Nitrate in Streams During Winter Low-Flow Conditions as an Indicator of Legacy Nitrate

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Abstract Winter low-flow (LF) conditions in streams provide a potential opportunity to evaluate the importance of legacy nitrate in catchments due to the dominance of slow-flow transport pathways and lowered biotic activity. In this study, the concentration, flux, and trend of nitrate in streams during winter low-flow conditions were analyzed at 320 sites in the conterminous United States. LF flow-normalized nitrate concentrations varied from <0.1 to >20 mg·N·L⁻¹ and LF conditions contributed between 2% and 98% of the winter nitrate flux. LF nitrate concentrations generally exceeded 2.5 mg·N·L⁻¹ in the upper Midwest, with smaller regions of high LF nitrate concentrations in eastern Texas and along the northern mid-Atlantic coast. Groundwater was inferred to be the primary or sole contributor of nitrate to streams during winter LF conditions at 140 of our 320 sites. Among these 140 sites, nitrate from groundwater comprised 45% or more of the winter nitrate flux at a quarter of the sites. Among the same 140 sites, concentrations of nitrate in streams during winter LF conditions generally increased between 2002 and 2012 at sites where 40% or more of the winter flux was from groundwater, suggesting that concentrations of nitrate in the contributing groundwater system were increasing. Using metrics developed herein, we characterize the potential importance of legacy nitrate at sites in this study and discuss methods to characterize sites with fewer samples than required by our models or at sites without continuous stream discharge measurements.

1. Introduction

Synthetic nitrogenous fertilizers have been used to increase agricultural production since the late 1940s. Fertilizer runoff and infiltration below the root zone have been linked to the eutrophication of surface waters, resulting in a loss of stream biodiversity, contributing to the development of harmful algal blooms, and increasing the occurrence of hypoxia in receiving waters (Rabalais & Turner, 2019; Turner & Rabalais, 1994; Vitousek et al., 1997). Tremendous effort has been put into reducing the use of nitrogen and mitigating the effects of excess nitrogen in stream systems (Bernhardt et al., 2005; Hassett et al., 2005; Rabotyagov et al., 2014). Despite these efforts, widespread decreases in nitrate fluxes in major rivers of the United States have not been observed (Stets et al., 2015). For example, nitrate fluxes from the Mississippi River basin to the Gulf of Mexico have been largely static since the mid-1980s (Sprague et al., 2011; Stets et al., 2015). Legacy nitrate—the lagged delivery of nitrate (and nitrate precursors) that has accumulated in groundwater and other storage areas, such as the root zones of agricultural soils (Van Meter et al., 2016) —is thought to be among the important reasons for a lack of observed improvement. Legacy nitrate is a worldwide concern (Howden et al., 2011; Puckett et al., 2011; Tesoriero et al., 2013), particularly as it relates to the eutrophication of streams and estuaries (Van Meter et al., 2018).

Groundwater is among the most important contributors of legacy nitrate to stream systems. The discharge of nitrate to a stream from its contributing groundwater system lags the recharge of nitrate to the groundwater system by the mean residence time of water in the aquifer (Puckett et al., 2011), which commonly is on the order of decades (Focazio et al., 1998; Plummer et al., 2000; Sanford & Pope, 2013; Van Meter et al., 2018). Microbially facilitated reduction of nitrate to nitrogen gas decreases the concentration of nitrate introduced during recharge in many groundwater systems (Postma et al., 1991; Puckett et al., 2002; Tesoriero et al., 2000); however, for various reasons, nitrate reduction often is limited or incomplete and nitrate from groundwater is delivered to streams (Böhlke & Denver, 1995; Green et al., 2008; Puckett et al., 2002). As a result, groundwater can be a large contributor of nitrate to stream systems and may be the dominant source during low-flow (LF) conditions when surficial transport processes are largely...
inactive. Stream chemistry during LF periods can be used to gain insight into the magnitude and trend of groundwater nitrate inputs to streams (Miller et al., 2016; Smakhtin, 2001; Tesoriero et al., 2013). Significant progress has been made in recent years in quantifying nitrate delivered to streams by groundwater systems. Hydrograph separation paired with discrete or continuous in-stream nitrate measurements has been used to assess the influence of groundwater nitrate on stream water quality at a limited number of sites (Miller et al., 2016; Spahr et al., 2010). Widespread application of these methods is limited by the data requirement to conduct these assessments, including measurements of stream discharge and a robust sampling of in-stream nitrate during LF conditions.

The objectives of our study were to describe the nitrate concentration and flux during winter LF conditions in a large number of streams of varying sizes across the United States and to evaluate the importance of groundwater as a source of nitrate. To achieve this goal, we developed a novel technique to generate catchment-integrated estimates of nitrate concentration and flux during winter LF conditions at 320 stream locations across the conterminous United States, accounted for nitrate inputs from point sources upstream from each site, and compared our results with published estimates. We provide a spatial overview of the in-stream winter LF nitrate concentrations and discuss regional patterns and trends in the winter LF nitrate concentration and flux, including at a subset of our sites where in-stream nitrate is predominantly or solely from groundwater. Implications for the role of legacy nitrate are discussed in relation to our results and we propose a rapid-assessment technique to identify streams where legacy N may be of concern.

2. Methods

2.1. Modeling In-stream LF Nitrate Concentration and Flux

Time series of daily LF flow-normalized (LFFN) nitrate concentrations and daily LFFN nitrate fluxes were developed for 471 stream sites across the United States and Puerto Rico for water years 2002–2012. The daily LFFN nitrate concentration and flux were extracted from daily time series of in-stream flow-normalized (FN) nitrate concentration and FN nitrate flux estimated using Weighted-Regressions on Time Discharge and Season (WRTDS; Hirsch et al., 2010). The WRTDS models and results were documented in Oelsner et al. (2017) and De Cicco et al. (2017) and served as the basis for this analysis. The modeling technique is briefly described below.

The WRTDS model is a multivariate regression model that generates estimates of a time series of daily concentration from discrete water quality measurements and a time series of daily discharge (Hirsch et al., 2010; Hirsch & De Cicco, 2015). The model generally provides more accurate and less biased estimates of concentration and flux compared to other concentration-discharge regression methods (Lee et al., 2016), and provides estimates for all possible concentration-flow regimes observed at a site. We exploit this latter feature to explore the behavior of nitrate in streams during LF conditions. The WRTDS regression model has the following form:

\[
\ln(C) = \beta_0 + \beta_1t + \beta_2\ln(Q) + \beta_3\sin(2\pi t) + \beta_4\cos(2\pi t) + \varepsilon
\]  

(1)

where \(C\) is the concentration, \(t\) is the sample day, \(Q\) is daily discharge, \(\beta_0 - \beta_4\) are fitted coefficients, and \(\varepsilon\) is the residual, unexplained variability.

