Groundwater contributions of flow and nitrogen in a headwater agricultural watershed

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Abstract
Nonpoint sources of nitrogen (N) and other nutrients are a major source of water pollution within the Chesapeake Bay watershed and other basins around the world. Human activities associated with agricultural practices can account for a large percentage of N loadings delivered to streams and rivers. This work aims to improve understanding of N transport from groundwater to surface waters, quantifying the principal hydrological processes driving water and N fluxes into and out of a headwater agricultural stream reach. The study site is a 175-m stream reach in a heavily cultivated 40-ha watershed in east-central Pennsylvania. This subwatershed is underlain by fractured shale bedrock, and receives most of its baseflow from groundwater, either by diffuse matrix discharge through the streambed or by localized discharge through riparian seeps. Samples of stream, seep, and shallow groundwater were collected approximately monthly under steady hydrologic conditions in 2017. Calculated matrix flow from hydraulic head and conductivity measurements paired with differential stream gauging was used to solve for the riparian seep flux using a mass balance approach. Riparian seep fluxes ranged from 45 to 217 m³/d, transporting 0.6–4.2 kg N d⁻¹ of nitrate-N from the fractured bedrock aquifer to the stream. Hydrochemical data suggest that the stream is mainly disconnected from the underlying aquifer and that seeps supply essentially all water and N to the system. Seeps are likely sourced with N in nearby agricultural fields and accelerated through the system with shorter residence times than shallow groundwater. Water isotope data reinforced this notion. This study underscores the importance of agriculture as a source of N to ground and surface waters. Identifying source areas that are causing groundwater enrichment of N and seep areas where N discharges to streams is beneficial for developing N pollution mitigation strategies and implementing management practices that aim to reduce nutrient loads to the Chesapeake Bay.

KEYWORDS
agriculture, groundwater, mass balance, nitrogen, seeps, watershed
1 | INTRODUCTION

Nitrogen (N) over-enrichment in the environment is a longstanding problem that has led to numerous adverse consequences around the world (Galloway et al., 2004; Sutton et al., ). Excess reactive N has led to widespread impairments of surface water quality, with watershed impacts related to acidification, eutrophication, and algal blooms (Bricker et al., 2008; Driscoll et al., 2003). Important sources of N inputs to the landscape include atmospheric deposition, fertilizers, manure, biological N fixation, and wastewater (septic and sewage) (Boyer et al., 2004; USEPA, 2011). N inputs to the landscape are subsequently stored in soils, taken up by crops or plants, released to air via denitrification processes, leached to groundwater through the soil, and/or transported to streams via hydrological flow pathways (Alexander et al., 2009; Boyer, Goodale, Jaworski, & Howarth, 2002). Nitrate is the most widespread pollutant in groundwater in the United States (Dubrovsky et al., 2010; Nolan & Hitt, 2006).

In many regions, streams receive the majority of total annual streamflow from groundwater flow pathways. Topography, water table gradients, and characteristics of the porous media dictate the movement of water through the landscape to surface water and groundwater (Winter, Harvey, Franke, & Alley, 1998). Primary flow paths of water and solutes through the riparian zone to streams include shallow and deep groundwater matrix flow, overland flow, and spring or seep flow. Matrix flow refers to the even flow of water through the soil matrix into the stream. In contrast, uneven and often rapid movement of water through the system is referred to as seepage flow; where seeps typically emerge within the riparian zone and flow downslope to the stream. Watersheds containing frequent riparian seeps are found throughout the northeastern U.S. (Pionke et al., 1988).

Stream seeps can often be the source of a large portion of flow delivered to streamflow and can have important implications for stream water chemistry (O’Driscoll & DeWalle, 2010). A growing body of literature exists on the role of seeps in groundwater-based N inputs in streams (Burns, Murdoch, Lawrence, & Michel, 1998; O’Driscoll & DeWalle, 2010; Stelzer, Strauss, & Coulibaly, 2017; Williams, Buda, Elliott, Singha, & Hamlett, 2015), but few studies have explicitly partitioned components of matrix and preferential groundwater flow in fractured aquifers. In fractured aquifers, hydraulic conductivities are often elevated, allowing for quick, lateral movements of water with low residence times, which facilitates N-rich waters to be transported to surface waters with little change to its chemistry (Gburek & Urban, 1990). Changes in N chemistry often occur when water takes a path of longer residence time through riparian or hyporheic sediments, which act as biogeochemical hotspots (McClain et al., 2003; Vidon et al., 2010; Zarnetske, Haggerty, Wondzell, & Baker, 2011).

The overall goal of this study was to identify the principal hydrogeological processes driving fluxes of water and N in a headwater stream polluted with agricultural runoff. More specifically, we coupled intensive streambed and reach-scale measurements during five multiday sampling campaigns to ascertain the reach-scale mass balance of water and N in a 175-m stream reach underlain by fractured shale bedrock. Samplings principally targeted periods of steady hydrologic conditions during the winter/spring recharge period. Our research questions included: (a) How much of the water and N load is attributed to groundwater seeps versus diffuse matrix flow through the streambed? (b) How is water entering the stream reach via groundwater seeps? Such information highlights the appropriate source areas in the landscape responsible for delivering N-rich waters to headwater agricultural streams and guides the development of targeted nutrient management strategies that can be used to mitigate these critical N sources.

