AGU PUBLICATIONS

Water Resources Research

RESEARCH ARTICLE

10.1002/2015WR017753

Quantifying watershed-scale groundwater loading and in-stream fate of nitrate using high-frequency water quality data

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Key Points:

- Daily groundwater and runoff N loads and in-stream retention are quantified from nitrate sensor data
- Groundwater contributes greater than half of the annual N load to the streams
- Ten to twenty-five percent of the annual N load is retained by the in-stream environment

Supporting Information:

- Supporting Information S1

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Citation:
Miller, M. P., A. J. Tesoriero, P. D. Capel, B. A. Pellerin, K. E. Hyer, and D. A. Burns (2016), Quantifying watershed-scale groundwater loading and in-stream fate of nitrate using high-frequency water quality data, *Water Resour. Res.*, *52*, 330–347, doi:10.1002/2015WR017753.

Received 26 JUN 2015
Accepted 22 DEC 2015
Accepted article online 28 DEC 2015
Published online 17 JAN 2016

Abstract We describe a new approach that couples hydrograph separation with high-frequency nitrate data to quantify time-variable groundwater and runoff loading of nitrate to streams, and the net in-stream fate of nitrate at the watershed scale. The approach was applied at three sites spanning gradients in watershed size and land use in the Chesapeake Bay watershed. Results indicate that 58–73% of the annual nitrate load to the streams was groundwater-discharged nitrate. Average annual first-order nitrate loss rate constants (k) were similar to those reported in both modeling and in-stream process-based studies, and were greater at the small streams (0.06 and 0.22 day^{-1}) than at the large river (0.05 day^{-1}), but 11% of the annual loads were retained/lost in the small streams, compared with 23% in the large river. Larger streambed area to water volume ratios in small streams results in greater loss rates, but shorter residence times in small streams result in a smaller fraction of nitrate loads being removed than in larger streams. A seasonal evaluation of k values suggests that nitrate was retained/lost at varying rates during the growing season. Consistent with previous studies, streamflow and nitrate concentrations were inversely related to k. This new approach for interpreting high-frequency nitrate data and the associated findings furthers our ability to understand, predict, and mitigate nitrate impacts on streams and receiving waters by providing insights into temporal nitrate dynamics that would be difficult to obtain using traditional field-based studies.

1. Introduction

Human activities such as food and energy production have resulted in a substantial increase in the amount of nitrogen (N) circulating in the biosphere [*Vitousek et al.*, 1997; *Galloway et al.*, 2008; *Schlesinger*, 2009] and delivered to watersheds where terrestrial and aquatic biogeochemical processes alter N concentrations and form. A net impact of increased N loading to groundwater [*Puckett et al.*, 2011] and surface water [*Howden et al.*, 2010] is the eutrophication of coastal waters [*Scavia et al.*, 2006; *Turner et al.*, 2006; *Mulholland and Webster*, 2010; *Testa et al.*, 2014]. For example, the delivery of N—along with phosphorus and sediment—has resulted in significant seasonal hypoxia in the Chesapeake Bay, which in turn has resulted in considerable investments into restoration activities.

To mitigate the impacts of N—particularly nitrate, which is often the dominant form of N—on streams and receiving waters, there is a need to quantify the time-variable loadings of nitrate to streams, and identify the temporal and spatial variability of the in-stream fate of nitrate. While field-based studies [*Burns*, 1998; *Peterson et al.*, 2001; *Duff et al.*, 2008; *Mulholland et al.*, 2008, 2009; *Tank et al.*, 2008; *Hall et al.*, 2009; *Mulholland and Webster*, 2010] and modeling approaches [*Jaworski et al.*, 1992; *Boynton et al.*, 1995; *Alexander et al.*, 2000, 2009; *Seitzinger et al.*, 2002; *Boyer et al.*, 2006; *Runkel*, 2007; *Ator and Denver*, 2012] have provided much needed information on reach and watershed-scale nitrate dynamics, the limited spatial extent and/or low temporal resolution of discrete data collection continues to be a challenge for quantifying loads and interpreting drivers of change in watersheds. Recent studies have demonstrated that the collection and interpretation of high-frequency nitrate data collected using water quality sensors can be used to better quantify nitrate loads to sensitive stream and coastal environments [*Ferrant et al.*, 2013; *Bieroza et al.*, 2014; *Pellerin et al.*, 2014], and provide insights into temporal nitrate dynamics that would otherwise be difficult to obtain using traditional field-based mass balance, solute injection, and/or isotopic tracer studies [*Pellerin et al.*, 2009, 2012; *Heffernan and Cohen*, 2010; *Sandford et al.*, 2013; *Carey et al.*, 2014; *Hensley et al.*,

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Table 1. Watershed Size, Land Use, Streamflow, Nitrate Concentrations and Loads, and In-Stream Reaction Rates for Water Year 2013 at the Three Study Sites

	Potomac River	Smith Creek	Difficult Run
Drainage Area (km^2)	29,950	250	150
Land Use[a]			
Developed (%)	10	9	51
Forest (%)	59	45	41
Agriculture (%)	30	46	3
Streamflow			
Average streamflow (m^3/s)	330	1.9	1.6
Average base flow index (fraction)	0.75	0.78	0.67
Nitrate			
Average [NO_3] (mg/L as N)	1.1	2.2	1.4
Groundwater-discharged end-member[NO_3](mg/L as N)	1.8 ± 0.1	2.9 ± 0.1	2.1 ± 0.1
Runoff end-member [NO_3] (mg/L as N)	1.1 ± 0.04	1.6 ± 0.1	0.8 ± 0.1
Watershed-Scale Loads[b]			
Nitrate load delivered to stream (kg/yr as N)	1.6×10^7	1.5×10^5	6.4×10^4
Groundwater-discharged nitrate load (kg/yr as N)	1.1×10^7 (69%)	1.1×10^5 (73%)	3.7×10^4 (58%)
Runoff nitrate load (kg/yr as N)	4.9×10^6 (31%)	3.9×10^4 (27%)	2.7×10^4 (42%)
Watershed-Scale In-Stream Reaction Rates[c]			
Average reaction rate constant (k, day^{-1})	0.05 ± 0.05	0.06 ± 0.05	0.22 ± 0.14
Average nitrate load retained/lost in the stream (%)	23	11	11

[a]Land use data are from the 2006 National Land Cover Data (http://www.mrcl.gov).
[b]These are the loads predicted to be discharged to the stream prior to being influenced by in-stream processes. The fraction of the total load delivered to the stream from the end-member (groundwater-discharged nitrate or runoff nitrate) is given in parentheses.
[c]Average reaction rate constants and percent of nitrate load retained/lost in-stream were calculated using only data for days on which in-stream nitrate concentrations were measured.

2014, 2015; *Outram et al*., 2014; *Crawford et al*., 2015]. Coupling these measurements with techniques for quantifying water sources and/or flow paths [*Gilbert et al*., 2013; *Bowes et al*., 2015; *Duncan et al*., 2015] provides further opportunity for understanding and managing the drivers of coastal eutrophication.

In this study, we describe a new approach for quantifying time-variable loadings of groundwater-discharged and runoff nitrate from three diverse sites in the Chesapeake Bay watershed by coupling high-frequency nitrate data with hydrograph separation techniques. In addition, these data are used to describe the retention or loss of nitrate in the river network and the hydrologic, chemical, and climatic conditions related to the net in-stream fate of nitrate at the watershed scale. Quantifying time-variable nitrate loading from groundwater and runoff, along with the retention of those loads in the drainage network, will help improve our understanding of N loads to receiving waters and therefore better inform best management practices to reduce them.

2. Methods

2.1. Study Areas and Data Collection

Three sites within the Potomac River watershed (a subwatershed within the Chesapeake Bay watershed) that span gradients in watershed size and land use were included in this study (Table 1 and Figure 1). The Potomac River (United States Geological Survey (USGS) gage 01646500) is a large river (seventh order) that drains an area of $\sim$30,000 km^2, and represents a mixed land use basin. Smith Creek (USGS gage 01632900), a predominantly agricultural watershed, and Difficult Run (USGS gage 01646000), an urban watershed, are third and fourth-order streams that drain areas of 250 and 150 km^2, respectively. There are multiple sources of N to these watersheds. For example, a Spatially Referenced Regression on Watershed attributes (SPARROW) model estimated that of the total nitrogen load at the Potomac River in 2002, 7% was from point sources, 11% from urban sources, 51% from fertilizer application and fixation by crops, 13% from manure, and 18% from atmospheric deposition [*Ator et al*., 2011]. The same model estimated that $<$1% of the total nitrogen load at Smith Creek and Difficult Run was from point sources, and there are no known point sources discharging to the study streams near the measurement locations. On average, 70–80% of the total nitrogen in the study streams is nitrate.