Unlike other regression-based methods (e.g., LOADEST; Runkel et al., 2004) that fit a single set of coefficients for the entire simulation period, WRTDS uses windows in time, season, and discharge space to estimate coefficients that best describe the water quality and streamflow conditions observed at each site during different flow conditions and time periods of the simulation. Thus, there are multiple sets of \(\beta\) coefficients for each site. For example, a site could have one value of \(\beta_2\) where \(Q \leq 100\) cubic meters per second (cms), and a different \(\beta_2\) where \(Q > 100\) cms. Similarly, a site where the concentration of nitrate increased until 2005 and then leveled off may have a different value of \(\beta_4\) before and after 2005. This unique feature of WRTDS provides more accurate estimates of concentration compared to a single set of fixed coefficients, particularly for conditions that occur rarely, such as unusually high or low flows. The estimated concentrations for a site are readily represented in time-discharge space as a shaded contour plot (Figure 1). The contour plot depicts the range of estimated nitrate concentrations for every day of the simulation, allowing the user to evaluate the effect of flow conditions on the concentration. For example, the historical range in...
gradient of the estimated nitrate concentration in mg N L⁻¹. The black line on the plot represents the 30th percentile of daily discharge. Estimated concentrations were generated using the model, Weighted Regressions on Time, Discharge, and Season (cms = cubic meters per second).

The WRTDS model also calculates a time series of FN concentrations, in which random, flow-related variability in the concentration estimates are eliminated. The FN concentration is the flow-frequency weighted mean of the concentrations estimated for a single day of a simulation period, that is, the weighted mean of a vertical daily “slice” of Figure 1. Estimates of flux and FN flux are generated from the estimated concentrations. Because variations in concentrations (and flux) due to changes in streamflow are eliminated, changes in the FN concentration and FN flux through time can provide insight into catchment processes, such as changing land use or evolving chemical use and management. The WRTDS model structure, function, and operation are discussed in greater detail in Hirsch et al. (2010) and Hirsch and De Cicco (2015).

2.2. Defining Low Flow

Low-flow conditions vary among streams and over time for each stream, and a variety of methods to describe them have been developed (Gao et al., 2009; Hamel et al., 2015; Ouyang, 2012; Vogel & Fennessey, 1994). In this analysis we define low flow as the 30th percentile of the daily discharge for the model period of record at each of our sites. The model period of record for each site is documented in Oelsner et al. (2017). The 30th percentile was selected as the LF threshold because (a) it minimizes the likelihood of the stream containing runoff from recent storms, (b) the flow percentile typically is encountered each year, and (c) it occurs frequently enough to have a sufficient number of water quality samples to accurately estimate LF concentrations in WRTDS. The use of this LF threshold captured the within site and between site variability among our study sites, which spanned several orders of magnitude in catchment area and streamflow volume. For example, at the Mississippi River at St. Francisville, LA, the 30th percentile of discharge on day 100 of the water year (early January) exceeds the highest discharge measured on day 250 (early June), while the 30th percentile of discharge on day 250 of the water year is lower than the lowest discharge measured on day 100 (Figure 2a). Similar variability is noted at streams of different sizes across the country (Figures 2b–2d).

2.3. Calculation of LF Flow-Normalized Nitrate Concentrations and Flux

Low-flow nitrate concentration values were extracted from the estimated WRTDS concentration data for each of the 471 nitrate models reported in Oelsner et al. (2017) and archived in De Cicco et al. (2017). Hereinafter, references to the source data will refer only to Oelsner et al. (2017) for brevity, and also because links to the source data and model output are provided in that report along with descriptions and discussions of the original nitrate model development. Concentrations falling below the 30th percentile of daily discharge (as defined in section 2.2) were extracted, and the daily LFFN nitrate concentration was calculated as the mean of the estimated LF concentrations for each day. Similarly, the daily LFFN nitrate flux was calculated as the mean of the product of each LF concentration and its corresponding streamflow value.

The WRTDS models of Oelsner et al. (2017) were developed from time series of water quality data having varying numbers of discrete nitrate measurements, and not all models had sufficient data to generate useful estimates of LFFN concentration and flux. A site was initially retained for our analysis if the slope of the concentration-discharge (CQ) relationship for the LF portion of the data was similar to the relationship for the full range of streamflow, or if the site met one of two LF sample count criteria described below. At sites where the relationship between concentration and discharge was similar during LF and across the full range of flows, a dearth of LF measurements will not affect the estimation of nitrate concentration during
low flows because it can be reliably estimated from measurements collected during higher flow periods. A change in the slope of the CQ relationship between LF and all flows was determined from the significance ($\alpha = 0.05$) of interaction term ($\beta_{3\text{lowflow} \times \log Q}$) in Equation 2:

$$\log C = \beta_1 \log Q + \beta_{2\text{lowflow}} + \beta_{3\text{lowflow} \times \log Q} + \varepsilon$$  \hspace{1cm} (2)$$

where $C$ is nitrate concentration, $Q$ is discharge, $\text{lowflow}$ is a binary operator designating a sample as having been collected on a day when discharge was less than the 30th percentile of daily discharge for the model period of record, and $\varepsilon$ is the residual unexplained variability. The linear models were developed in R (R Core Team, 2017). At sites where the slope of the CQ relationship differed ($n = 165$), one of two minimum sample count screens were implemented. A site was retained if

1. the original WRTDS model for the site was calibrated using at least 50 LF samples collected during the period 2002–2012. LF samples were defined as samples collected on days when the daily discharge was less than or equal to the 30th percentile of daily discharge for the model period of record, or
2. the original WRTDS model was calibrated using at least 25 LF samples collected during the period 2002–2012, the number of LF samples was at least 25% of the total number of samples, and the number of LF samples was less than or equal to 75% of the total number of samples.

Figure 2. Annual hydrographs over the period of analysis for four monitoring stations of differing catchment area: (a) Mississippi River near St. Francisville, LA (USGS station number 07373420); (b) Sacramento River at Freeport, CA (USGS station number 11447650); (c) Rappahannock River near Fredericksburg, VA (USGS station number 01668000); and (d) Fountain Creek near Colorado Springs, CO (USGS station number 07103700). Black dots show all discharge observations and yellow dots show the 30th percentile of discharge for each day (cms, cubic meters per second; sq km, square kilometer).
The LF sample count criteria were designed to ensure that the WRTDS calibration windows included a large number of LF samples from the time period of interest. Of the 471 nitrate models obtained from Oelsner et al. (2017), 387 were retained. These 387 sites were further evaluated for geographic redundancy (primarily those located within 50 km on same stream or using the same streamflow data) and poor model fit (most commonly temporal structure in the model residual that could affect trends); 320 sites passed our screens and were retained for our final analysis (Table S1 in the supporting information).