2 | METHODS

2.1 | Site description

The study was conducted at the United States Department of Agriculture’s WE-38 research watershed, which is located in the north-central portion of the Mahantango Creek watershed in east-central Pennsylvania (Figure 1). The WE-38 watershed is situated within the Upper Chesapeake Bay watershed in the non-glaciated Ridge and Valley physiographic province. There is variability in elevation, terrain, and landscape characteristics across the overall WE-38 watershed and its sub-basins, leading to localized differences in hydrologic responses (Gburek, Folmar, & Urban, 1999). Average yearly rainfall is around 108 cm, with rainfall relatively evenly distributed throughout the year. Soil depth varies considerably across the watershed. The shallowest soils (less than 2 m) are composed of silt loams typically found on ridges and along hill slopes (Gburek & Folmar, 1999; Pionke & Urban, 1985), while the deepest soils (greater than 10 m) are found in foot slopes and riparian areas of the valleys. There is an extensive history of research on agriculture and water quality in WE-38 (Williams et al., 2015; Buda et al., 2011; Church et al., 2011). Previous research in WE-38 revealed that nitrate-N concentrations increase with increasing agricultural land area and decreasing stream order (Kang, Lin, Gburek, Folmar, & Lowery, 2008), groundwater seeps are generally elevated in nitrate-N concentrations (Pionke et al., 1988), and that the majority (~75%) of nitrate-N losses in surface water occur during baseflow conditions (Zhu, Schmidt, Buda, Bryant, & Folmar, 2011). Williams et al. found that seeps exert strong controls on stream discharge and N chemistry under baseflow conditions and that seep water is mainly sourced from lateral flow in the underlying aquifer that emerges through fractures in the shallow bedrock (Williams et al., 2014, 2016; Williams, Buda, Elliott, Singha, & Hamlett, 2015). Williams et al. (2015) also linked seep N concentrations to agricultural practices in upslope recharge areas within the watershed.

We focused our measurements on a headwater sub-catchment of WE-38 (7.3 km²), referred to as RS (Figure 1b). RS is a 40-hectare basin with about 75% land cover devoted to agriculture. We chose a 175-m stream reach that was bounded by two flumes: flume 1 (upstream) and flume 2 (downstream). Though the upland agricultural landscape clearly influences the experimental stream reach, most of the reach itself flows through a forested riparian area before entering a clearing where vegetation transitions to a mix of perennial grasses and shrubs. The watershed area upslope of the uppermost flume (flume 1) was agricultural, with fields planted in corn and
soybeans and with forested areas in the southwest portion (Figure 1b). RS is situated on highly fractured and weathered shallow bedrock (Wyrick & Borchers, 1981). These fractures can exert a significant influence on groundwater flow in the area rather than rock type, and they allow for the high prevalence of groundwater seeps within the riparian zone (Gburek et al., 1999; Gburek & Urban, 1990; Williams et al., 2014). Previous studies in the WE-38 watershed (which includes RS) generally show that deeper groundwater is primarily recharged on the forested ridges, having relatively low nitrate-N concentrations. In contrast, the shallower groundwater aquifers are influenced more by agricultural land use and typically have much higher concentrations of nitrate-N (Gburek, Urban, & Schnabel, 1991). The groundwater source in RS is principally recharged within the surrounding crop fields that have N application rates of 0–250 kg N ha\(^{-1}\) yr\(^{-1}\) (Williams, Buda, Elliott, Collick, et al., 2015).

2.2 | Reach-scale mass balance

Reach-scale N mass balance studies are used widely across watershed studies to infer fluxes of N (Kaushal et al., 2014; Newcomer Johnson, Kaushal, Mayer, & Grese, 2014). Other studies have used streambed-scale measurements, such as hydraulic conductivity, hydraulic head, and N concentrations (Gilmore et al., 2016; Kennedy, Genereux, Reide Corbett, & Mitasova, 2009a, 2009b). These two methods are sometimes coupled (Duff, Tesoriero, Richardson, Strauss, & Munn, 2008; Stelzer, Drover, Eggert, & Muldoon, 2011) but mainly focus on the in-stream processing and retention of N at different spatial scales. Few studies (Stelzer et al., 2017) have used these two techniques to separate different inputs of groundwater. This coupling provides more accurate insights into groundwater contributions and assists in locating N sources.

The study consisted of five separate mass-balance calculations for a 175-m stream reach during the winter and spring of 2017. For each mass balance calculation, field data were collected over a period of 2 to 3 days under relatively stable hydrologic conditions (10% variation in streamflow, on average) compared to increases in streamflow of 29% and nitrate-N flux of 27% along the stream reach. A mass balance equation was used to estimate riparian seep water and N inputs to the stream. Total groundwater discharge (\(Q_{gw}\)) was calculated as the difference between stream discharge at the start (\(Q_{in}\)) and end (\(Q_{out}\)) of the reach:

![Figure 1](image-url)
\[ Q_{\text{gw}} = Q_{\text{out}} - Q_{\text{in}} - P + E \pm \Delta S \]  

