Insights into Nitrogen Fluxes: Quantifying Variations in Groundwater-Stream Hydrologic Connectivity

Cassandra L. Cosans
Winchester, Virginia

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Janet S. Herman,
Thesis Advisor

Aaron L. Mills,
Thesis Co-Advisor

Thomas A. Smith,
Director of Distinguished Major Program

ABSTRACT

Significant nutrient nitrogen (N) that degrades coastal waters comes from groundwater that discharges through base flow in streams; thus, understanding the movement of N from groundwater to streams is essential. Nitrate in the groundwater and streamwater was studied at four low-relief, gaining coastal streams on the Delmarva Peninsula of Virginia with the goal of identifying factors important in controlling N flux. Saturated hydraulic conductivity (K_s) was measured by rising and falling head tests in piezometers installed at depths of 60, 100, and 150 cm below the sediment surface and in 70-cm-long sediment cores taken at each stream. Percent organic matter was determined along the sediment cores through weight-loss on ignition. Percent organic matter was inversely related to K_s, but both were extremely variable among the different samples at each stream, differing as much within a single stream as among streams. K_s was between <0.006 and 0.24 cm/sec, while organic matter content ranged from 0.3 to 42%. Nitrate concentrations in the streamwater were fairly similar among the streams and were always less than 8 mg NO_3^--N L^{-1}, although Tommy's Ditch consistently had the highest concentrations. Tommy's Ditch also had the lowest groundwater NO_3^- concentrations. Cobb Mill Creek had groundwater NO_3^- concentrations that ranged from 8.5 to 13.3 mg NO_3^--N L^{-1}, which were dramatically larger than the groundwater at the other streams (range of <0.1 to 3 mg NO_3^--N L^{-1}). The notable differences in the N content of water at Cobb Mill Creek compared to the other streams is likely a direct result of their respective hydrologic settings. The relatively great topographic relief at Cobb Mill Creek favors deep groundwater circulation, and such a flowpath results large hydraulic gradients and higher N concentrations persisting at very shallow depths under the stream channel.

ACKNOWLEDGEMENTS

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INTRODUCTION

Nitrogen pollution of natural waters, particularly the Chesapeake Bay, is of pressing concern and has recently received a great deal of public and legislative attention. Due to its action as a limiting nutrient, excess nitrogen can lead to severe environmental problems including eutrophication and fish kills (Nixon, 1995). Declining water quality, decreased biodiversity, reduction of aesthetic and recreational value, and loss of income from fisheries are some of the impacts of nitrogen pollution (Lowrance et al., 1997). Excess nitrogen is derived primarily from anthropogenic sources, particularly agricultural fertilizer application and livestock waste management (Galloway et al., 2003). The VA Dept. of Environmental Quality and the US Environmental Protection Agency are working to reduce nitrogen contamination in waterways (Denver et al., 2004). However, as a non-point source pollutant, nitrogen is very difficult to monitor and regulate. Determining nitrogen fluxes from specific watersheds and scaling up to regional nutrient loads to receiving waters are current challenges. Understanding nitrogen mobility is crucial in determining the most effective reduction measures (Kennedy et al., 2009a; Kennedy et al., 2009b).

About half of the nitrogen load to the Chesapeake Bay is first stored in groundwater before being discharged through base flow in streams (Phillips and Lindsey, 2003), making understanding the movement of nitrogen from groundwater essential (Sanford and Pope, 2013). Mills et al. (2008) have been studying the role of nitrate-rich groundwater discharging to surface streams draining the Delmarva Peninsula as a major factor in watershed nutrient flux. Microbially mediated denitrification has been demonstrated to significantly lower the concentration of nitrate (e.g., Hill et al., 2000; Kennedy et al., 2009b), yet details of the groundwater hydrology been shown determine the extent to which denitrification occurs. In some cases, nitrate-rich groundwater bypasses the riparian zone and enters the stream without any loss of nitrate (Tesoriero et al., 2005). In other cases, denitrification leads to nearly complete removal of nitrate from groundwater as it moves through streambed sediments (Gu at al., 2007). Further investigation points to the role for residence time in determining the efficacy of denitrification in a given groundwater—stream-water system (Flewelling et al., 2012). Additionally organic carbon availability has been shown to be a limiting factor in denitrification (Hill et al., 2000). Yet, the predictive characteristics of an individual stream for anticipating its nitrate flux to coastal waters remain largely unidentified.