2.4. Seasonal Differences in Low-Flow Nitrate Concentration

In-stream LFFN nitrate concentrations were lower during summer (July–September) compared to winter (January–March) at 82% of our sites (Figure 3), which is attributed to higher in-stream, streambed, and riparian zone biological activity due to warmer temperatures and more hours of solar insolation during summer months. Riparian shading has been shown to limit stream photosynthetic activity during summer months in some forested streams (Ledford et al., 2017; Roberts & Mulholland, 2007) and may explain why summer concentrations exceeded winter concentrations at some of our sites. We explored the potential impact of shading at our sites using a dataset of riparian forest canopy cover in a 200-meter wide buffer along all stream reaches upstream from each of our sites (Falcone, 2017). Riparian cover upstream of our sites ranged from 0.1% to 93.4%. The median seasonal difference of the in-stream LFFN nitrate concentrations were largest (1.2 mg-N L⁻¹) at sites having less than 33 percent riparian canopy cover (n = 130). The median seasonal difference was smallest (0.1 mg-N L⁻¹) at sites with more than 67% riparian canopy cover (n = 52); only one site in this high-cover group had a seasonal difference greater than 0.5 mg-N L⁻¹. These observations suggest that low-shade sites do experience more in-stream removal of nitrate during the summer than more heavily shaded sites. However, among the sites where summer concentrations exceeded winter concentrations (n = 58), only 18 sites had more than 67% riparian canopy cover and there were 9 sites that had less than 33% riparian canopy cover. So, although riparian shading influences the magnitude of the observed differences in the seasonal variation of in-stream LF nitrate concentrations, shading does not affect the direction of the change at most sites: in-stream winter LFFN nitrate concentrations exceed summer concentrations at most of our sites. We attribute the higher winter concentrations to lower in-stream removal resulting from a combination of cooler temperatures and less solar insolation due to fewer daylight hours and lower sun angle (Holmes et al., 1996; Schaefer & Alber, 2007; Starry et al., 2005). In-stream nitrate production is unlikely to account for the larger winter concentrations because the combined effect of in-stream denitrification and uptake generally exceeds nitrate production (Arango et al., 2008; Bernhardt et al., 2002; Jarvie et al., 2018). Subsequent analyses of the in-stream LF nitrate concentration and flux data in this paper were limited to winter months. At sites without appreciable nitrate from upstream point source discharges, the median winter LFFN nitrate concentration can provide a conservative estimate of nitrate delivered to the stream from the groundwater system (Miller et al., 2016; Stelzer et al., 2020).

2.5. Calculation of Trends in Low-Flow Nitrate Concentration

Sen’s trend slope was calculated on the median winter LFFN concentrations for the period 2002 through 2012 in R (R Core Team, 2017) using the sens.slope function from the package, trend (Pohlert, 2018). The p value reported by the sens.slope function was converted to a likelihood statistic for comparability with Oelsner et al. (2017) and was calculated as follows:

\[
\text{Likelihood} = \left( 1 - \left( \frac{p \text{ value}}{2} \right) \right)
\]  

(3)

where p value is the p value calculated and reported by the sens.slope function. The likelihood statistic is the functional equivalent of the p value but avoids the strict, binary interpretation of significance inherent
in the use of a fixed p value. Trends having likelihood values greater than 0.7 were interpreted as “somewhat likely” to be trending in the indicated direction, while those with likelihood values greater than 0.85 were “likely” to be doing so. Hirsch et al. (2015) provide a more detailed discussion of the history, rationale, and application of the likelihood statistic for trend analysis.

2.6. Calculation of Median Winter Low-Flow Flux Fraction

The median winter LF flux fraction \( F_{LF} \) provides a measure of the proportion of the winter in-stream nitrate flux that occurs during LF conditions and was calculated as the ratio of the daily LFFN nitrate flux (defined in section 2.3) to the daily FN nitrate flux obtained from the original models reported by Oelsner et al. (2017) for the months of January, February, and March for water years 2002–2012. In streams without appreciable nitrate additions from point source discharges, \( F_{LF} \) provides a conservative estimate of the fraction of nitrate entering the stream from the groundwater system during winter LF conditions.

2.7. Nongroundwater Sources of Nitrate in Streams During LF Conditions

In catchments with little or no industrial or municipal activity, groundwater is the primary source of water and dissolved nitrate to streams during LF conditions. During LF periods, slow transport paths control the movement of water and associated solutes and nonpoint, quick-flow transport paths (e.g., rainfall runoff) are virtually nonexistent. Discharges of nitrate from point sources, including municipal wastewater treatment plants (WWTPs), industrial outfalls, and aquaculture, generally are independent of stream discharge and, where present, serve as year-round sources of nitrate to stream systems during all flow conditions. An accounting of the nitrate from point sources upstream from each of our sampling locations was undertaken to identify sites where these sources are potentially important to the in-stream LF nitrate budget, and conversely, to identify sites where in-stream LF nitrate is predominantly or exclusively derived from groundwater discharge.

Skinner and Wise (2019) estimated the discharge of total nitrogen (TN) from permitted sources in the U.S. Environmental Protection Agency National Pollutant Discharge Elimination System (NPDES) for 2012; a comparable data set is not available for nitrate. The compilation does not capture unpermitted sources or illegal discharges, but represents the best available national compilation of nitrogen from point sources. These data were used to calculate the load of TN released from point sources upstream from each of our sites. WWTPs accounted for the majority of the TN point source load at most of our sites, but releases from industrial, mining, and aquaculture facilities exceeded WWTPs at some sites. Seasonal measurements of TN discharge were unavailable for most of the sources in the NPDES database, so we assumed TN discharge from each source was constant throughout the year and divided the annual TN load by 365 to estimate the daily flux of TN.

The relative importance of nitrate from point sources at each stream site was determined by calculating the ratio of the daily TN flux from NPDES sources to the median winter LF in-stream nitrate flux \( R_{NPDES} \). The use and limitation of \( R_{NPDES} \) are discussed further in section 3.1.

2.8. Comparison of Low-Flow Nitrate Concentration and Low-Flow Flux Fraction With Published Baseflow Nitrate Estimates

Published estimates of baseflow nitrate concentration \( (n = 10; \text{Miller et al., 2016; Spahr et al., 2010}) \) and baseflow nitrate flux fraction \( (n = 11; \text{Miller et al., 2016; Spahr et al., 2010; Tesoriero et al., 2013}) \) were identified for 10 of our sites and compared to our estimates of winter LFFN nitrate concentration and \( F_{LF} \), respectively. The common sites spanned the conterminous United States and were located on streams draining catchments ranging from 44 to 29,967 km². Baseflow nitrate concentration and flux from Spahr et al. (2010) and Tesoriero et al. (2013) were modeled using discrete samples of in-stream nitrate collected during baseflow periods and daily baseflow estimates developed using a graphical hydrograph separation technique. The values from Miller et al. (2016) were developed from high-frequency measurements of in-stream nitrate using nitrate sensors paired with daily baseflow estimates developed using a low-pass filter on daily streamflow.

Our estimates of winter LFFN nitrate concentration were highly correlated with estimates of baseflow nitrate concentration from all three studies \( (n = 10; \text{Spearman’s } r = 0.98, \text{two-sided } p \text{ value } < 0.0001) \) and demonstrates that our winter LFFN nitrate concentration estimates are reasonable representations of
the baseflow nitrate concentration. Overall, our estimates of $F_{LF}$ were not as well correlated with the published estimates of baseflow nitrate flux fraction ($\rho = 0.55; \text{two-sided } p = 0.0780$). However, 8 of the 11 pairs of flux fraction values were highly correlated ($\rho = 0.83$, two-sided $p = 0.0154$) and exhibited a nearly 1:1 relation ($\text{slope} = 1.03, \text{intercept} = 0.03$); the published baseflow nitrate flux fraction estimates exceeded our $F_{LF}$ in the other three pairs, including both values from Miller et al. (2016) and one estimate from Spahr et al. (2010). The high degree of correlation among the paired estimates for concentration and most flux fraction estimates suggests methodological or site-specific issues with the hydrograph separation technique used to estimate baseflow discharge as the source of the discordance at the three sites falling off the 1:1 relation.