High-frequency nitrate sensor measurements were made at all sites at 15 min intervals during the study period (water year 2013—1 October 2012 to 30 September 2013) with Submersible Ultraviolet Nitrate

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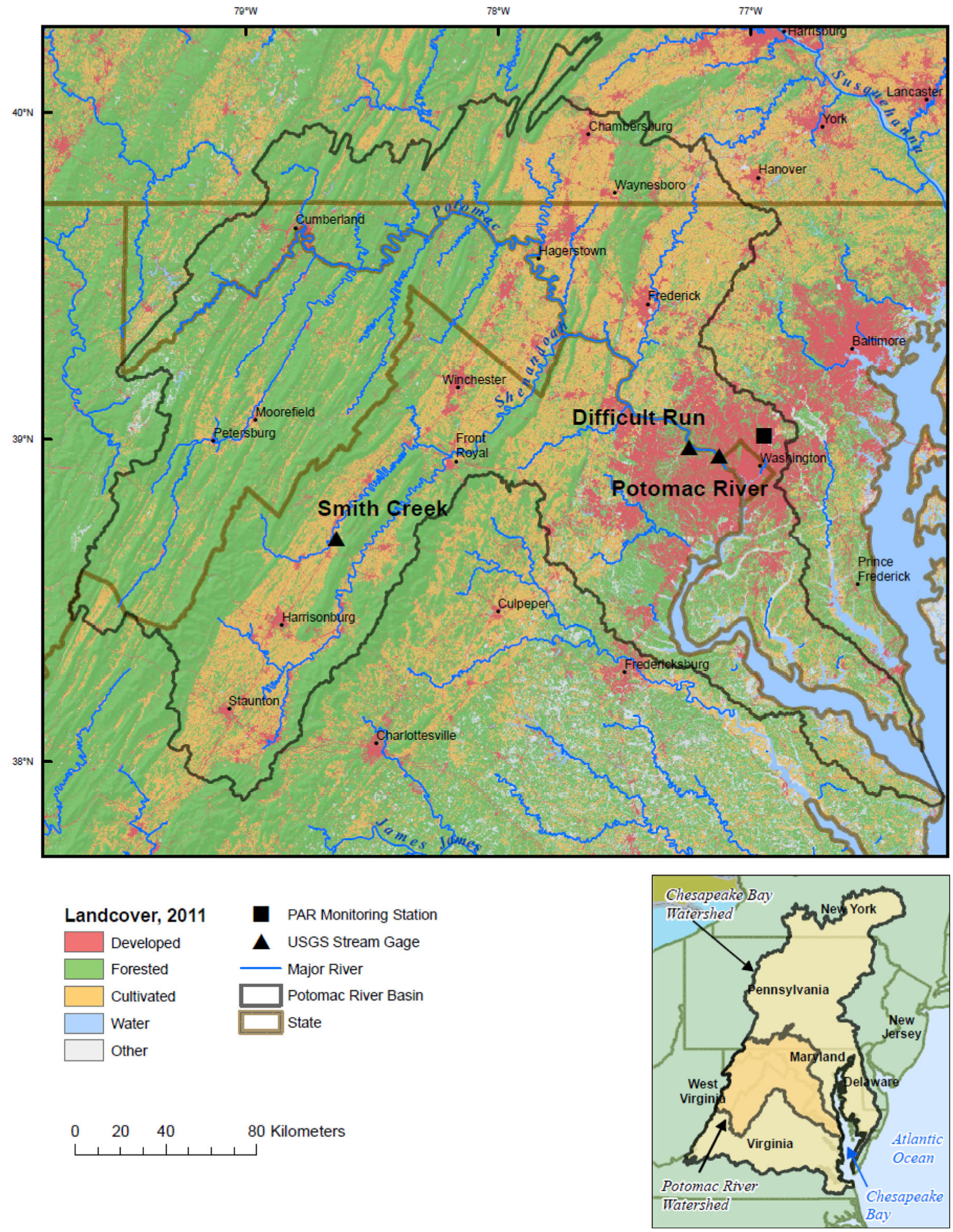

Figure 1. Map showing the locations of the sampling sites and the photosynthetically active radiation (PAR) monitoring station. The inset shows the location of the Chesapeake Bay and Potomac River watersheds in the northeastern U.S. Land cover data from *Homer et al*. [2015].

Analyzers (SUNA) with a 10 mm optical path length (Version 1; Satlantic, Nova Scotia, Canada). There were days with missing nitrate values at all sites, and analyses of the nitrate data were conducted only on those days with available data. High-frequency temperature measurements were also measured at all three sites, and high-frequency dissolved oxygen measurements were made at Smith Creek and Difficult Run during

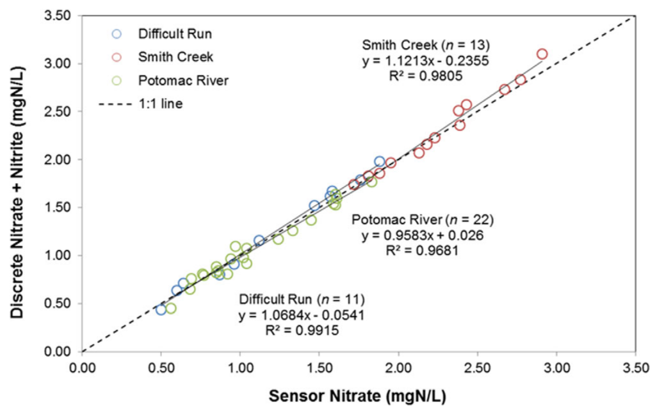

Figure 2. Relationship between nitrate concentrations measured in the laboratory from discrete water quality samples and concentrations measured by the in situ sensors at Potomac River, Smith Creek, and Difficult Run.

the study period using a luminescent-based sensor (6-Series YSI 6150 ROX, Yellow Springs, OH). In the Potomac River, the SUNA was mounted on an instrument cage and deployed vertically on a fixed I-beam. At Smith Creek, the SUNA was mounted to exposed bedrock in the approximate center of the stream channel. At the Difficult Run site, the SUNA was attached to a boulder on the right edge of the stream bank that extended out into the stream flow. All instruments were equipped with an external nylon brush wiper (Zebra-Tech, New Zealand) that cleaned the optical windows prior to every sampling interval. Nitrate sensor performance was checked prior to and during field deployments as explained in *Pellerin et al*. [2013]. Briefly, this includes blank and standard checks, as well as comparison to discrete samples collected at or near the site. Reported SUNA accuracy (0.03 mgN/L or 10% of the reading, whichever is greater) and precision (0.0028 mgN/L) are based on the manufacturers specifications. The SUNA was operated in freshwater mode (i.e., without bromide temperature compensation). In situ nitrate concentrations were measured by the SUNA at a sampling rate of ~1 Hz over a short burst window at each sampling interval, which typically resulted in ~20 measurements of nitrate concentrations per burst that were averaged on the SUNA or an external data logger. Additional information that describes the burst variability and spectral data such as the root-mean-square error (RMSE) of the algorithm fit were used to flag erroneous data from the time series when available. While the SUNA does not explicitly account for absorbance by nitrite in the range of 210–220 nm, the concentration of nitrite is almost always negligible in surface waters and has little effect on reported concentrations in most surface waters. Therefore, we refer to the sensor measurements as nitrate in units of mg/L as N.

Depth and width-integrated discrete water quality samples were collected at the same location as the sensor at Smith Creek and Difficult Run, but were collected approximately 1.5 km downstream of the sensor on the Potomac River at Chain Bridge (USGS gage 01646580). Samples were filtered and stored at 4°C until analyzed at the USGS National Water Quality Laboratory for major ions and for nitrate plus nitrite using the enzymatic reduction method [*Patton and Kryskalla*, 2011]. A regression of depth and width-integrated discrete nitrate plus nitrite concentrations with sensor nitrate concentrations on 11–22 dates shows that the two were strongly correlated ($r^2 = 0.97$–0.99) across a range of flow conditions at all three sites (Figure 2). Sensor bias relative to laboratory measurements were corrected as described in *Pellerin et al*. [2013]. This is the primary step in our postprocessing, as burst data and metadata (such as the fitting parameter) are used in real-time to assure high data quality.

Fifteen minute streamflow data for each site for water year 2013 and long-term mean annual streamflow data were obtained from the U.S. Geological Survey (USGS) National Water Information System database (http://nwis.waterdata.usgs.gov/nwis). Fifteen minute streamflow and water quality data were averaged to generate daily mean streamflow (hereafter Q_{Stream}), nitrate concentration (hereafter $[NO_3]_{Stream}$), and temperature values. While the averaging approach results in the loss of information at time steps less than 1 day, using daily mean values is likely adequate for assessing patterns in in-stream data over extended time periods, such as the 1 year duration of this study. Further, the averaging approach, which uses the 15 min sensor data to generate daily mean values, provides daily values that are true daily means, and more accurately represent the system than daily values obtained from other commonly applied approaches, such as daily grab samples obtained by automatic samplers. All samples were collected and processed using established USGS protocols [*U.S. Geological Survey*, 2014]. Photosynthetically active radiation (PAR) data collected at the U.S. Department of Agriculture UV-B monitoring and Research Program, Beltsville, MD (tp://uvb.nrel.colostate.edu/UVB/index.jsf) site were used as estimates of PAR at all three sampling sites (Figure 1), and as a potential predictor variable in regression models relating environmental characteristics to in-stream nitrate reaction rate constants (see below for detailed description of regression modeling).