My own research over the past two years as part of the larger UVA effort has been focused on water flux from a set of four streams representing a range of watershed sizes and land-use practices in the region (Cosans et al., 2014). Information on the details of N occurrence and transformation within the context of my water-flux study has been lacking. Ultimately, the desired research outcome is to quantify regional-scale N flux. In order to use the detailed sampling of just a few watersheds to generalize to a regional outcome, the controlling factors in groundwater--surface-water connections must be elucidated. My goal is to determine the effect that differences in the (1) hydrologic connectivity between groundwater and streamwater and (2) sediment biogeochemical properties has on nitrogen flux variation among various watersheds.

Hydrologic connectivity derives from the physical characteristics of the porous medium at the groundwater—surface-water interface, i.e., saturated hydraulic conductivity and relative elevation head. Sediment biogeochemistry is embodied in organic carbon content and in porewater nitrate concentrations. I will examine these hydrologic and biogeochemical factors among my four streams of study, along with groundwater and stream-water nitrate levels, to gain insights into the factors controlling the differences in N flux variation among these watersheds.

METHODS

Study Site

The combined field and laboratory investigation focused on four streams that I have already studied for stream discharge and water flux. All four are low-relief, low-order coastal streams that drain to seaside lagoons along the Delmarva Peninsula of Virginia. The stream sites are along a roughly north to south transect approximately 45 miles long. From northernmost to southernmost the stream study sites are Bundick's Creek at 37°46'58" N and 75°36'23" W, Phillip's Creek at 37°26'07" N and 75°53'07" W, Cobb Mill Creek at 37°19'29" N and 75°56'08" W, and Tommy's Ditch at 37°09'55" N and 75°56'05" W. The Cobb Mill Creek study site is located at the bottom of a forested hillslope that separates the creek from an adjacent crop field. The flat-lying terrain bounding the other side of the creek is also forested. The hillslope is about 100 m wide with a change in elevation of 7.5 m. Bundick's, Phillip's, and Tommy's are all in relatively flat areas with changes in elevation of about 2 m or less. Bundick's Creek flows directly through a crop field and has a narrow riparian zone vegetated with grasses. Phillip's Creek passes between a crop field on one side and a wooded area on the other. Between the stream and the crop field, there is a riparian buffer about 20 m wide and vegetated in grasses. Tommy's Ditch flows between a field that has been fallow for at least 6 years and a forest. All crop fields near the streams grow a rotation of soybeans, corn, and winter wheat.

Daily precipitation during the period of study from June 2014 through February 2015 was obtained for the VA Cape Charles weather station from the NOAA National Climatic Data Center (http://www.ncdc.noaa.gov/crn/report).

Field Methods

Several hydrological and geochemical methods of study were leveraged to characterize groundwater-stream interactions. Piezometer nests were installed in the center of each stream channel in order to measure hydraulic gradients and obtain groundwater samples (Galavotti, 2004). Piezometers consist of 2.5 cm i.d. PVC pipe sealed at the end with a pointed solid PVC tip. Using a hand-held electric drill, four holes ¼ inch in diameter were drilled in a ring near the capped bottom. The exact distance from the top lip of the pipe to the level of the holes was measured. Each nest is composed of three piezometers that open to discrete depths of approximately 60, 100, and 150 cm below the surface of the streambed. The nested design allows for direct measurement of hydraulic gradient through water level measurements in the piezometers relative to the stream surface.

Water samples were collected from the piezometers using a peristaltic pump. During sampling, the piezometer was initially pumped dry or drained of a minimum of three full volumes of water to ensure that the sample obtained is fresh groundwater. For the remainder of the report, water sampled from the piezometers will be referred to exclusively as groundwater. The groundwater and streams were sampled concurrently six times ranging from June 2014 through February 2015. All water samples were kept on ice after collection, transported to the laboratory, and refrigerated.