(1)

where additions of precipitation (P) were zero, and evaporative losses (E) and storage changes in the stream channel (\(\Delta S\)) were assumed to be zero over the short sampling intervals (2-3 days). Since \(Q_{\text{gw}}\) is the combination of seep discharge (\(Q_{aa}\)) and diffuse streambed matrix flow (\(Q_{aq}\)), as well as \(\Delta S\), the change in aquifer storage, which is assumed to be 0 over a few days, the total seep discharge (\(Q_{\text{seep}}\)) can be found using:

\[ Q_{\text{seep}} = Q_{\text{out}} - Q_{\text{in}} - Q_{aq} \]  

(2)

The streambed matrix flow \(Q_{aq}\) was estimated using Darcy’s Law, \(q = JK\), with \(J\) being hydraulic head gradient and \(K\) hydraulic conductivity. Hydraulic head gradient was calculated by the change in head (\(\Delta h\)) divided by the distance (\(L\)) from the streambed to the middle of the piezometer screen \((J = \Delta h/L)\). Kennedy, Generaux, Corbett, & Mitasova, 2007. Air-water manometers with a side-port for sampling (Kennedy et al., 2007; Winter, Labaugh, & Rosenberry, 1988) were used to obtain values of \(\Delta h\) between surface water and groundwater. Hydraulic conductivity measurements were determined using falling-head slug test measurements originally outlined in Hvorslev (1951). To estimate \(Q_{aq}\) for the whole reach (volumetric flux), the entire seepage face of the streambed was incorporated in Darcy’s Law. Streambed area (\(A\)) was calculated as the product of the stream length and the mean stream width, which was determined from field measurements every 12.5 m.

\[ Q_{aq} = J \times K \times A \]  

(3)

The same concept was applied to the N mass balance equation using nitrate-N concentrations (\(C\)), solving for \(N\) in the diffuse matrix flow (\(N_{aq}\)).

\[ N_{aq} = J \times K \times A \times C \]  

(4)

Finally, N inputs from the seeps (\(N_{\text{seep}}\)) were estimated from the following equation,

\[ N_{\text{seep}} = N_{sw(down)} - N_{sw(up)} - N_{aq} + N_{\text{uptake}} \]  

(5)

where \(N_{sw(down)}\) and \(N_{sw(up)}\) refer to N flux measured in stream water at the upstream and downstream reach locations, and where \(N_{\text{uptake}}\) is in-stream biotic uptake or denitrification of \(NO_3^-\). A slug injection of 180.7 g of NaCl and 42.2 g of KNO3 dissolved in stream water was used to estimate \(N_{\text{uptake}}\) in our stream reach in April 2018, using methods similar to Tank, Rosi-Marshall, Baker, and Hall (2008). Downstream recoveries of \(Cl^-\) and \(NO_3^-\) were 98 and 109%, respectively, suggesting minor or negligible in-stream N uptake relative to N inputs from groundwater. Considering this information, we assumed \(N_{\text{uptake}} = 0\) on the temporal and spatial scales of our study, but acknowledge that N uptake is ubiquitous in streams, even those with chronic N inputs (O’Brien, Dodds, Wilson, Murdock, & Eichmiller, 2007).

### 2.3 | Field and lab measurements

#### 2.3.1 | Sampling overview

Each sampling campaign was split into a 2- to 3-day process. Day 1 included sampling stream water at flumes and each of the 15 piezometer locations. Any visible seeps were sampled on this day. Then, air–water manometers with a port for collection of groundwater were installed at the 15 sites and allowed to equilibrate for 24 hr before reading (Baxter, Hauer, & Woessner, 2003). Day 2 consisted of recording head differences from the manometers. Afterward, each piezometer was purged with a hand pump, and riparian wells were purged with a peristaltic pump to be sampled the following day. In addition to flume data, discharge measurements were made at three points in the stream between the flumes and at major seep inputs. On day 2 or 3, all piezometers and riparian wells were sampled using a hand pump. All measurements were conducted during relatively steady hydrologic conditions, with streamflow from the reach varying by 10% (on average).

#### 2.3.2 | Stream discharge measurements

To measure stream discharge at the start and end of the stream reach, we used two 1-m H-flumes installed in the stream (Open Channel Flow, 2018). On each sampling visit, the instantaneous discharge was measured in each flume using manual stage height measurements. Stage height in each flume was also monitored every 5 min with a Decagon CTD sensor. Two methods were used to measure streamflow discharge rates at locations along the stream reach between the flumes and seeps in this shallow headwater stream. The first was the bucket and stopwatch method, funnelling the stream into a large PVC pipe and collecting the water into a 19-L bucket for a known amount of time \((Q = V/t)\) (Guberuk & Folmar, 1999). The second method employed a Marsh-McBirney flow meter to measure the average velocity of water flowing through a makeshift flume (\(-0.25 \times 1\) m) that was temporarily installed in the stream during the field visit. The streamflow discharge was calculated as the product of water velocity, flume width, and water depth.

