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RESEARCH ARTICLE

Assessing the importance of seepage and springs to nitrate flux in a stream network in the Wisconsin sand plains

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Abstract

Evaluating the flow paths that contribute to solute flux in stream networks can lead to greater understanding of the linkages between biogeochemistry and hydrology. We compared the contributions of groundwater in spring brooks and in seepage through the streambed to nitrate flux in the Emmons Creek network in the Wisconsin sand plains. We predicted that spring brooks would contribute disproportionately to nitrate flux due to the presumed higher advection rates in springs and less opportunity for nitrate removal relative to seeps. Nitrate flux was measured in 15 spring brooks that entered Emmons Creek. Nitrate flux from seepage was measured at the locations of 30 piezometers, based on Darcy's Law, and by a reach-scale injection of Rhodamine water tracing (RWT). When seepage discharge was estimated from the RWT release, groundwater inputs from seepage and springs accounted for the discharge gain in the Emmons Creek channel. Springs brooks and seepage (based on the RWT release) contributed 37% and 63%, respectively, to nitrate flux inputs in the study reach. Contrary to our prediction, seeps contributed disproportionately to nitrate flux relative to their discharge. Relatively high rates of seepage discharge and higher than anticipated nitrate concentrations in the shallow pore water at seepage locations contributed to the unanticipated result.

KEYWORDS

flow path, groundwater, hydraulic conductivity, nitrogen, seepage, springs

1 | INTRODUCTION

There is a long history in the fields of hydrology and biogeochemistry of determining the sources of solute fluxes in rivers, particularly where solute loads are elevated due to anthropogenic influences (Alexander, Boyer, Smith, Schwarz, & Moore, 2007; Flewelling, Herman, Hornberger, & Mills, 2012; Mulholland, 1992; Tesoriero, Duff, Saad, Spahr, & Wolock, 2013; Tesoriero, Duff, Wolock, Spahr, & Almendinger, 2009; Yevenes & Mannaerts, 2012). Soil type, bedrock presence and permeability, terrain, and urbanization are some of the factors that influence the dominant routing pathways for solutes in watersheds (Buda & DeWalle, 2009; Hiscock, 2005). Streams in agricultural watersheds often contain elevated concentrations of nitrate and other mobile forms of nutrients, especially where soil conditions (high porosity) and flow alteration (e.g., tile drains) facilitate rapid subsurface transport and reduce opportunities for nutrient processing. Elevated nitrate supply in streams and rivers contributes to ecosystem degradation in freshwater and marine coastal regions (Diaz & Rosenberg, 2008; Erisman et al., 2013).

In streams draining watersheds with low topographical relief groundwater is typically the major routing pathway for water and solutes, particularly during base flow (Tesoriero et al., 2013). There are several possible pathways by which solutes in groundwater can enter streams in these types of landscapes including groundwater emerging in springs drained by spring brooks (outflows from springs, i.e., rheocrene springs; Kurz, Martin, Cohen, & Hensley, 2015; Roy, Zaitlin, Hayashi, & Watson, 2011), groundwater seepage through soil or fractures in bedrock (O'Driscoll & DeWalle, 2010; Williams, Buda, Elliot, Singha, Hamlet, 2015; Williams et al., 2014), groundwater seepage through streambeds (Binley et al., 2013; Fitzgerald, Roy, & Smith, 2015; Grimaldi et al., 2004; Kennedy, Genereux, Corbett, & Mitasova, 2009a; Lansdown et al., 2015; Stelzer & Bartsch, 2012), and diffusion (Kurz et al., 2015). In this manuscript, we refer to groundwater that moves through streambed sediments as seeps or seepage. Several investigators have quantified the inputs of nitrate or ammonium to streams from riparian seepage (O'Driscoll & DeWalle, 2010; Williams et al., 2014), streambed seepage (Fitzgerald et al., 2015; Heppell et al., 2014), and springs (Roy et al., 2011). Studies that have quantified multiple sources of nitrogen, including groundwater, to streams (Buda & DeWalle, 2009; Fitzgerald et al., 2015; Grimaldi et al., 2004; Mulholland, 1992; Tesoriero et al., 2009; Yevenes & Mannaerts, 2012) have become increasingly common.

Dissolved forms of nitrogen, including nitrate, are readily taken up by organisms during assimilatory and dissimilatory processes (Burgin & Hamilton, 2007). The capacity for nitrate transformation depends on several factors including the quantity and type of biota, the presence of dissolved oxygen, and the availability of suitable electron donors such as organic carbon (Schlesinger & Bernhardt, 2013; Tiedje, 1982). The transport rate of water through sediments will also influence the capacity by which nitrate can be transformed. The ratio of reaction rate to transport rate (Damköhler number) influences the degree of nitrate transformation in sediments. In general, when transport rates are low, bacteria and algae will have a greater opportunity to affect nitrate concentration than when transport rates are higher (Flewelling et al., 2012; Lansdown et al., 2015; Zarnetske, Haggerty, Wondzell, Bokil, & González-Pinzón, 2012). The capacity for nitrate to be transformed likely differs among the major pathways by which nitrate in groundwater enters streams. Where groundwater seeps through carbon-rich sediments, the availability of organic carbon and relatively long-transport time would tend to favor nitrate transformation. Seepage through sediments with low quantity or quality of organic carbon would be expected to experience low-reaction rates and high-transport rates (sediment grains less likely to be clogged with particulate organic matter) resulting in less nitrate transformation (Stelzer, Scott, & Bartsch, 2015; Stelzer, Scott, Bartsch, & Parr, 2014). Rates of nitrate transformation may be lower in springs, which are locations with preferential discharge of groundwater. In springs and spring brooks, higher transport rates may reduce the capacity for nitrate transformation compared with seepage through the streambed in which transport rates are expected to be lower, particularly when fine, organic-rich sediments are present (Flewelling et al., 2012; Tesoriero et al., 2009; Zarnetske et al., 2012).

Our primary objective was to compare the influence of two major routing pathways, springs and seeps, on the flux of nitrate in a stream network. We predicted that springs contribute disproportionately more to nitrate flux than what would be expected based on their discharge because of less opportunity for nitrate uptake and removal in these systems than in seeps. Our secondary objective was to assess spatial variation in nitrate concentrations and fluxes among springs and seepage locations in the Emmons Creek network.

2 | METHODS

2.1 | Site description

The Emmons Creek network is located in Portage County, Wisconsin, in the Central Sand Ridges ecoregion (CSRE). Portage County contains crystalline rocks of Precambrian age and sandstone of Cambrian age (Holt, 1965). The bedrock is overlaid by well-sorted sand and gravel till and outwash. The Emmons Creek watershed is in a region with unconfined sandy aquifers about 30 m thick (Holt, 1965). The main stem of the network, Emmons Creek, is a third-order stream fed by surface water from Fountain Lake and Carden Feeder Creek, by groundwater from seeps that occur throughout most of the stream channel and by numerous small tributaries (spring brooks) that drain springs (Figure 1). These rheocrene springs likely receive groundwater from shallow flow paths (Susan Swanson, Beloit College—personal communication). The discharge of Emmons Creek tends to be relatively stable due to the large contribution of groundwater that is