2.2. Hydrograph Separation

There are many approaches for graphical hydrograph separation which rely on streamflow data alone to separate the hydrograph into base flow and runoff components, including, for example, HYSEP [*Sloto and Crouse*, 1996], PART [*Rutledge*, 1998], and Eckhardt's recursive digital filter method [*Eckhardt*, 2005]. Tracer mass balance methods [*Pinder and Jones*, 1969], which rely on streamflow data and concentrations of chemical constituents in the stream, are also commonly used to separate hydrographs, and are often considered to be more objective than graphical hydrograph separation approaches [*Stewart et al*., 2007; *Zhang et al*., 2013; *Miller et al*., 2015]. We applied a graphical hydrograph separation approach to estimate base flow and runoff because the conductivity of stream water in the study streams is likely altered by application of road salts during high flow conditions in the winter months [*Sanford et al*., 2011], thereby limiting the use of a tracer mass balance approach to estimate base flow and runoff at these sites.

Quantifying base flow and runoff contributions to streamflow is difficult and values can depend on the method used. While true values of base flow and runoff are unknown, the recursive digital filter method is a stable, reproducible, and objective method of base flow separation when compared to smoothed minima methods [*Nathan and McMahon*, 1990] and has been used for national assessments of base flow [*Santhi et al*., 2008]. Eckhardt's recursive digital filter method [*Eckhardt*, 2005] was found to be the most hydrologically plausible of seven commonly used graphical hydrograph separation methods [*Eckhardt*, 2008]. The *Eckhardt* [2005] digital filter can be described as follows:

$$b_i=\frac{(1-\beta)\propto b_{i-1}+(1-\propto)\beta Q_{Stream}}{1-\alpha\beta} \quad (1)$$

where b is estimated base flow at time step i, α is the recession constant, which is objectively defined using recession analysis [*Nathan and McMahon*, 1990], and β is the long-term ratio of base flow to total streamflow. This approach assumes that the outflow from an aquifer is linearly proportional to its storage, and may overestimate base flow in large watersheds because of longer travel times to the catchment outlet resulting in dispersion of runoff peaks. Nonetheless, it has been shown that the linear model is generally a good approximation [*Chapman*, 1999] for recessions of duration up to about 10 days. α was defined for the study streams using the RECESS program [*Rutledge*, 1998] with the minimum number of days required to detect a recession period set to 10, and using only the linear segments of the recession limbs. Until recently, β has been defined a priori based on the dominant geological characteristics of the watershed [*Eckhardt*, 2005]. *Collischonn and Fan* [2013] described an objective backward filtering approach which uses streamflow data to define β. For these reasons—the finding that the Eckhardt approach is the most hydrologically plausible graphical hydrograph separation method and the ability to objectively estimate α and β from measured streamflow data—we chose to use Eckhardt's recursive digital filter [*Eckhardt*, 2005] with the backward filtering approach of *Collischonn and Fan* [2013] as a simple and objective approach for separating the stream hydrograph into base flow and runoff at a daily time step. The base flow index (BFI) was calculated as the ratio of base flow to streamflow. Base flow (b) and runoff ($Q_{Stream} - b$) estimates served as proxies for groundwater and runoff discharge to the stream, respectively, and are hereafter referred to as groundwater discharge (Q_{GWD}) and runoff discharge (Q_{RO}). Lumping of many different flow paths into these two end-members is a simplification of the system, necessitated by the long duration of the study period and varying sizes of the watersheds. Groundwater discharge represents multiple slowly varying subsurface flow paths that contribute to stream discharge, whereas runoff discharge represents multiple rapidly varying flow paths that contribute to the stream, including shallow lateral subsurface flow.

2.3. Groundwater-Discharged Nitrate Loads

In this study, we define the in-stream environment as including the stream channel and the proximal subsurface and surface environments (e.g., hyporheic and riparian zones), whereas we define the terrestrial environment as comprising the distal subsurface and surface portions of the watershed. $[NO_3]_{Stream}$ provides an integrated signal of all sources of nitrate to the stream (e.g., agricultural fertilizer/manure, atmospheric deposition, etc.) that have undergone biogeochemical processing in the terrestrial and in-stream ecosystems within the watershed. We assumed that in-stream processing of nitrate was minimal during winter, an assumption that is supported by the data presented below and numerous studies that have shown positive relationships between N processing and temperature [*Holmes et al.*, 1996; *Strauss et al.*, 2002; *Schaefer and Alber*, 2007; *Starry et al.*, 2005]. In turn, $[NO_3]_{Stream}$ during winter provides an integrated signal of all sources of nitrate to the stream that have undergone terrestrial biogeochemical processes such as nitrification, denitrification, and assimilatory uptake, but prior to any in-stream biogeochemical processing. Therefore, site-specific linear-regression equations defining the relationship between $[NO_3]_{Stream}$ and BFI during winter were used to differentiate between and approximate the concentrations of nitrate discharged to the in-stream environment from the terrestrial environment as groundwater ($[NO_3]_{GWD}$) and runoff ($[NO_3]_{RO}$). $[NO_3]_{GWD}$ and $[NO_3]_{RO}$ represent end-member concentrations that were estimated by setting BFI = 1.0 and BFI = 0.0, respectively, in the regression equations that define the line of best fit during winter at each site, and were assumed to be temporally invariant. This assumption and potential implications are discussed below. The daily load of groundwater-discharged nitrate to the stream was calculated as the product of daily Q_{GWD} and $[NO_3]_{GWD}$. Similarly, daily Q_{RO} was multiplied by $[NO_3]_{RO}$ to estimate the daily load of runoff nitrate to the stream.

2.4. In-Stream Fate of Nitrate

The sum of groundwater-discharged and runoff nitrate loads represents the sum of all sources of nitrate to the streams, and reflects the mass of nitrate discharged to the stream after terrestrial biogeochemical processes have taken place, but prior to any in-stream biogeochemical processing. The in-stream fate of nitrate was quantified by comparing the estimated input nitrate concentration to the stream ($[NO_3]_{in}$) from groundwater discharge and runoff with the measured nitrate concentration in the stream ($[NO_3]_{Stream}$) and assuming first-order kinetics [*Alexander et al.*, 2009]. $[NO_3]_{in}$ was estimated at a daily time step as:

$$\left[NO_3^-\right]_{in}=\frac{\left[NO_3^-\right]_{GWD}Q_{GWD}+\left[NO_3^-\right]_{RO}Q_{RO}}{Q_{Stream}} \tag{2}$$

Average watershed-scale first-order reaction rate constants (k; units of day^{-1}) were quantified at a daily time step as:

$$k=-\frac{\ln\left(\frac{\left[NO_3^-\right]_{Stream}}{\left[NO_3^-\right]_{in}}\right)}{t} \tag{3}$$

where t (day) is average watershed-scale travel time (described below). Positive values of k indicate net average watershed-scale in-stream retention/loss and negative values indicate net average watershed-scale export. Note that when k is positive, it is not possible to differentiate between permanent loss of nitrate from the system via denitrification or retention via assimilatory uptake; hence the use of the term, "net in-stream retention/loss." Similarly, when k is negative, it is not possible to identify the specific process contributing to net export, which may include nitrification, mobilization of nitrate from the hyporheic zone, or a decrease in biotic uptake.