#### 2.3.3 | Water sampler installation

A total of 15 drive point, stainless steel piezometers (Solinst Model 615) were installed in the streambed along the stream reach, spaced approximately 12.5 m apart starting at the upstream flume (flume 1). Kennedy, Generaux, Mitasova, Reide Corbett, and Leahy (2008) suggest that a sampling density of 0.08 points m\(^{-2}\) gives a realistic image of spatial variability within the experimental reach. With a stream area of about 195 m\(^2\), 15 points were deemed adequate. The piezometers were hammered into the stream with 46 cm between the streambed and the middle of the well screen, enough to provide an accurate measure of streambed hydraulic conductivity. To observe shallow
groundwater, observation wells were installed in the riparian zone in a transect perpendicular to the stream. Three pairs were put on each side of the stream, one shallow (~1 m) and one deep (~3 m) for a total of 12 wells. The wells were installed using a SIMCO Earth Probe 200, where a 5 cm auger was used to drill the holes and was cased with a 5-cm diameter PVC pipe. The bottom 30.5 cm of each well contained a screen and filter sock. A sand pack was added to the height of the well screen in each well and the remaining space was filled in with bentonite clay from the top of the screen to the ground surface. Decagon CTD sensors were used to measure water level, electrical conductivity, and water temperature every 5 min.

2.3.4 | Thermal imaging

Thermal imaging techniques are useful for locating groundwater seep inputs into the stream. In winter, the groundwater coming into the stream is warmer than the water on the surface, so the difference in temperature was used to locate discrete groundwater inputs. The camera used in this study was the FLIR T640bx. The entire stream reach was surveyed with the camera during each field visit, and seep inputs were identified and flagged for sampling and discharge measurements. Hare, Briggs, Rosenberry, Boutt, and Lane (2015) report that shallow streams are ideal for thermal imaging because their thermal signatures are easily transferred to the water surface.

2.3.5 | Water sample collection

Surface water samples were collected in pre-cleaned HDPE bottles using grab sample techniques (Lurty & Kolbe, 2000) about once a month throughout the study period. Surface water samples were denoted with a number indicating the downstream distance (m) from flume 1. Seeps were sampled concurrently with surface water samples. Seeps were labelled with an R or L to denote whether they were on the right (west) or left (east) side of the stream. Piezometers and wells were thoroughly purged and then sampled the next day using a hand-held vacuum pump to extract water. Piezometers were labelled as PZ and the number indicated the distance from flume 1. Wells were labelled with GW and the number increased as the wells got further from the stream. An R or L was also used, and an S or D represented whether it was a shallow or deep well. A subsample of each type of water described was set aside in a 5 ml glass vial for water isotope analyses. All samples were filtered in the field using a 0.45 μm syringe filter and stored on ice during transit.

2.3.6 | Laboratory methods

Prior to analysis, samples were stored in a 4°C cold room. The samples were analysed for nitrate-N and ammonium-N by colorimetry (QuikChem Methods FIA+ 8000 Series, Lachat Instruments, Loveland, Colorado). Total N was determined on unfiltered samples by alkaline persulfate digestion following the method of Patton and Kryskalla (2003). Nitrate-N represented on average over 90% of total N in surface water, thus nitrate-N was the focus of this study. Concentrations of dissolved metals (Ca, Mg, Si, etc.) were determined by analysing filtered samples with inductively coupled plasma optical emission spectroscopy (ICP-OES). Unfiltered samples were digested with 1% aqua regia (25% 12 M HNO₃ + 75% 12 M HCl) and then analysed with ICP-OES to determine total elemental concentrations. Water isotopes (δD and δ¹⁸O) were analysed using a Picarro L2140-i cavity ring-down spectrometer (Picarro, Santa Clara, California). Isotope abundances are presented in δ notation (δ = Rsample/Rstandard where R = ¹⁸O/¹⁶O), and the Vienna Standard Mean Ocean Water–Standard Light Antarctic Precipitation (VSMOW–SLAP) was used as a reference scale (0 ‰) (Coplen, 1996). Samples were analysed along with three water reference standards calibrated to the VSMOW–SLAP scale.

3 | RESULTS

3.1 | Physical measurements

In summer/fall of 2016, the stream had little to no visible flow of water, reflecting a persistent drought that precluded stream sampling in the 6 months leading up to the study (July to December 2016). Notably, this drought may have exacerbated N losses from the watershed during the study period from January to June in 2017 (Outram et al., 2014). Rainfall amounts (~42 cm) were well below the 30-year average (~57 cm) for this 6-month period. The start of the study in January 2017 represented a transition to increasingly wetter conditions, with more frequent precipitation events enabling the stream to recover from the previous season’s drought. Rainfall throughout the study period remained slightly less (~4 cm) than the 30-year average of 53 cm for this period. Precipitation values were highest at the end of April and through May, with one large precipitation event in March (Figure 2). Stream discharge during the study ranged from about 86.4 to 4320 m³/d (1 to 50 L/s) using measurements from flume 2 at the outlet of the reach. Except for the end of January, discharge increased into the spring, peaked at the end of March and April (4320 m³/d maximum), and then dropped and levelled off at the end of May and June. April had the highest discharge values of any month (Figure 2). Sampling occurred during relatively stable flow conditions (coefficients of variation: range, 3–19%; mean, 10%) with stream discharge averaging 230 to 682 m³/d across each of the 2- to 3-day sampling periods.