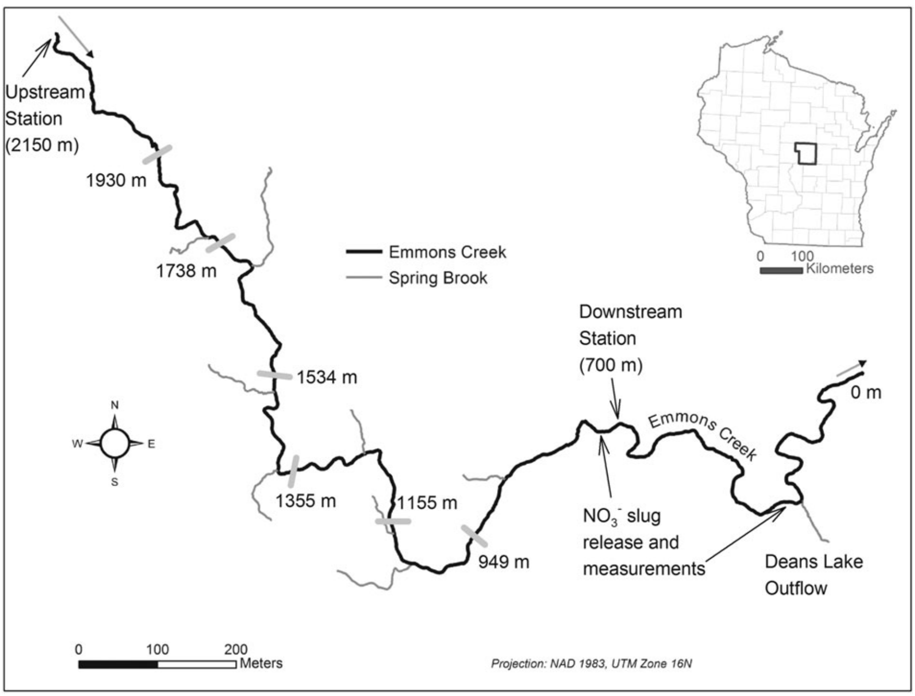

FIGURE 1 Emmons Creek network including locations of the upstream and downstream stations and the tributaries that drain prominent springs. Piezometer transects (widths exaggerated) are indicated with gray bars and positions (m) relative to a downstream reference station (0 m)

facilitated by high-recharge rates in the CSRE. The sandy soil and thick sandy aquifer in the CSRE result in oxic groundwater throughout much of the region (Stelzer & Bartsch, 2012; Tesoriero et al., 2013). The sediment of Emmons Creek is dominated by sand and secondarily by silt, gravel, and pebble with occasional stretches of coarser sediment (cobble and boulder) in riffles. Concentrations of nitrate in the surface water (2.2 to 2.7 mg NO_3–N/L) and shallow groundwater (<0.01 to 3.5 mg NO_3–N/L) associated with Emmons Creek are high compared to historical estimates for streams in this region (Smith, Alexander, & Schwarz, 2003), due primarily to the influence of agriculture in the watershed. Land cover in the Emmons Creek watershed is a mix of forests, savanna, wetlands, and vegetable and dairy farms.

2.2 | Overall approach

The following mass balance model describes the primary fluxes (mg/s) of solutes in the Emmons Creek network.

$$DS_{\text{flux}} = US_{\text{flux}} + S_{\text{flux}} + P_{\text{flux}} - U \tag{1}$$

where

DS_{flux} is the solute flux at a downstream station (Figure 1).
US_{flux} is the solute flux at an upstream station,
S_{flux} is the solute flux from spring brooks,
P_{flux} is the solute flux from groundwater seepage through the streambed, and
U is the net uptake of the solute in the stream channel.

We applied this mass balance model to nitrate and chloride fluxes. Chloride tends to behave conservatively and was considered to evaluate the water balance in the network. The study reach began at the Third Avenue Bridge and ended about 1,450 m downstream at the downstream station (Figure 1). To determine if spring brooks or seepage had disproportionate impacts on reach-scale nitrate flux, we compared the contributions of spring brooks and seepage to the gain in nitrate flux in the study reach (DS_{flux} – US_{flux}). The analysis was based on two measurement periods—late June (June 19–July 3) and late July (July 15–31) of 2015. Measurements of discharge and solute concentrations occurred during base flow.

2.3 | Main channel discharge and solute flux

Mean daily discharge at the downstream station was estimated by using a rating curve based on a relationship between discharge and water depth, determined at 10-min intervals with a Solinst 3001 Gold Levelogger deployed at the downstream station. Discharge at the downstream station was measured using the dilution-gauging method based on a continuous injection of sodium bromide for several hours on June 12, 2015, during the falling limb of the hydrograph.

A whole-reach continuous injection of Rhodamine water tracing (RWT) was performed on June 19, 2015, to determine how discharge changed longitudinally in Emmons Creek (Kilpatrick & Cobb, 1985; Kurz et al., 2015). The injection was also used to measure discharge at the upstream station and to corroborate the discharge estimate from the rating curve at the downstream station. Longitudinal changes in discharge in the Emmons Creek channel, based on the RWT release, were used to corroborate direct measurement of discharge from spring brooks entering the reach and to estimate seepage inputs in subreaches that did not contain springs (see below). A concentrated solution of RWT (3.92 g/L) was injected continuously at a rate of 61 ml/min for 8 hr at the upstream station with a Watson Marlow 504S peristaltic pump. The RWT was added to a turbulent section of the thalweg to facilitate mixing. An MS5 Hydrolab Sonde, equipped with an RWT optical sensor and temperature transducer, was used to measure RWT concentration in the stream. After RWT concentrations reached plateau at a location about 2,150 m downstream from the injection site (0 m in Figure 1), RWT concentration was measured at 25-m intervals in the thalweg by personnel walking in an upstream direction. RWT concentrations measured during the plateau phase were corrected for temperature (Wilson, Cobb, & Kilpatrick, 1986) and background concentration. Discharge was estimated at each 25-m interval based on the RWT concentration in the stream and the concentration and injection rate of the RWT solution, according to dilution-gauging principles (Kilpatrick & Cobb, 1985). Measurements of RWT at lateral transects during the plateau phase indicated that the RWT became well mixed throughout the stream channel at about 100 m downstream from the injection point. Discharge at the upstream station on June 19, 2015, was estimated based on the RWT release. Discharge at the upstream station on other dates was estimated based on the discharge at the downstream station determined from the rating curve described previously. We assumed that the ratio of discharge at the downstream and upstream stations was constant.

Water samples for nitrate and chloride were collected from the thalweg of Emmons Creek at the downstream and upstream stations (typically every 2 to 4 days) during the June and July measurement periods. Samples were immediately filtered through Whatman GF/F filters in the field, returned to the lab on ice, and stored at −20 °C until analysis. Mean daily solute fluxes at the downstream and upstream stations were determined by multiplying solute concentrations by mean daily discharge.

2.4 | Spring brook discharge and solute flux

Nitrate and chloride fluxes from the spring brooks (S_{flux} in mg/s) were estimated based on the following equation:

$$S_{\text{flux}} = \sum_{i=1}^{n} Q_i \, C_i \tag{2}$$

where

Q_i is the discharge (L/s),
C_i is the solute concentration (mg/L), and
n is the number of springs.

Discharge was measured directly in the spring brooks during two periods (June 24–26 and July 22, 2015) using the velocity area method. Water velocities, measured with a Marsh McBirney Flo-Mate 2000 electromagnetic flowmeter, and water depths were determined at a lateral transect established in each spring brook about 5 to 10 m from the confluence with the main channel of Emmons Creek. In the June period, discharge was measured in every spring brook that exceeded 0.4 L/s in discharge (15 total). In the July period, discharge was only measured in six relatively large (>3 L/s) spring brooks. Discharge in the other, mostly smaller spring brooks, was estimated for the July period based on a linear relationship (least squares regression, r^2 = 0.83) between discharge during the two time periods at the six larger springs. Total discharge from spring brooks during each period was determined by summing the discharges of individual spring brooks.