The strong correlation between our estimates of LFFN nitrate concentration and $F_{LF}$ with similar published metrics of baseflow nitrate demonstrates the comparability of our estimates with previously published methods to characterize nitrate in baseflow. Further, it circumvents limitations inherent in other methods, namely, (1) the use of hydrograph separation techniques to estimate baseflow discharge, which have known issues in many stream systems (Miller et al., 2015; Stewart et al., 2007), and (2) the subjective decision of deciding which discrete samples are representative of baseflow conditions.

### 3. Results

#### 3.1. Sites Dominated by Groundwater During Low-Flow Conditions

Of the 320 sites in our analysis (Figure 4a), 49 had no documented TN discharge from permitted NPDES facilities upstream of the monitoring location ($R_{NPDES} = 0$; Table 1). At 91 additional sites, the potential contribution of nitrate from permitted discharges was $\leq 20\%$ of the median winter LFFN nitrate flux ($0 < R_{NPDES} \leq 0.2$), assuming all of the TN from permitted facilities was discharged as nitrate and was delivered to the monitoring location without uptake or degradation. The actual nitrate from permitted discharges delivered to the LF monitoring sites likely is much less than the discharged TN load because (1) nitrate represents a fraction of the TN discharged from most permitted sites (Chen et al., 2011) and (2) the potential for some in-stream removal of nitrate during the winter months (Roberts et al., 2007). That nitrate represents a fraction of the permitted TN discharged is supported by the fact that $R_{NPDES}$ exceeded 1.0 at 70 sites. At the 140 sites where $R_{NPDES} \leq 0.2$ (Figure 4b), the median winter LFFN nitrate concentration and flux were assumed to be representative of nitrate discharging from the contributing groundwater systems less any in-stream and streambed metabolic uptake and transformation. The LFFN concentration and flux estimates may reflect small amounts of nitrate generated in the stream, for example, nitrification of ammonia; however, removal processes are expected to exceed generation processes in most systems (Arango et al., 2008; Bernhardt et al., 2002; Jarvie et al., 2018) and both are expected to small during winter months. The winter LFFN nitrate concentration and flux at these 140 stream sites provide a minimum estimate of the catchment-integrated nitrate concentration and flux from groundwater during winter LF periods. Hereinafter, these 140 sites are referred to as LF groundwater dominated.

#### 3.2. Spatial Variability in Winter Low-Flow Nitrate Concentration, 2002–2012

Regional patterns in the distribution of median winter LFFN nitrate concentrations at our stream sites were evident (Figure 4a). Regions having multiple sites with concentrations exceeding 2.5 mg-N L$^{-1}$ included the Snake River Plain, Colorado, the Midwest, the northern Atlantic coast, and a north-south corridor running through central Oklahoma and eastern Texas. The median LFFN nitrate concentration generally was less than 1.0 mg-N L$^{-1}$ in the Pacific Coast states, Kansas, Missouri, Arkansas, and in the middle and southern Atlantic Coast states. Many of the highest LFFN nitrate concentrations were associated with high-density metropolitan areas, including Chicago, Dallas, Houston, northern Ohio, and the region between Washington, D.C., and New York City. Most of these sites are notably absent from the group of LF groundwater-dominated sites (Figure 4b) and illustrate the importance of nitrate from point sources (most likely WWTPs) during LF conditions in streams near major centers of population. Several clusters of sites where the LFFN nitrate concentrations exceeded 2.5 mg-N L$^{-1}$ do not correspond to areas of high population, most notably, Iowa and western Maryland (Figure 4a). However, both regions correspond to areas of high fertilizer and manure application (Figure 4b). In general, the correlation between agricultural nitrogen application and winter in-stream LFFN nitrate concentration generally is observed.
Figure 4. Distribution of median winter low-flow normalized nitrate concentration at (a) the 320 sites used in this study overlain on county population estimates for 2017 (Esri, 2020) and (b) the subset of 140 low-flow groundwater-dominated sites ($\text{R}_{\text{NPDES}} \leq 0.2$) overlain on county estimates of applied nitrogen from fertilizer and manure for 2006 (Gronberg & Spahr, 2012). The point colors correspond to the median winter LFFN nitrate concentration for water years 2002–2012 (mg N L$^{-1}$ = milligrams of nitrogen per liter; kg/ha = kilogram per hectare).

Table 1
Summary of $R_{\text{NPDES}}$ at Study Sites

| $R_{\text{NPDES}}$ | Number of sites | Comment |
|--------------------|-----------------|---------|
| 0                  | 49              | Groundwater is sole source of nitrate during low flow |
| >0 to $\leq$0.2    | 91              | Groundwater is dominant source of nitrate during low flow |
| 0.2 to $\leq$1.0   | 110             | NPDES discharges may be an important source of nitrate during low flow |
| >1                 | 70              | NPDES discharges are likely an important source of nitrate during low flow |

Note. NPDES, National Pollutant Discharge Elimination System.
among all the LF groundwater-dominated sites and highlights the importance of this source to in-stream LF nitrate across the country. Although indicative of the source, the county-scale nitrogen application estimates may not be a good predictor of the magnitude of in-stream LF nitrate at the continental scale due to large variations across the United States in soil permeability (enhancing or limiting nitrate infiltration) and denitrification during groundwater transport (affecting the proportion of infiltrating nitrate that reaches the stream channel).

The spatial distribution of nitrate concentrations among our LF groundwater-dominated sites (Figure 4b) is not substantially different from that observed among the entire group of sites (Figure 4a), and they serve as a reasonable sample of the larger group. The uneven distribution of sites across the United States reflects the source data used by Oelsner et al. (2017) and was a result of the availability of streamflow and discrete nitrate samples required to calibrate the original WRTDS models. The additional constraints we imposed to ensure that a sufficient number of LF discrete samples were used to calibrate the models reduced the density of sites but did not substantially change the overall distribution. The western Great Plains and Intermontane West are poorly represented in our data, which largely is due to generally arid conditions and limited surface water compared to more humid portions of the conterminous United States. Many streams in these western regions are intermittent and are not routinely included in long-term streamflow and water quality monitoring networks. Perennial streams in these regions tend to be located in mountainous areas which are not well suited for farming and have limited artificial nitrogen inputs, and therefore, tend to be excluded from state and Federal water quality monitoring programs—the source for most of the data used by Oelsner. Spatial gaps elsewhere in the conterminous United States were driven by state-specific data limitations as illustrated by a lack of sites in Alabama, Mississippi, Tennessee, and most of the New England states.

