



INFLUENCE OF RIPARIAN SEEPAGE ZONES ON NITRATE VARIABILITY IN TWO AGRICULTURAL HEADWATER STREAMS¹

Mark R. Williams, Anthony R. Buda, Herschel A. Elliott, Kamini Singha, and James Hamlett²

ABSTRACT: Riparian seeps have been recognized for their contributions to stream flow in headwater catchments, but there is limited data on how seeps affect stream water quality. The objective of this study was to examine the effect of seeps on the variability of stream NO₃-N concentrations in FD36 and RS, two agricultural catchments in Pennsylvania. Stream samples were collected at 10-m intervals over reaches of 550 (FD36) and 490 m (RS) on 21 occasions between April 2009 and January 2012. Semi-variogram analysis was used to quantify longitudinal patterns in stream NO₃-N concentration. Seep water was collected at 14 sites in FD36 and 7 in RS, but the number of flowing seeps depended on antecedent conditions. Seep NO₃-N concentrations were variable (0.1-29.5 mg/l) and were often greater downslope of cropped fields compared to other land uses. During base flow, longitudinal variability in stream NO₃-N concentrations increased as the number of flowing seeps increased. The influence of seeps on the variability of stream NO₃-N concentrations was less during storm flow compared to the variability of base flow NO₃-N concentrations. However, 24 h after a storm in FD36, an increase in the number of flowing seeps and decreasing streamflow resulted in the greatest longitudinal variability in stream NO₃-N concentrations recorded. Results indicate seeps are important areas of NO₃-N delivery to streams where targeted adoption of mitigation measures may substantially improve stream water quality.

(KEY TERMS: groundwater seep; nonpoint source pollution; semi-variogram; variability; water quality; nitrogen.)

Williams, Mark R., Anthony R. Buda, Herschel A. Elliott, Kamini Singha, and James Hamlett, 2015. Influence of Riparian Seepage Zones on Nitrate Variability in Two Agricultural Headwater Streams. *Journal of the American Water Resources Association* (JAWRA) 1-15. DOI: 10.1111/1752-1688.12335

INTRODUCTION

Transfers of nitrogen (N) from terrestrial to aquatic ecosystems contribute to watershed impairment and can lead to eutrophication of coastal zones (where N is often the limiting nutrient) (Carpenter *et al.*, 1998). Agriculture is an important source of N

to surface waters (Craig and Weil, 1993; Tesoriero *et al.*, 2000) and accounts for approximately 37% of the N load delivered to the Chesapeake Bay (U.S. Environmental Protection Agency, 2008). Recent work by Peterson *et al.* (2001) and Alexander *et al.* (2007) point to the importance of headwater streams as major contributors of N to downstream (higher order) systems. Thus, identifying sources of N to

¹Paper No. JAWRA-14-0043-P of the *Journal of the American Water Resources Association* (JAWRA). Received January 29, 2014; accepted December 9, 2014. © 2015 American Water Resources Association. **Discussions are open until six months from issue publication.**

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headwater streams and evaluating the effects of these sources on water quality is essential for the attainment of downstream water quality goals.

In the Northeast United States (U.S.), groundwater-sustained wetlands, springs, or emergent groundwater seeps (hereafter referred to as seeps) represent a potentially significant source of water and N to many headwater streams. Burns *et al.* (1998) found that perennial seeps were the principal source of streamflow and nitrate-N ($\text{NO}_3\text{-N}$) in a forested headwater catchment in New York. Similarly, seep $\text{NO}_3\text{-N}$ concentrations in a forested headwater catchment in Pennsylvania were linked with stream water $\text{NO}_3\text{-N}$ concentrations (O'Driscoll and DeWalle, 2010). In agricultural headwater catchments, recent work by Shabaga and Hill (2010) and Williams *et al.* (2014) also suggest that seeps are a potential source of $\text{NO}_3\text{-N}$ to streams.

Riparian seeps are characterized by zones of groundwater discharge that flow over land via concentrated flow paths before entering the stream at discrete points along the channel (Pionke *et al.*, 1988). As a result, $\text{NO}_3\text{-N}$ inputs from seeps may influence spatial patterns of $\text{NO}_3\text{-N}$ concentration in headwater streams similar to the effects of tributary inputs on higher order streams. For example, Haggard *et al.* (2001) examined the effect of point sources on water chemistry and nutrient retention during summer base flow in a karst watershed. They found that discharge from a waste water treatment plant not only increased stream $\text{NO}_3\text{-N}$ concentrations at the point of discharge, but also influenced stream $\text{NO}_3\text{-N}$ concentrations at distant downstream locations. Scanlon *et al.* (2010) also observed that variable $\text{NO}_3\text{-N}$ concentrations along the main stem of a stream network were caused by tributary inputs that tended to have lower $\text{NO}_3\text{-N}$ concentrations compared to the main stem. Thus, seep inputs to headwater streams may potentially influence stream $\text{NO}_3\text{-N}$ concentrations at the point of seep discharge as well as $\text{NO}_3\text{-N}$ concentrations along the length of the stream channel.

Semi-variogram analysis is a geospatial tool for exploring the variability of constituents in terrestrial and aquatic ecosystems (see reviews by Peterson *et al.*, 2013; Isaak *et al.*, 2014). This method has been used in a variety of fields including ecology (e.g., organism response to environmental heterogeneity), soil science (e.g., distribution of nutrient concentrations), and geology (e.g., estimation of ore reserves). Semi-variograms quantify the strength, pattern, and extent of spatial dependence by examining how nutrient concentrations (or other data) co-vary as a function of the distance between sampling locations (Cooper *et al.*, 1997). The utility of semi-variograms in exploring longitudinal $\text{NO}_3\text{-N}$ variability in streams is that they can aid in the identification of potential sources of $\text{NO}_3\text{-N}$ to the stream (Rossi *et al.*, 1992) such as seep inputs (as

explicitly considered in this article), or areas along the stream channel where instream nutrient processing and hyporheic exchange remove or retain N.

Several studies have used semi-variogram analysis to quantify the variability of nutrients in higher order streams. Dent and Grimm (1999) found that nutrient concentrations were extremely variable along a 10 km stream reach in Arizona. The authors concluded that $\text{NO}_3\text{-N}$ was consistently more spatially heterogeneous than phosphorus or conductivity. Elsewhere, Peterson *et al.* (2006) evaluated pH, $\text{NO}_3\text{-N}$, and sulfate ($\text{SO}_4\text{-S}$) in a stream network. They showed that patterns of spatial correlation differed between each chemical response variable dependent on hydrologic and biogeochemical processes acting in the stream network. While many of the studies examining instream variability of nutrients have been conducted at base flow, the study by Dent and Grimm (1999) indicated that instream N variability can substantially decrease during higher flows. Distinguishing between different flows (i.e., base flow *vs.* storm flow) is important because seeps are seen as a major contributor at base flow, but less so during storms.

In this study, we examined the influence of groundwater-fed seeps on the longitudinal variation of $\text{NO}_3\text{-N}$ concentrations in FD36 and RS, two agricultural headwater streams possessing differing numbers of seeps in their riparian areas. We conducted our assessments at different times of the year and under different flow conditions (base flow and storm flow) to evaluate the effects of seasonality and hydrology on instream $\text{NO}_3\text{-N}$ patterns in both watersheds. We expected the semi-variogram range, which specifies the average distance over which instream $\text{NO}_3\text{-N}$ values are spatially correlated, to be shorter in streams with highly variable $\text{NO}_3\text{-N}$ concentrations and longer in streams with more homogeneous $\text{NO}_3\text{-N}$ concentrations. Our central hypothesis was that seep inputs would exert a first-order control on instream $\text{NO}_3\text{-N}$ variability, and that this variability would depend on time of year and on hydrology. Specific study objectives were to (1) quantify the downstream variability of $\text{NO}_3\text{-N}$ concentrations in each stream; (2) determine the influence of seeps on spatial patterns of stream $\text{NO}_3\text{-N}$ concentrations; and (3) examine the controls of base flow and storm flow on instream $\text{NO}_3\text{-N}$ variability.