Water samples were collected for nitrate and chloride concentrations from all spring brooks larger than 0.4 L/s on June 24–26, 2015, and July 22, 2015. Samples were collected from the thalweg of the spring brooks about 5 to 10 m from the confluence with the main channel and filtered and preserved as described previously. We assumed that discharge and solute concentrations, and therefore solute fluxes, did not change in the spring brooks within the June (June 19–July, 3, 2015) and July (July 15–31, 2015) measurement periods. Although fluxes likely varied somewhat within these periods, this is probably a reasonable simplifying assumption because the measurements of discharge and solute sampling were performed at base flow, and base flow conditions occurred throughout most of the study periods.

2.5 | Darcian seepage discharge and solute flux

Solute flux to the main channel due to seepage was quantified in two different ways. First, solute flux was measured based on estimates of seepage discharge according to Darcy's Law. Second, solute flux was measured based on estimates of seepage discharge from the RWT release described previously.

In the Darcian approach, seepage flux (P_{flux} in mg·m^{-2}·s^{-1}) was estimated using the following equation:

$$P_{flux} = C_5 \; q \tag{3}$$

where

C_5 is the solute concentration (mg/L) in pore water collected 5 cm beneath the sediment surface, and

q is the specific discharge (cm^3·m^{-2}·s^{-1}).

Piezometers, constructed with chlorinated polyvinyl chloride (1.2 cm inner diameter) with the terminal 4.5 cm screened (3 mm holes covered with 100-μm Nitex mesh), were installed for measurement of specific discharge in six transects spanning the wetted width of Emmons Creek at approximately 200 m intervals (Figure 1). Each transect consisted of five piezometers spaced at 0.5 to 0.75 m intervals. Piezometers were installed at midscreen sediment depths ranging from about 17 to 25 cm.

Specific discharge (q, cm^3·m^{-2}·s^{-1}) was estimated based on Darcy's Law using the following equation:

$$q = K_v \left(\frac{\Delta h}{\Delta l}\right) \tag{4}$$

where

K_v is the vertical hydraulic conductivity,

Δh is the difference between the static head and stream surface water level (cm), and

Δl is the depth of the piezometer into the sediment (cm).

Horizontal hydraulic conductivity (K_h) was measured using falling-head slug tests (Hvorslev, 1951; Stelzer, Drover, Eggert, Muldoon, 2011). The slug tests were performed by adding 200 ml of water to each piezometer, measuring the return time to the static head level, and back-calculating the time lag (T_0) for the water to return to 37% of the initial change in head level (Hvorslev, 1951). Slug tests were performed in duplicate in each piezometer (additional replicates were added if the duplicate tests yielded inconsistent results) on at least one occasion during the study period (June 24 or 29, 2015), and mean values of T_0 were used to estimate q. We made the simplifying assumption that K_v was equal to K_h. K_h may be higher than K_v (Dahm, Valett, Baxter, & Woessner, 2006), but without direct estimates of K_v, we decided to assume unity. Vertical hydraulic gradient (VHG; $\Delta h/\Delta l$) was measured in each piezometer as described in Dahm et al. (2006) and Stelzer, Drover, et al. (2011). Measurements for VHG were collected when slug tests were performed in June (June 24 or 29, 2015) and again during the July study period (July 28 or 31, 2015). We assumed that K_v did not vary temporally throughout the entire study period and that VHG did not vary within the June or July study periods.

Pore water was collected for nitrate and chloride concentrations at 5 cm sediment depth using MINIPOINT samplers (see Stelzer et al., 2015) inserted within a 5-cm horizontal radius of each piezometer. Based on our previous research in Emmons Creek (Stelzer, Bartsch, et al., 2011; Stelzer, Drover, Eggert, Muldoon, 2011), the hyporheic zone is very shallow. We assumed that the pore water collected at 5 cm consisted of groundwater. Pore water samples were collected for each of the June (on July 1 or 3, 2015) and July (on July 28 or 31, 2015) study periods. Water samples were processed and preserved as described previously. We assumed that the solute concentrations at 5 cm depth did not change within each of the June and July study periods.

Seepage discharge at each piezometer location was estimated using Equation 4, and seepage discharge to the entire reach was estimated for the June and July periods by multiplying the average of the individual seepage discharge measurements (N = 30) by the wetted channel area (5,208 m^2) of the study reach. The wetted channel area was estimated at base flow by measuring wetted channel widths at 20-m intervals throughout the study reach. Seepage solute flux at each piezometer location was determined by multiplying the specific discharge by the solute concentration at 5 cm sediment depth (Equation 3). The average of these solute flux measurements was multiplied by the wetted channel area of the reach to estimate the solute flux due to seepage at the reach scale.

2.6 | Seepage discharge and solute flux from the Rhodamine WT release

Seepage discharge to Emmons Creek was also estimated by measuring longitudinal changes in discharge in the main channel, based on the RWT release, along subreaches (four total) that did not contain any springs with a discharge exceeding 1 L/s. The total discharge from spring brooks to all of these subreaches combined was less than 1.5 L/s. We assumed that gains in discharge in these subreaches were due solely to groundwater seepage through the streambed. The discharge gain due to seepage (L·s^{-1}·m^{-1}) in each of the four subreaches was estimated by linearly regressing discharge in the main channel on longitudinal position in each subreach. We assumed average seepage rates did not differ between subreaches with negligible inputs from springs and those with substantial inputs. Therefore, we multiplied the mean gain in discharge in the subreaches with negligible spring inputs by the total length of the reach to estimate the seepage discharge to the entire study reach. Solute flux from seepage was estimated by multiplying reach-scale seepage discharge by the mean groundwater discharge-weighted solute concentrations of pore water at 5 cm sediment depth. Because the RWT release occurred on June 19, solute flux from seepage based on the RWT release was only used during the June study period.

2.7 | Surface water nitrate uptake and transient storage measurement

We performed a slug release of nitrate in a 440-m reach downstream of the study reach on August 21, 2015, in order to estimate net nitrate uptake in the channel of Emmons Creek (Equation 1, Figure 1). To measure net nitrate uptake, we compared the downstream transport of a nitrate tracer versus that of a conservative RWT tracer. We dissolved 614 g of $NaNO_3^-$ and 40 ml of RWT into approximately 30 L of stream water and released the solution into the stream as a single pour slug. Following the release, RWT concentrations were measured at 10 s intervals with a Hydrolab DS5 equipped with a Turner Designs RWT sensor 440 m downstream of the release location. RWT concentrations were temperature corrected using the relationships given by Wilson et al. (1986). Grab samples were collected at approximately 30 s intervals, at the same location where RWT was measured, for determination of nitrate concentrations. Peak (background corrected) downstream RWT and nitrate concentrations were 46 µg RWT/L and 3 mg NO_3–N/L, respectively, and the travel time until peak concentrations was 21 min. Background-corrected breakthrough curves for RWT and NO_3–N are shown in Figure 2a. Nitrate uptake metrics were calculated by integrating under the breakthrough curves using the equations from Tank, Rosi-Marshall, Baker, and Hall (2008).

Transient storage was measured immediately following the whole-stream nitrate uptake measurement in the same 440-m reach using a 42-min RWT injection. An RWT solution was injected into the stream at a rate of 66 ml/min using a Fluid Metering, Inc., battery-powered pump (model QB-Q2CKC-W). Downstream plateau concentration was 38 µg/L and was maintained for 18 min (Figure 2b). Transient storage parameters were determined by modeling the RWT concentrations with the advection or dispersion equations including parameters for lateral flux and transient storage (Stream Solute Workshop, 1990). Model simulations were completed using OTIS and OTIS-P software (Runkel, 1998). The final model values were then used to calculate $F_{med}{}^{200}$, the fraction of median travel time due to transient storage at a standard reach distance of 200 m (Runkel, 2002).

$$F_{med^{200}} \left(1 - e^{-L\,(\alpha/u)}\right) \frac{A_s}{A + A_s} \tag{5}$$

where

- L is the reach length and is fixed at 200 m for $F_{med}{}^{200}$,
- α is the storage exchange coefficient (s^{-1}),
- u is the average stream velocity (m/s; estimated by dividing stream discharge [m^3/s] by the average cross sectional area of the stream [A; m^2]), and
- A_s is the cross-sectional area of the transient storage zone (m^2).