Average watershed-scale travel times were estimated at a daily time step for water year 2013 at each site. Reach-scale estimates of length, mean annual streamflow, and drainage area were obtained from the 1:100,000-scale national hydrography data set (NHD; http://www.horizon-systems.com/NHDPlus/index.php). This data set includes 12,155 reaches upstream of the gage on the Potomac River, 25 reaches upstream of the gage on Smith Creek, and 94 reaches upstream of the gage on Difficult Run. The ratio of the reach-scale mean annual streamflow (from NHD) to the annual mean streamflow measured at the gage was calculated for each reach. This reach-specific ratio was then multiplied by the daily mean streamflow measured at the gage on each day of the year to provide estimates of daily streamflow for each reach. Water velocity estimates in each reach for each day of the year were determined from the reach-scale estimates of daily streamflow and drainage area using the equation developed by *Jobson* [1997]:

$$v=0.02+0.051x\ (D_a)^{0.821}x\ \left(\frac{Q}{Q_a}\right)^{-0.465}x\frac{Q}{D} \tag{4}$$

where v is daily velocity (m s^{-1}), Q is daily discharge (m^3 s^{-1}), Q_a is the mean discharge (m^3 s^{-1}) for the period of record, D is drainage area (m^2), and D_a is the dimensionless drainage area defined as:

$$D_a = \frac{D^{1.25}\sqrt{g}}{Q_a} \tag{5}$$

where g is the acceleration of gravity (m s^{-2}). Daily travel times for each reach were calculated as reach length divided by estimated daily water velocity times 0.5 (one half of the reach travel, which is the expected mean travel time for a single reach) [*Alexander et al*., 2009]. A network node-navigation algorithm was used to sum the daily travel times along the flow path from each reach to the downstream watershed outlet, thus providing a distribution of the expected travel times within the watershed for each day. The mean and standard deviation of each daily distribution of travel times for all reaches in each watershed were calculated first, from which overall estimates of the average daily watershed-scale travel time and variability in travel time were then determined. Limitations to this approach for estimating travel time and subsequently average watershed-scale k values include the assumptions that the ratios of the reach-scale mean annual streamflow to the annual mean streamflow measured at the gage are constant across a range of streamflow values, that there are no lags between flow conditions at a given reach and flow conditions measured at the downstream gage, and that nitrate sources are distributed uniformly throughout the watershed. Nonetheless, this approach provides a means to account for the effects of differences in stream network geometry and hydrologic conditions on the spatial and temporal variability in travel times and reaction rates present in each watershed.

2.5. Statistical Methods

The nonparametric Wilcoxon rank-sum test [*Wilcoxon*, 1945] was used to compare differences in nitrate reaction rate constants among seasons. Multiple linear-regression models were developed for each site to describe the relationship between daily k estimates (response variable) and Q_{Stream}, $[NO_3]_{Stream}$, stream temperature, and PAR. A natural logarithm transformation was applied to all explanatory variables so that the data approximated normal distributions. The regression models are specific to each site, and are not intended as predictive tools, but rather as a means to provide insight into the nature of the relationship between the response and explanatory variables. Kendall's tau correlation coefficients (τ) [*Kendall*, 1975] and Kendall-Theil lines [*Theil*, 1950] were generated to describe the relationships between k and daily variability in dissolved oxygen concentration. All statistical analyses were conducted using R (http://r-project.org).

The errors in daily estimates of $[NO_3]_{in}$, groundwater-discharged nitrate loads, and k values were estimated using the root-mean-square error propagation approach [*Topping*, 1972]. The addition/subtraction (equation (6)) or multiplication/division (equation (7)) rules were used individually or in combination as required for error propagation:

$$E_P = \sqrt{\left(E_a^2 + E_b^2 + E_n^2\right)} \tag{6}$$

$$E_P = \sqrt{\left(\frac{E_a}{a}\right)^2 + \left(\frac{E_b}{b}\right)^2 + \left(\frac{E_n}{n}\right)^2} \tag{7}$$

where E_P is the probability range in error, n is the number of sources of error, and a. . .n are the potential sources of error.

Potential sources of error in $[NO_3]_{in}$ include errors associated with the estimation of $[NO_3]_{GWD}$, $[NO_3]_{RO}$, Q_{GWD}, and Q_{RO} as well as errors in Q_{Stream} measurements. Errors associated with $[NO_3]_{GWD}$ and $[NO_3]_{RO}$ were obtained from the standard errors associated with the regression model used to describe the relationship between $[NO_3]_{Stream}$ and BFI during winter. Errors associated with Q_{GWD} and Q_{RO} were obtained following the approach of *Eckhardt* [2012]. Specifically, the sensitivity values for the α and β parameters used in the estimation of Q_{GWD} and Q_{RO} were calculated and multiplied by the relative error in each parameter. The relative errors of α and β are unknown, and were assumed to be 10%. We believe this to be a conservative estimate of relative errors because both parameters were calculated using measured streamflow data. Errors in Q_{Stream} measurements were assumed to be 5%, which is also a conservative estimate [*Sauer and Meyer*, 1992].

Potential sources of error in estimated groundwater-discharged nitrate loads include errors associated with $[NO_3]_{GWD}$ and Q_{GWD}. Errors associated with these variables were defined as described above. The error in the annual groundwater-discharged nitrate load was calculated by taking the square root of the sum of the squared daily groundwater-discharged load error estimates (i.e., quadrature).

Potential sources of error in k include errors associated with $[NO_3]_{Stream}$, $[NO_3]_{in}$, and travel time. Using the 30 s sensor burst measurements from the sensor at the Potomac River (burst data are not available at Smith Creek and Difficult Run), the average percent error in $[NO_3]_{Stream}$ was calculated to be 0.5%. Given the low-percent error from the burst data at the Potomac River and the fact that the same model of nitrate sensors were deployed at all three sites, an error of 0.5% was assumed for errors associated with $[NO_3]_{Stream}$ at all sites. Errors associated with $[NO_3]_{in}$ were calculated as described above. The error in travel time was obtained from the standard deviation associated with the travel time estimates.

3. Results and Discussion

3.1. Patterns in Streamflow and Nitrate Concentrations

Average streamflow for water year 2013 was greater at the Potomac River (330 m^3/s) than at Smith Creek and Difficult Run (1.9 and 1.6 m^3/s, respectively), and was 102%, 90%, and 84% of the long-term mean annual streamflow at these sites, respectively. The period of record used to calculate long-term mean annual streamflow values was 1930 to present at the Potomac River, 1960 to present at Smith Creek, and 1935 to present at Difficult Run. All three sites are groundwater dominated, as indicated by annual mean BFI values of 0.75 (Potomac River), 0.78 (Smith Creek), and 0.67 (Difficult Run; Table 1). These estimates compare favorably with BFI estimates (generated using PART) [*Rutledge*, 1998] of 0.73 at Smith Creek and 0.58 at Difficult Run for the period March 2007 to August 2008 [*Sanford et al*., 2011]. The parameters used for hydrograph separation (see equation (1)) at the Potomac River, Smith Creek, and Difficult Run, respectively, were $\alpha = 0.973$, 0.980, 0.980 and $\beta = 0.655$, 0.632, and 0.406. Q_{GWD} was nearly equal to Q_{Stream} at all sites during low flow conditions, but accounted for a smaller fraction of streamflow during high flow events (Figure 3). The annual mean nitrate concentration at the agricultural stream—Smith Creek—was greater (average of 2.2 mg/L as N) than at the Potomac River and Difficult Run (1.1 and 1.4 mg/L, respectively; Table 1). Daily in-stream nitrate concentrations were variable over time and among sites during water year 2013, with short-term changes in response to high flow events (generally dilution), and longer-term seasonal changes, including generally higher concentrations during the winter months (Figure 3).

3.2. Groundwater-Discharged Nitrate Loads

The BFI is a measure of the relative contribution of groundwater and runoff discharge, and can be used to quantify the associated nitrate in groundwater and runoff end-members discharging to the stream. In a hypothetical setting, where $[NO_3]_{GWD}$ and $[NO_3]_{RO}$ are stationary over time, $[NO_3]_{GWD}$ is greater than $[NO_3]_{RO}$, and there are no effects of in-stream processing (i.e., conservative behavior), in-stream concentrations increase in a linear fashion as BFI goes from 0.0 (0% groundwater) to 1.0 (100% groundwater) with a R^2 of 1.0. In-stream processing of nitrate is a source of deviation from the perfect fit in a plot of BFI versus in-stream nitrate concentration. Daily measured in-stream nitrate was plotted seasonally as a function of BFI at each site. R^2 values were highest during the winter at all three study sites ($R^2 = 0.62$–0.76; $p < 0.001$; Figure 4), supporting the assumption of minimal effects of in-stream processing on in-stream nitrate concentrations during the winter months. In contrast, there were poor fits during the spring, summer, and fall months, with R^2 values ranging from <0.01 to 0.28 (Figure 4), likely due to the effects of in-stream processing on concentration during these times. Therefore, end-member concentrations for groundwater discharge and runoff were determined using the winter BFI-nitrate relationships. Groundwater-discharged end-member concentrations (1.8 ± 0.1–2.9 ± 0.1 mg/L as N), which represent the nitrate concentration in the slowly varying subsurface flow paths contributing to the stream, were greater than runoff end-member concentrations (0.8 ± 0.1–1.6 ± 0.1 mg/L as N; Table 1 and Figure 3), which represent nitrate concentrations in the more rapidly varying flow paths contributing to the stream.