METHODS

Site Location and Characteristics

The study was conducted in two headwater catchments (FD36 [40 ha] and RS [45 ha]) located within

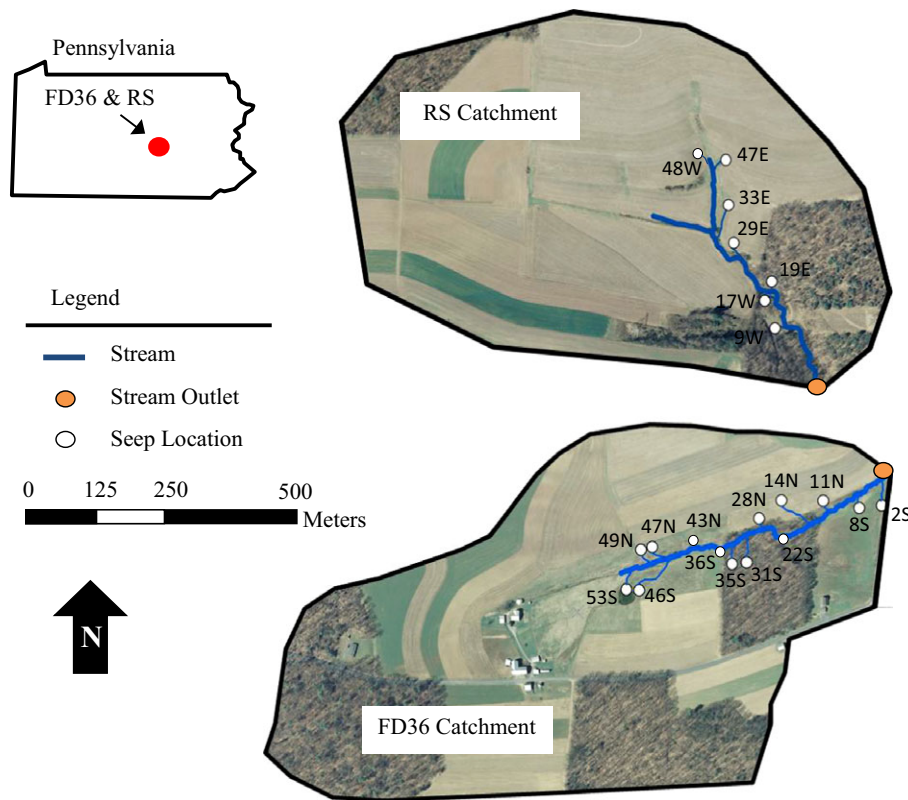


FIGURE 1. Aerial Photograph of FD36 and RS with Locations of Groundwater-Fed Seeps. FD36 and RS are sub-catchments of WE-38 (7.3 km²), which is located in central Pennsylvania.

the Appalachian Ridge and Valley physiographic region of Pennsylvania (Figure 1). FD36 and RS are located within WE-38, a 7.3 km² experimental watershed that has been operated by the USDA-ARS since 1968 (Bryant *et al.*, 2011). Elevations in the catchments range from 242 m above mean sea level (outlet) to 294 m amsl (ridgeline) in FD36 and from 238 m amsl (outlet) to 293 m amsl (ridgeline) in RS. Bedrock geology is largely consistent between the two catchments, with the main rock types being siltstones, mudstones, and sandstones of the Irish Valley and Sherman Creek Members of the Catskill Formation.

Both catchments possess numerous groundwater seeps in the riparian area, with well-drained residual soils on the hillslopes and somewhat poorly drained soils along the valley floor (Needleman, 2002). The well-drained soils are stony, silt loams (Leck Kill, Calvin, Berks series), while the somewhat poorly drained soils (Albrights and Hustontown series) have a moderately well developed fragipan beginning at a depth of 0.4-0.8 m. The dominant land use in FD36 and RS is agriculture (56 and 75% of the catchment, respectively) (Figure 1). Crops are planted on upslope fields and the riparian zones are variable in width (2-20 m) and planted with warm and cool season grasses. Annual farmer surveys show that most N is

applied during the spring and fall as commercial fertilizer, dairy manure, or swine manure. Nitrogen application rates in RS are greater than N application rates in FD36 (Table 1) due to the presence of a confined animal feeding operation that land-applied their animal manures in the RS catchment.

The streams that drain FD36 and RS flow for most (if not all) of the year. The stream channel in FD36 follows a gentle gradient (3%) from the headwaters to the outlet. The stream channel in RS is steeper than that of FD36, with a gradient of about 6%. Unlike FD36, which is gauged in four locations, the RS catchment is ungauged. Nonetheless, flows in FD36 should be representative of those in RS due to the proximity of both watersheds, as well as their similarities in size, soils, and geologic conditions (Bryant *et al.*, 2011).

Stream and Seep Water Sampling

Stream study reaches were established in FD36 (550-m long) and RS (490-m long) to monitor variations in N concentrations in stream and seep water. In each study reach, stream and seep water were sampled on 21 occasions (14 at base flow; 7 during or following storm events) between April 2009 and

TABLE 1. Nitrogen Management Data from FD36 and RS (2007-2011).

Year	FD36			RS		
	N Applied kg	Area ha	Mean N Application Rate kg/ha	N Applied kg	Area ha	Mean N Application Rate kg/ha
2007	2,182	15.4	142	3,982	19.6	203
2008	2,279	15.0	152	5,796	27.3	212
2009	1,773	12.8	139	4,773	22.5	212
2010	1,456	14.0	104	6,011	28.2	213
2011	2,148	15.3	140	4,228	26.6	159

Note: Data were collected from annual surveys of farmers in both catchments. The amount of N applied in FD36 and RS was a combination of fertilizer, dairy manure, and swine manure. Nitrogen content in manure was determined using the Penn State Agronomy Guide (2007).

January 2012. On each sampling date, stream water was collected from the thalweg at 10-m intervals moving from the stream outlet upstream to the top of the reach (i.e., 55 and 49 sampling points in FD36 and RS, respectively). The 10-m sampling interval was chosen, in part, because preliminary surveys in both watersheds showed that the minimum distance between any two seep inputs was about 10 m. Sampling that coincided with storm events occurred within 12 h of the end of the storm. For one summer storm event in FD36 (July 29, 2009), an additional set of stream water samples was collected 24 h after the event ceased. Stream discharge was monitored continuously (5-min) at the outlet of FD36 using a recording H-flume. Discharge was not monitored in RS, but we anticipate that it would be similar to what was measured in FD36.

During each stream survey, the locations of flowing groundwater seeps were identified by walking the length of the stream channel (Figure 1). Seeps were defined as areas in which groundwater emerged onto the land surface and was transported via surface flow paths to the stream channel. In order to be sampled, seeps had to have visible movement of water across the land surface, have a surface flow path longer than 1 m, and have a surface connection between the seep water and the stream channel. Seep water samples were collected 0.5 m from the stream edge to ensure there was no mixing between seep and stream water.

Water Quality Analysis

All water samples were preserved at 4°C until they could be analyzed for total N, NO₃-N, ammonium-N (NH₄-N), and chloride (Cl⁻) concentrations. Concentrations of total N were determined for unfiltered samples following alkaline persulfate digestion (Patton and Kryskalla, 2003). For dissolved constituents, water samples were filtered (0.45 μm) within 24 h of collection and then analyzed colorimetrically with a

Lachat QuikChem FIA+ autoanalyzer (QuikChem Methods FIA+ 8000 Series, Lachat Instruments, Loveland, Colorado). The analytical detection limit was 0.1 mg/l for NH₄-N and NO₃-N, and 0.2 mg/l for total N. Prior to analysis, the average holding time for water samples in cold storage was 30 days, and internal quality assurance and quality control measures showed no significant changes in concentrations over this time frame. Only 6% of the stream and seep samples collected had NH₄-N concentrations greater than the analytical detection limit; therefore, we chose not to report these values. Nitrate-N comprised 90-99% of total N on all sampling dates. Thus, the main focus of this article is on NO₃-N.