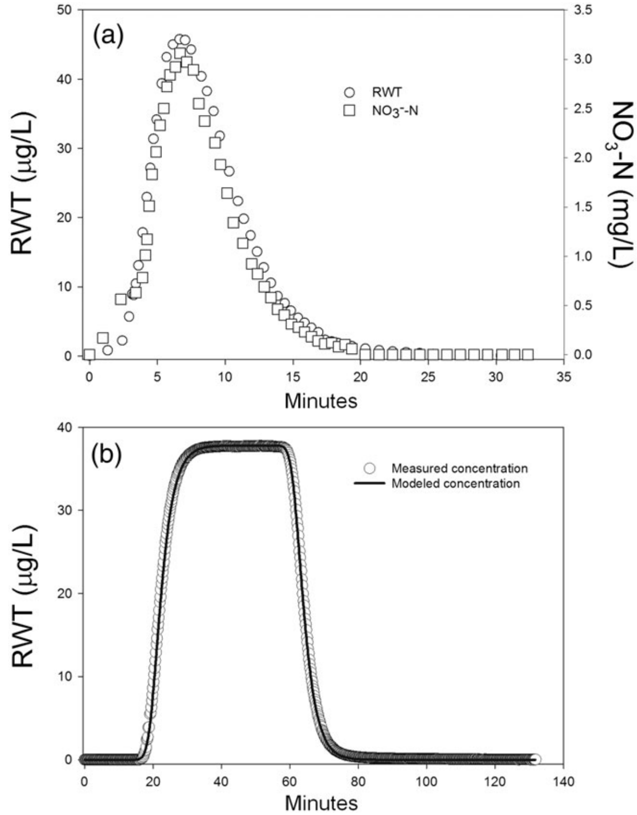

FIGURE 2 (a) NO_3–N and Rhodamine water tracing (RWT) concentrations, following a slug injection of NO_3^- and RWT, plotted against time elapsed after RWT first appeared at the downstream location. (b) Measured and modeled RWT concentrations during a 42-min sustained injection of RWT plotted against time elapsed after the injection. Injections occurred in Emmons Creek on August 21, 2015, and sampling was performed 440 m downstream of the injection site

2.8 | Solute and statistical analysis

Nitrate samples collected for the estimate of nitrate uptake in the stream channel were measured on a Lachat QuikChem 8500. For all other samples, nitrate and chloride concentrations were measured with a Dionex ICS-1000 ion chromatograph equipped with an IonPacAS14A column. Paired *t* tests (Systat v13) were used to compare nitrate concentrations (from spring brooks and shallow pore water) and hydraulic data (VHG and seepage discharge) between June and July periods.

3 | RESULTS

3.1 | Water balance

Discharge in the main stem of Emmons Creek increased by about 200 L/s (a two-fold gain) in the 1,450-m study reach (Table 1, Figure 3). The gain in discharge decreased from 211 L/s at the

TABLE 1 Discharge (L/s) balance in the Emmons Creek network

Date	Downstream Station (*DS*)	Springs	Seepage (RWT)	Seepage (Darcian)	Discharge gain (*DS* − *US*)	Inputs (springs + seepage$_{RWT}$)	Inputs (springs + seepage$_{Darcy}$)
6/19/2015	413	87	123	36	211	210	123
6/24/2015	390	87	123	36	199	210	123
6/26/2015	380	87	123	36	194	210	123
6/29/2015	383	87	123	36	195	210	123
7/1/2015	365	87	123	36	186	210	123
7/3/2015	360	87	123	36	184	210	123
7/15/2015	364	63	—	39	186	—	102
7/22/2015	353	63	—	39	180	—	102
7/24/2015	355	63	—	39	181	—	102
7/28/2015	351	63	—	39	179	—	102
7/31/2015	345	63	—	39	176	—	102

Note. *DS* = downstream station; RWT = Rhodamine water tracing; *US* = upstream station, upstream location at Third Avenue Bridge. On June 19, 2015, discharge at *DS* and *US* was based on the RWT injection. On all other dates, discharge at *DS* and *US* was based on a rating curve (see Section 2).

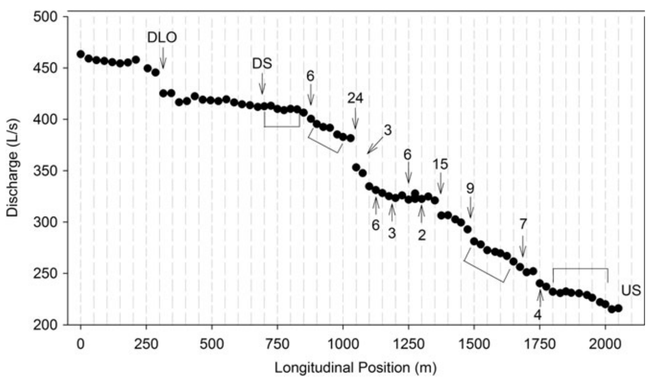

FIGURE 3 Discharge (L/s) profile in the Emmons Creek channel based on a Rhodamine water tracing release on June 19, 2015. Longitudinal position is relative to a downstream reference station. *DS* and *US* indicate the positions of the downstream and upstream stations. DLO indicates Deans Lake outflow. The positions and discharge (L/s) of spring brooks in June are identified with arrows. Subreaches that receive zero or negligible inputs from spring brooks are indicated with brackets

beginning of the study (June 19, 2015) to 176 L/s at the end (July 31, 2015). The estimate of discharge at the downstream station on June 19, 2015, based on a rating curve (375 L/s) was similar but lower than the estimate from the RWT release on the same date (413 L/s, Table 1). Total discharge from spring brooks and seepage, when estimated based on Darcy's Law, could account for 63 to 87 L/s (34% to 47%) and 36 to 39 L/s (17% to 22%), respectively, of the discharge gain in the study reach (Table 1). Seepage discharge estimated from the RWT release during June was 123 L/s, over 3 times higher than the Darcian estimate. The sum of RWT-based seepage discharge and spring discharge in the June period was 210 L/s that accounted for the gain in discharge (184 to 211 L/s) between the downstream and upstream stations (Table 1).

3.2 | Spring brooks

Mean discharge ranged from 0.5 to 21 L/s among spring brooks with a grand mean of 5 L/s (Table 2). Spring brooks were predominantly located in the downstream portion (700 to 1,400 m) of the study reach (Figures 1 and 3). The entry locations of five of the larger spring brooks (at 875, 1,060, 1,370, 1,495, and 1,680 m), which accounted for 50 L/s and 67% of the total discharge from spring brooks, on average, were associated with step increases in the discharge of Emmons Creek similar in magnitude to the discharges of the spring brooks (Figure 3). Discharge from spring brooks declined 26%, on average, between the June and July study periods.

Mean nitrate concentration in the spring brooks was 2.13 mg NO_3–N/L and ranged from 1.17 to 3.24 mg NO_3–N/L (Table 2). Mean discharge-weighted nitrate concentration in the spring brooks was 1.95 mg NO_3–N/L. Mean nitrate concentration in the spring brooks was slightly higher in July on average (2.16 mg NO_3–N/L) than in June (2.10 mg NO_3–N/L; paired t test, $t = -3.03$; $df = 14$; $p < .01$). Mean chloride concentration in the spring brooks was 2.73 mg Cl^-/L and ranged from 1.69 to 4.21 mg Cl^-/L. Total nitrate flux from spring brooks, which was dominated by the larger spring brooks, was 163 and 126 mg NO_3–N/s, respectively, in the June and July study periods (Table 3). Chloride flux from the spring brooks was 238 and 188 mg Cl^-/s in the June and July study periods (Table 4).