The assumption that $[NO_3]_{GWD}$ and $[NO_3]_{RO}$ are temporally static is a limitation of the approach as currently applied, and is used here as a first approximation in calculations of groundwater discharged and runoff nitrate loads. Possible drivers of seasonal change in end-member concentrations include anthropogenic activities in the watershed (e.g., fertilizer application), temperature-dependent rates of biogeochemical processes, or changes in flow paths to the stream. While seasonal variations in end-member concentrations driven by these processes cannot be ruled out, we expect a minimal influence of seasonality on $[NO_3]_{GWD}$

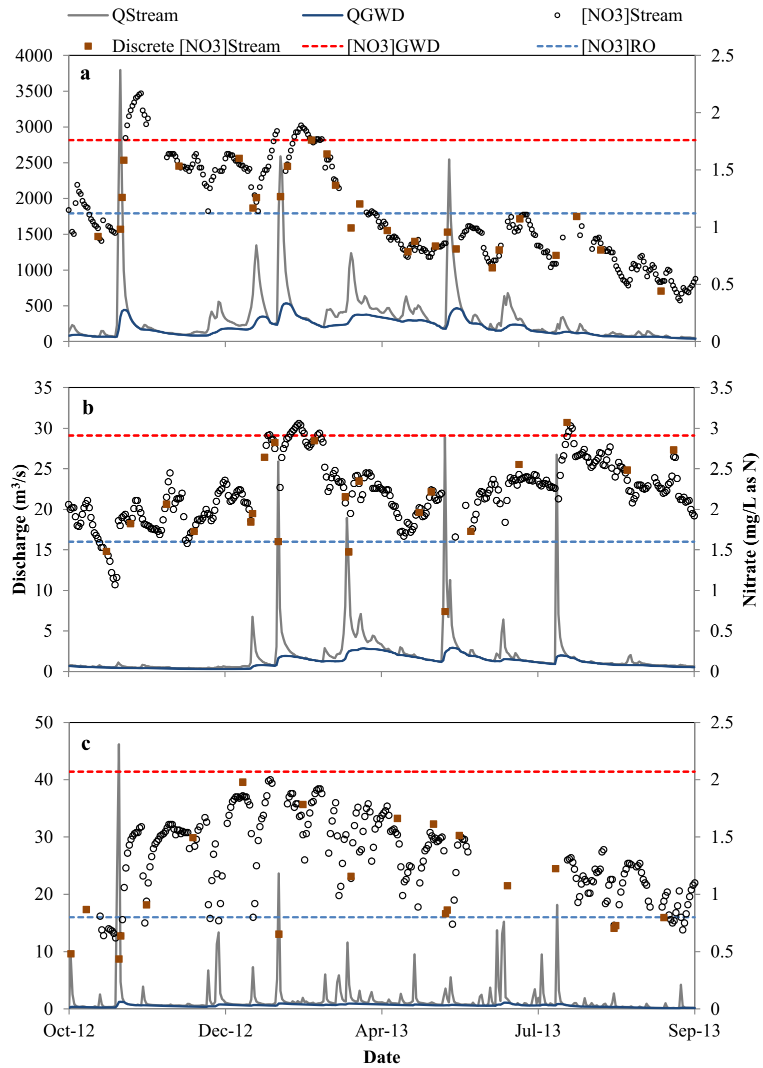

Figure 3. Streamflow (Q_{Stream}), groundwater discharge (Q_{GWD}), sensor measured in-stream nitrate concentrations ($[NO_3]_{Stream}$), and estimated groundwater-discharged and runoff end-member nitrate concentrations ($[NO_3]_{GWD}$ and $[NO_3]_{RO}$, respectively) at (a) Potomac River, (b) Smith Creek, and (c) Difficult Run. Also shown are the analytically determined nitrate concentrations from discrete sampling events. Note the variability in ranges on the *y* axes.

and $[NO_3]_{RO}$ at our study sites. Watersheds with high BFI (>0.40) may be responding to land use activities that occurred decades ago [*Sanford and Pope*, 2013; *Tesoriero et al.*, 2013]. Indeed, the age of groundwater in the Potomac River watershed has been estimated to range from 10 to 20 years [*Michel*, 1992; *Phillips et al.*, 1999]. The apparent age of groundwater determined from chlorofluorocarbon (CFC) analysis of water sampled from springs near the study sites described here was 10 years for the Potomac River and Difficult Run and 22 years for Smith Creek [*Focazio et al.*, 1997]. In light of the long groundwater travel times in these watersheds, seasonal variation in anthropogenic activities likely has little effect on the $[NO_3]_{GWD}$ end-member concentrations. Further evidence suggesting that a dominant shift in groundwater flow paths among seasons at these sites is unlikely provided by the finding that major ion concentrations in these streams were similar over the year during high BFI (>0.8) days, when groundwater discharge to streams is the dominant source water (supporting information Figure S1). However, a greater number of discrete samples for major ion chemistry collected at high BFI conditions would be necessary to evaluate this assumption in greater detail. Because low BFI values coincide with high flow conditions at these sites, when the influence of groundwater-discharged nitrate and in-stream retention/loss are expected to be minimal, nitrate concentrations measured in the stream during these times are likely similar to the runoff end-member concentrations, and could be used to define seasonally variable $[NO_3]_{RO}$. We did not have

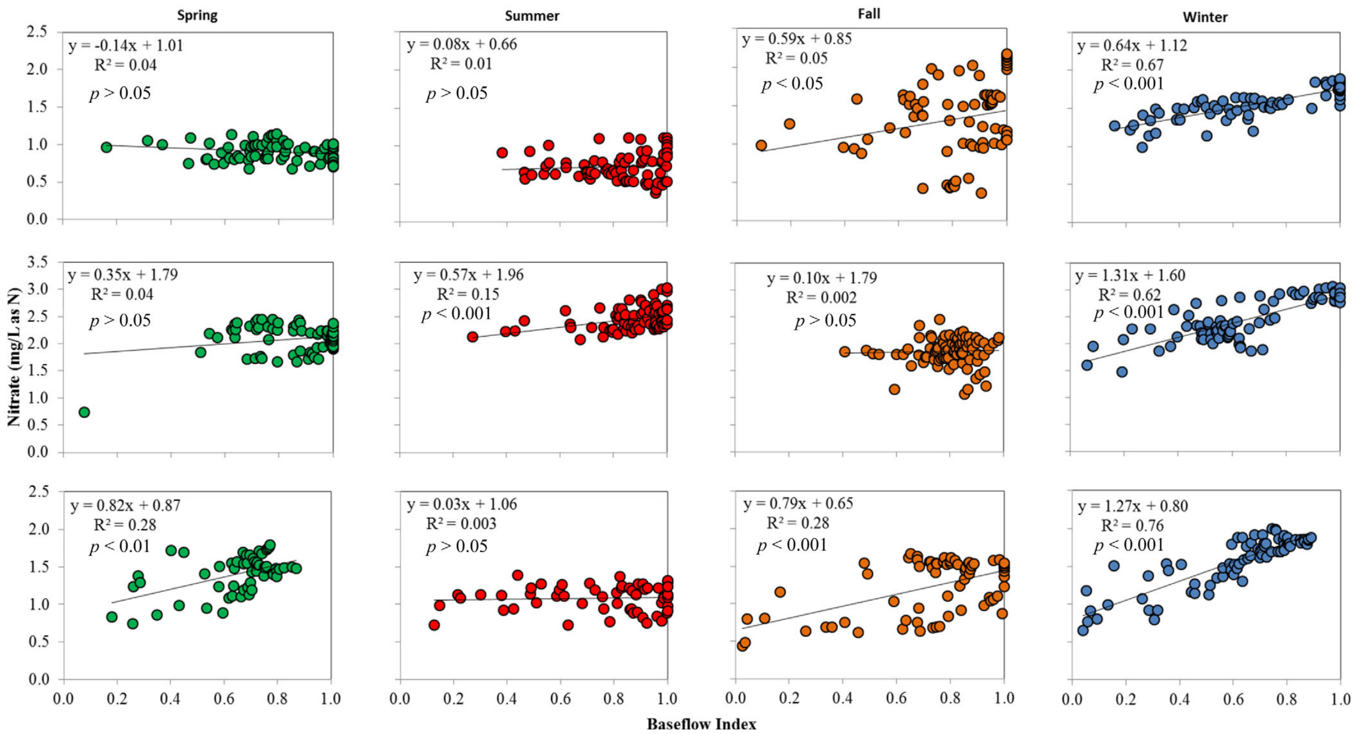

Figure 4. In-stream nitrate concentrations versus the fraction of streamflow estimated to be base flow (Base flow Index) by season at (top row) Potomac River, (middle row) Smith Creek, and (bottom row) Difficult Run. The groundwater-discharged ($[NO_3]_{GWD}$) and runoff ($[NO_3]_{RO}$) nitrate end-member concentrations were estimated by setting BFI = 1.0 and BFI = 0.0, respectively, in the regression equations that define the line of best fit during winter at each site. Note the variability in ranges on the *y* axes.

adequate data on low BFI days during each season at each site to employ this approach (see limited data availability at low BFI during each season in Figure 4), but provide an example of how this approach could be applied in the supporting information. There was relatively little seasonal variability in $[NO_3]_{Stream}$ on the low BFI days for which nitrate concentration data are available (Figure 4), suggesting that the assumption of constant $[NO_3]_{RO}$ may be reasonable. While future efforts to characterize temporal variability in end-member concentrations are warranted (e.g., additional seasonal discrete samples during extreme BFI conditions), the approach applied here provides a first approximation of groundwater-discharged and runoff nitrate loads and in-stream retention at the watershed scale.