Data Analysis and Basic Statistics

The ill-defined nature of seep surface flow paths precluded the establishment of permanent gauging stations on seeps. To ascertain individual seep contributions to streamflow, we estimated the relative contribution of upstream and seep sources of streamflow using Cl⁻ concentrations as a proxy. Chloride concentration was utilized because it is nonreactive and serves as a conservative tracer of water flow pathways (Davis *et al.*, 2006). The fraction of seep water relative to upstream sources of streamflow was estimated with a simple mixing model by

$$\frac{Q_{\text{str}}}{Q_t} = \frac{C_2 - C_1}{S - C_1} \quad (1)$$

where Q_{str}/Q_t is the percent of Cl⁻ derived from the seep relative to upstream sources of Cl⁻, C_1 is the stream water Cl⁻ concentration at the nearest stream sampling location upstream of the seep's confluence with the stream, C_2 is the stream water Cl⁻ concentration 10 m downstream of C_1 , and S is the Cl⁻ concentration of seep water entering between C_1 and C_2 . In using this approach, it was assumed that the only source of Cl⁻ entering the stream channel between C_1 and C_2 was from the seep.

The effect of seeps on NO₃-N concentrations within individual stream segments of the studied reaches were assessed using data from the longitudinal stream surveys. First, downstream NO₃-N concentration was subtracted from the upstream NO₃-N concentration in each 10-m stream segment. Stream segments receiving inputs from flowing seeps were classified as “seep” and stream segments lacking seepage inputs were classified as “non-seep.” Since limited data on stream segments with seeps were available for any given sampling date, we grouped the stream segment data by season (spring: Mar.-May; summer: Jun.-Aug.; fall: Sept.-Nov.; winter: Dec.-Feb.) and by flow condition (base flow; storm flow) prior to analysis. One sample *t*-tests were then conducted in R statistical software (R Development Core Team, 2013) to determine whether changes in NO₃-N concentration in “seep” and “non-seep” segments were significantly different from zero change in concentration for each season and flow condition. This approach was similar to the one employed by Dent *et al.* (2001), who used one sample *t*-tests to assess changes in nutrient concentrations in concave and convex stream segments.

Since stream and seep surveys were collected recurrently over time, we applied repeated measures analysis of variance (ANOVA) to assess catchment level differences in the semi-variogram range and in stream and seep water NO₃-N concentrations. The repeated measures ANOVA incorporated an autoregressive variance structure (AR[1]) in the model to compensate for temporal autocorrelation in the data. Pairwise comparisons were made using Tukey’s Studentized Range test in order to separate treatment means. This analysis completed using R statistical software and a probability level of 0.05 was used to evaluate significance.

To evaluate whether the number of seep inputs to the streams affected the spatial variability of stream water NO₃-N concentrations, we tested whether a statistically significant correlation existed between the semi-variogram range and the number of flowing seeps, grouping the data by catchment and by flow condition. Instead of using a standard Pearson correlation test, we applied the Dutilleul modified *t*-test, which calculates an effective sample size based on the amount of autocorrelation in the data, adjusts the degrees of freedom accordingly, and calculates a modified significance value of the test (Dutilleul, 1993). The Dutilleul modified *t*-tests were run using version 2 of the Pattern Analysis, Spatial Statistics, and Geographic Exegesis (PAS-SaGE) software package (Rosenberg and Anderson, 2011).

Semi-Variogram Analysis

Semi-variograms show how differences between data points change with increasing distance between them (referred to as the lag; *h*) (Figure 2). Semi-variance (γ) is calculated as

$$\gamma(h) = \frac{1}{2n} \sum [g(x) - g(x + h)]^2 \quad (2)$$

where *n* is the number of sample pairs, *g* is the NO₃-N concentration, *x* denotes the position of one sample in the pair and *x + h* denotes the other. Semi-variance will not increase with increasing lag distance if data are spatially independent (Figure 2; Random Model). If, however, data points closer together tend to be more similar than data points that are farther apart, semi-variance will increase with separation distance and the data are considered spatially dependent. Semi-variance may increase for all lags, which suggests that points located further apart become continuously more different (Figure 2; Linear Model). Semi-variance may also level off to an asymptote, called the sill (Figure 2; Spherical Model). At the lag distance of the sill, called the range or patch size, data are no longer considered to be spatially dependent. Thus, the range denotes the lag distance over which data are spatially correlated (Rossi *et al.*, 1992). The apparent y-intercept of a semi-variogram, called the nugget, is often greater than zero and represents

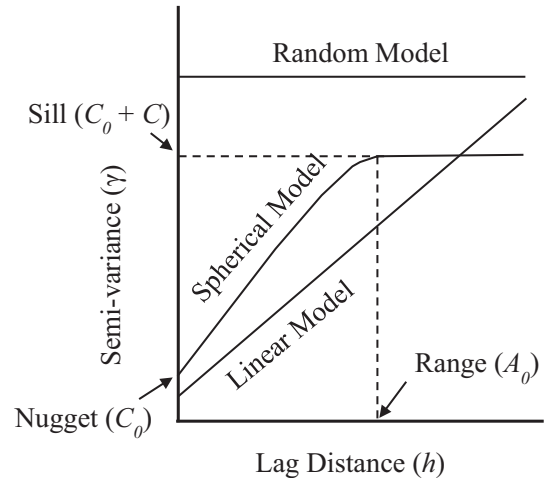


FIGURE 2. Semi-Variogram Models Showing the Semi-Variance (γ) as a Function of Increasing Lag Distance (*h*). For spatially independent data, semi-variance does not increase with lag (Random Model). For spatially dependent data, semi-variance may increase for all lags (Linear Model) or level off to an asymptote, called the sill (Spherical Model). The range or patch size indicates the distance over which data are spatially correlated. Figure adapted from Dent and Grimm (1999).

either measurement error or variability at scales smaller than the sampling interval (Rossi *et al.*, 1992).

Semi-variogram analysis was applied in the downstream direction in order to quantify spatial patterns in stream NO₃-N concentration. Following the methods of Dent and Grimm (1999), downstream trends in NO₃-N concentration were first removed using linear regression and the resultant regression residuals were used in the analysis. A lag interval of 10 m, which corresponded to our sampling interval, was used and we extended our analysis to a maximum lag of 200 m. The maximum lag was equivalent to 35 and 40% of the study reach in FD36 and RS, respectively, and was chosen based on the number of sample pairs required for accurate semi-variogram calculation (Dent and Grimm, 1999). We then applied the technique of Cressie (1985) to determine the values of the sill, range, and nugget. Briefly, spherical models were fit to the semi-variogram in R statistical software using weighted least-squares analysis. In the spherical model, if $h < A_0$, then

$$\gamma(h) = C_0 + C\left[1.5\frac{h}{A_0} - 0.5\left(\frac{h}{A_0}\right)^3\right] \quad (3)$$

where h is the lag interval, A_0 is the range, $\gamma(h)$ is the semi-variance at lag h , C_0 is the nugget variance, and C is the structural variance (variance attributed to autocorrelation). If $h \geq A_0$, then

$$\gamma(h) = C_0 + C. \quad (4)$$

RESULTS

General Trends in Precipitation and Streamflow

Annual precipitation measured at the rain gauge in FD36 showed that rainfall amounts were similar in 2009 and 2010, but substantially greater in 2011. In 2009 and 2010, rainfall amounts were 887 and 914 mm, respectively, which was slightly less than the long-term (40 year) mean rainfall of 1,080 mm in FD36 (Buda *et al.*, 2011). Relative to 2009 and 2010, the amount of rainfall nearly doubled in 2011, as 1,811 mm of rain was recorded. The increased rainfall in 2011 was caused by two large storm systems (remnants of Hurricane Irene [Aug. 27] and Tropical Storm Lee [Sept. 8]) that yielded 645 mm of rain.

