with the SIMMr package in *R* (Parnell, 2021; R Core Team, 2020) using the software JAGS (Just Another Gibbs Sample; Plummer, 2003) and was modified to provide source proportions by sampled loading (Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022). Model equations, parameters, and sources of uncertainty are discussed in Supporting Information S1 (Text S4).

2.7. Analysis of Sampling Frequency Impact on Export Estimates

Weekly grab sampling and occasional storm sampling for solute chemistry is often combined with flow gauging to produce discharge-concentration (QC) relationships from which a timeseries and annual solute export is estimated (Janke et al., 2014; Shields et al., 2008). We evaluated the performance of high frequency in situ measurement of NO_3^-, TDN, and DOC concentrations and export relative to grab sampling derived estimates of concentration and export. Seasonal QC relationships were generated for each catchment. Linear, log, and binomial relationships were tested between concentration and flow for each season, catchment, and solute and the relationship with the lowest *p* value was selected for the model using our full stream sample data set of 227–383

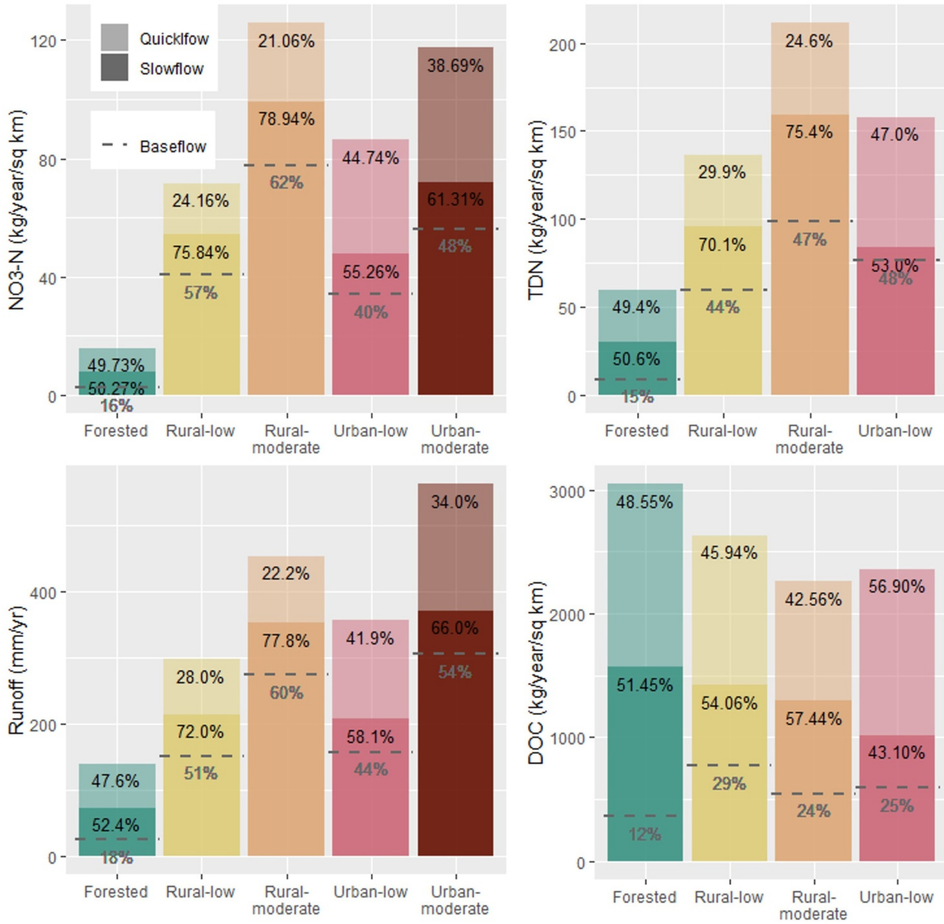

Figure 5. Barplots of total runoff, nitrate export, total dissolved nitrogen export, and dissolved organic carbon export for study catchments. Estimated slowflow and quickflow runoff and export components are designated by light and dark colors with the percentage on the bars. The conservative estimate of baseflow runoff and export (assuming negligible event scale variation) is shown as the gray dotted line. Values are presented for the Forested, septic served (Rural-low), developed portion of the septic served (Rural-moderate), Urban-low, and Urban-moderate study catchments.

samples per catchment. Uncertainty propagation in export was estimated by quadrature of the standard errors of the QC relationships and the water level-discharge rating curves. We compared how well the high-frequency in situ measurements and seasonal QC relationships predicted variation in solute concentration and compared estimates of total annual export.