Seventy-three percent (1.1×10^5 kg) of the annual nitrate load discharged to the stream, prior to any in-stream processing, was estimated to be from groundwater at Smith Creek, the site with the highest BFI (Table 1). At the intermediate and lowest BFI sites—the Potomac River and Difficult Run—groundwater-discharged nitrate accounted for 69% (1.1×10^7 kg) and 58% (3.7×10^4 kg) of the total annual load discharged to the stream, respectively. The positive relationship between BFI and the fraction of total loads estimated to be groundwater-discharged loads is consistent with studies that have identified positive relationships between BFI and in-stream loads during base flow conditions [*Tesoriero et al*., 2009, 2013; *Spahr et al*., 2010].

Uncertainties in the estimated contributions of groundwater-discharged nitrate loads are due to a number of factors, including the parameterization of the Eckhardt model [*Eckhardt*, 2012], estimated end-member concentrations, and analytical errors associated with sensor and discrete data. The average error estimates for daily groundwater-discharged nitrate loads were 5% at the Potomac River and Smith Creek and 14% at Difficult Run, while the error in the annual groundwater-discharged nitrate loads (based on the square root of the sum of the squared daily loads) was <1% at the Potomac River and Smith Creek and 1.3% at Difficult Run. While not explicitly quantified here, wastewater discharge has been shown to be an important contributor of N to urban streams during base flow conditions [*Kaushal et al*., 2011]. A Chesapeake Bay SPARROW model estimates that <1% of the total nitrogen load at the Smith Creek and Difficult Run sites and 7% at the Potomac River site was from point sources in 2002 [*Ator et al*., 2011]. Further, there are no known point

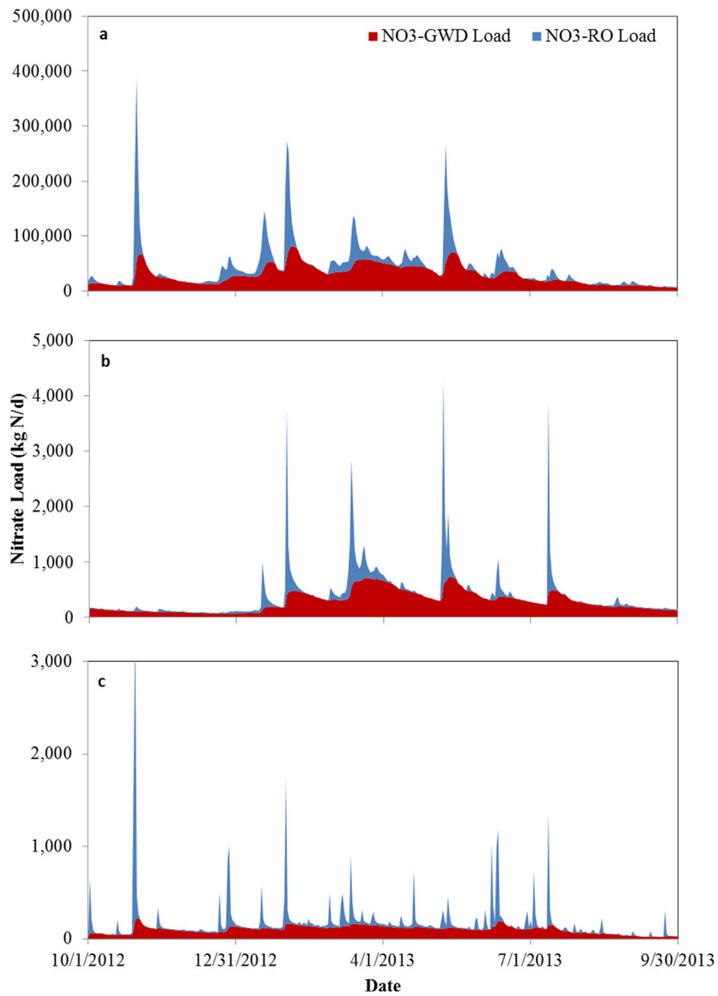

Figure 5. Predicted groundwater-discharged (GWD) and runoff (RO) nitrate loads at (a) Potomac River, (b) Smith Creek, and (c) Difficult Run. The GWD and RO nitrate loads are the estimated loads delivered to the stream, prior to any in-stream biogeochemical processing of nitrate. The sum of these loads is different than the load measured at the gage, which reflects the influence of in-stream processing. Note the variable ranges on the *y* axes.

source discharges to the study streams near the measurement locations, and point source discharges to streams in the Potomac River basin have been decreasing in recent years due to upgrades to waste water treatment plans [*Woods et al.*, 2013]. Therefore, it is expected that point source wastewater discharge to the study streams is unlikely to have a significant effect on the in-stream nitrate concentrations.

Similar to previous studies [*Royer et al.*, 2006; *Carey et al.*, 2014], we observed increases in total loads during and directly following high flow events; this was also the case for both the groundwater-discharged and runoff fractions of the nitrate load (Figure 5). The loads shown in Figure 5 are the estimated groundwater-discharged and runoff nitrate loads delivered to the stream, prior to any in-stream biogeochemical processing of nitrate. The sum of these loads is different than the load measured at the gage, which reflects the influence of in-stream processing. Runoff nitrate loading increased and decreased rapidly during and following high flow events, whereas there was generally a rapid rise and gradual recession of the groundwater-discharged loads until the next high flow event. For example, see the rapid rise and decline in runoff loading following the high flow event on 31 October at the Potomac River, and the rapid rise, but gradual decline in groundwater-discharged loads until the next high flow event on 22 December (Figure 5a).

3.3. In-Stream Fate of Nitrate

Previous studies have suggested that large streams can retain/remove a greater fraction of nitrate loads than small streams because of longer residence times, but that nitrate retention/loss efficiency is greatest in small streams where there is a larger ratio of streambed area to water volume [*Seitzinger et al.*, 2002; *Mulholland et al.*, 2008]. Our estimates of net average watershed-scale in-stream nitrate retention/loss are consistent with these findings. All three sites were, on average for the year, net sinks for nitrate (Table 1). The fraction of total nitrate retained/lost in the stream over the course of the year was greatest at the Potomac River, where 23% of the total incoming load was retained/lost, whereas 11% of the incoming loads were retained/lost at Smith Creek and Difficult Run (Table 1). These values are similar to other estimates of in-stream N removal, including an estimated 24% loss via benthic denitrification of the annual nitrate load to the Mississippi River [*Donner et al.*, 2004], and 16% (denitrification) and 33% (denitrification plus assimilation) loss of dissolved inorganic nitrogen (DIN) loads to the 400 km^2 Ipswich River network [*Wollheim et al.*,

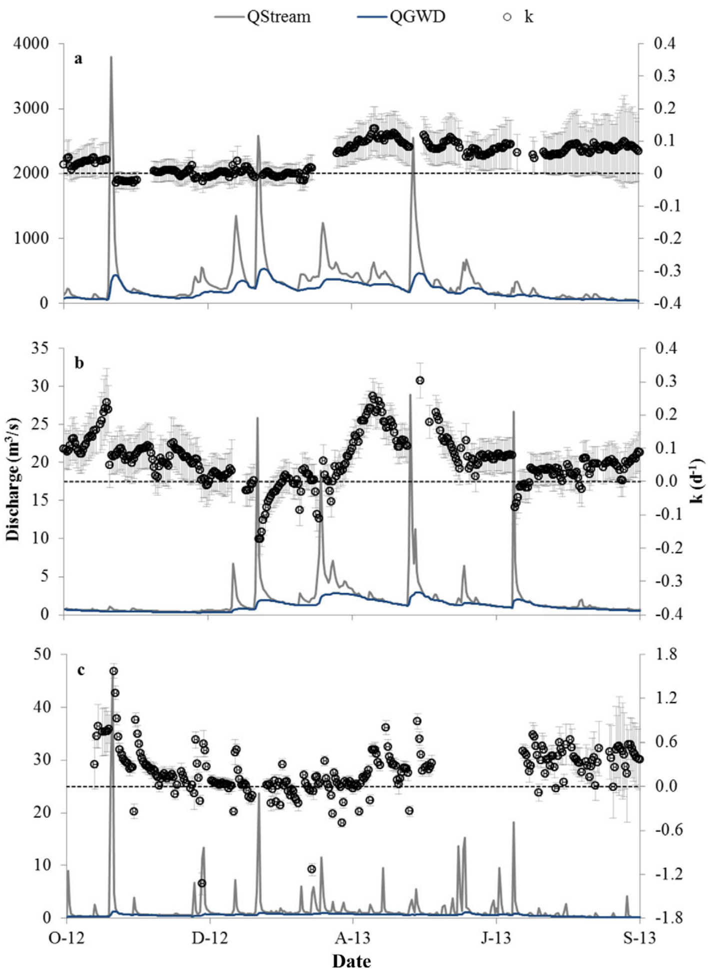

Figure 6. First-order average watershed-scale nitrate reaction rate constant (k, day^{-1}) and error estimates at (a) Potomac River, (b) Smith Creek, and (c) Difficult Run. The horizontal dashed lines indicate conservative behavior of nitrate (no gains or losses). Positive values of k indicate net watershed-scale in-stream retention/loss and negative values indicate net export. Also shown are streamflow (Q_{Stream}) and groundwater discharge (Q_{GWD}). Note the variability in ranges on the *y* axes.