Rising head tests were performed in the piezometers by measuring recovery after drawdown using water level tape and a timer. The saturated hydraulic conductivity (K_s) was calculated using:

$$K_s = (\pi r^2/A_{y)}*(1/t)*\ln(z_0/z_t) \quad (1)$$

where r is the piezometer radius, A_y is a shape factor in units of length, t is the time since the initial drawdown, z_0 is the initial distance between the water level in the piezometer and the equilibrium water level, and z_t is the distance between the water level in the piezometer and the equilibrium water level at time t (Bouwer and Rice 1976). The Hvorslev shape factor equation for a piezometer was used

$$A_y=2\pi L/\ln[(L/D)+[1+(L/D)^2]^{1/2}] \quad (2)$$

where D is the diameter of the piezometer and L is the diameter of the holes drilled in the piezometer or the height of the screened portion (Chapuis 1989). To process the field data, z_0/z_t was graphed on a logarithmic axis against time (seconds) elapsed since the starting point, generating an approximately straight line. The time was selected that would yield a ratio of z_0/z_t equal to 0.37 so that the equation reduces to (Domenico and Schwartz 1990)

$$K_s= (\pi r^2/A_{y)})*(1/t) \quad (3)$$

This time was determined either directly from the data if there was enough resolution in that region of the curve, or it was calculated from an exponential fit of the line.

In addition to groundwater and stream samples, three cores of sediment were obtained from each of the four streams of study. The cores were collected using PVC cylinders (5.1 cm i.d., 120 cm length) driven into the streambed sediment, sealed with a compression cap after filling the head space with water, and manually wrenched out of the streambed. The other end of the cylinder was sealed immediately with another compression cap. The collected cores were placed over ice and transported to the laboratory for analysis.

Laboratory Methods

The vertical chemical gradient in the sediment cores was analyzed through subsampling porewater through sample ports created using a hand-held electric drill to create a hole (~ 3 mm diameter) in the PVC pipe at 10 cm intervals along the length of the cores (Gu et al., 2007). Porewater was extracted using a syringe placed through each sampling port in turn. For the remainder of the report, water sampled from the cores will be referred to exclusively as porewater.

Within 72 hours of collection, all water samples were pushed through 0.45 µm syringe-tip membrane filters, collected in HDPE bottles, and refrigerated until chemical analysis. Dissolved anion concentrations, specifically NO_3^- and Cl^-, were measured by ion chromatography using a Dionex ICS-2100. Units of NO_3^- concentration were converted to units of NO_3^--N for all subsequent discussion of N in this report. Duplicate samples for groundwater and streamwater and single samples for porewater were injected using an automated Dionex AS-DV sampler in 50 sample batches. Sample sequences were programmed with the Chromeleon Software version 6.8 to run at a column temperature of 35°C, 1 mL/min flow rate, 34 mM KOH eluent concentration, 90 mA suppressor current, and a runtime of 15 minutes.

Once the porewater samples were obtained, two of the three cores from each stream were analyzed for hydraulic conductivity and percent organic matter. A hollow core drill bit (2 cm diameter) was used to drill through the PVC pipe at 10 cm intervals along the length of the cores at an offset radial position from the porewater sampling ports to avoid collecting disturbed sediments in the subcore. In some instances these points were not aligned with the porewater sampling ports in the PVC pipe due to sediment settling upon dewatering. Once the hole was created in the PVC pipe, a de-tipped plastic 10 cm^3 syringe was pushed through the hole into the sediments to collect a horizontal subcore (Thomas, 2003). Using the sediment-filled syringe, mini-permeameters were constructed (Figure 1). Falling head tests were performed using these mini-permeameters to obtained saturated hydraulic conductivity (K_s) in horizontal subcores along the same 10 cm interval used for water samples (Mills et al., 2002). K_s was calculated using

$$K_s = A_t / A_c * L / t * \ln(H_0/H_1) \qquad (4)$$

where A_t is the cross-sectional area of the falling head reservoir, A_c is the cross-sectional area of the sample chamber, L is the length of the sediment column, and t is the time for the water level to fall from H_0, the initial water level above the base level, to H_1, the final water level (Mills et al., 2002).