As watershed storage increased, some seeps within the reach “turned on” adding to the total flow in the stream. Thermal imaging, along with manual stream temperature measurements, allowed us to identify seep areas (Figure 3). Hydrochemical data were also used to corroborate the seepage sources of water contributing to streamflow. At the start of the study, only two seeps were identified and sampled; by May 2017, eight seeps were sampled. Conversely, when conditions got drier and discharge decreased in June, only one seep could be identified and sampled. We primarily found instances of
bank seepage, as well as several small, macroporous seeps in the channel itself.

Only one seep, seep 100, flowed continuously throughout the entire study period, keeping a stable discharge value of around 17.3 m$^3$/d. In January 2017, stream discharge increased from 174 to 292 m$^3$/d from flume 2 to a point roughly 15 m upstream of flume 1, and then dropped to 239 m$^3$/d at flume 1. This general discharge pattern was observed throughout the study. The gain in flow in the reach was consistent even as overall discharge values increased, by up to around sixfold, into the spring. Nitrate fluxes in and out of the reach also showed a net increase in N at each sampling date, with an increase of 1.37 g/d in January. We observed differences in the amount of water and N entering and leaving the reach, revealing the gains from groundwater (Table 1). Each sampling date yielded a positive increase in both water (84.7–205.6 m$^3$/d) and N (0.61–3.99 kg/d), with April and May having the highest gains (205.6 m$^3$ water d$^{-1}$; 3.99 kg N d$^{-1}$ and 203.0 m$^3$ water d$^{-1}$; 3.85 kg N d$^{-1}$, respectively).

Hydraulic head gradients were mostly negative (Redder, 2018), indicating that stream water was moving downward through the streambed, recharging groundwater. There was no obvious pattern of hydraulic gradients from upstream to downstream, and gradients over time either remained constant or changed by an order of magnitude (Redder, 2018). The month of June had the greatest number of piezometers with a positive hydraulic gradient (6 of 15); May had 4; April had 3, and January and February each had 1. Therefore, as time progressed and conditions became wetter, a greater proportion of the piezometers indicated that groundwater was discharging into the stream. Like hydraulic head gradients, there was no predictable pattern throughout the reach in the measured values of hydraulic conductivity. Locations varied in hydraulic conductivity by several orders of magnitude and ranged from 0.0009 to 8.27 m/d (Redder, 2018).
Concentrations of nitrate-N in stream water (Figure 4a) were relatively stable throughout the stream reach and throughout the study period. Nitrate-N concentrations typically stayed at about 19–20 mg/l; while May, the wettest month, had the highest values at around 21 mg/l. In-stream piezometer samples were highly variable in nitrate-N concentrations, with values ranging from about 1 to 21 mg/l (Figure 4b). Streambed groundwater measured with in-stream piezometers was almost always lower in nitrate-N concentrations than the stream water.

Shallow groundwater sampled within riparian zone wells (Figure 5a) had the lowest average nitrate-N concentrations (~0–14 mg/l). Riparian seep waters were the most variable ranging from about 3 to 32 mg/l nitrate-N (Figure 5b). Shallow groundwater (GW) in the riparian wells on the right side (9 mg/l average) of the stream bank had statistically higher nitrate-N concentrations than those on the left (10 mg/l average, \( U = 181, p < .001 \)).

Though groundwater (GW) sampled within the shallow riparian wells had the lowest average nitrate-N concentrations, they had the highest levels of dissolved silica (~8–10 mg/l) (Figure 6). Silica in surface and seep waters was generally similar, with surface waters having, on average, about 1 mg/l lower dissolved silica concentrations than seep waters. Piezometer (PZ) waters sampled in the streambed plotted in between seeps/surface waters and riparian groundwater. Dissolved silica concentrations in the piezometer water were about half that in the shallow groundwater samples and had double the nitrate-N concentrations.

Water isotopes values were plotted as \( \delta^{18}O \) versus \( \delta D \) for each sample (Figure 7). Using a t test for regression slopes (Zar, 1984), we found that the slopes of the \( \delta^{18}O \) versus \( \delta D \) lines for seeps and surface waters did not differ significantly (\( t = 0.105, \text{ d.f.} = 62 \);
Zar, 1984). Seeps and surface waters had greater ranges in $\delta^{18}O$ than waters from the in-stream piezometers and shallow riparian groundwater samples. The $\delta^{18}O$ values of seeps and surface waters spanned from about $-10$ to $-5$‰ while piezometers and shallow groundwater ranged from about $-10$ to $-8$‰. The $\delta^{18}O$ versus $\delta D$ for groundwater seems to mirror the local meteoric water line (LMWL), while the $\delta^{18}O$ versus $\delta D$ line for piezometer samples is in between $\delta^{18}O$ versus $\delta D$ lines for seeps/surface water and groundwater. None of the waters exhibited as much variability and range as the precipitation (LMWL, $R^2 = 0.8606$).

### 3.3 Mass balance calculations

Hydraulic head gradients were primarily negative, meaning the stream was losing water and N to the streambed. Daily matrix flow fluxes ranged from 0.76 to 13.23 m$^3$/d of water and 0.02 to 0.25 kg/d of N leaving the stream through diffuse streambed seepage in the reach (Table 2). These numbers were an order of magnitude lower than the inputs calculated from seeps. Seeps provided anywhere from 45 to 217 m$^3$/d of water and 0.63 to 4.21 kg/d of N to the stream. Two to three of the eight total visible seeps could be gauged, and only one reliably during the entire study period. These seeps accounted for anywhere from 29 to 82% of water and 41 to 124% of N that was estimated to be discharged into the stream via seeps from the mass balance. Seep 100 alone, which was visibly
flowing at every sampling date, supplied 72% of the calculated seep N to the reach in June 2017.