3.3 | Seepage (Darcian)

Seepage discharge estimated based on Darcy's Law varied among and within piezometer transects (Figure 4). Transects at 949, 1,155, and 1738 m revealed higher groundwater seepage discharge (grand mean of 12.5 $cm^3 \cdot m^{-2} \cdot s^{-1}$) than transects at 1,355, 1,534, and 1,930 m (grand mean of 1.9 $cm^3 \cdot m^{-2} \cdot s^{-1}$; Figure 4). Variation in seepage discharge among transects reflected variation in K_v and VHG. The three transects with high-seepage discharge had a mean K_v of 0.0054 cm/s and a mean VHG of 0.259, whereas the three transects with low-seepage discharge had means of 0.0034 cm/s and 0.088. Variation in seepage discharge within transects was especially pronounced at 949 m where the range was 1.3 to 55.2 $cm^3 \cdot m^{-2} \cdot s^{-1}$ (Figure 4). VHG did not differ statistically (paired t test, $t = -0.314$; $df = 29$; $p = .756$) between the June (0.171) and July (0.176) study periods, which resulted in similar estimates of mean seepage discharge for the periods (7.0 and 7.4 $cm^3 \cdot m^{-2} \cdot s^{-1}$; paired t test, $t = -0.567$; $df = 29$; $p = .575$).

TABLE 2 Attributes of spring brooks entering Emmons Creek

Spring (m)	Length (m)	Q (L/s)	Water temperature (°C)	Specific conductance (μS/cm)	NO_3–N (mg/L)	Cl^- (mg/L)	NO_3–N flux (mg/s)	Cl^- flux (mg/s)
875	50	4.8	13.9	367.0	1.89	2.07	9.12	10.00
975	25	0.7	14.8	390.0	2.61	1.72	1.84	1.22
1,060	150	20.9	12.2	367.5	1.95	3.38	40.66	70.60
1,100	25	2.7	13.4	383.5	2.45	2.94	6.51	7.78
1,125	50	5.2	14.3	390.5	1.87	1.74	9.71	8.97
1,182	25	2.9	13.3	375.8	1.72	3.01	4.9	8.3
1,240	75	5.2	17.2	392.0	2.02	2.26	10.42	11.70
1,290	50	1.7	14.3	407.0	2.70	2.05	4.66	3.52
1,370	100	10.8	15.7	362.5	1.19	2.13	12.73	22.71
1,495	100	7.9	14.9	400.8	1.99	3.17	15.62	24.87
1,651	25	0.5	11.0	440.0	1.88	3.53	0.94	1.76
1,680	175	6.0	14.4	395.5	2.42	4.10	14.45	24.45
1,747	25	1.3	13.0	419.5	3.17	3.12	4.16	4.08
1,749	75	4.3	14.0	430.0	1.84	2.56	7.94	11.03
1,828	25	0.6	12.3	441.5	2.23	3.13	1.25	1.75

Note. Values are means for the June and July sampling periods. Springs are indicated as relative positions (m) from a downstream reference station.

TABLE 3 Nitrate fluxes (mg NO_3–N/s) in the Emmons Creek network

Date	Downstream station (*DS*)	Springs	Seepage (RWT)	Seepage (Darcian)	Flux gain (*DS* − *US*)	Inputs (springs + $seepage_{RWT}$)	Inputs (springs + $seepage_{Darcy}$)
6/19/2015	967	163	278	82	445	441	246
6/24/2015	913	163	278	82	427	441	246
6/26/2015	892	163	278	82	418	441	246
6/29/2015	884	163	278	82	417	441	246
7/1/2015	861	163	278	82	400	441	246
7/3/2015	846	163	278	82	390	441	246
7/15/2015	847	126	—	89	394	—	215
7/22/2015	843	126	—	89	389	—	215
7/24/2015	831	126	—	89	387	—	215
7/28/2015	820	126	—	89	380	—	215
7/31/2015	818	126	—	89	379	—	215

Note. *DS* = downstream station; RWT = Rhodamine water tracing injection; *US* = upstream station, upstream location at Third Avenue Bridge.

TABLE 4 Chloride fluxes (mg Cl^-/s) in the Emmons Creek network

Date	Downstream station (*DS*)	Springs	Seepage (RWT)	Seepage (Darcian)	Flux gain (*DS* − *US*)	Inputs (springs + $seepage_{RWT}$)	Inputs (springs + $seepage_{Darcy}$)
6/19/2015	1,520	238	322	99	544	560	337
6/24/2015	1,402	238	322	99	492	560	337
6/26/2015	1,370	238	322	99	473	560	337
6/29/2015	1,447	238	322	99	516	560	337
7/1/2015	1,331	238	322	99	457	560	337
7/3/2015	1,321	238	322	99	434	560	337
7/15/2015	1,401	188	—	97	508	—	285
7/22/2015	1,364	188	—	97	486	—	285
7/24/2015	1,371	188	—	97	482	—	285
7/28/2015	1,381	188	—	97	466	—	285
7/31/2015	1,332	188	—	97	459	—	285

Note. *DS* = downstream station; RWT = Rhodamine water tracing injection; *US* = upstream station, upstream location at Third Avenue Bridge.

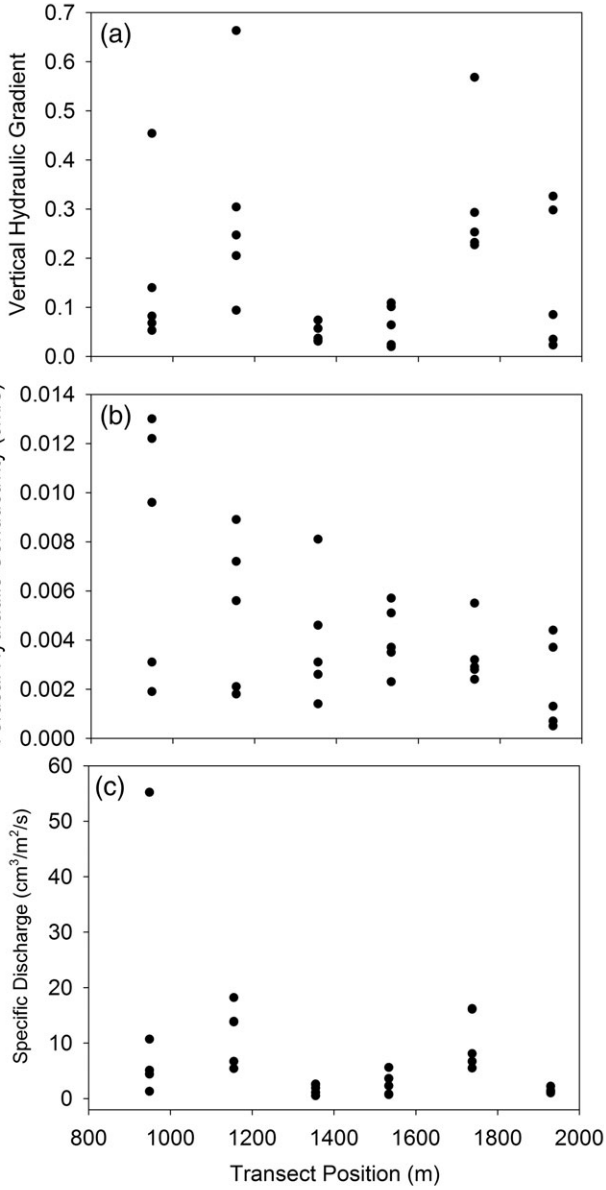

FIGURE 4 (a) Vertical hydraulic gradient. (b) Vertical hydraulic conductivity (K_v) (c) Specific discharge (q). Values based on measurements at piezometers from six transects (positions are indicated relative to a downstream reference station) in Emmons Creek. All values are means (N = 2) except K_v (N = 1)