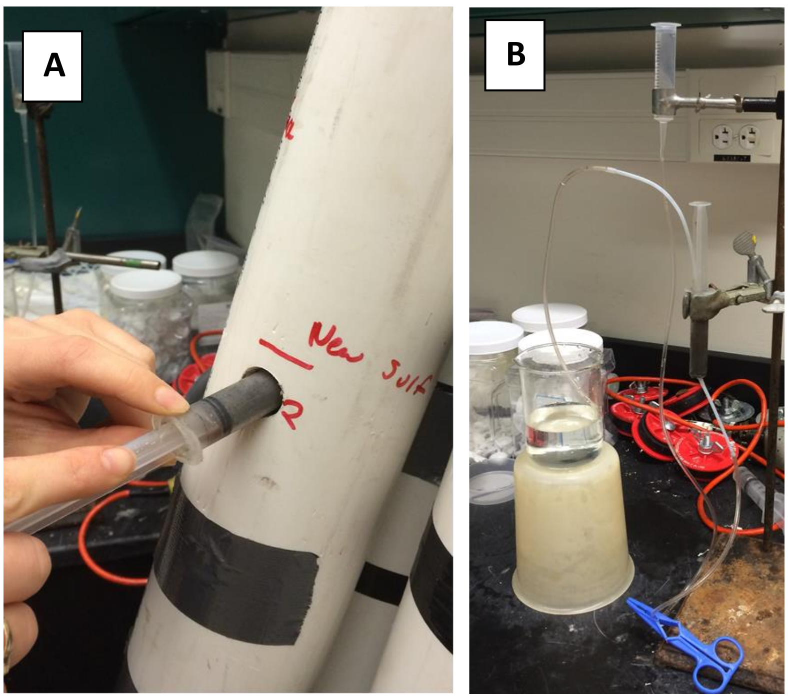

Figure 1: Sample collection from sediments cores. A: A subcore is extracted in a detipped syringe. B: The mini-permeameter setup includes a syringe falling head tank, the subcore, and a beaker for base level.

Finally, the contents of the mini-permeameter were pushed into a pre-weighed aluminum boat. The sediment samples were dried at 104°C for 24 hours, cooled and weighed, then ashed in a 500ºC oven and cooled and reweighed for mass loss on ignition that quantifies the total organic carbon content of the sediment (McFadden, 2013).

RESULTS

Over the sampling period, groundwater and streamwater samples were collected on six occasions (Figure 2): June 5 (the day piezometers were installed), June 23, July 10, September 27, and December 13, all in 2014, and February 14, 2015. Streambed sediment cores were collected on July 10, 2014. Precipitation was lowest during June; while July and August were fairly wet months and early September had the heaviest precipitation of the study period (Figure 2). The majority of sampling dates occurred after at least a few dry days and captured baseline conditions (Figure 2).