3. Results

3.1. Total Runoff and Solute Export

Total runoff generally increased with catchment development intensity, but N export per unit area was greatest for the septic served catchment (Rural-moderate) (Figure 5). The sampling periods total precipitation was 1,272 mm, 136 mm higher than the 30-year average. The Forested catchment NO_3^- export was just 12.8%–22.5% of the export of all other catchments and Forested catchment TDN export was 28.6%–44.2% of the export of all other catchments with TDN analysis. Nitrate makes up only 26.2% of TDN export for Forested whereas NO_3^- export makes up between 50.8% and 56.9% of TDN export for Rural-low, Rural-moderate, and Urban-low. Nitrite and NH_4^+ were not significant components of N load in our study catchments (Delesantro et al., 2021) meaning that dissolved organic nitrogen (DON) accounts for most of the primarily forested catchment TDN export. DOC export was greatest for the primarily forested catchments and generally decreased with development intensity (Figure 5). Metrics of development intensity were significant drivers of variation in runoff and solute export across the five study catchments. Runoff was positively correlated to road density and parcel density (Road Dens.:

$R^2 = 0.86$, $p = 0.02$; Parcel Dens.: $R^2 = 0.95$, $p < 0.01$). Solute export was also positively correlated to population metrics with parcel density being the best predictor (NO_3^- ~ Parcel Dens: $R^2 = 0.75$, $p = 0.05$, TDN ~ Parcel Dens: $R^2 = 0.99$, $p < 0.01$, DOC ~ Parcel Dens: $R^2 = 0.95$, $p = 0.03$).

3.2. Flow Component Runoff and Solute Export

Across catchments we estimate that slow-moving flows, which likely have a substantial subsurface flow path contribution, export the majority of NO_3^- and TDN across both septic and sewer served developed catchments (Figure 5). Estimated baseflow and slow-moving flow runoff and N export was highest at the septic served Rural-low and Rural-moderate catchments, accounting for up to 78.9% of annual NO_3^- export (Table 2). The conservative estimates of baseflow, with little to no event scale variation, attributed between 39.5% and 61.8% of NO_3^- and TDN export to baseflows across developed catchments. Even inter-storm baseflow, excluding any stormflow period export, contributed 38.6%–62.9% of total NO_3^- and TDN export across developed catchments. Baseflow and slow-moving flow in the developed catchments did not deliver as much of the total DOC and TDN export as it did the total NO_3^- export, indicating that higher flows may be required to mobilize these solutes. It is also notable that the estimated contribution of baseflow and slow-moving flow to runoff and N export was greater for developed catchments than the primarily forested catchments.

3.3. Cumulative Frequency Distributions of Flow and Solute Export

Cumulative flow duration and cumulative export curves were used to compare the runoff and solute export regimes across catchments (Figures 6a–6d) and key values were extracted (Table 2). The cumulative runoff of the Forested catchment was distributed over a larger range of flows relative to the developed catchments where runoff was largely concentrated within a narrow range of flow consistent with steady baseflow (Figure 6a). There was less seasonal variation in runoff from Urban-low and Urban-moderate than the Forested catchment and Rural-low (Figure 3). The highest observed flows across catchments ranked by development intensity, lowest for Forested and highest for Urban-moderate. We assessed rare extreme flows by the duration of flows which account for the top 25% of runoff, where shorter durations represent greater high or extreme flows. All catchments show evidence of rare extreme flows with 25% of total flow occurring from less than 1% of the sampling period (Table 2), but across developed catchments, extreme flows increased with developed cover and developed feature density.

Solute export from the Forested catchment and Rural-low was largely driven by higher flows in seasonally wet periods (Table 2, Figures 6, Figure 3) while export from Urban-low and Urban-moderate was not as sensitive to seasonal export variation. For Forested and Rural-low respectively, 88.0% and 92.2% of NO_3^- export occurred during the wettest half of the sampling period, while it was just 68.5% and 67.8% for Urban-low and Urban-moderate respectively (Table 2). Across the developed catchments the NO_3^- export F75 increased with developed cover and developed feature density. Twenty five percent of NO_3^- export was attributed to 0.74%, 0.55%, and 0.35% of the highest flows for Rural-low, Urban-low, and Urban-moderate respectively. For Urban-moderate these flows correspond to just 20.5 hr of the 11.8-month sampling period. The forested catchment exhibited a threshold in export at flows around 20 mm/day where the percentage export increases dramatically across solutes (Figure 6).