Pore water nitrate and chloride (data not shown) concentrations at 5 cm sediment depth also varied among and between piezometer locations (Figure 5) but did not differ between June and July study periods (paired t tests, $p > .492$). Mean pore water nitrate and chloride concentrations at 5 cm were 2.31 and 3.27 mg/L for the June period, respectively, and 2.34 and 3.15 mg/L for the July period, respectively. Groundwater discharge-weighted NO_3–N and Cl^- concentrations at 5 cm were 2.26 and 2.62 mg/L for the June period, respectively, and 2.30 and 2.51 for the July period, respectively. Nitrate fluxes in seepage were one to two orders of magnitude higher in transects at 949, 1,155, and 1,738 m than in the other three transects (Figure 5). Variation in nitrate fluxes also occurred within transects, generally within one order of magnitude range. There was no consistent pattern in the location of the highest nitrate fluxes within transects. At the reach scale, nitrate fluxes from seepage inputs based on Darcy's Law were estimated at 82 and 89 mg NO_3–N/s for the June and July periods (Table 3). respectively. Chloride fluxes from seepage were 99 and 97 mg Cl^-/s for these periods (Table 4).

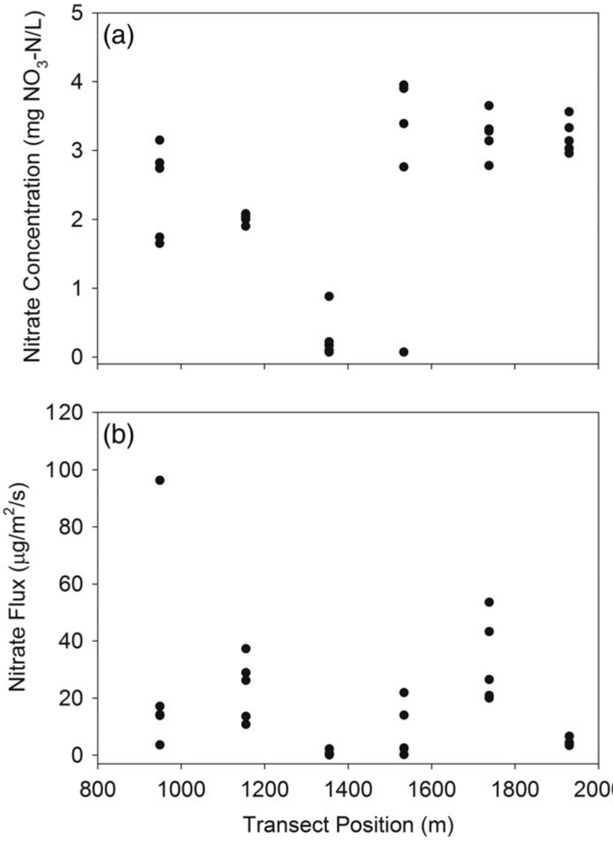

FIGURE 5 (a) Pore water nitrate concentration and (b) nitrate flux based on measurements from six transects in Emmons Creek at 5 cm sediment depth. Values are means (N = 2)

3.4 | Seepage (RWT release)

The discharge gains in the four subreaches of Emmons Creek that contained negligible inputs from springs were 5 L/s (700 to 850 m), 15 L/s (900 to 1,029 m), 14 L/s (1,500 to 1,625 m), and 20 L/s (1,775 to 2,050 m). The mean discharge gain in these subreaches was 0.084 $L{\cdot}s^{-1}{\cdot}m^{-1}$. Estimates of nitrate and chloride fluxes from seepage for the June study period, based on the RWT release, were 278 mg NO_3–N/s and 322 mg Cl^-/s (Tables 3 and 4), respectively. These flux estimates were over 3 times higher than when seepage was estimated using Darcy's Law due to the higher estimates of seepage discharge based on the RWT release.

3.5 | Whole-stream nitrate uptake and transient storage

Mean nitrate concentrations in the surface water of Emmons Creek were 2.46 (0.03, standard deviation) and 2.35 (0.02) mg NO_3–N/L at the upstream and downstream stations during the study period. During the nitrate and RWT slug release on August 21, 2015, downstream recoveries of the added RWT and nitrate tracers were 100% and 105%, respectively, indicating that both tracers traveled through the reach conservatively. Consequently, we were unable to calculate any net nitrate uptake. The assessment of the transient storage zone in Emmons Creek based on OTIS-P modeling of the 42-min RWT injection indicated that the stream does not have extensive storage and solute transport is relatively unobstructed. The modeled values of the breakthrough curve fit the measured values very well (adjusted $R^2 = 0.9998$, $p < .0001$, linear regression of the observed vs. modeled values). The modeled cross-sectional area of the transient storage zone (A_s) was determined to be 0.141 m^2 (95% CI [0.110, 0.172]), the storage exchange coefficient (α) was 0.000919 (95% CI [0.000565, 0.00127]), and the storage zone relative to stream area (A_s/A) was 0.101. The fraction of median travel time due to transient storage at a standard reach distance of 200 m (F_{med}^{200}) was 4.0%.

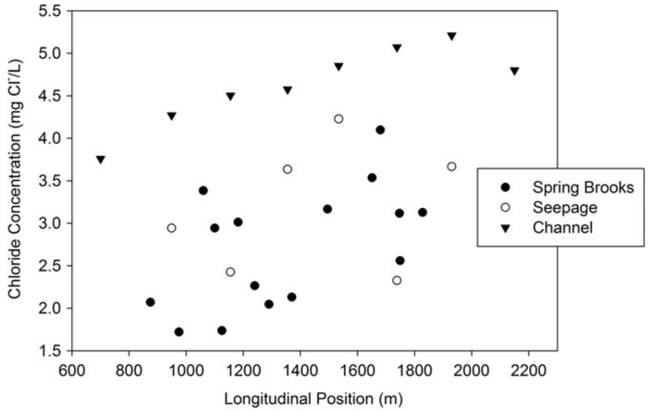

FIGURE 6 Mean chloride concentrations of spring brooks (N = 2), seepage (N = 10), and main channel (N = 1 or 2) in the Emmons Creek network

3.6 | Mass balance model

When seepage discharge was estimated based on Darcy's Law, groundwater nitrate flux from seepage and springs only accounted for about 55% to 63% of the gain in nitrate flux in Emmons Creek based on the difference between downstream and upstream fluxes (Table 3). Total groundwater nitrate flux from seepage and springs accounted for about 99% to 113% of the gain in nitrate flux in Emmons Creek when seepage was estimated from the RWT release (Table 3). Chloride inputs from RWT-estimated seepage and springs accounted for 102% to 129% of the chloride flux gain between the upstream and downstream locations. Chloride inputs from Darcian-estimated seepage and springs were lower, accounting for 56% to 78% of the gain in the Emmons Creek channel (Table 4).

Nitrate input to Emmons Creek from seepage, based on the RWT release, was 71% higher than nitrate input from spring brooks during the June study period (Table 3). Discharge to Emmons Creek from seepage, based on the RWT release, was 41% higher than discharge from spring brooks (Table 1) in the June period. Thus, of the two primary nitrate-routing pathways to the study reach of Emmons Creek, groundwater seepage made a disproportionately larger contribution to nitrate flux at the downstream station.

3.7 | Longitudinal trends

Chloride concentration in spring brooks, near the locations where they entered Emmons Creek, decreased in a downstream direction along the main channel (Figure 6). Pore water chloride concentrations at 5 cm depth (seepage) also showed a similar longitudinal trend. These trends were reflected in the chloride concentrations in the main channel, which also decreased in a downstream direction (Figure 6). No longitudinal trends were present in nitrate concentration (data not shown).