2008]. The Ipswich River estimates of DIN removal were based on application of removal rates measured during summer to other seasons. This likely contributes to the greater estimates of in-stream removal reported for the Ipswich River relative to our estimates of annual retention/loss for the two similarly sized Smith Creek and Difficult Run watersheds.

The lowest annual average watershed-scale nitrate reaction rate constant and largest error (as percent) was at the Potomac River (0.05 ± 0.05 day^{-1}), followed by Smith Creek (0.06 ± 0.05 day^{-1}) and Difficult Run (0.22 ± 0.14 day^{-1}). These estimates are within the range of model-derived estimates of k for permanent removal of total N ranging from 0.45 day^{-1} in small streams to 0.005 day^{-1} in the Mississippi River watershed [*Alexander et al*., 2000], and to 0.34 day^{-1} in small streams to 0.01 day^{-1} in larger streams in the Chesapeake Bay watershed [*Ator et al*., 2011].

Average watershed-scale nitrate reaction rate constants were often negative during storm events, suggesting in-stream production of nitrate in the system (Figure 6). This is likely a result of multiple interacting factors, including, for example, mobilization of nitrate from the hyporheic zone or stream sediments and a decrease in biotic uptake due to the scouring of streambed biota [*Cirmo and McDonnell*, 1997; *Marti et al*., 1997; *Smith et al*., 2006; *Gu et al*., 2008]. Seasonally, our results suggest that nitrate behaved conservatively during the winter months at all three sites with median k values near 0.0; which were significantly ($p < 0.001$) less than median k values during all other seasons at all sites (Figure 7). The result of estimated k values near 0.0 during the winter is expected based on our assumption that in-stream processing is minimal in the winter. Nonetheless, the lack of scatter about the lines of best fit in the plots of BFI versus nitrate in winter (Figure 4) support this assumption. Further, this result is consistent with studies that identified decreases in nitrate loss during winter conducted at similar latitudes [*Royer et al*., 2004; *Triska et al*., 2007; *Böhlke et al*., 2009]. Nitrate reaction rate constants were significantly different ($p < 0.001$) among all seasons at the Potomac River, with the highest median values during the spring (0.10 day^{-1}), followed by summer (0.07 day^{-1}) and fall (0.01 day^{-1}). The greatest median k was also observed during the spring at Smith Creek (0.12 day^{-1}), but during summer at Difficult Run (0.40 day^{-1}). In contrast to the low median k in the fall at the Potomac River, median k values were greater during the fall months in the smaller streams, with values of 0.09 day^{-1} at Smith Creek and 0.29 day^{-1} at Difficult Run. These seasonal patterns in k are consistent with patterns in denitrification rate coefficients observed in sediments of headwater agricultural streams [*Royer et al*., 2004].

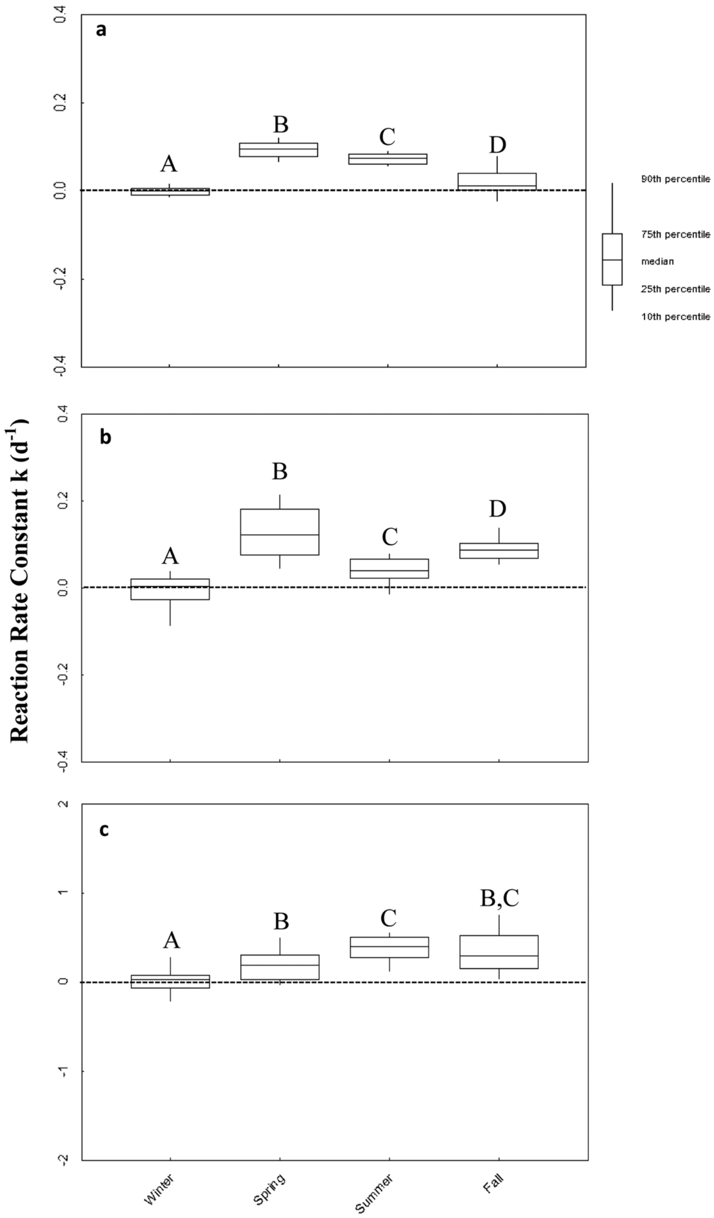

Figure 7. Box plots for first-order average watershed-scale nitrate reaction rate constants (k) versus season at (a) Potomac River, (b) Smith Creek, and (c) Difficult Run. The horizontal dashed lines indicate conservative behavior of nitrate (no gains or losses). Positive values of k indicate net watershed-scale in-stream retention/loss and negative values indicate net export. Different capital letters above boxes indicate significantly different ($p < 0.001$) reaction rate constants among seasons. Note the variability in ranges on the *y* axes.

Studies that have employed mass balance, isotopic, nutrient enrichment, modeling, or a combination of these approaches to quantify in-stream nitrate reaction rate constants (commonly denitrification rate constants) generally indicate that nitrate reaction rates are inversely related to stream nitrate concentrations and streamflow [*Alexander et al.*, 2000; *Royer et al.*, 2004; *Brigand et al.*, 2007; *Alexander et al.*, 2009; *Böhlke et al.*, 2009]. The results of our regression analysis are largely consistent with the results of these studies. Assessment of normal probability plots and plots of the model residuals versus predicted k values indicated that the assumptions of normality of the distribution and the independence and homoscedasticity of the model residuals were upheld for our regression models. Variance inflation factors [*Marquardt*, 1970] were less than three for all explanatory variables for the models at each site, indicating that muticollinearity was not a problem. There was a negative relationship between nitrate concentration and k at all sites ($p < 0.001$; Table 2). However, this is due in part to the concentration dependence of the approach used to estimate k (equation (3)). Daily k values were positively related to streamflow at the Potomac River ($p < 0.001$), unrelated to streamflow at Smith Creek, and negatively related to streamflow at Difficult Run ($p < 0.001$). The positive relationships between k and stream temperature and PAR at the three sites are consistent with previously reported relationships (Table 2). For example, the influence of denitrification was found to be greatest during low flows and warm temperatures in two streams draining agricultural watersheds in New York [*Burns et al.*, 2009]. Further, groundwater-discharged nitrate removal was largely attributed to biotic uptake [*Duff et al.*, 2008], which has been shown to be positively related to light availability [*Peipoch et al.*, 2014]. The positive relationships between k and stream temperature are also consistent with the Chesapeake Bay total nitrogen SPARROW model estimates of k, which were lower at colder temperatures [*Ator et al.*, 2011].

As a means to further assess the reliability of the approach applied to estimate watershed-scale nitrate reaction rate constants, k values were compared with diel variability in dissolved oxygen concentration.