Differences in the solute cumulative export distribution across flows suggest distinct sources of flow paths of N and C across the sampled catchments (Figures 6b–6d; Table 2). Patterns in NO_3^-, TDN and DOC export across flow are largely consistent within the Forested catchment which may support a common source of all solutes. However, at Rural-low the F75 for NO_3^- is 2.95 mm/day, while it is 10.45 mm/day for TDN, and 74.70 mm/day for DOC, indicating that higher flows facilitate the transport of TDN and especially DOC, relative to NO_3^-. At Urban-low, patterns in NO_3^- and TDN export across flows are largely consistent and have F75 values of 27.17 mm/day and 27.40 mm/day respectively, but the F75 of DOC is 35.14 mm/day, indicating that N sources are primarily transported by similar flows, but higher flows facilitate the transport of DOC.

3.4. Nitrate Sources

Stormflows mobilized and mixed a greater diversity of N sources than baseflows and across all study catchments there was much greater variation across stormflow samples than baseflow samples (Figure 7). The primarily forested catchment showed inter-storm baseflow isotopic values in the range reported for soil N, shifting toward greater contribution from NH_4^+ nitrification during stormflows (Figure 8, Table S2 in Supporting Information S1).

Table 2
Measurement and Metrics of Catchment Runoff and Export Dynamics

Metric	Units	Study WS ID				
		Forested	Rural-low	Rural-moderate	Urban-low	Urban-moderate
Runoff	mm/yr	141.12 ±2.96	297.42 ±7.90	450.41 ±8.44	371.15 ±8.40	565.68 ±6.18
Perc. runoff	%	11.10	23.38	35.49	29.18	44.72
Total NO3-N load	kg/km2/yr	15.51 ±0.74	68.18 ±2.05	119.40 ±2.19	85.93 ±2.32	116.08 ±1.49
Total TDN load	kg/km2/yr	60.61 ±2.3	136.14 ±3.30	209.99 ±4.03	160.28 ±3.68	–
Total DOC load	kg/km2/yr	3,092.85 ±44.24	2655.24 ±39.98	2262.13 ±59.63	2348.23 ±42.72	–
The flow at 75% of cumulative export						
NO3 F75	mm/day	67.01	2.95	–	27.17	49.11
TDN F75	mm/day	67.31	10.45	–	27.40	–
DOC F75	mm/day	74.91	74.70	–	35.14	–
Duration of sampling period accounting for top 25% of export						
Runoff	% duration	0.12	0.74	–	0.55	0.35
NO3	% duration	0.11	1.90	–	0.38	0.24
TDN	% duration	0.10	0.44	–	0.38	–
DOC	% duration	0.08	0.08	–	0.24	–
Slow-moving flow including baseflow and likely subsurface stormflow contribution to total export						
Runoff	%	52.41	71.99	77.78	58.13	66.05
NO3	%	50.27	75.84	78.94	55.26	61.31
TDN	%	50.64	70.14	75.43	53.02	–
DOC	%	51.45	54.06	57.44	43.10	–
Conservative baseflow parametrized to excluding event scale variation contribution to total export						
Runoff	%	18.04	50.74	60.43	44.06	54.9125
NO3	%	16.49	56.84	61.76	39.51	47.86
TDN	%	14.93	43.80	46.68	48.40	–
DOC	%	11.96	29.34	24.23	25.21	–
Inter-storm baseflow contribution to total export						
Runoff	%	11.17	55.21	53.34	46.15	57.85
NO3	%	9.45	62.91	62.72	40.47	50.92
TDN	%	8.17	53.10	52.17	38.55	–
DOC	%	3.45	28.38	26.88	21.95	–
Contribution to total export during the wettest half of the sampling period						
Runoff	%	87.81	87.10	–	63.63	66.68
NO3	% load	87.99	92.24	–	68.50	67.84
TDN	% load	88.51	91.38	–	64.86	–
DOC	% load	94.28	89.30	–	73.58	–

The rural septic served catchment (Rural-low) NO_3^- contribution from wastewater was dominant at baseflow and supplemented again by NH_4^+ nitrification during stormflows. The Urban-low and Urban-moderate catchments showed inter-storm baseflow isotopic values consistent with mixing of fertilizer/rain NH_4^+ nitrification, soil N,