4 | DISCUSSION

4.1 | Water balance and groundwater seepage

We think that the estimates of discharge in the Emmons Creek channel determined from the RWT release were accurate for two reasons. First, the estimate of mean daily discharge at the downstream station based on the June 9, 2015, RWT release was similar to the estimate derived from the rating curve at that location. Second, the step increases in channel discharge based on the RWT release were similar in location and magnitude to the direct estimates of discharge from the larger spring brooks. When seepage discharge was estimated from the RWT release, inputs of water from seepage and spring brooks could account for the gain in discharge between the downstream and upstream stations. Spring brooks and seepage estimates based on Darcy's Law could only account for about 50%–60% of the discharge gain in the main channel. In addition, when seepage was estimated from the RWT release, total inputs of chloride to the reach (springs and seepage) accounted for the gain in chloride flux between the upstream and downstream stations. Inputs of chloride that included Darcian seepage measurements underestimated the gain in chloride flux in the channel. On the basis of these collective results, we think that the nitrate and chloride flux estimates from seepage based on the RWT release were more accurate than those estimated from Darcy's Law, and we will emphasize the former estimates hereafter.

4.2 | Nitrate-routing pathways

We predicted that springs would contribute disproportionately to nitrate flux in the Emmons Creek network because springs, particularly those with relatively high discharge, are locations with preferential groundwater discharge and likely low-Damköhler values (Marzadri, Tonina, & Bellin, 2012; Zarnetske et al., 2012). These conditions suggest reduced opportunities for nitrate removal (Flewelling et al., 2012; Zarnetske et al., 2012). We predicted that the nitrate concentrations in springs, and by extension spring brooks, would be higher on average than in groundwater seeping through the streambed because of predicted higher water transport rates in springs and lower nitrate retention in springs than in seeps. Our previous studies in Emmons Creek (Stelzer, Bartsch, et al., 2011, Stelzer et al., 2015, 2014) and those of investigators working in other streams (Duff, Tesoriero, Richardson, Strauss, & Munn, 2008; Lansdown et al., 2015) have documented considerable nitrate loss along seepage flow paths in streambeds, particularly in sediments that are rich in organic matter. The nitrate concentrations in pore water at 5 cm sediment depth were higher than we predicted at most locations. The mean nitrate concentration at 5 cm depth (2.33 mg NO_3–N/L) was only slightly lower than the mean concentration from samples collected at 25 cm sediment depth at the same locations (2.55 mg NO_3–N/L, data not shown; paired *t* test, *t* = −2.388; *df* = 59; *p* = .010), suggesting low-nitrate retention in seepage flow paths, on average. These results are consistent with pore water dissolved oxygen data (mean of 5.9 mg/L; Stelzer, unpublished data) collected from 5 cm sediment depth at the transect locations that suggests that redox conditions in the shallow sediments were not favorable for denitrification. Our nitrate results contrast with those of Tesoriero et al. (2009) who found much lower nitrate concentrations in the shallow pore water than in the surface water in groundwater-receiving reaches of several agricultural streams, which suggested nitrate removal. The relatively low-net nitrate retention in the sediments was likely influenced by their properties. The dominant surficial substrate at all of the piezometer transects was sand, which was also the most common surficial substrate in the study reach. Other investigators (Flewelling et al., 2012; Heppell et al., 2014) have measured, or inferred, low- or zero-nitrate retention along groundwater flow paths in streambeds containing sandy or coarser sediments with relatively fast transport times. These conditions favor high-transport rates of groundwater nitrate to streams (Tesoriero et al., 2013).

The lack of net nitrate uptake in the channel of Emmons Creek is consistent with the results of our mass balance model. When nitrate uptake in the channel was set to 0, nitrate inputs from springs and seepage (based on the RWT release) could account for the gain of nitrate flux in the Emmons Creek channel. Our results suggest that in the summer months, nitrate behaved conservatively in the channel. The slug release of nitrate was performed to evaluate nitrate uptake by processes in the stream channel such as assimilatory uptake by periphyton, heterotrophic microbes and submergent macrophytes, which were sparsely distributed. This approach was likely less sensitive to processes expected to occur over longer time scales such as denitrification in hyporheic flow paths. The high-nitrate concentrations in the surface water of Emmons Creek and the exceptionally high ratio of available N:P (NO_3–N:PO_4–P, >1,000:1; Stelzer, unpublished data) suggest that there was low biological demand for nitrogen in the channel. The lack of net nitrate uptake in the Emmons Creek channel measured in August 2015 contrasts with measurements made in the same reach in October 2014 when we determined an uptake rate of 544 mg NO_3–N·m^{-2}·d^{-1} and an uptake length of 4.96 km. We speculate that this higher nitrate uptake in the autumn might be caused by higher primary production and/or microbial production. During autumn, Emmons Creek experiences significant leaf litter inputs and heightened light penetration through the stream riparian because of leaf fall. These conditions could increase autotrophic and/or heterotrophic populations resulting in higher nitrate uptake. We did not take measurements of nitrate uptake in the channels of the spring brooks. The channel lengths between the spring outflows and the Emmons Creek channel were relatively short (Table 1) that makes it unlikely that nitrate uptake in these channels substantially reduced nitrate contributions from the springs. However, even small to moderate amounts of nitrate uptake in the spring brooks (O'Driscoll & DeWalle, 2010; Williams, Buda, Elliot, Collick, et al., 2015) could partially explain why spring brooks contributed a disproportionately lower amount of nitrate flux to Emmons Creek than seepage.

Estimates of groundwater and nitrate fluxes in seepage based on Darcy's Law were lower than those based on the sustained RWT injection on June 12, 2015, which is consistent with the results reported by Kurz et al. (2015) in a karst river—If K_v was lower than K_h (we assumed unity), this would have led to even larger discrepancies between the Darcy's Law and RWT injection approaches. There are several possible reasons why the seepage estimates based on Darcy's Law were lower than from the RWT injection in our study. First, although the six piezometer transects were positioned at approximately equal distances throughout the study reach, it is possible that their locations were, on average, in subreaches with lower groundwater discharge than what occurred throughout the entire reach. The juxtaposition of transect locations (Figure 1) and the longitudinal gains in surface water discharge from seepage (Figure 3) do not provide support for this hypothesis. However, hydraulic conductivity tends to be inherently variable in streams with diverse sediment types, particularly at small (<1 m) scales (Genereux, Leahy, Mitasova, Kennedy, & Corbett, 2008; Kalbus, Reinstorf, & Schirmer, 2006), and it is conceivable that the array of piezometers did not fully reflect variability in seepage throughout the reach. Second, the RWT injection to estimate seepage discharge occurred on June 9, 2015, whereas the Darcy's Law measurements (slug tests and measurements of VHG) occurred on June 24 or 29, 2015. Although base flow conditions prevailed when the measurements were taken, it is possible that groundwater discharge variance among dates contributed to the differences in seepage discharge estimates. Third, uncertainty in either the RWT or Darcy's Law (Lu, Chen, Cheng, Ou, & Shu, 2012) approach may have contributed to the discrepancy. We assumed that RWT behaved conservatively in the channel. If RWT sorption (Sutton, Kabala, Francisco, & Vasudevan, 2001) occurred in the study reach, this could have led to an overestimation of groundwater seepage. Although we cannot discount this source of bias, we think if RWT sorption occurred it was minimal. In support of this assertion, our results from the 42-min RWT injection for estimating transient storage showed that downstream RWT concentrations rapidly reached and maintained plateau (Figure 2) indicating sorption and desorption was in a steady state condition. In addition, the good agreement between surface water discharge determined by the RWT release and by a rating curve, described previously, suggests the RWT approach yielded accurate results. Another possible source of the difference between the RWT- and Darcy's Law-based estimates of seepage was lateral inflow of soil water or groundwater through the stream banks. Water entering the stream through the stream banks would have likely been incorporated in the RWT-based estimate but not that based on Darcy's Law. There is considerable inherent uncertainty in point-based methods to estimate groundwater discharge, including approaches based on Darcy's Law and seepage meters, and the appropriateness of different methods for estimating groundwater discharge is scale dependent (Kalbus et al., 2006). For estimating groundwater seepage at the reach-scale of Emmons Creek, we think the RWT method yielded more accurate results. However, the Darcy's Law approach allowed us to quantify spatial heterogeneity in seepage within the reach at a scale that the tracer-based approach did not allow.