4 DISCUSSION

4.1 Coupling streambed and stream-reach measurements

This study highlights the importance of selecting the right method for estimating the reach mass balance, similar to Gilmore et al. (2016). Using these two methods—reach mass balance and streambed point measurements—facilitates a more complete picture of the transport of N in these headwater stream systems at multiple scales. The mass balance approach is a convenient and simple method for evaluating N flow in agricultural streams (Schwientek & Selle, 2016). With the high degree of variability between the seeps and the difficulties associated with locating and gauging them, a reach mass balance provides insight into groundwater and N transport to the entire reach. As stream reaches get larger, individual point measurements become less feasible. However, the point measurements in the streambed enable a clear distinction between groundwater inputs from matrix flow and riparian seeps. Additionally, the streambed measurements provided understandings into the fate of N at different stages of flow in this headwater stream.

4.2 Fluxes of flow and nitrogen in the stream reach

The appearance of more seeps and increases in seep discharges occurred during periods with the highest stream discharge values. In January, 2 seeps were observed and sampled for nitrate analysis; 6 in February; 7 in April; 8 in May; and 6 in June. Stream discharge values were highest when more seeps were observed (April/May), emphasizing that seeps may have a considerable influence on the total discharge of the stream. As time progressed, plant growth around the stream increased, potentially causing the severe drop in discharge throughout May and June even as precipitation increased, and seep flow became more prominent. Evapotranspiration rates likely increased throughout the study period, causing a greater water loss and decreased discharge values. Overall, based on the physical data, the seeps did not appear to be connected to one another and each varied in activity and discharge. Although the stream reach increased in discharge values downstream, head gradients indicated a net loss of stream water to groundwater. Therefore, the increases in stream discharge downstream are attributed groundwater seeps. Any continuously significant decreases in discharge may be attributed to negative head gradients, relatively large hydraulic conductivities, and no additional inputs of water.
Within the reach, nitrate-N concentrations of the different waters have significantly large ranges, approximately 0 to approximately 36 mg/l. Physical evidence suggested that these seeps were not well connected and acted independently from one another, which is further supported by chemical data. Seeps had the highest range of nitrate-N (1.7–36.2 mg/l) concentrations. Nitrate-N in stream water stayed relatively constant throughout the reach and the study; approximately 19–20 mg/l. Piezometer waters had more variation in nitrate-N levels than surface waters, likely due to varying hydraulic heads and hydraulic conductivities, mixing between surface and shallow groundwater, and/or biogeochemical reactions such as denitrification in the streambed. Lastly, riparian wells had considerable variation in nitrate-N concentrations, ranging from near 0 to 17.6 mg/l, yet were generally lower than seep waters. These results suggest that seep water is not derived from shallow groundwater, or that there are additional processes affecting its chemistry.

The hydraulic conductivity of the streambed sediments is so low at some locations that there is little connection of stream water to the underlying aquifer. In areas with higher hydraulic conductivities, head gradients are primarily negative, so the stream is losing water into the streambed. Therefore, virtually all the water and nitrate-N accumulated throughout the reach can be attributed to point discharges via riparian seeps. Riparian seeps supply 45–36.2 mg/l concentrations. Nitrate-N in stream water stayed relatively constant throughout the reach and the study; approximately 19–20 mg/l. Piezometer waters had more variation in nitrate-N levels than surface waters, likely due to varying hydraulic heads and hydraulic conductivities, mixing between surface and shallow groundwater, and/or biogeochemical reactions such as denitrification in the streambed. Lastly, riparian wells had considerable variation in nitrate-N concentrations, ranging from near 0 to 17.6 mg/l, yet were generally lower than seep waters. These results suggest that seep water is not derived from shallow groundwater, or that there are additional processes affecting its chemistry.

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Notably, our study found larger stream nitrate-N concentrations with less variation than a previous multiple-year study in RS by Williams, Buda, Elliott, Singha, and Hamlett (2015). However, the study by Williams et al. took place over multiple years during both baseflow and storm conditions, and the experimental stream reach was not only longer (490 m) but also extended further upstream where nitrate-N concentrations were considerably more variable. Our study, on the other hand, featured a much shorter reach (175 m) and sampling generally targeted lower flow regimes. Williams et al. found that the influence of seeps on stream nitrate-N variability was less during storm events, attributed to increased mixing and homogenization of the variable nitrate-N inputs. Other factors could cause changes at a given site from year to year, such as differences in sources (e.g., from N fertilization rates, N fixation rates, or atmospheric N deposition rates), as well as differences in storages and losses, mediated by the distribution of precipitation and wetness (or dryness) over time (Galloway et al., 2004).