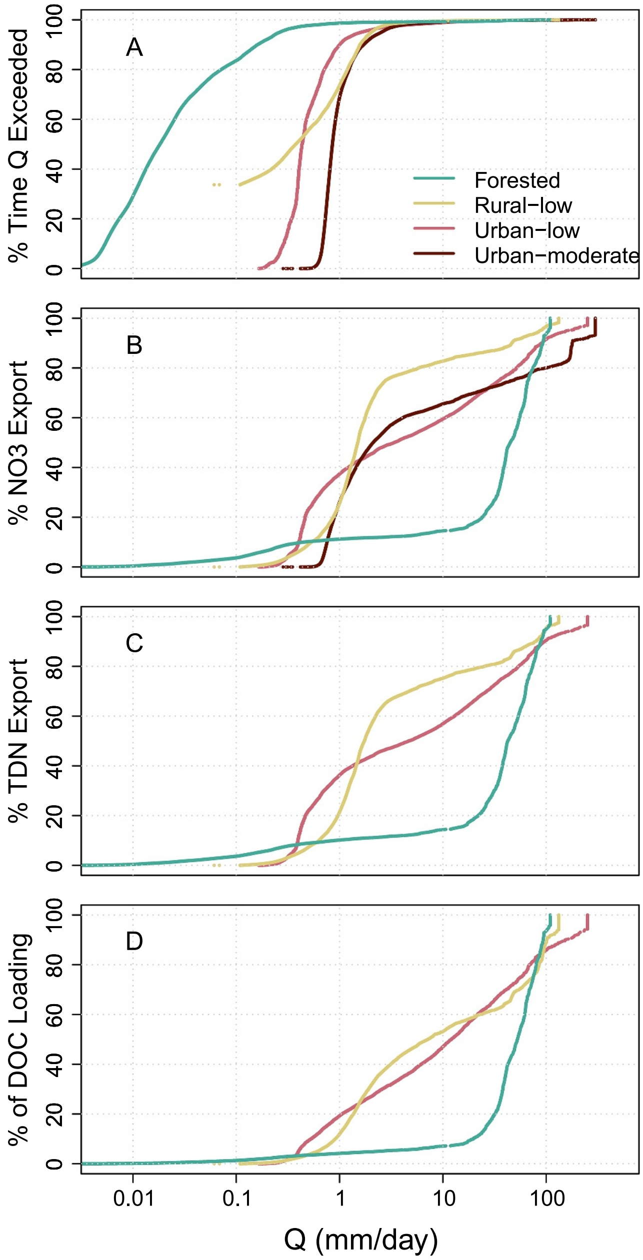

Figure 6. Cumulative flow duration (a) and cumulative percent nitrate (b), total dissolved nitrogen (c), and dissolved organic carbon export (d) across observed flows and the primarily forested (Forested), septic served (Rural-low), Urban-low, and Urban-moderate study catchments.

and wastewater. We cannot differentiate these sources with high confidence because they lie on the same mixing line. However, NO_3^- export from the urbanized catchments was four to six times greater than the forested catchments suggesting mixing of wastewater and fertilizers sources likely outweigh soil N. This is captured by the large range in the probability distribution of the source contribution for urban catchment soil N (Figure 8). Wastewater is the likely dominant NO_3^- source at Urban-low during baseflow with sources shifting toward greater contribution from fertilizers during stormflows. The more developed Urban-moderate catchment has a greater variation in isotopic values at baseflow than all other catchments, and greater likely baseflow contribution from fertilizers. While several stormflow samples had isotopic signatures reflecting atmospheric NO_3^-, particularly at Urban-moderate, these samples had very low concentration and the contribution to observed export was small, likely less than 8.8% across catchments (Figure 8). δ15N- NO_3^- values were generally negatively correlated to log normalized flow (Figure S6 in Supporting Information S1). These trends are consistent with a shift from wastewater and soil N dominated inter-storm baseflow to more widely mixed sources including surface sources such as atmospheric deposition and fertilizers (Figure 8).

3.5. Sampling Frequency Impact on Export Estimates

Seasonal discharge-concentration (QC) relationship based on 227–383 discrete baseflow and storm flow stream samples per catchment explained less than 31.0% of variation in concentration across study catchments and solutes (Table S1 in Supporting Information S1). By comparison, high frequency sensor measurements explained greater than 84.8% of the variation in concentration across catchments and solutes (Figure S1 in Supporting Information S1) demonstrating that the sensors were more accurate at estimating concentration and loading than using seasonal QC relationships. Averaged across all study catchments, seasonal QC estimated annual export deviated by ±16.7% from the high frequency in situ monitoring estimated export. Annual export estimates of NO_3^- and TDN based on seasonal QC relationships varied widely, between −19.2% and 33.4% of estimates obtained from high frequency monitoring for all catchments except Rural-low for which estimates generally agreed (2.5%–6.1%) (Table S1 in Supporting Information S1). Uncertainty in load estimation was on average 2.06 times greater for the QC method versus the high frequency monitoring. The deviation in both load estimation and the estimated uncertainty between the two methods was greatest for the most developed catchment (Urban-moderate).