4.3 | Focused discharge and nitrate flux

We found evidence of focused groundwater discharge both among and within transects when seepage was estimated based on Darcy's Law. Several other investigators have observed a high degree of spatial variation in groundwater discharge (Binley et al., 2013; Lowry, Walker, Hunt, & Anderson, 2007; Malzone & Lowry, 2015; Rosenberry, Briggs, Delin, & Hare, 2016) or hydraulic conductivity (Genereux et al., 2008) in streambeds. Based on the finding of other investigators and our previous work in Emmons Creek (Stelzer, Drover, et al., 2011), the determination of focused discharge in the study reach was not surprising. We suspect that focused discharge was widespread throughout the reach, and its range may have exceeded the range determined at the piezometer transects. Focused discharge can be a source of uncertainty when scaling up from point-based determinations of groundwater discharge. The spatial variation in groundwater seepage to Emmons Creek, coupled with the spatial variation in pore water nitrate concentration, tended to magnify the variation in nitrate flux, particularly among transects (Figure 5). Although we noted variability in groundwater nitrate fluxes within transects, we did not observe any patterns with respect to lateral position in the channel. Kennedy et al. (2009a) reported lower nitrate flux in the center of the thalweg in a coastal plain stream, which they attributed to older groundwater with lower nitrate concentration. The range of nitrate fluxes in groundwater seepage to Emmons Creek was comparable to rates of nitrate flux reported by other investigators (Heppell et al., 2014; Kennedy, Genereux, Corbett, & Mitasova, 2009b).

There was some indication of a relationship between Darcian seepage rates and RWT-based seepage rates in Emmons Creek. The three transects that had high rates of Darcian seepage (949, 1,155, and 1738 m; Figure 4) were located in subreaches where discharge in the main channel was gaining at relatively rapid rates due to seepage based on the RWT release (Figure 3). The transects with much lower Darcian seepage rates (1,355, 1,534, and 1,930 m) were associated with subreaches with apparent low- (1,355 and 1,930 m) and high- (1,534 m) discharge gains from seepage, inferred from the RWT release. However, several of the piezometer transects were located in subreaches that contained inputs from spring brooks, which made it difficult to assess the contributions of seepage to discharge gain. Measurements of groundwater discharge at additional transect locations would have allowed us to better determine if seepage rates estimated from the two methods were correlated.

4.4 | Springs

Springs contributed about 40% to the discharge gain and 36% to the gain in nitrate flux in the study reach, on average. The contribution of springs to surface water discharge is comparable to the contributions from surface water seeps that have been documented by other investigators (O'Driscoll & DeWalle, 2010; Williams, Buda, Elliot, Singha, et al., 2015). The nitrate concentrations of spring brooks varied within a two-fold range in most cases (Table 2). Variation in the land use at recharge locations of springs (Menció, Boy, & Mas-Pla, 2011) and variation in nitrate uptake among spring brooks (O'Driscoll & DeWalle, 2010) are two potential sources for these differences.

Emmons Creek network springs provide an important source of cold water necessary for brown trout (*Salmo trutta*), which are abundant in Emmons Creek, and other coldwater fish species. In addition, spring brooks provide an important nursery habitat for salmonids in the Emmons Creek network (Louison & Stelzer, 2015) as headwater streams do in other ecosystems (Cunjak, Linnansaari, & Caissie, 2013). The data on discharge and solute dynamics from springs in this study will provide a baseline for comparison in future decades. Groundwater pumping for irrigated agricultural and municipal water demand has been increasing rapidly in the Central Sands area of Wisconsin (Kraft, Clancy, Mechenich, & Haucke, 2012), which includes the Central Sand Ridges ecoregion where Emmons Creek is located. Increased groundwater withdrawal in the Emmons Creek groundwater watershed could impact the discharge from both springs and seepage across the streambed to Emmons Creek, which may impact the brown trout population and other biota.

Despite there being a relatively small percentage of the Emmons Creek watershed in active agriculture, the nitrate concentrations of springs and of groundwater in seeps were elevated and likely much higher than concentrations before marked increases in fertilizer use in Central Wisconsin during the latter part of the 20th century (Smith et al., 2003). The relatively high-nitrate concentrations in shallow groundwater associated with Emmons Creek may be partly due to the legacy of agricultural activity in the watershed (Browne & Guldan, 2005; Tesoriero, Sprull, Mew, Farrell, & Harden, 2005).

4.5 | Transient storage

The results of the transient storage modelling suggest that surface water or hyporheic transient storage zones were small relative to the streambed area (A_s/A) that suggests that hyporheic processes played a minor role, if any, on nitrate retention in Emmons Creek. Our value of the hyporheic exchange coefficient (α) fell in the midrange of values computed for other sandy streams based on literature data compiled by Stofleth, Shields, and Fox (2008). However, our A_s/A value was lower than most of the values available in Stofleth et al. (2008).

4.6 | Broader implications

Our results demonstrate the importance of taking measurements at multiple spatial scales in hydrological studies. If point measurements (Darcian) of groundwater discharge and groundwater nitrate flux had been used exclusively to quantify groundwater inputs to the study reach estimates of groundwater discharge and nitrate flux would have been grossly underestimated. This approach would have inappropriately deemphasized the importance of groundwater seepage through the streambed, relative to springs, as a source of nitrate to the main channel. Whole-stream tracer injections allow for hydrological and biogeochemical processes to be integrated over larger spatial scales than point-based approaches. The advancement of distributed (e.g., fiber optic) temperature sensors and associated thermal modeling (Briggs, Lautz, Buckley, & Lane, 2014; Koch et al., 2015) have the potential to yield more accurate estimates of groundwater flux than traditional Darcian-based approaches. One advantage of these thermal-based methods is their potential to capture groundwater dynamics at spatial and temporal scales that were not possible in the point-based approach (piezometer transects and parameter estimation based on discrete measurements such as falling-head slug tests) that we employed for part of our study.

5 | CONCLUSIONS

Spring brooks and groundwater seepage were both important sources of nitrate in the Emmons Creek network, contributing 126–163 and 278 mg NO_3–N/s, respectively, and accounted for the gain in nitrate flux along the main channel in June. Contrary to our prediction, seepage contributed disproportionately to nitrate flux in the stream network relative to the discharge contribution from seeps. Relatively high rates of seepage discharge and higher than anticipated nitrate concentrations in the shallow pore water at seepage locations contributed to the unanticipated result. Based on the Darcian estimates of groundwater seepage, there were one to two orders of magnitude differences among piezometer transects in nitrate flux and less variation within transects. Discharge and nitrate fluxes in spring brooks ranged from 0.5 to 21 L/s and 1 to 41 mg NO_3–N/s, respectively. Baseline information on the discharge and nitrate fluxes from springs and other sources of groundwater in this watershed are important due to the rapid increases in groundwater pumping in the Central Sands Region of Wisconsin and the known impacts of this pumping on groundwater discharge (Kraft et al., 2012).

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