### 3.3. Spatial Patterns in Low-Flow Flux Fraction ($F_{LF}$)

The low-flow flux fraction metric ($F_{LF}$) provides a means to quantify the proportion of nitrate in a stream that enters during LF periods. Sites where $F_{LF}$ is low receive most of their nitrate from processes active during high-flow periods, for example, runoff from agricultural field or lawns. In contrast, sites where $F_{LF}$ is high receive most of their nitrate loading during LF periods. The median $F_{LF}$ was 0.33 across all sites in the study and 0.29 at LF groundwater-dominated sites ($R_{NPDES} \leq 0.2$) (Table 2), indicating that runoff processes dominate nitrate transport at most sites during the winter.

Regional patterns are evident in the distribution of $F_{LF}$ among the 140 LF groundwater-dominated sites (Figure 5b), which likely reflect similarities in the permeability and redox characteristics of the contributing aquifers within regions. Sites in the Intermontane West, Wisconsin, Minnesota, Pennsylvania, New Jersey, eastern Maryland, and Florida generally had $F_{LF}$ greater than 0.4, whereas sites in Virginia, North Carolina, Iowa, Illinois, Indiana, Ohio, and Arkansas generally had $F_{LF}$ less than 0.4. Although there was regional cohesion in both $F_{LF}$ and winter LFFN nitrate concentrations among the LF groundwater-dominated sites, the two LF metrics were poorly correlated (Spearman’s rho = 0.04, two-sided p value = 0.6556). As an

### Table 2

|                      | n  | Min | 25th percentile | Median | 75th percentile | Max | Median Winter LFFN Nitrate Concentration, Median Winter LFFN Nitrate Flux, and Low-Flow Flux Fraction ($F_{LF}$) |
|----------------------|----|-----|-----------------|--------|-----------------|-----|----------------------------------------------------------------------------------------------------------------------------------|
| $C_{LFFN\text{-NO}_3}$ |    |     |                 |        |                 |     |                                                                                                                                |
| All sites            | 320| <0.1| 0.3             | 0.9    | 2.6             | 20.4|                                                                                                                                |
| LF groundwater-dominated sites | 140| <0.1| 0.3             | 0.8    | 2.4             | 15.0|                                                                                                                                |
| Flux$L_{LFFN\text{-NO}_3}$ |    |     |                 |        |                 |     |                                                                                                                                |
| All sites            | 320| <1  | 118             | 684    | 3,052           | 1,246,281|                                                                                                                                |
| LF groundwater-dominated sites | 140| <1  | 39              | 206    | 1,273           | 14,716|                                                                                                                                |
| $F_{LF}$             |    |     |                 |        |                 |     |                                                                                                                                |
| All sites            | 320| 0.02 | 0.19           | 0.33   | 0.49           | 0.98|                                                                                                                                |
| LF groundwater-dominated sites | 140| 0.03 | 0.18           | 0.29   | 0.45           | 0.97|                                                                                                                                |

Note: LF, low flow; n = number of samples; min = minimum; max = maximum; $C_{LFFN\text{-NO}_3}$ = median winter LFFN nitrate concentration, in milligrams of nitrogen per liter; Flux$L_{LFFN\text{-NO}_3}$ = median winter LFFN nitrate flux, in kilograms of nitrogen per day.
example, LFFN nitrate concentrations exceeded 2.5 mg-N L\(^{-1}\) at most LF groundwater-dominated sites in Iowa, Illinois, Indiana, and Ohio where \(F_{LF} < 0.4\). In contrast, LFFN nitrate concentrations in Virginia and North Carolina were generally less than 0.1 mg-N L\(^{-1}\) at sites where \(F_{LF} < 0.4\). The poor correlation may be due to \(F_{LF}\) being influenced by characteristics of the contributing aquifer (e.g., permeability and redox state), while the magnitude of the winter LFFN nitrate concentration is largely dictated by the amount of nitrogen used in the contributing catchment.

The same general regional patterns noted for the 140 LF groundwater-dominated sites were observed in the full suite of 320 sites (Figure 5a). In addition to the broadly similar regional patterns, the influence of point sources of nitrate (predominately WWTPs) was evident at sites near major metropolitan areas. Many sites near Chicago, Dallas, Atlanta, and Charleston, and along the corridor between Washington, D.C., and Boston had \(F_{LF} > 0.6\), while \(F_{LF}\) generally was lower at sites farther from the cities in those same regions. As was observed in the concentration results, point sources of nitrate are an important contributor to the LF nitrate flux in many streams draining urban areas of the United States.

Figure 5. Distribution of low-flow flux fraction (\(F_{LF}\)) at (a) the 320 sites used in this analysis and (b) the subset of 140 low-flow groundwater-dominated sites (\(R_{NPDES} \leq 0.2\)). The point color corresponds to the value of the median winter \(F_{LF}\) for water years 2002–2012.
3.4. Trends in Low-Flow Nitrate Concentrations, 2002–2012

Trends in LFFN nitrate concentration at the 140 LF groundwater-dominated sites for the period 2002–2012 were predominately downward (Table 3). At sites where $F_{LF} \leq 0.4 (n = 92)$ there were twice as many downward trends than upward trends. However, the situation was reversed at sites where $F_{LF} > 0.4 (n = 48)$; at these sites, there were twice as many upward trends as there were downward trends. The prevalence of upward trends at sites where much of the winter LF nitrate flux is from groundwater discharge is of potential concern in these systems and suggests concentrations in the downgradient portions of the contributing groundwater systems are still increasing.

The distribution of upward and downward trends in LFFN nitrate concentration was not random. There were large regions where trends were generally upward or generally downward, although sites with opposite trends often are found nearby in many regions (Figure 6). Regions of upward trends included the interior Pacific Northwest, Minnesota, Wisconsin, northern Arkansas, Florida, and northern Virginia, Maryland, and Delaware. Generally downward trends were found at sites along the Pacific Coast, Colorado, Virginia, North Carolina, Georgia, and the Corn Belt states of Iowa, Illinois, Indiana, and Ohio.

### Table 3

| $F_{LF}$ | Downward | Upward | No trend | Ratio of downward to upward trends |
|----------|----------|--------|----------|-----------------------------------|
| <0.2     | 26       | 12     | 1        | 2.2                               |
| 0.2–0.4  | 34       | 17     | 2        | 2.0                               |
| 0.4–0.6  | 10       | 18     | 3        | 0.6                               |
| 0.6–0.8  | 4        | 9      | 2        | 0.4                               |
| >0.8     | 0        | 2      | 0        | 0.0                               |
| Total    | 74       | 58     | 8        | 1.3                               |

*Note. $F_{LF}$, median winter low-flow flux fraction.*

#### 3.5. Relation Between Low-Flow Flux Fraction ($F_{LF}$) and Baseflow Index

The stream baseflow index (BFI) has been used to evaluate the relative importance of groundwater to streamflow and more recently has been used to understand the contribution of groundwater-sourced nitrate to stream systems (Tesoriero et al., 2013; Webster et al., 2019). Streams with high BFI values receive more of their streamflow from groundwater discharge compared to streams with low BFI values, which are dominated by rainfall runoff. Tesoriero et al. (2013) found a strong correlation between BFI and annual nitrate load from baseflow at seven locations in the United States. We also found a strong positive correlation (Spearman’s rho = 0.68, two-sided p value < 0.0001) between the $F_{LF}$ and BFI (Figure 7a) at our 140 LF groundwater-dominated sites, indicating that the BFI is a good predictor of the proportion of the nitrate flux entering a stream from groundwater. Not surprisingly, BFI is a markedly poorer predictor of the LF nitrate flux among sites that receive appreciable amounts of nitrate from upstream point sources ($R_{NPDES} > 0.2$; Spearman’s rho = 0.39, two-sided p value < 0.0001; Figure 7b).