4. Discussion

4.1. Land-Use Impacts on Solute Loading Across Flows

The magnitude and flow contribution of annual NO_3^-, TDN, and DOC loading varied greatly with development intensity and infrastructure use across the study gradient. Nitrogen loading generally increased with development intensity across the five study catchments, except for the rural developed catchment served by septic systems (Rural-moderate) which had the highest export of N per unit area (Figure 5). The export from Rural-moderate exceeded the export from both urban catchments. Previous research in the region which included these study catchments has shown that baseflow period nonpoint source N loading is not generally higher from septic served catchments relative to similar population density sewer served catchments in the region (Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022). The rural septic served catchments studied in Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al. (2022) generally had higher vegetative landcover to similar population density urban catchments and lower baseflow runoff which offset the impact of N enrichment of streamflow from wastewater. However, the high

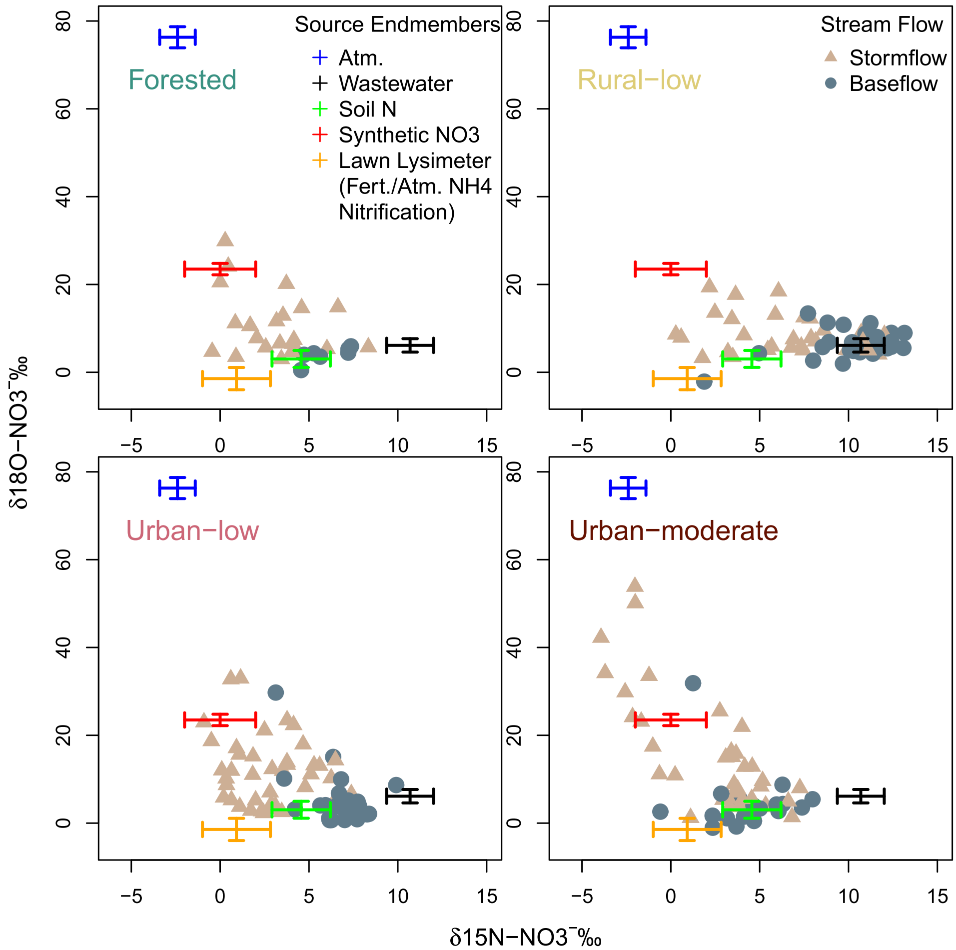

Figure 7. Nitrate isotope values for nitrate source endmembers and analyzed samples from the Forested, septic served (Rural-low), Urban-low and Urban-moderate catchments across inter-storm baseflow periods (gray circles) and stormflow periods (yellow triangles).

frequency monitored runoff from Rural-moderate was consistent with that of the urban catchments and paired with elevated stream N concentration, largely associate with wastewater (Figure 8), resulted in the highest N loading observed in this study. This suggests that nonpoint source loading from rural septic served catchments can exceed that of more developed catchments when runoff is not sufficiently mediated by ET demand.