Stream discharge at the outlet of FD36 averaged 7.2×10^{-3} cubic meters per second (cms) from April 2009 through January 2012. Flow ranged from dry (i.e., no flow) to 0.5 cms, with the lowest measurable

flow occurring in September 2010 and the highest flow occurring September 2011 (Figure 3). On dates of stream surveys, stream discharge averaged 5.8×10^{-3} and 3.8×10^{-2} cms for base flow and storm flow, respectively (Figure 3). Stream discharge during storm flow sampling ranged from 5.0×10^{-3} to 0.1 cms, whereas, stream discharge was relatively consistent during base flow sampling (Figure 3). Relative estimates of seep contributions to the stream relative to upstream sources of water are presented in a subsequent section.

Stream Water NO₃-N Concentrations and Spatial Variability

Base Flow. Stream NO₃-N concentrations were significantly less in FD36 compared to RS ($p = 0.002$). Nitrate-N concentrations in FD36 ranged from 0.6 to 6.1 mg/l, whereas in RS, NO₃-N concentrations ranged from 10.8 to 14.7 mg/l. Nitrate-N concentrations were significantly different among seasons in FD36 ($p = 0.013$) (Figure 4A). In FD36, mean stream NO₃-N concentrations were lower during the summer compared to the spring and fall, and winter. Temporal variability in stream NO₃-N concentration over the study period is shown in Figure 5. In both FD36 and RS, there was a strong positive linear relationship between NO₃-N concentration and downstream distance on all sampling dates ($p < 0.001$) (Table 2), with NO₃-N concentrations increasing downstream on all sampling dates in both catchments. Spatial variability in stream NO₃-N concentration, measured by the coefficient of variation (CV), ranged from 4 to 94% in FD36 and 7 to 36% in RS. Mean NO₃-N concentration variability in FD36 was significantly greater in the summer (CV = 65%) compared to the spring and winter (CV = 10 and 6%, respectively) ($p = 0.003$). Variability in NO₃-N concentrations in RS was similar across all seasons (CV = 18-26%).

Spherical models were fit to the experimental semi-variogram on all base flow sampling dates to quantify longitudinal patterns in stream NO₃-N concentration (Table 2). Stream NO₃-N concentrations in both FD36 and RS showed spatial patchiness within the scale of the survey; however, the range where concentrations became spatially dependent was significantly less in FD36 (82 m) compared to RS (151 m) ($p < 0.001$). Spatial patterns of stream NO₃-N concentrations varied in both catchments with season ($p = 0.029$) (Figure 4B). In FD36, patch sizes of NO₃-N concentrations were significantly larger during the summer and fall compared to spring and winter. Patch sizes of NO₃-N concentrations in RS were significantly larger in the summer compared to the fall. Semi-variogram nugget values were relatively low

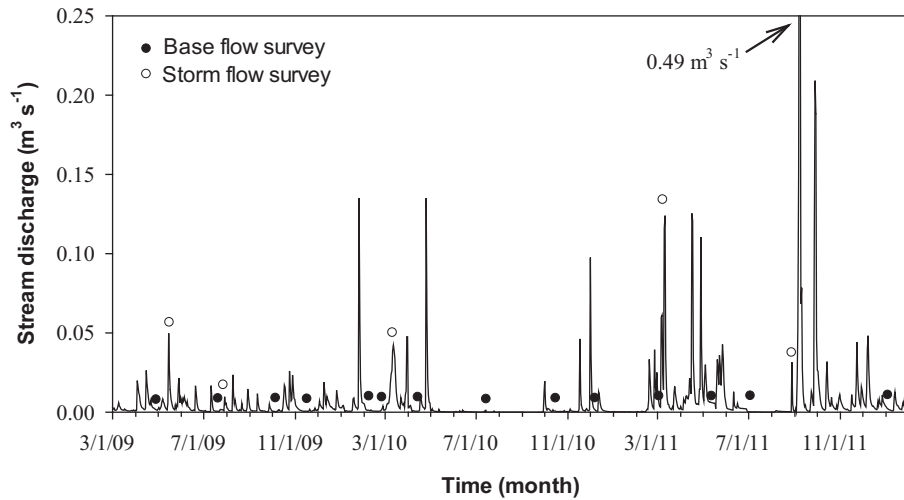


FIGURE 3. Daily Average Stream Discharge at the Outlet of FD36. Stream discharge was measured with a recording H-flume at 5-min intervals and averaged daily. Base flow and storm flow stream and seep survey dates are labelled.

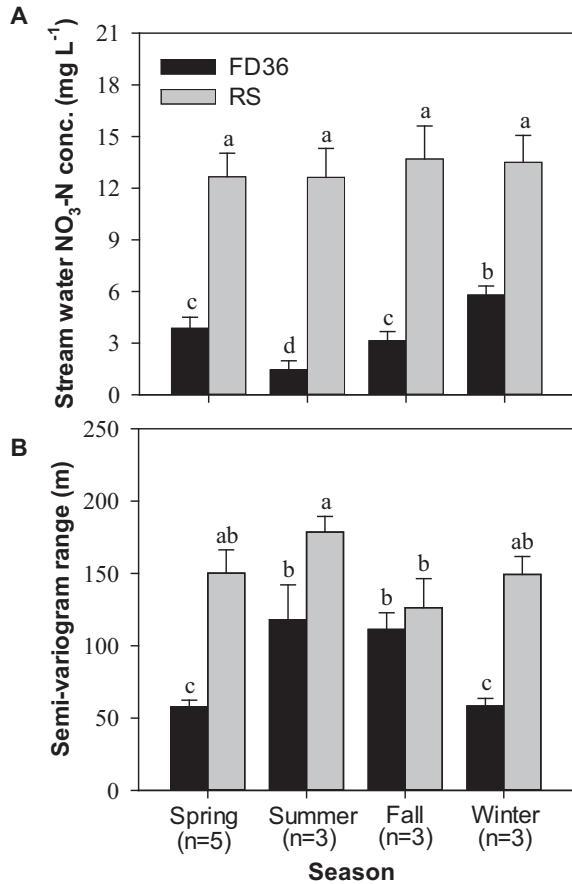


FIGURE 4. (A) Base Flow Stream Water $\text{NO}_3\text{-N}$ Concentrations from FD36 and RS. (B) Spatial patterns in base flow stream water $\text{NO}_3\text{-N}$ concentrations from FD36 and RS. Semi-variogram range values indicate the distance over which stream water $\text{NO}_3\text{-N}$ concentrations are spatially dependent. Error bars represent one standard error. Letters above bars denote statistical significance ($p < 0.05$).

compared to the sill on all base flow sampling dates, which resulted in high structural variance (Table 2). Values for structural variance averaged 0.85; thus, on average, 15% of the observed variability in stream $\text{NO}_3\text{-N}$ concentration was either due to measurement error or variability at lag distances < 10 m.

Storm Flow. Storm events did not significantly impact mean stream $\text{NO}_3\text{-N}$ concentration in either catchment (Table 2). Compared to base flow $\text{NO}_3\text{-N}$ concentrations, $\text{NO}_3\text{-N}$ concentrations following storm events were slightly lower on average (Figure 5). Similar to base flow, there was a strong positive linear relationship between $\text{NO}_3\text{-N}$ concentration and downstream distance on all storm sampling dates in both FD36 and RS ($p < 0.001$). Overall spatial variability of stream water $\text{NO}_3\text{-N}$ concentrations tended to decrease during storm events compared to base flow (Table 2). Based on data from storm events in this study, events occurring in the summer appeared to decrease $\text{NO}_3\text{-N}$ variability more than events occurring in the spring. For example, in FD36, the CV changed by $< 1\%$ following spring storm events compared to summer events in which the CV decreased by more than 30%. Figure 6 shows how stream $\text{NO}_3\text{-N}$ concentration and spatial patterns changed from base flow, to immediately following a summer storm (6 h), to 24 h after the storm in FD36.