![Figure 6. Map of trends in low-flow-normalized nitrate concentration at the 140 low-flow groundwater-dominated sites ($R_{NPDES} \leq 0.2$).](image)
3.6. Correlation Between Low-Flow Flux Fraction ($F_{LF}$) and the Slope of the Concentration-Discharge (CQ) Relation

The slope of the CQ relation (coefficient $\beta_1$ of Equation 2) describes how the nitrate concentration in the stream varies with changing stream discharge. The CQ relationship for dissolved and suspended constituents in stream systems is the foundation for many commonly used regression models used to estimate concentrations on unmonitored days and to calculate annual loads (Hirsch et al., 2010; Runkel et al., 2004) and also is an important indicator of the predominant processes of constituent mobilization and transport (Godsey et al., 2009; Moatar et al., 2017). One would expect a negative CQ slope in streams where the flux of nitrate from groundwater is larger than the flux of nitrate from runoff processes—increasing streamflow has a diluting effect on the in-stream nitrate concentration. In contrast, streams where the nitrate flux is driven by runoff processes should have a positive CQ slope—increasing streamflow increases the nitrate concentration. The relationship between the CQ slope and $F_{LF}$ provides an alternative method to BFI to gauge the relative importance of groundwater to nitrate flux during LF conditions. At our 140 LF groundwater-dominated streams, $F_{LF}$ was inversely correlated to the CQ slope (Spearman’s rho = $-0.60$; $p$ value < 0.0001; Figure 8a) demonstrating that the fraction of nitrate delivered during LF is directly related to this simple relation between concentration and discharge. The strength of the relation is similar to the relation between $F_{LF}$ and BFI. However, unlike the relation between $F_{LF}$ and BFI, the relationship is stronger among sites having varying amounts of nitrate from point sources ($R_{NPDES} > 0.2$; Spearman’s rho = $-0.72$, two-sided $p$ value < 0.0001; Figure 8b). Not unexpectedly, the relationship between CQ slope and $F_{LF}$ among all sites together was similarly robust (Spearman’s rho = $-0.3586$ and intercept = 0.3740).

4. Discussion

The groundwater component of a stream nitrate budget can be difficult to directly assess due to spatially heterogeneous geochemical conditions in the contributing aquifer system and spatial and temporal heterogeneity in groundwater discharge to the stream. Streams integrate these heterogeneities, but an understanding of the groundwater chemistry and dynamics are confounded by nitrate delivered by runoff mechanisms, point source discharges, and by in-stream biological removal and production. Numerous methods to isolate and estimate the contribution of groundwater discharge to a stream exist (Eckhardt, 2005; Sloto & Crouse, 1996; Stewart et al., 2007; Wahl & Wahl, 1995), but methods to obtain estimates of discharging groundwater chemistry, including nitrate, are more limited and depend on hydrograph separation to accurately estimate groundwater discharge and subjective decisions about discrete stream samples being representative of groundwater (Miller et al., 2016; Spahr et al., 2010; Tesoriero et al., 2013). Instrumenting catchments and modeling play a crucial role in understanding the movement of nitrate from the groundwater system to receiving waters. These types of studies have been instrumental in raising awareness of the time lag between nitrate input to groundwater systems and its discharge to receiving waters and the role of denitrification in mitigating nitrate concentrations in some groundwater systems (Böhlke & Denver, 1995; Tesoriero et al., 2013). However, the expense, complexity, time requirements, and relatively small scale of most studies inherently limit their application to large areas and large numbers of
locations, such as may be desired by a management organization or regulatory agency needing to prioritize limited staff and funding resources.

Utilizing publicly available data, we quantified in-stream nitrate concentration and flux at 140 stream locations spanning the conterminous United States where groundwater was the primary source of nitrate to the stream during winter LF conditions. The focus on LF conditions emphasizes groundwater contributions to streamflow (Smakhtin, 2001), and the focus on in-stream nitrate concentrations during LF can inform our understanding of the nitrate concentrations in the contributing groundwater system (Tesoriero et al., 2009). Our estimates of LF concentration and LF nitrate flux fraction ($F_{LF}$) agreed well with previously published estimate of baseflow nitrate concentration and flux at 10 overlapping sites that were determined using two different methods. These results indicate that our method offers a new route to estimating in-stream nitrate during winter baseflow conditions that eliminates the need for hydrograph separation. LFFN nitrate concentrations and $F_{LF}$ varied considerably among sites, but, in general, were regionally coherent (Figure 4; Figure 5), which likely reflects similar nitrate loading and transport processes, for example, corn-soybean agriculture on soils derived from glacial till at many sites in the Midwest. Although our methods provide no direct measurements of the residence time of nitrate in the groundwater systems contributing to our sites, comparing the trends in the winter LFFN in-stream nitrate concentration with historical changes in the use and management of nitrate in the contributing catchments may provide some indication of the time scale of expected response. Compiling time series of catchment-wide nitrate use and management necessary for this evaluation was beyond the scope of this study but could be a starting point for follow-up work.

Trends in the LFFN nitrate concentration were calculated at these 140 LF groundwater-dominated sites for the period 2002–2012, which can serve as a proxy for the long-term trend in nitrate discharging from the groundwater system upstream from the sampling location over that time period. Although the in-stream LFFN nitrate concentration may be somewhat lower than the actual nitrate concentration of discharging groundwater due to in-stream nitrate removal processes, the magnitude and direction of the trend in winter LFFN nitrate concentration in the stream should remain a robust estimate of the magnitude and direction of the trend in nitrate of discharging groundwater in most cases. The difference in nitrate concentration between the stream and discharging groundwater is expected to be small because nitrate removal and production processes typically are lowest during the winter months (Jarvie et al., 2018; Roberts et al., 2007; Stelzer et al., 2020), and the in-stream concentration is expected to be lower than groundwater in most cases because the combined effect of in-stream denitrification and uptake generally exceeds production (Arango et al., 2008; Bernhardt et al., 2002; Jarvie et al., 2018). A disconnect between the measured trend in nitrate in the stream and discharging groundwater could occur if a site was affected by a series of unusually warm or cold winters that increase or suppress in-stream removal—for example, a downward in-stream trend could be observed at a site where there is no trend in the nitrate concentration of discharging groundwater if the end of the trend period was uniformly warmer than the beginning of the trend period and instream removal was slightly higher than in latter years. A disconnect could also occur if the nitrate concentration of discharging groundwater was low enough to be largely consumed by winter in-stream removal processes—for example, no in-stream trend could be observed at a site where there is an increasing trend.