Nitrogen export from the primarily Forested catchment was largely consistent with similar forested catchments in the region (Boggs et al., 2013, 2016) and deviated from the developed study catchments in magnitude, constituents, and timing. The Forested catchment exported between 29% and 44% of the TDN of the developed catchments and up to 74% of the loading was as DON. In contrast, the developed rural catchment which had similar forest cover and composition, but also housed a population consistent with the studied urban catchments, exported four times as much TDN, with the majority as NO_3^-. The percent of N export at baseflow was also much lower for Forested than the developed catchments, suggesting that forest cover can effectively transform and retain external N inputs during inter-storm baseflow periods when residence times are longest. However, the high N export from the similarly forested, but also developed rural catchment, suggests that anthropogenic inputs of N, alterations to hydrology, and impacts to ecosystem services can overwhelm the natural retention and removal capacity, even at low development intensity.

4.1.1. The Role of Baseflow and Subsurface Flow in Loading Across Development Intensity

Baseflow and slow-moving stormflows, likely traveling along subsurface flow paths, are likely responsible for most of the N loading across our study's low and medium development intensity catchments. These results are in

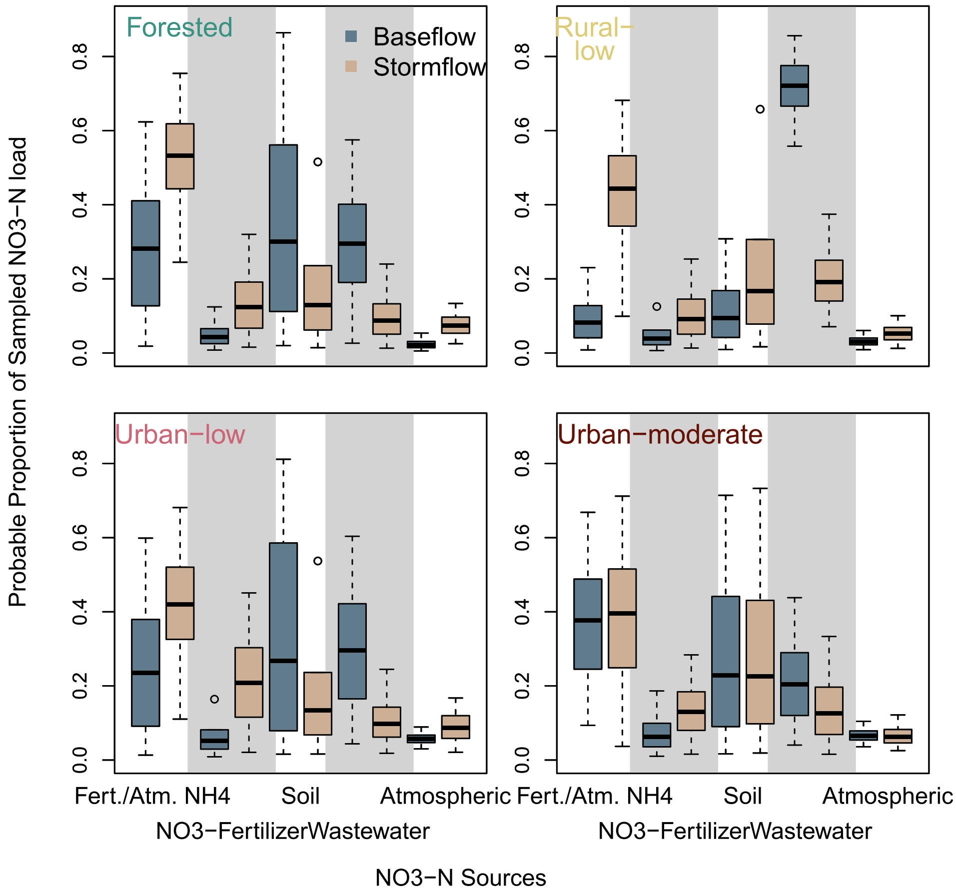

Figure 8. Boxplots of the probability distribution for the proportion by mass (load) of NO_3^--N sources for targeted grab sampling at the Forested, septic served (Rural-low), Urban-low and Urban-moderate catchments across inter-storm baseflow periods and stormflows.

general agreement with previous studies (Janke et al., 2014; Kincaid et al., 2020; Shields et al., 2008), but are informed by high frequency in situ measurement of N concentrations across a gradient of urban development intensity and infrastructure use. Up to 75% of TDN loading was derived from estimated subsurface flows at the septic served Rural-moderate catchment. The conservative baseflow estimate, with little inter-storm baseflow variation, suggests baseflows still contribute greater than 44% of TDN loading across all developed study catchments. This contribution represents the constant supply of N likely from groundwater and leaky infrastructure between and through events (Figure 1b). Inter-storm periods of baseflow account for greater than 39% of TDN loading across developed catchments. These inter-storm periods represent flows with the longest residence times and most easily mediated by stream restorations. Baseflows and subsurface stormflows are not addressed by surface water BMPs which are primarily targeted to mediate surface stormflows and may be exacerbated by infiltration-based designs that can increase subsurface flushing.