Spherical models were fit to storm event semi-variograms on all dates in both FD36 and RS except for the event on July 30, 2009, which was fitted with a linear model (Figure 2). The range where stream $\text{NO}_3\text{-N}$ concentration became spatially dependent was generally greater following a storm event compared

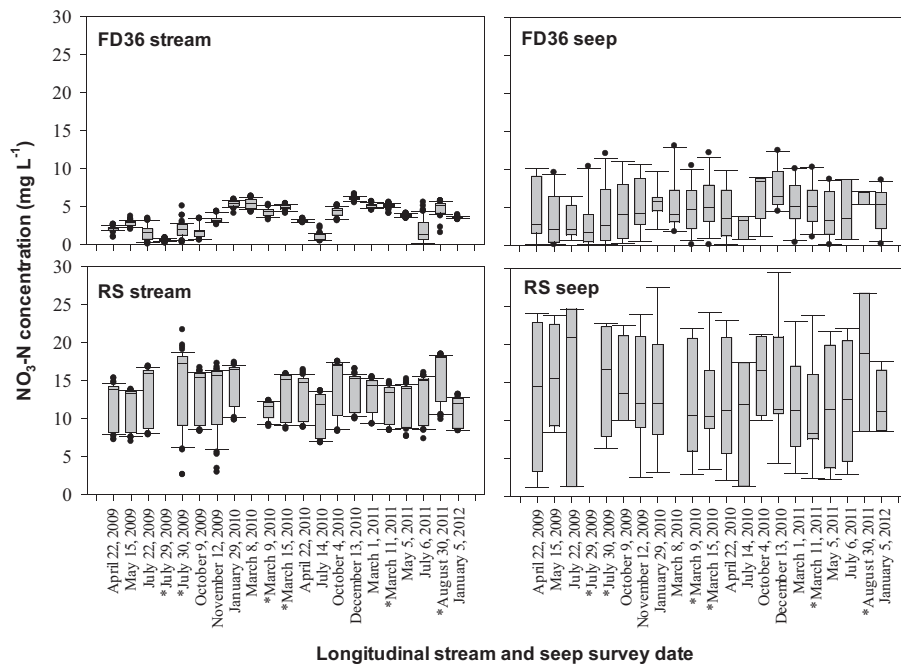


FIGURE 5. Box-and-Whisker Plots Showing the Variation in Stream and Seep Water $\text{NO}_3\text{-N}$ Concentrations in FD36 and RS on 21 Sampling Dates between April 2009 and January 2012. Asterisks indicate storm flow sampling dates.

to base flow conditions (Table 2). In FD36, the mean patch size of stream $\text{NO}_3\text{-N}$ concentration increased from 71 m at base flow to 111 m immediately following storms, while an increase from base flow to storm flow of 151 to 157 m was observed in RS. Stream $\text{NO}_3\text{-N}$ concentrations therefore became less spatially variable following storm events. Notably, $\text{NO}_3\text{-N}$ concentrations in FD36 became continuously more different along the reach (Figure 6) 24 h following a summer storm event (July 2009), suggesting that stream $\text{NO}_3\text{-N}$ concentration variability changes markedly over the course of a single event (i.e., base flow, to immediately following (6 h) the event, to 24 h following the event) (Figure 6).

Seep $\text{NO}_3\text{-N}$ Concentration Variability

The number of seeps that were sampled in FD36 and RS ranged from an absolute minimum of 2 seeps in RS to a maximum of 13 seeps in FD36 (Table 2). Seep surface flow paths in RS tended to have a greater slope than seep flow paths in FD36 (Table 3). The mean number of seeps sampled on each date was significantly greater in FD36 compared to RS ($p < 0.001$). On average, 64% of seeps were sampled in FD36, whereas 71% of seeps were sampled in RS (Table 3). Mean seep water $\text{NO}_3\text{-N}$ concentrations in FD36 (4.7 mg/l) were significantly less than mean $\text{NO}_3\text{-N}$ concentrations measured in RS (13.4 mg/l) ($p < 0.001$; Figure 5). In both catchments, seeps

located immediately downslope of cropland tended to have the highest $\text{NO}_3\text{-N}$ concentration, but some seeps located below forest also had high concentrations (e.g., RS, seep 19W) (Table 3).

Seep water $\text{NO}_3\text{-N}$ concentrations significantly differed among seasons in FD36 ($p = 0.03$). In FD36, mean seep water $\text{NO}_3\text{-N}$ concentrations were less during the summer compared to the winter. Storm events did not have a significant effect on seep $\text{NO}_3\text{-N}$ concentrations in either catchment, but seep concentrations tended to decrease following storm events compared to base flow (Figure 5).

The Influence of Seeps on Stream Water $\text{NO}_3\text{-N}$ Concentration and Variability

Stream and seep water Cl^- concentrations were used in two-component mixing models to estimate seep contributions to streamflow relative to upstream sources of stream water (Table 3). Estimates of seep contributions ranged from 0 (i.e., seep was not flowing) to 58% of streamflow relative to upstream sources of water. On average, individual seep contributions to streamflow ranged from 2.0 to 20.9% (Table 3). In both catchments, the location of the seep along the stream reach influenced the relative contribution of the seep to streamflow. Seeps located the furthest from the catchment outlet accounted for a relatively larger proportion of streamflow compared to seeps located downstream (Table 3).

TABLE 2. Mean NO₃-N Concentrations Across the Study Reach, Downstream Trends, Number of Flowing Seeps, and Indices of Spatial Variability for Stream Water in FD36 and RS.

Date	FD36							RS						
	Seeps <i>n</i>	Concentra- tions and Downstream Trends		Spherical Model Parameters				Seeps <i>n</i>	Concentra- tions and Downstream Trends		Spherical Model Parameters			
		NO ₃ -N mg/l	R ^{2†}	Nugget [‡] C ₀	Sill [§] C ₀ + C ₁	Range [¶] <i>m</i>	R ^{2*}		NO ₃ -N mg/l	R ^{2†}	Nugget [‡] C ₀	Sill [§] C ₀ + C ₁	Range [¶] <i>m</i>	R ^{2*}
2009														
Apr. 29	8	2.0	0.52	0.006	0.044	50	0.56	4	12.0	0.59	0.670	5.87	155	0.99
May 15	9	2.8	0.51	0.013	0.099	120	0.90	5	11.6	0.67	0.279	3.55	150	0.99
Jul. 22	7	1.6	0.85	0.032	0.175	71	0.88	3	13.8	0.64	0.886	7.44	159	0.99
Jul. 29	10	0.6	0.57	0.002	0.015	107	0.94	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Jul. 30	12	1.9	0.49	—	—	—	0.91	4	14.3	0.58	—	—	—	0.95
Oct. 9	6	1.7	0.84	0.014	0.121	96	0.88	4	13.4	0.67	0.851	5.60	135	0.97
Nov. 12	7	3.3	0.51	0.015	0.127	104	0.91	6	12.9	0.54	4.160	11.36	88	0.82
2010														
Jan. 29	9	5.3	0.87	0.004	0.016	57	0.60	6	14.7	0.63	0.140	4.41	144	0.98
Mar. 8	11	5.3	0.85	0.018	0.073	45	0.85	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Mar. 9	12	4.3	0.76	0.011	0.083	84	0.91	6	11.2	0.64	0.003	0.97	181	0.98
Mar.15	13	4.9	0.66	0.006	0.035	60	0.81	7	13.3	0.78	0.124	3.45	193	0.99
Apr. 22	8	3.1	0.27	0.005	0.016	89	0.84	5	13.2	0.56	0.133	6.00	155	0.99
Jul. 14	3	1.1	0.85	0.023	0.167	151	0.97	3	10.8	0.49	0.010	6.53	196	0.99
Oct. 4	5	4.3	0.62	0.022	0.205	134	0.98	4	14.7	0.66	0.680	6.01	156	0.99
Dec. 13	10	6.1	0.16	0.012	0.052	68	0.90	7	13.8	0.65	0.074	2.44	131	0.97
2011														
Mar. 1	11	4.1	0.53	0.005	0.040	56	0.69	6	13.1	0.56	0.486	4.31	110	0.87
Mar. 11	13	5.1	0.48	0.006	0.033	86	0.80	9	13.2	0.74	0.247	1.90	158	0.98
May 5	10	3.8	0.42	0.001	0.021	49	0.83	4	12.3	0.68	0.195	4.23	181	0.98
Jul. 6	3	1.7	0.56	0.038	0.080	132	0.94	2	13.7	0.57	0.649	5.89	181	0.99
Aug. 30	5	4.8	0.52	0.034	0.379	168	0.98	6	15.9	0.63	0.321	5.94	150	0.99
2012														
Jan. 5	11	5.9	0.10	0.002	0.011	50	0.55	4	11.2	0.48	0.353	3.05	173	0.99

Notes: Bolded rows indicate sampling dates that coincided with storm events.