Denitrification and biotic uptake are two of the main factors for transforming and removing nitrate-N in streams (O’Driscoll & DeWalle, 2010; Sebestyen, Shanley, Boyer, Kendall, & Doctor, 2014; Vidon et al., 2010). The two streambed water samples with the lowest N concentrations also had the lowest streambed hydraulic conductivities. Denitrification could play a large role in reducing nitrate-N concentrations in the low hydraulic conductivity sites. Denitrification occurs throughout the stream and streambed, but longer residence times could lead to higher denitrification rates. Mulholland et al. (2008) assessed stream denitrification of 72 streams across the United States and Puerto Rico and found that the percentage of nitrate uptake decreased with increasing nitrate-N concentrations in small streams (<100 L/s or 8640 m$^3$/d). Streams with nitrate-N concentrations of about 15 mg N L$^{-1}$ lose around 10% of nitrate from biotic removal. Studying a first-order stream in an agricultural watershed, Rahimi, Essaid, and Wilson (2015) found that water in the streambed lost between 89 and 99.5% of its nitrate to denitrification. This could explain why nitrate-N values in the streambed in RS were much lower than the stream, yet higher than the shallow groundwater. Residence time plays a key role in nitrate removal/transformations (Boyer et al., 2006; Lindsey et al., 2003; Zarnetske et al., 2011).

Riparian zones with groundwater-fed surface pathways can differ significantly in their ability to reduce nitrate levels due to differences in soils and residence times (Shabaga & Hill, 2010). The relatively low nitrate-N concentrations in riparian wells are consistent with data from Mehnert et al. (2007). They found that significant denitrification was occurring in the shallow groundwater, with denitrifying bacteria being discovered up to 10 m below the surface. This study, along with Roer, David, and Gentry (2006), found that preferential flow originating in agricultural fields had significantly higher N concentrations than the wells. These flow paths could be analogous to the seeps in RS. Nitrogen-rich water leaving the cropped fields and travelling quickly to the stream would not have ample time for denitrification and uptake to occur and would exhibit higher N concentrations than well waters. Different sources and flow paths could explain the variability in the seep nitrate-N levels and water chemistry. This study found that waters originating from the right side of the stream that regularly receives swine slurry applications had higher concentrations of major ions than waters on the left side, so different recharge zones can have a considerable influence on seep chemistry (Williams, Buda, Elliott, Collick, et al., 2015).
4.3 | Hydrochemical evidence of groundwater contributions

The concept that the stream water is primarily supplied by riparian groundwater seeps is further supported by hydrochemical evidence (Figure 5). The monthly averages for seeps and surface waters overlap, while piezometers have higher Si and lower nitrate-N. The one value of seeps that is lower in nitrate-N may be a result of seep 143-I, often high in nitrate-N, being inaccessible (i.e., not flowing) during June. The shallow groundwater has both lower nitrate-N and higher silica concentrations than the other waters, implying that the shallow aquifer is disconnected from the overlying stream and chemically different from seep waters. The higher silica concentrations of the shallow groundwater indicate a longer residence time (Peters, Burns, & Aulenbach, 2014). Prolonged contact with soil and bedrock often facilitates more silica dissolution, so the lower silica concentrations in seeps suggest they are moving quickly through the system than shallow aquifer water. The bedrock in RS is composed mainly of mudstone, siltstone, and sandstone (Trexler & Wood Jr., 1968a, 1968b). The different amounts of silica contained within these rocks could also account for some variation in dissolved silica content.

Water isotope data also support the notion that groundwater seeps are the primary source of N to the stream (Figure 6). Surface water and seep samples plotted almost identically in $\delta^{18}$O versus $\delta$D space, and their linear regression slopes did not differ significantly. Piezometers plotted in between the seep/surface water lines and the shallow groundwater line, but the similar range in $\delta^{18}$O values suggest piezometer water more closely resembles shallow groundwater. Groundwater is typically well mixed, and isotope values are dampened as it moves through the soil column (Majumdar, Miller, & Parizek, 1990). However, the groundwater values fall around the LMWL and have a similar slope. The broader range in $\delta^{18}$O values of seeps and surface waters support the hypothesis that the seeps have shorter residence times and quicker flow pathways to the stream. When water travels quickly through a system there is less time for mixing and homogenization of isotope values, as well as denitrification, which is one factor contributing to the high levels of nitrate-N in the Mahantango watershed (Lindsey et al., 2003). Piezometer water seems to be derived from shallow groundwater, but some isotopic fractionation processes may be occurring to result in a smaller slope value in $\delta^{18}$O versus $\delta$D space, or there could be some mixing of stream and shallow groundwater.

The lower slope values of $\delta^{18}$O versus $\delta$D lines for seep and stream waters indicate that fractionation had occurred (Kendall & Doctor, 2003). One of the most common forms of fractionation on water is evaporation. It seems that seep, and therefore stream, water has significant evaporation causing a smaller slope in $\delta^{18}$O versus $\delta$D. Gibson, Birks, and Edwards (2008) estimated that soil water in this area would have an evaporation line with a slope of about 3 or 4, so the observed seep slope (2.51) and stream water slope (2.55) were in line with this prediction. However, flow from the seeps is too large to be just soil water, so near surface evaporation of the seep water in the riparian zone may also explain the low slope values of the seep and stream water. While the seep/stream samples plotted with a smaller slope, they still fell within the range of precipitation values. Sprenger, Tetzlaff, and Soulsby (2017) suggest that monthly sampling can miss critical transition periods in a climate that has isotopic seasonal variability in its precipitation, especially during the spring and fall seasons. This can lead to an incomplete assessment of isotopic signatures in the upper portion of the critical zone, and the selective sampling once a month does not make it possible to explore what happens to these seeps during storm events.