4.1.2. The Role of Extreme Flows

Estimated quick flow or stormflow runoff increased with development intensity across developed catchments as did the component of NO_3^- and TDN loading. All catchments were sensitive to rare high flows, but at the most developed study catchment (Urban-moderate) 25% of NO_3^- loading came from just 0.24% of the sampling period driven by the highest flows. In other terms, 25% of the annual nitrate load was delivered in a cumulative period of 21.3 hr. However, the analyzed sampling period excludes two tropical storms for which reliable data could not be obtained and the Urban-moderate catchment represents only moderate intensity development for the region (Delesantro et al., 2021, 2022), suggesting that even higher loading is possible from larger storms and more highly developed landscapes.

Although TDN loading from the primarily forested catchment was much lower than in the developed catchments, there is a striking threshold of around 20 mm/day above which solute export increases dramatically (Figure 6) and we hypothesize that catchment retention efficiency sharply declines. However, this result is contradictory to the work of Shields et al. (2008) which found that the F75 for a forested Piedmont catchment (Pond Branch) in Maryland, USA was lower than other developed catchments in the region. While Pond Branch was almost entirely forested, this study's Forested catchment contains several anthropogenic impacts including 2.6 km of roads and associated ditches, and the peak runoff observed was 100 mm/day, lower than for the study developed catchments, but an order of magnitude higher than the peak runoff at Pond Branch from 1998 to 2004. While further study is required, these results may indicate that even very low levels of development may be sufficient to generate rare extremes in loading which exceed catchment retention capacity. This may be increasingly important as climate change results in increased storm intensity which may mobilize nutrients previously retained at lower peak flows.

4.2. Solute Mobilization and Sources

Patterns in NO_3^-, TDN, and DOC loading across flow are largely consistent for the primarily forested catchment which suggests a common source of solutes across flows, likely soils. However, solute loading patterns vary significantly for developed catchments indicating that higher flows are required to mobilize DON and DOC relative to NO_3^-. This suggests that across the developed catchments there are disparate sources of NO_3^- and DON/DOC which are flushed by different flows. This is also supported directly by analysis of nitrate isotopes.

Across the studied developed catchments, the nitrate isotope mixing model results suggests that storm flows likely mobilized and mixed all potential NO_3^- sources while baseflow export was generally driven by wastewater (Rural and Urban-low) or a combination of fertilizer and wastewater (Urban-moderate). Stormflow in urbanized landscapes is generally thought to be driven by the rapid connection of surface runoff to streams by impervious cover and stormwater sewers. Previous studies of urbanized catchments have identified a nearly singular mixing line between a wastewater source endpoint and an atmospheric source endpoint across storm sampling (Divers et al., 2014; Guo et al., 2022; Kaushal et al., 2011). By comparison, our stormflow sampling captured greater variation along the NH_4^+ (fertilizers)—Soil N—wastewater mixing line (Figure 7) and although urban catchments were served by separate stormwater and sanitary sewers, the stormflow NO_3^- contribution from wastewater exceeded that from atmospheric deposition (Figure 8). Our results suggest that stormflow paths across our study's exurban and urban catchments are more complicated than routing from impervious surfaces to streams, and that stormflows can transport N sources from lawns, soil, and even subsurface sources like leaking sanitary infrastructure. Most of the developed landscape, locally and globally, is characterized by low to moderate population density and impervious cover (Angel et al., 2011; Delesantro et al., 2021; Dijkstra & Poelman, 2014; Richards, 2006; Seto et al., 2012) and across these catchments intermediate event throughflow is likely a major contributor to N export (Figure 1B).

4.3. High Frequency Monitored Loading Compared to Grab Sampled Estimates

We compared estimates of total NO_3^-, TDN, and DOC loading derived from high frequency in situ monitoring and seasonal discharge-concentration (QC) relationships derived from grab sampling. Our grab sampling consisted of 227–383 samples per catchment in a 2-year period, but even with a high density of baseflow and targeted storm samples, seasonal QC relationships only agreed with in situ monitoring of N loading for the septic served Rural-low catchment. The Rural-low catchment N loading was likely dominated by few sources (Figure 8), mainly wastewater, which may generate more consistent QC relationships relative to catchments with more dynamic solute sourcing. The failure of QC relationships to predict loading from small, urbanized catchments, even with substantial storm sampling, demonstrates the high temporal heterogeneity in loading and sources which is also captured by NO_3^- isotope analysis (Figure 7). Fazekas et al. (2020) similarly found that QC relationships informed by insufficient sampling frequency misclassified the transport versus source limitation status of catchments and our results demonstrate that high frequency monitoring is also necessary for accurate estimation of total annual loads, particularly in environments with several temporally variable N sources. Other regression methods for estimating loading based on grab samples may provide better estimates in specific cases (e.g., WRTDS, LOAD Est, etc.), but also have various limitations and additional research will be needed to comprehensively compare load estimation methods and monitoring for urbanized catchments.