*Linear relationship between semi-variance and spherical model.

†Linear relationship between NO₃-N and downstream distance.

‡Measurement error or variability at scales < 10 m.

§Maximum semi-variance (i.e., where semi-variance levels off).

¶Distance over which NO₃-N concentration is spatially dependent.

Downstream changes in NO₃-N concentration for stream segments (10 m) with and without seeps (i.e., non-seep) are shown in Figure 7. In both FD36 and RS, mean seep NO₃-N concentration was greater than mean stream water NO₃-N concentration; thus, seeps resulted in an increase in stream NO₃-N concentration. During base flow, mean increases of 0.24 and 0.26 mg/l NO₃-N were observed for stream segments with seeps in FD36 and RS, respectively. Mean increases in NO₃-N concentration as a result of seep inputs were significant across all seasons in FD36, but only during the spring and summer in RS (Figure 7). The influence of seeps on changes in stream NO₃-N concentration was also significant during storm flow in both FD36 and RS (Figure 7). In contrast to stream segments with seeps, non-seep stream segments had a mean downstream decrease in NO₃-N

concentration during base flow in both FD36 and RS, and during storm flow in RS (Figure 7). One nonseep stream segment in RS, however, consistently resulted in large increases in stream water NO₃-N concentration of up to 6.0 mg/l. Since there were no visible additions of water at this location, it was assumed that groundwater with high NO₃-N concentration was discharging directly into the stream channel.

The number of seeps sampled during each stream survey significantly influenced spatial patterns in stream water NO₃-N concentration in both FD36 and RS (Figure 8). A significant linear relationship was observed between the number of seeps sampled during base flow and the semi-variogram range for stream water NO₃-N concentration (FD36, $p = 0.040$; RS, $p = 0.026$). During base flow, the more seeps that were sampled, the smaller the semi-variogram range

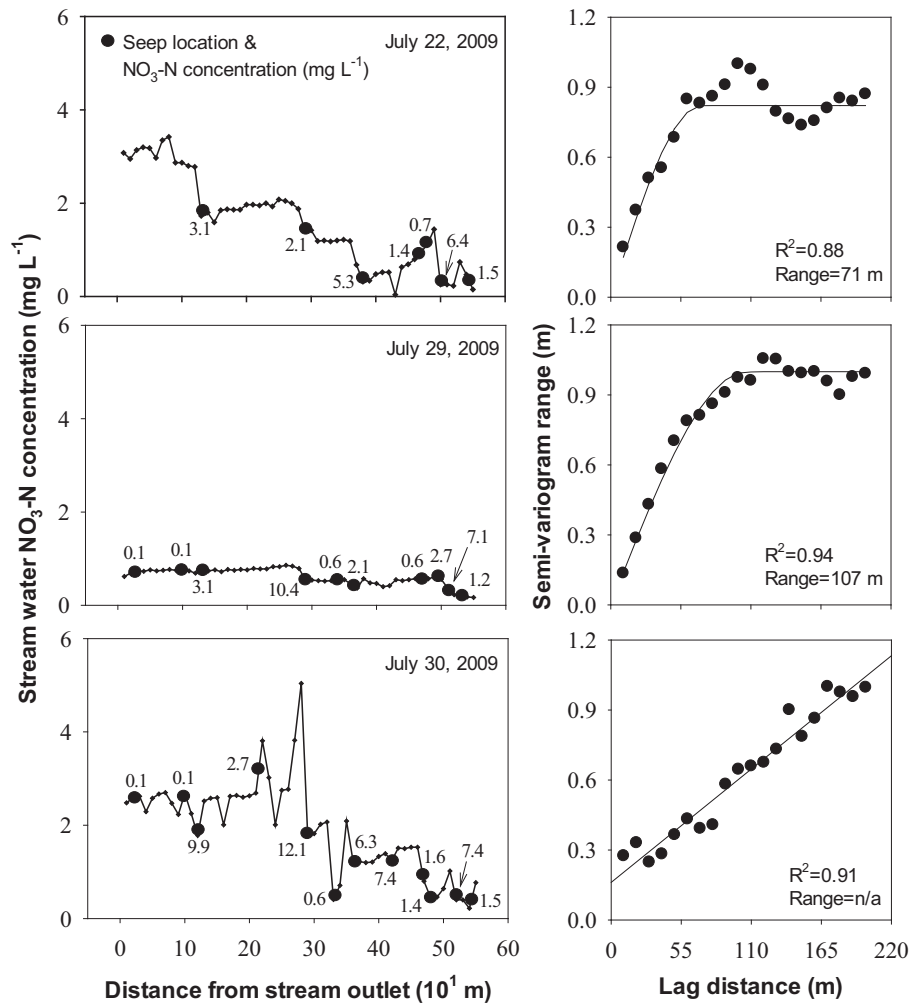


FIGURE 6. Stream Water NO₃-N Concentration (left column) and Semi-Variograms (right column) from FD36 before (July 22), Immediately Following (July 29), and 24 h After (July 30) a Storm Event (2.9 cm). Seep locations along the stream reach and NO₃-N concentrations are shown. Spherical models were fit to the July 22 and 29 semi-variograms. A linear model was used to describe the July 30 semi-variogram. Semi-variance was standardized by dividing through by its maximum value on each date. Indices of spatial variability are given in Table 2.

(or patch size) (Figure 8); therefore, an increase in the number of point inputs from seeps yielded more spatial variability in stream water NO₃-N concentrations. In contrast, no such correlations were observed between the number of seeps sampled during storm flow and the semi-variogram range for stream water NO₃-N concentration (FD36, $p = 0.171$; RS, $p = 0.693$).

DISCUSSION

Variability of NO₃-N in Stream and Seep Waters

Results from longitudinal monitoring of stream reaches in FD36 and RS suggest that NO₃-N additions primarily occurred where seeps entered the

stream. Seeps essentially function as a drainage outlet for larger areas of the catchment (although the extent of this area is difficult to determine); therefore, they have the potential to deliver large volumes of agriculturally influenced groundwater to the stream (Angier and McCarty, 2008). In FD36 and RS, stream segments with seeps comprised between 5 and 16% of the total stream length and we estimated that individual seeps were supplying between 2 and 21% of streamflow relative to upstream sources of stream water. Since seep NO₃-N concentrations were on average greater than stream NO₃-N concentrations, the addition of water from seeps to the stream resulted in significant increases in stream NO₃-N concentrations downstream of the seep input (0.25 mg/l). Stream segments that were not receiving seep inputs exhibited small decreases in NO₃-N concentration indicating that instream uptake, denitrification, and/or dilution were also likely occurring

TABLE 3. Length of Flow Path, Slope, Immediate Upslope Land Use, NO₃-N Concentration Mean and Range, Estimated Flow Contribution Relative to Upstream Sources, and Percentage of Sampling Days Each Seep Was Flowing in FD36 and RS.