![Figure 8. Relation between slope of the concentration-discharge (CQ) relation and low-flow flux fraction ($F_{LF}$) at (a) low-flow groundwater-dominated sites ($R_{NPDES} \leq 0.2$) and (b) sites that may have appreciable nitrate from upstream point source discharges ($R_{NPDES} > 0.2$).](image-url)
in nitrate in the discharging groundwater if in-stream removal processes reduce the in-stream nitrate concentration below the detection level every winter. Regional coherence among trends observed at the 140 LF groundwater-dominated sites (Figure 6) and lack of longitudinal or latitudinal gradients in trends indicate disconnects between trends in the in-stream LFFN nitrate concentration and discharging groundwater are uncommon, and that in-stream trends of nitrate concentration during winter LF conditions are indeed a good proxy for nitrate trends of discharging groundwater.

Although our study focused on winter LF conditions to minimize the influence of light and temperature dependent biological processes, conclusions about concentrations and trends of nitrate in discharging groundwater at our sites may be applicable year-round if the chemistry of discharging groundwater is temporally stable across seasons. Miller et al. (2016) make a similar assumption in their work arguing that seasonal changes in the chemistry of discharging groundwater that is decades old are unlikely, although this assumption may not be appropriate at sites draining catchments where groundwater discharges to streams from karst or fractured rock (Mahler & Garner, 2009; Rugh & Burbey, 2008). Support for this assumption in some hydrologic settings is provided by Stelzer et al. (2020) who observed relatively constant concentrations of nitrate in discharging groundwater over a 10-year period. In that study, groundwater nitrate concentrations exhibited no seasonality and had considerably lower variability than the stream into which it discharged.

Two assumptions underlie our attribution of LF nitrate concentration and flux and to groundwater discharge at the 140 LF groundwater-dominated sites: (1) the EPA NPDES database adequately captures all major sources of nitrate entering a stream during LF conditions and (2) in-stream uptake and denitrification of nitrate during winter LF conditions consumes a small fraction of the nitrate discharged from groundwater. The scope of our study precluded an in-depth evaluation of these assumptions at each site and it would be useful to investigate them further in future work. Our assumption that the nitrogen discharged from point sources was entirely nitrate is almost certainly an overestimation of nitrate loading from these sources and likely provides a buffer for errors in the reported discharge and minor sources that were unaccounted for. Evidence that using the NPDES TN loads greatly overestimate the nitrate loads is provided by the 70 sites where \( R_{NPDES} > 1 \). In-stream removal of nitrate through uptake and denitrification during winter LF conditions almost certainly occurs to some degree in all streams, and our estimates represent the residual of that process. Although we cannot say how much nitrate was lost due to in-stream removal, the fact that the residual in-stream nitrate exhibits considerable spatial variability with some regional coherence indicates it is providing important insight into regional catchment-scale nitrate transport processes.

Additionally, we observed a good correlation between the \( F_{LF} \) and the BFI at LF groundwater-dominated sites (Figure 7a). A reasonably strong correlation between \( F_{LF} \) and BFI is expected at sites where groundwater contributes the majority of the nitrate to the stream during LF because the volume of groundwater discharge is a component of both variables. Variability in the \( F_{LF} \)-BFI relationship at LF groundwater-dominated sites is expected due to variability in the concentration of nitrate in the discharging groundwater among sites. Some additional variability in the relationship may occur due to variations in the removal of nitrate in the stream resulting from such factors as differences in light availability, water temperature, stream channel geometry, and nutrient availability.

### 4.1. Legacy Nitrate at Low-Flow Groundwater-Dominated Sites

At nearly half our sites (140), groundwater discharge was the sole or dominant source of nitrate in streams during LF conditions. The range of nitrate concentrations during winter LF conditions at these sites ranged from <0.1 to 15 mg-N L\(^{-1} \) and the fraction of nitrate contributed during winter months (\( F_{LF} \)) ranged from 0.03 (runoff dominated) to 0.97 (groundwater dominated) (Table 2). A bivariate plot of these two metrics provides a framework to evaluate the relative importance of legacy nitrate within each catchment (Figure 9). The lines separating the regions of concern in the figure are subjective and may be drawn differently depending on the primary management goal(s), for example reducing eutrophication or meeting drinking water standards. Our principal goal is to provide a structure for conceptualizing the potential importance of legacy nitrate, and in doing so, we have attempted to balance both environmental and human health goals in drawing the regions.

Sites where winter LFFN nitrate concentration is low (here defined as <0.5 mg-N L\(^{-1} \)) are generally not a concern for legacy nitrate across the entire range of \( F_{LF} \) and are characterized as “lowest concern” in
Figure 9. Characterization of the potential for concern for legacy nitrate at 140 low-flow groundwater-dominated streams in this study ($F_{NPDES} \leq 0.2$) (mg-N L$^{-1}$ = milligrams of nitrogen per liter; LF, low-flow; LFFN, low-flow flow-normalized).

Figure 9. The flux of nitrate in streams during LF conditions may be a substantial portion of the winter nitrate, but the concentration delivered to the site is low and close to the natural background concentration in most areas (Dubrovsky et al., 2010). Sites of lowest concern for legacy nitrate may still have issues with quick-flow (runoff) sources of nitrate. There may also be concerns for elevated nitrate in the contributing groundwater system, but biogeochemical processes during and after the groundwater discharges to the stream have reduced concentrations to the point of low concern. Sites falling in the “moderate concern” range of Figure 9 are characterized by larger fluxes of nitrate from groundwater during the winter ($F_{LF} > 0.33$) at slightly elevated concentrations ($0.5–1.0$ mg-N L$^{-1}$), or by having less than one third of their winter nitrate flux from groundwater at moderately elevated concentrations ($0.5–2.0$ mg-N L$^{-1}$). In the “greatest concern” region, groundwater contributes a substantial portion of the overall winter nitrate flux at moderately elevated concentrations or the concentration is large enough to warrant concern no matter how much it contributes to the overall winter flux of nitrate. Sites in the region of “greatest concern” have LFFN nitrate concentrations that considerably exceed natural background concentrations in most stream systems (Dubrovsky et al., 2010). Among sites in the “lowest concern” region, trends in winter LFFN nitrate were predominantly downward (29 of 50 sites), whereas an equal number of upward and downward trends (27 each) were identified among sites in the “highest concern” region (56 sites). And, as noted previously in the trend results (section 3.4), increasing trends in LFFN concentrations of nitrate were identified at 67 percent of the sites where $F_{LF} \geq 0.40$ (Table 3). Increasing winter LFFN nitrate concentrations at sites where groundwater already contributes a substantial fraction of the total winter nitrate flux or at sites where the LFFN nitrate concentrations already exceed $1$ mg-N L$^{-1}$ indicates the legacy of nitrogen use and management in these catchments will cause continued deterioration of stream water quality during LF conditions into the near-term future.