4.4. Management Implications

This study suggests that across residential rural, low, and medium development intensity landscapes, most non-point source N is transported by baseflows and subsurface stormflows, but also demonstrates that rare high flows representing less than 1% of the sampling period, largely driven by surface runoff and increasing with development intensity, are responsible for over 25% of annual loading. These findings are illustrated in the conceptual figure (Figure 1). Subsurface flows in rural and low development intensity landscapes drive loading, particularly when these flows intersect subsurface sources of N such as septic systems or leaking sanitary sewers. High flows, and associated loading increases with development intensity as impervious cover and stormwater infrastructure redirect loads to streams across fast moving surface flow paths. However, even within the studied medium development intensity catchment most N was transported by baseflows and subsurface stormflows. Best management practices in developed catchments are generally built to address surface flows from stormwater (Delleur, 2003; Loperfido et al., 2014), but these BMPs will not mediate the loading from baseflows and subsurface stormflows. Our findings support the need for both baseflow and stormflow nutrient management. A holistic approach toward nutrient management should be taken in which SCMs curb flows and peak loads in support of targeted regional baseflow N management. Because 38%–63% of TDN loading occurs during inter-storm periods with longer residence times, effective mitigation of N throughout stream networks can address a significant portion of total loading. Because 55%–75% of TDN export is transported by baseflow and subsurface pathways, effective placement of upland green spaces and maintenance or restoration of bottomlands and riparian zones to promote vegetation uptake and denitrification can address an even larger portion of N loading. For the restoration of streams, bottomlands, and riparian zones to be sustainable, erosive, and scouring peak flows must be reduced (Bernhardt et al., 2008). Mediating baseflow loading at the source could be accomplished by reducing fertilizer inputs or addressing sanitary infrastructure through rehabilitation or retrofit focused on infrastructure in wet areas of the landscape (Delesantro, Duncan, Riveros-Iregui, Blaszczak, et al., 2022) and conversion of septic systems to sanitary sewer systems. However, stormflows mobilize and mix all sources with no clear primary source (Figures 7 and 8).

5. Conclusions

In this study we answered three primary questions. First, we asked what is the relative role of baseflow loading versus stormflow loading across a gradient of development intensity and sanitary infrastructure? The findings of this study demonstrate that baseflows and subsurface flows can contribute a greater portion of total solute loading than surface stormflows in the most expansive low and moderate development intensity catchments. These loads are not treated by surface water BMPs primarily targeted to manage stormflows. However, these lower flows may be more amenable to enhanced retention measures, including green infrastructure in the terrestrial phase, and stream and riparian restoration. Although subsurface flow paths dominated total dissolved N delivery, the contribution of rare high flows generally increased with development intensity and short periods accounted for outsized contributions to total annual loading. To support restorations addressing loading over the full flow regime, stormflows must be curbed to prevent stream channel degradation and resulting loss of retention.

Next, we asked how nitrate source change across flows. Stormflows mobilized and mixed a wide diversity of NO3- sources, in stark contrast to baseflow sources which were fewer and more consistent in time. The diversity of N sources demonstrated that in the studied low to moderate development intensity catchments, surface flows, throughflow, and baseflow were all significant contributors to storm event loading. The evaluation of N source export across flow conditions may allow researchers to further parse flow paths and allow more targeted management intervention. We sampled five storms for isotopic analysis. While this was sufficient to reveal clear trends between catchments, additional data will be necessary to determine drivers of event-to-event variation in N sources.

Finally, we evaluated the sensitivity of loading estimates to concentration observation method and temporal resolution. Loading estimated by seasonal discharge-concentration relationships of stream grab samples rarely agreed with the in situ monitoring. High frequency monitoring in urban environments may be necessary to capture rapidly shifting loading dynamics of mixed N sources. The ability to accurately assess loads across all flows and seasonal conditions without several years of monitoring can allow managers to address water quality issues more quickly and efficiently.

Data Availability Statement

The data supporting the analyses and results of this paper are publicly available on HydroShare (Delesantro, Duncan, Riveros-Iregui, & Band, 2022) and geospatial data can be found in previous publications and associated materials (Delesantro et al., 2021, 2022).

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