Seep	n* %	Length m	Slope m m ⁻¹	Land Use [†]	NO ₃ -N Concentration		Flow Contribution [‡]	
					Mean	Range	Mean	Range
					mg/l		%	
FD36								
2S	29	33	0.028	Meadow	0.3	0.1-1.1	3.1	0.0-6.5
8S	71	12	0.051	Meadow	1.5	0.1-4.5	4.6	0.0-11.7
11N	81	8	0.076	Crop	8.5	3.1-12.2	3.2	0.0-14.3
14N	24	55	0.030	Crop	8.7	6.3-10.2	3.5	0.0-6.7
22S	33	3	0.079	Forest	1.5	0.5-2.4	2.0	0.0-4.7
28N	76	2	0.053	Crop	9.4	2.1-13.1	8.5	0.0-37.9
31S	76	29	0.045	Forest	2.3	0.3-4.8	7.6	0.0-22.6
35S	24	20	0.041	Forest	4.9	3.7-5.7	3.7	0.0-9.7
36S	90	2	0.043	Forest	5.4	2.1-8.8	10.5	0.0-29.4
43N	38	5	0.029	Crop	5.6	3.0-7.4	5.3	0.0-18.9
46S	71	76	0.012	Meadow	2.8	0.1-5.8	10.5	0.0-32.7
47N	43	35	0.030	Crop	4.3	0.7-8.2	7.3	0.0-31.5
49N	95	17	0.045	Crop	7.1	3.8-9.1	11.0	0.0-19.2
53S	100	17	0.027	Meadow	3.6	0.8-6.8	20.1	0.0-58.5
RS								
9W	90	8	0.114	Forest	17.6	11.3-21.0	10.8	0.0-38.0
17W	90	10	0.091	Crop	23.3	17.6-29.5	6.5	0.0-29.7
19E	57	2	0.126	Forest	2.7	1.2-4.4	2.9	0.0-14.6
29E	81	14	0.214	Crop	10.6	8.2-13.2	6.9	0.0-25.5
33E	19	64	0.156	Crop	10.9	8.0-12.5	6.8	0.0-15.2
47E	19	22	0.130	Crop	9.0	1.4-12.0	13.6	0.0-20.8
48W	67	2	0.124	Crop	10.2	7.6-13.2	20.9	0.0-44.2

Notes: Seep IDs denote their distance from the stream outlet (e.g., 11S is 110 m from the stream outlet; 28N is 280 m from the stream outlet) and location relative to the stream (e.g., N = north).

*Percent of sampling dates when the seep was flowing.

†Immediate upslope land use. All seep flow paths are located in the riparian zone.

‡Estimate of seep contributions relative to upstream flow in the stream channel. Estimates are based on two-component mixing models using seep and stream Cl⁻ concentrations from base flow sampling dates.

along the stream channel (Peterson *et al.*, 2001; Alexander *et al.*, 2007). The influence of instream NO₃-N removal mechanisms, however, was minimal compared to cumulative seep NO₃-N inputs as stream water NO₃-N concentrations increased downstream during all stream surveys.

Nitrate-N concentrations varied substantially among individual seeps in FD36 and RS. Variations in seep chemistry have also been documented in a forested catchment in Pennsylvania (O'Driscoll and DeWalle, 2010) and in the Catskill Mountains of New York (Burns *et al.*, 1998). Seep NO₃-N concentrations in these forested catchments, however, had a much smaller absolute range (< 2 mg/l) in concentration compared to those found in FD36 and RS. Variability in seep NO₃-N concentrations has been attributed to differences in physical, chemical, and biological processes occurring in the upslope contributing area (e.g., Cirno and McDonnell, 1997). In addition to differences in biogeochemical processes among the areas draining to seeps, N application rates and land use in agricultural catchments often vary at the field-scale.

Nitrogen application rates in areas draining to seeps are likely related to seep NO₃-N concentrations, as seeps in FD36 and RS immediately below cropland tended to have higher concentrations than other land uses. However, there is little research on the potential link between seeps and upslope N management. We hypothesize that in agricultural catchments differences in N management determine seep NO₃-N concentration, whereas in forested catchments, differences in biogeochemical processes likely play a larger role in seep NO₃-N concentration.

Once groundwater is discharged from a seep, flow paths and residence times within the seep can also affect the chemistry of seep water entering the stream (Hill, 1996). A tracer study in New Zealand pasture demonstrated that approximately 24% of NO₃-N could be removed along a seep surface flow path (Rutherford and Nguyen, 2004). Groundwater and NO₃-N transported in these flow paths, however, are more likely to bypass the mitigating features of the riparian zone (Warwick and Hill, 1988; Angier

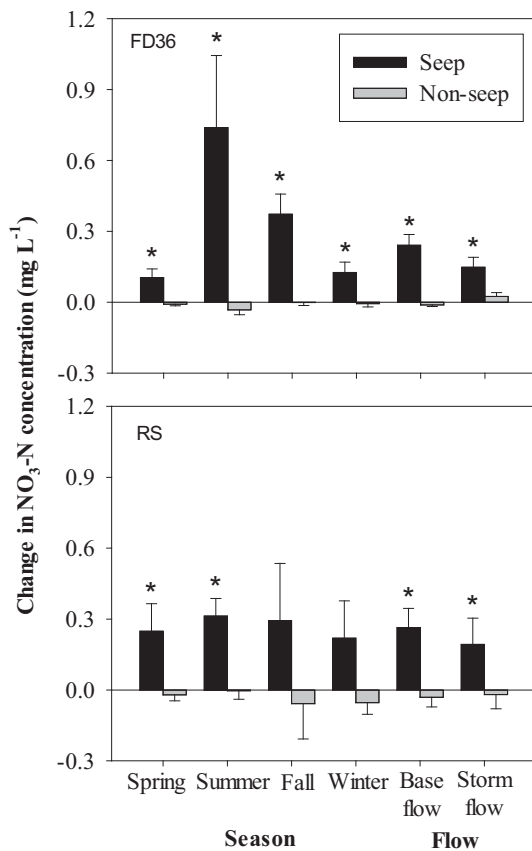


FIGURE 7. Changes in Stream Water NO₃-N Concentration between Sampling Locations Along the Study Reaches in FD36 and RS. Changes were calculated over a 550- and 490-m stream reach in FD36 and RS, respectively, at 10-m intervals. Seasonal data only includes base flow surveys. Error bars represent one standard deviation. Asterisks indicate that the change in NO₃-N concentration was significantly different from zero change in concentration ($p < 0.05$).

et al., 2002, 2005). In contrast, NO₃-N concentrations in shallow groundwater have been reported to decrease by 90-95% due to high denitrification rates in saturated riparian zone soils (Peterjohn and Correll, 1984; Lowrance, 1992). Since both surface and subsurface flow paths occur along the length of a seep, it is possible that a single seep could function as both a conduit and barrier for NO₃-N delivery. In FD36, seep NO₃-N concentrations were greater during the winter and spring compared to the summer. During the winter and spring, higher seep discharge could lead to more of the downseep flow being transported along rapid surface flow paths as opposed to slower, subsurface paths. This would decrease the potential for NO₃-N removal and result in higher concentrations delivered to the stream (Gold *et al.*, 2001). Alternatively, during the summer, lower seep discharge and longer residence times could promote NO₃-N removal.

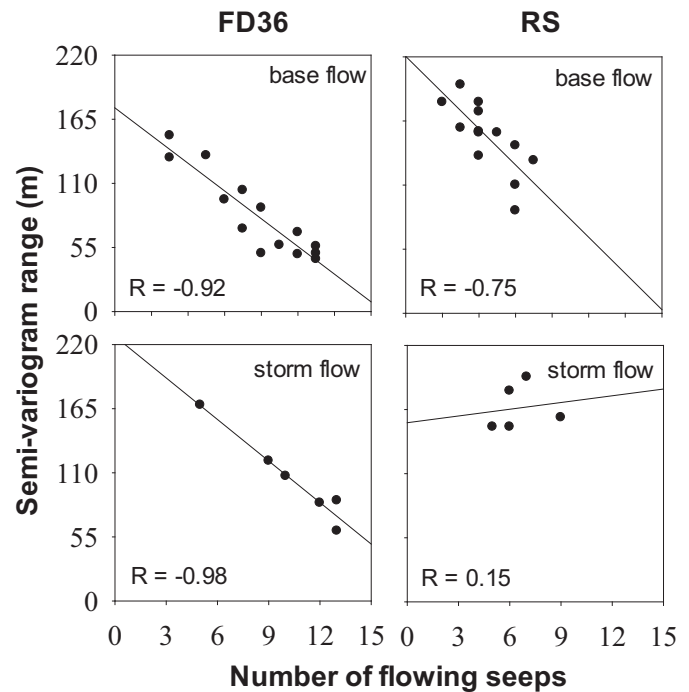


FIGURE 8. Number of Flowing Seeps on Each Sampling Date Compared with the Semi-Variogram Range (m) for Base Flow and Storm Flow Stream Surveys in FD36 and RS. The semi-variogram range indicates the distance over which stream water NO₃-N concentrations were spatially dependent.