In sum, multiple lines of physical and chemical evidence suggest that seeps supply the majority of N exported by streamflow in the RS catchment. Coupled use of streambed and reach-scale measurements showed that groundwater discharges of N emerged as seeps in the riparian zone and that groundwater discharges through the streambed were not a significant source of N in surface water. Fractures and macropores allow for water to mobilize from agricultural fields with large amounts of nitrate-N to streams with minimal denitrification that usually occurs in the shallow groundwater. This would explain why more seeps continued to appear as conditions got wetter throughout the spring. Unsaturated soils would not result in a flow of water through the subsurface.

5 | CONCLUSIONS

This study reveals the importance of groundwater seepage as a delivery mechanism of flow and solutes to streams within headwater regions of the Mahantango Creek research watershed, where seeps can be a significant source of N loading. Our results add to the growing body of literature on preferential flow paths of nitrate from groundwater to surface water. We note that the geological setting can greatly influence results. For example, in their study of the effects of groundwater springs on nitrate concentrations in streams issuing from the Catskill Mountains, Burns et al. (1998) also explored the potential role of seeps in affecting streamflow. That study was conducted in a watershed characterized by glacial geology (till reworked into thick alluvium deposits) and describes two sources of groundwater: a shallow flow system that discharges groundwater from a hillside and a deeper flow system that supplies groundwater to springs (Burns et al., 1998). In contrast, the RS catchment overlies unglaciated, fractured shale bedrock. During our study period, the hydrology of RS is completely fed by riparian seeps, with mostly losing head gradients between the stream and groundwater.

Our results indicate that seeps and other macropore flows should be considered when devising techniques and management practices to mitigate nutrient pollution problems. A large amount of fractured bedrock in this area allows for the accumulation of N-rich water to flow from nearby agricultural fields to this headwater stream. Kang et al. (2008) investigated the Mahantango creek watershed and observed that nitrate concentrations in stream water increase with decreasing stream order. It is critical to target these headwater streams when implementing mitigation techniques to fix the issue at the source. Typical restoration techniques, like the implementation of
traditional best management practices in riparian zones, may not be the most effective mitigation strategies in systems where the N is moving rapidly from source areas in the landscape to the stream via preferential flow pathways. Even so, Easton, Bock, and Stephenson (2019) suggest that large springs and seeps with elevated nitrate-N levels could be effectively targeted with woodchip bioreactor technologies, though whether such technologies could be applied to the small seeps in headwater agricultural streams has not been well studied. Over the longer term, sources of N to these seeps and groundwater recharge zones may need to be reduced to see a decrease in stream N concentrations in headwater basins like RS (Böhlke & Denver, 1995; Lindsey et al., 2003). Plonke, Gburek, and Sharpley (2000) estimated excess N inputs of about 57 kg ha\(^{-1}\) yr\(^{-1}\) in WE-38 based on farmer surveys within the watershed. Williams, Buda, Elliott, Collins, et al. (2015) showed the linkage between N application rates and seep nitrate-N concentrations. Therefore, an overall decrease in nitrogenous fertilizer use would likely result in lowering N concentrations being discharged into the streams via riparian seeps, and, in turn, decreasing nutrient loads to downstream receiving waters such as the Chesapeake Bay.

Further, our results underscore the importance of agriculture as a source of N to groundwaters and surface waters, and agricultural lands are the primary source of N issuing from most large mixed land use watersheds in the mid-Atlantic region of the United States (Boyer et al., 2002). Within the Chesapeake Bay watershed, nutrients are a pervasive and longstanding water quality problem (NRC, 2011; Bricker et al., 2008; USEPA, 2010). Agricultural sources account for about 43% of the N delivered to the Bay, and many regions, including south-eastern Pennsylvania, have among the highest concentrations of nitrate in groundwater observed nationwide (NRC, 2011; USEPA, 2010). Both observational and modelling studies of the region have shown the most significant N yields, both incremental (from the local drainage area to an individual stream segment) and delivered (to downstream receiving waters) originate from agricultural regions of the watershed (Ator, Brakebill, & Blomquist, 2011). In an investigation of the differential effects of land use on water quality across the state of Pennsylvania, Clune, Crawford, Chappel, and Boyer (2020) demonstrated that land use strongly influenced nutrient water quality conditions, where long-term median stream concentrations of total nitrogen are about 11 times higher in agricultural areas compared to undeveloped areas. Identifying source areas that potentially cause of groundwater N enrichment, and seepage areas where N is discharging to streams, are necessary for developing N pollution mitigation strategies toward achieving water quality goals.

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CONFLICT OF INTEREST

The authors declare no conflicts.

DATA AVAILABILITY STATEMENT

All data presented in this manuscript are provided in BR’s master’s thesis (Redder 2018), where there also are additional site photos and further details of the study. Additional data from the Mahantango Creek Experimental Watershed are available from the U.S. Department of Agriculture through the database delivery system called STEWARDS, as detailed here: https://www.ars.usda.gov/north-east-area/up-pa/pswmru/docs/watershed-data/.

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