The comparison of $F_{LF}$ and LFFN nitrate concentration just described provides a preliminary assessment of the potential for legacy nitrate at the catchment scale that can be useful for prioritizing more in-depth work. A more complete understanding of catchment-scale legacy nitrate requires additional information unavailable from an assessment of LF nitrate conditions alone, including (1) the loading and trend of nitrate use and management in the catchment, (2) the travel time (or mean residence time) of nitrate through the groundwater system, (3) identifying and characterizing all sources of legacy nitrate in the catchment, and (4) characterizing the biological and geochemical processes controlling the addition or removal of nitrate in the aquifer and stream.

4.2. Characterizing Concern for Nitrate Loading During Low-Flow Conditions

Understanding the dominant transport path of nitrate to a stream is essential for developing meaningful nitrate mitigation strategies. The $F_{LF}$ metric can be used to characterize the relative importance of LF and runoff sources to the delivery of nitrate to a stream during winter—values of $F_{LF}$ less than 0.5 indicate most nitrate flux is from sources operating during higher flows (most likely rainfall runoff), whereas values of $F_{LF}$ greater than 0.5 indicate most nitrate flux occurs during LF conditions (groundwater and point sources)—and this information can inform nitrate management strategies. For example, strategies designed to reduce rainfall runoff from farm fields may not be particularly effective in reducing nitrate in a stream where most of the flux occurs during LF periods (e.g., $F_{LF} = 0.65$), whereas promoting infiltration of water containing nitrate in a system such as this potentially exacerbates legacy nitrate problems.

The characterization of concern for legacy nitrogen presented in section 4.1 can be expanded to include all of our sites and expressed as a concern for nitrate loading during winter LF conditions in general, regardless of the source of nitrate during LF (Figure 10). As before, the regions on the figures are somewhat subjective and reflect our attempt to balance environmental and human health concerns and should be adjusted to meet...
specific analytic objectives. Nearly one third of our sites \((n = 101)\) fall in the region of lowest concern where the LFFN nitrate concentration \(<0.5 \text{ mg-N L}^{-1}\) and indicating that LF nitrate is likely not of concern regardless of the proportion of nitrate delivered during LF conditions. It also can be seen that there is a somewhat larger group of sites \((n = 136)\) where the flux and concentration of LF nitrate is likely of concern due to elevated nitrate concentration or a large \(F_{LF}\).

This analysis could be expanded to many more sites than the 320 we used in our study by relying on the relationship between \(F_{LF}\) and the slope of the concentration-discharge (CQ) relationship (Figure 8). The sites we used in this study generally had 100 to 200 measurements collected over 10 or more years, which enabled Oelsner et al. (2017) to use WRTDS to generate a time series of daily estimates of nitrate for each stream system. However, an estimate of the slope of the CQ relationship can be developed using fewer data—several dozen measurements of nitrate and streamflow discharge across a range of flow conditions would likely be sufficient to determine the slope with reasonable accuracy. The \(F_{LF}\) metric could be estimated from the slope of CQ the relationship or the slope could be used directly and as a surrogate for \(F_{LF}\) (second y axis in Figure 10). Minimally, the slope of the CQ relationship likely could be bounded as being positive, negative, or neutral (near zero) thus narrowing the potential range of \(F_{LF}\) values. A large amount of data exist that could be used to expand understanding LF nitrate across the United States. The Water Quality Portal (National Water Quality Monitoring Council, 2019) contains nitrate data from more than 67,000 stream sites in the United States. These data represent an immense opportunity for a more comprehensive assessment of the role of LF nitrate in the Nation’s streams by identifying sites therein that have streamflow data from a gage or discrete measurements. An additional analysis to evaluate NPDES nitrogen loads upstream of each site would then allow reasonable estimates of the relative importance of groundwater and point source discharges to the nitrate loading at the site.

5. Summary and Conclusions

Quantifying the nitrate concentration and flux of groundwater discharging to streams at the catchment scale is a difficult but important task in the mitigation and management of nitrate contamination in streams. Direct measurements of nitrate in groundwater may not be representative of the nitrate concentration in discharging groundwater because wells access a discrete point along a flow path whereas streams integrate a multitude of flow paths. Additionally, the concentration of nitrate measured in a well may undergo denitrification before discharging to the stream, either in the aquifer or as it upwells through the streambed. Streambed measurements of nitrate concentration and flux are known to be spatially and temporally heterogeneous (Puckett et al., 2008; Rosenberry & LaBaugh, 2008) and techniques to directly measure groundwater discharge can be problematic for various reasons (Murdoch & Kelly, 2003; Rosenberry & LaBaugh, 2008). Watershed models can be useful but are resource intensive at small scales, and larger, regional models often do not capture site-specific details needed for management. Analyses of stream low flow (LF) or baseflow conditions currently are among the best methods to understand nitrate discharge from groundwater at the catchment scale (Miller et al., 2016; Tesoriero et al., 2013; Webster et al., 2019).

Our analysis of in-stream nitrate concentration and flux during winter LF conditions was conducted at 320 stream sites across the conterminous United States. The concentration and flux data were extracted from existing, published time series of in-stream nitrate developed using the model WRTDS (Oelsner et al., 2017), and our technique represents a new method to estimate nitrate during LF conditions without the use of hydrograph separation. Our LF nitrate concentrations compared favorably with previously published estimates, as did our estimates of the proportion of the winter nitrate flux in the stream that occurred during LF periods. Low-flow conditions were responsible for one third or more of the winter nitrate flux at half
of our sites, demonstrating the importance of LF conditions to the delivery of nitrate at many sites across the United States.

In-stream nitrate during LF was determined to be predominantly or solely from groundwater discharge at 140 of these sites that had minimal or no total nitrogen discharged from point sources upstream of the monitoring location. At the 140 LF groundwater-dominated sites, our estimates of nitrate concentration and flux are inferred to represent catchment-integrated groundwater. Trends in the winter LF nitrate concentrations at these sites likely reflect the trend in nitrate discharged from groundwater in the contributing catchment and provide insight into the expected trajectory of in-stream nitrate during LF conditions in the near-term future. Trends in nitrate from discharging groundwater likely reflect the nitrate loading history in the contributing catchment, but additional work is needed to quantify the time lag between nitrate loading at the surface and discharge to streams at these sites.

To facilitate the evaluation of legacy nitrate at more sites and prioritize sites for additional study or monitoring, we developed a graphical method to characterize the nitrate condition of streams based on the winter LF concentration and flux of nitrate. Additionally, we suggest methods for extending this technique to sites that are less data rich than those we used in this study. The graphical method is flexible and users can readily apply their own thresholds of concern to categorize sites. Among our 140 sites where groundwater was the sole or primary source of nitrate in streams during winter LF conditions, nitrate was determined to be of “moderate concern” or “greatest concern” at 64% of the sites.

**Data Availability Statement**

The modeled daily nitrate concentration and flux data from which our LF concentration and flux estimates were made are archived and publicly available from De Cicco et al. (2017), the point source data are archived and publicly available from Skinner and Wise (2019), and the site characteristics and riparian canopy data are archived and publicly available from Falcone (2017).

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