Effects of Seeps on Stream Water NO₃-N Variability

Differences in the number of seeps and their NO₃-N concentrations among sampling dates resulted in spatial patterns of stream water NO₃-N concentrations that reflected the variability of seep inputs. Semi-variogram analysis showed that stream NO₃-N concentrations in FD36 and RS were not only spatially dependent at small scales (i.e., semi-variance increased with increasing lag distance), but also patchy within the scale of the survey. Given the unidirectional flow of stream water, it is not surprising that NO₃-N concentrations at nearby downstream locations were more similar than locations separated by longer distances. We found mean patch sizes of stream NO₃-N concentration were greater in FD36 compared to RS, which suggests that NO₃-N in FD36 was more spatially variable than in RS. This coincided with FD36 having more seeps, on average, compared to RS. In addition, the greater the number of seeps in both catchments on a single base flow sampling date, the greater the spatial variability of stream NO₃-N concentrations (i.e., decreased patch size). This suggests that in FD36 and RS, spatial patterns of stream NO₃-N concentrations were tightly coupled with variable inputs of NO₃-N from seeps.

Stream NO₃-N concentrations in FD36 and RS exhibited a substantial amount of longitudinal varia-

tion. For example, the annual variation in $\text{NO}_3\text{-N}$ concentration at the outlet of FD36 determined by weekly sampling (Zhu *et al.*, 2011) was 2-3 times less than the variation we observed over the 550-m stream reach during the summer (annual [2009] $\text{CV} = 32\%$ for 50 samples; CV on July 22, 2009 and July 6, 2011 = 61 and 94%, respectively, for 55 samples). Few studies, however, have quantitatively assessed spatial patterns in stream $\text{NO}_3\text{-N}$ concentrations as a result of seep inputs. Dent and Grimm (1999) found that patch sizes of stream $\text{NO}_3\text{-N}$ concentrations were approximately 400 m in length, but their study was conducted on a much larger desert stream. Although the size of the stream was much larger in the study by Dent and Grimm (1999), the effect of discrete point inputs on spatial patterns of stream $\text{NO}_3\text{-N}$ concentrations were similar to the finding from FD36 and RS reported herein. Dent *et al.* (2001) found that localized groundwater upwelling zones within the stream channel that had high $\text{NO}_3\text{-N}$ concentration had a strong influence on spatial patterns of stream water $\text{NO}_3\text{-N}$, which is similar to the effects of point inputs from riparian seepage zones.

Research on spatial patterns of nutrients in soils can also provide a useful comparison to the observations obtained from stream sampling in FD36 and RS. For example, studies have shown that most nutrients in forest soils are spatially dependent at distances ranging from 2 to 5 m (Palmer, 1990; Lechowicz and Bell, 1991), whereas in agricultural soils, nutrients are found to be spatially dependent over distances of up to 100 m (Robertson *et al.*, 1997). The high spatial variability of nutrient concentrations found within terrestrial soils is likely not reflected in seeps as areas draining to seeps tend to integrate the effects of different land uses, flow paths, and biogeochemical processes. Stream $\text{NO}_3\text{-N}$ concentrations observed in FD36 and RS would therefore be expected to be less variable than soil $\text{NO}_3\text{-N}$ concentrations within each catchment. In addition, downstream transport of $\text{NO}_3\text{-N}$ may lengthen the distance over which concentrations are spatially dependent compared to soils by carrying products away from where they are formed or enter the stream (Wagener *et al.*, 1998).

Influence of Storm Events on Instream $\text{NO}_3\text{-N}$ Variability

Nitrate-N concentrations in stream water became less spatially variable immediately following storm events compared to base flow in FD36 and RS. Although the number of flowing seeps increased immediately following storm events, patch sizes also increased following storm events. The diminished

influence of seeps on spatial patterns in stream $\text{NO}_3\text{-N}$ concentrations immediately following storm events compared to base flow coincided with decreased changes to stream water $\text{NO}_3\text{-N}$ concentrations where seep water entered the stream. During storm events, rain falling directly into the stream channel and surface runoff from the landscape increased stream discharge and most likely diluted stream $\text{NO}_3\text{-N}$ concentrations (Pionke *et al.*, 1988). Increased stream discharge also likely resulted in more turbulent streamflow and greater mixing of the stream water, which would have homogenized $\text{NO}_3\text{-N}$ concentrations throughout the reach. Similar findings have been reported in both aquatic and terrestrial environments. For example, flooding of a desert stream decreased $\text{NO}_3\text{-N}$ concentration variability (Dent and Grimm, 1999). In addition, the distance over which soil nutrient concentrations are spatially dependent is typically greater for cultivated (i.e., well mixed) agricultural fields compared to undisturbed fields (Robertson *et al.*, 1993).

The increased patch sizes of stream $\text{NO}_3\text{-N}$ concentrations that were observed immediately following a small summer storm event in FD36 (July 29, 2009; Figure 6), however, were reversed one day following the event as stream $\text{NO}_3\text{-N}$ concentrations became continuously more different along the entire reach (July 30, 2009; Figure 6). We explain this pattern using the conceptual model of storm flow generation developed by Pionke *et al.* (1988). This model, developed in a neighboring catchment to FD36 and RS, describes a five-step sequence where streamflow cycles from base flow dominated, to rainfall-diluted base flow, to surface runoff dominated flow, to subsurface discharge dominated flow, and then back to base flow. In our study we infer that as streamflow cycled from rainfall-diluted and surface runoff dominated flow to subsurface discharge dominated flow, the influence of seep inputs on spatial patterns of stream water $\text{NO}_3\text{-N}$ concentrations in FD36 and RS likely reached its maximum. During this transition period, the number of flowing seeps was likely at its greatest and stream discharge was receding back to base flow. It is also likely that stream water $\text{NO}_3\text{-N}$ concentrations would become less variable and patch sizes would return to base flow values as time passed after the storm and inputs from seeps declined.

CONCLUSION

This study applied longitudinal sampling of stream and seep water quality to provide valuable insight into factors influencing the spatial variability of $\text{NO}_3\text{-N}$

concentrations in headwater streams draining the FD36 and RS catchments. Concurrent sampling of riparian seeps with stream water provided evidence that instream $\text{NO}_3\text{-N}$ concentrations were increasingly variable as the number of seep inputs to streams increased. In contrast, during storm events, $\text{NO}_3\text{-N}$ concentrations became less variable as streamflow transitioned from base flow to storm flow, owing to increased mixing and homogenization of the variable $\text{NO}_3\text{-N}$ inputs from seeps to stream water. Findings from this study suggest that variable inputs of $\text{NO}_3\text{-N}$ from riparian seeps impart identifiable patterns of $\text{NO}_3\text{-N}$ variability in stream water, especially during base flow conditions. Collectively, these results pinpoint seeps as important sources of $\text{NO}_3\text{-N}$ to streams and highlight the need to target seep contributing areas for conservation and nutrient management programs, as well as for possible mitigation measures where $\text{NO}_3\text{-N}$ levels in seeps are consistently elevated. Future research exploring the linkage between $\text{NO}_3\text{-N}$ variability in seep water and variable land management activities in upslope seep contributing areas will be critical to developing strategies to protect water quality in seeps and streams in the northeast U.S.

DISCLAIMER

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

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