Table 2. Multiple Linear Regression Results for Estimated Daily First-Order Reaction Rate Constants as a Function of the Natural Log of Measured Streamflow, Stream Nitrate Concentrations, Stream Temperature, and Photosynthetically Active Radiation (PAR)

Explanatory Variables and Model Statistics	Potomac River	Smith Creek	Difficult Run
ln Streamflow (m^3/s)			
Coefficient	0.02	0.001	−0.11
Standard Error	0.001	0.004	0.02
p-value	<0.001	0.91	<0.001
ln Nitrate (mg/L as N)			
Coefficient	−0.09	−0.30	−0.75
Standard Error	0.004	0.02	0.6
p-value	<0.001	<0.001	<0.001
ln Stream Temperature (°C)			
Coefficient	0.01	0.02	−0.02
Standard Error	0.002	0.003	0.02
p-value	<0.001	<0.001	0.43
ln PAR ($\mu mol/m^2/d$)			
Coefficient	0.003	0.01	0.04
Standard Error	0.002	0.003	0.02
p-value	0.06	<0.001	0.02
Intercept			
Coefficient	−0.15	0.09	−0.27
Standard Error	0.02	0.04	0.28
p-value	<0.001	<0.001	0.34
Model Statistics			
Number of Observations	291	322	248
Residual Standard Error	0.02	0.04	0.21
R^2	0.84	0.62	0.57

Diel variability in dissolved oxygen concentration has long been used as a measure of primary productivity [*Odum*, 1956]. At constant reaeration rates, greater diurnal variability in DO is generally indicative of greater photosynthetic rates [*Chapra and DiToro*, 1991]. It follows that because nutrients are essential for autotrophic activity, that nitrate retention/loss rates should be positively correlated with diel variability in dissolved oxygen. Indeed, others have demonstrated positive relationships between primary productivity and N assimilation [*Roberts and Mulholland*, 2007; *Valett et al.*, 2008; *Hall et al.*, 2009; *Heffernan and Cohen*, 2010]. At Smith Creek and Difficult Run, the two sites for which high-frequency in situ dissolved oxygen data were available, there were statistically significant ($p < 0.001$) positive correlations between the daily percent change in dissolved oxygen concentration and estimated nitrate reaction rate constants (Figure 8). These positive relationships provide additional confidence in the approach described here for estimating net in-stream nitrate reaction rate constants.

3.4. Future Applications and Implications

The approach presented here couples hydrograph separation with high-frequency nitrate data to describe the estimation of time-variable groundwater-discharged and runoff nitrate loads to streams and the net in-stream fate of nitrate at the watershed scale. Despite the assumptions of this approach, it results in estimates of in-stream nitrogen removal and rate constants that are similar to rates reported in both modeling and in-stream process-based studies. However, future efforts to combine hydrograph separation techniques with continuous water quality data to evaluate source and processing will benefit from further consideration of a few key points. First, the assumption of constant end-member nitrate concentrations is currently a limitation of the approach. While data suggest that this assumption may be reasonable at these study sites, targeted collection of discrete nitrate samples during high flow, low BFI conditions among seasons would allow for definition of seasonally variable runoff end-member concentrations. Ratios of nitrate to chloride concentrations have been used to differentiate between hydrological (e.g., dilution) and biogeochemical (e.g., denitrification) processes influencing nitrate concentrations [*Messer et al.*, 2012; *Billy et al.*, 2013; *Tesoriero et al.*, 2013]. Targeted sampling for major ions (including nitrate and chloride) during high BFI days among seasons would allow for assessments of the time-variable nature of groundwater-discharged end-member concentrations. Second, we were not able to fully account for within-watershed spatial variability in groundwater concentrations or k. Within-watershed spatial variability in groundwater concentrations is accounted for, in part, by the fact that the in-stream chemistry provides an integrated signal of the spatially variable flow paths and nitrate in those flow paths contributing the stream. Nonetheless, development of spatially variable source-weighted residence time estimates for nitrate would allow for more accurate estimates of N sources and transport. Nutrient uptake velocities (based on surface area) may be a better metric than k (based on volume) for assessing watershed-scale nutrient retention/loss [*Wollheim et al.*, 2006] because k has been shown to decline with increasing river size [*Alexander et al.*, 2000]. Future development of spatially variable streambed area or depth data sets would allow for calculation of uptake velocities. Finally, it is not currently possible to identify the relative importance of the mechanism of nitrate retention/loss (e.g., assimilatory biological uptake versus denitrification) using single-station data at the watershed

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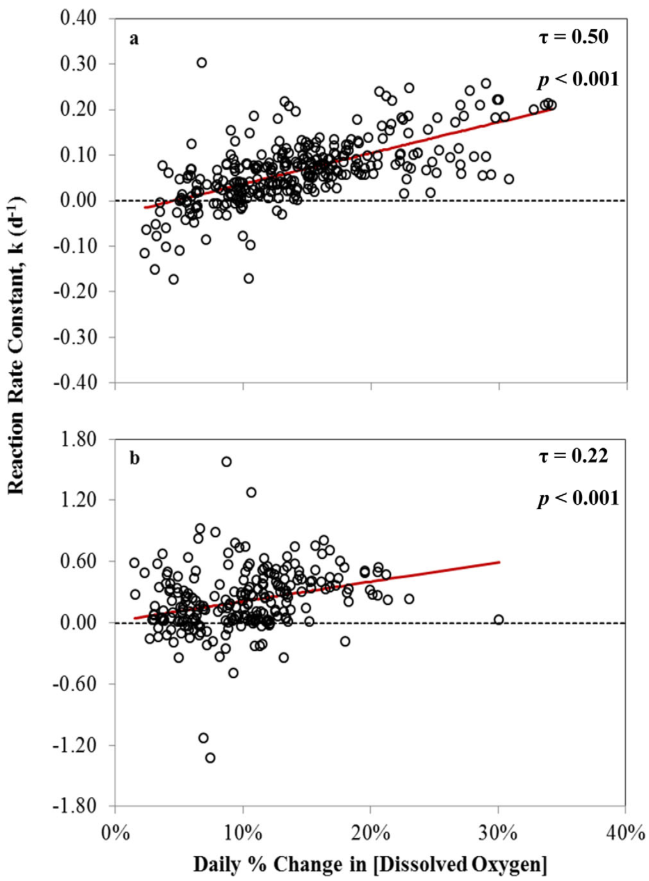

Figure 8. The daily percent change in dissolved oxygen concentration (mg/L) versus first-order watershed-scale nitrate reaction rate constants (k, day^{-1}) at (a) Smith Creek and (b) Difficult Run. Positive values of k indicate net watershed-scale in-stream retention/loss and negative values indicate net export. The horizontal dashed lines indicate conservative behavior of nitrate (no gains or losses). The red lines are the nonparametric Kendall-Theil lines. Also shown are the Kendall's tau correlation coefficients between the percent change in dissolved oxygen concentration and nitrate reaction rate constants. Note the variability in ranges on the *y* axes.

scale. Applying methods to quantify time-variable assimilative nitrate uptake and denitrification using high-frequency water quality data [*Heffernan and Cohen*, 2010; *Hensley et al.*, 2014] in larger river basins warrants further attention. To this end, combining the approach described here with estimates of stream metabolism from dissolved oxygen data is a potential avenue of future research. While further insights may be gained from these suggested refinements, the proposed approach for quantifying time-variable groundwater-discharged and runoff nitrate loads to streams and the net in-stream fate of nitrate at the watershed-scale improves our understanding of N loads to receiving waters.

Mitigation of the environmental and economic impacts of N on receiving waters, such as the Chesapeake Bay, requires an understanding of N transport and processing from the time that N first enters the watershed to when it is discharged downstream. The approach described here for quantifying nitrate loading to streams from the terrestrial environment, in either groundwater-discharge or runoff, and in-stream retention/loss addresses part of this need. For example, our estimate that 58–73% of the annual nitrate loads delivered to the study streams is from groundwater suggests that mitigation actions aimed at intercepting nitrate in runoff may have a smaller impact on nitrate loads than anticipated at these streams. Coupling this approach for quantifying N loading to streams and in-stream retention/loss with methods that estimate N transport and removal along groundwater flow paths, such as recent work demonstrating that decades old nitrate is being discharged to streams in the Chesapeake Bay watershed and elsewhere [*Sanford and Pope*, 2013; *Tesoriero et al.*, 2013], will provide a more holistic understanding of watershed-scale N processing and transport.

Acknowledgments
This work was funded by the U.S. Geological Survey National Water Quality Assessment Integrated Watershed Studies program. We thank Jessica Hopple and Silvia Terziotti for assistance with data compilation and figure preparation. James Webber maintained the sensors and organized data collection at Smith Creek and Difficult Run. Richard Alexander assisted with estimation of travel times and provided helpful comments on an earlier draft of the manuscript. We thank Jeannie Barlow, the Associate Editor, and an anonymous reviewer for their feedback on the manuscript. The data for this paper are publicly available at the websites referenced in the text or by contacting the corresponding author.

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