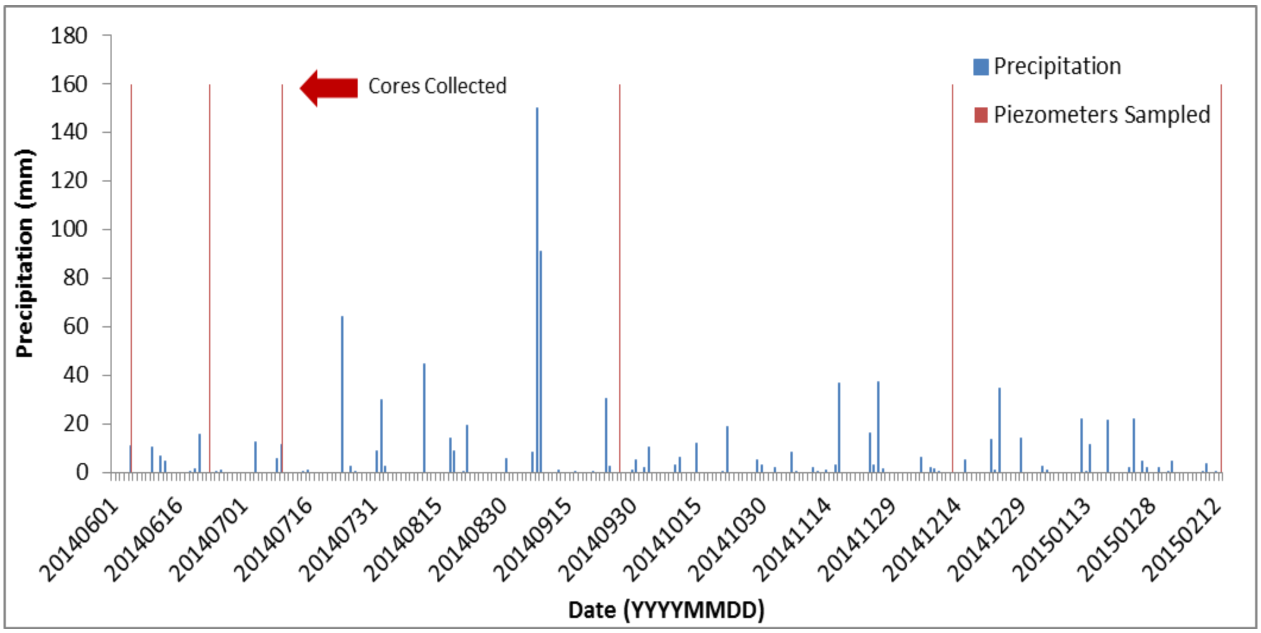

Figure 2: Daily precipitation (in blue) from June 2014 to February 2015 with sampling dates indicated by red bars. Groundwater samples were collected twice in June, and once in July, September, December and February. Cores were collected on the same day in July that groundwater was sampled.

Despite the change in seasonal conditions from late spring to winter, all groundwater and streamwater nitrogen (NO_3^--N) concentrations follow the same general trends (Figure 3). Cobb Mill groundwater is consistently far more concentrated in N than the other three streams at ~150, 100, 60 cm below the streambed (Figure 3). Bundick's, Phillip's, and Tommy's all tend to have lower concentrations of N in the groundwater than in the stream (Figure 3). Cobb Mill Creek displays the opposite relationship with much lower N concentrations in the stream than in the groundwater (Figure 3). Note that Cobb Mill Creek chloride concentrations are similar or greater in the stream compared to the groundwater (Appendix A). Tommy's Ditch often has the lowest groundwater N concentrations and yet has the highest levels of N in streamwater for all sampling dates (Figure 3). Phillip's Creek deep and mid-level groundwater N concentrations are highest in the cold months of December and February, while the N concentrations at the shallow groundwater level remain low at all times (Figure 3). In February Bundick's follows a similar pattern (Figure 3). For both Phillip's and Bundick's chloride concentrations remain the same or increase while N decreases moving from the groundwater to the stream (Appendix A).

Hydrological qualities of the streambed were tested through the piezometers by examining hydraulic gradients and conductivity at the deep, mid, and shallow levels. The hydraulic gradient at all four streams was consistently great enough that equilibrium water levels in piezometers were always higher than the streamwater surface (Figure 4). Cobb Mill Creek had larger hydraulic gradients than the other three streams (Figure 4). With the exception of the September measurement, Tommy's typically had the smallest hydraulic gradients (Figure 4). Saturated hydraulic conductivity values determined from rising head tests range from 0.0006 cm/sec for the Cobb Mill Creek deep piezometer to 0.0088 cm/sec for the Phillip's deep piezometer (Table 1). Phillip's mid- and deep-level values were the highest compared to the other streams (Table 1). Conductivity was typically quite different at the separate depths of each stream (Table 1). Two duplicate pilot tests from December demonstrate reasonably consistent results (Table 1).

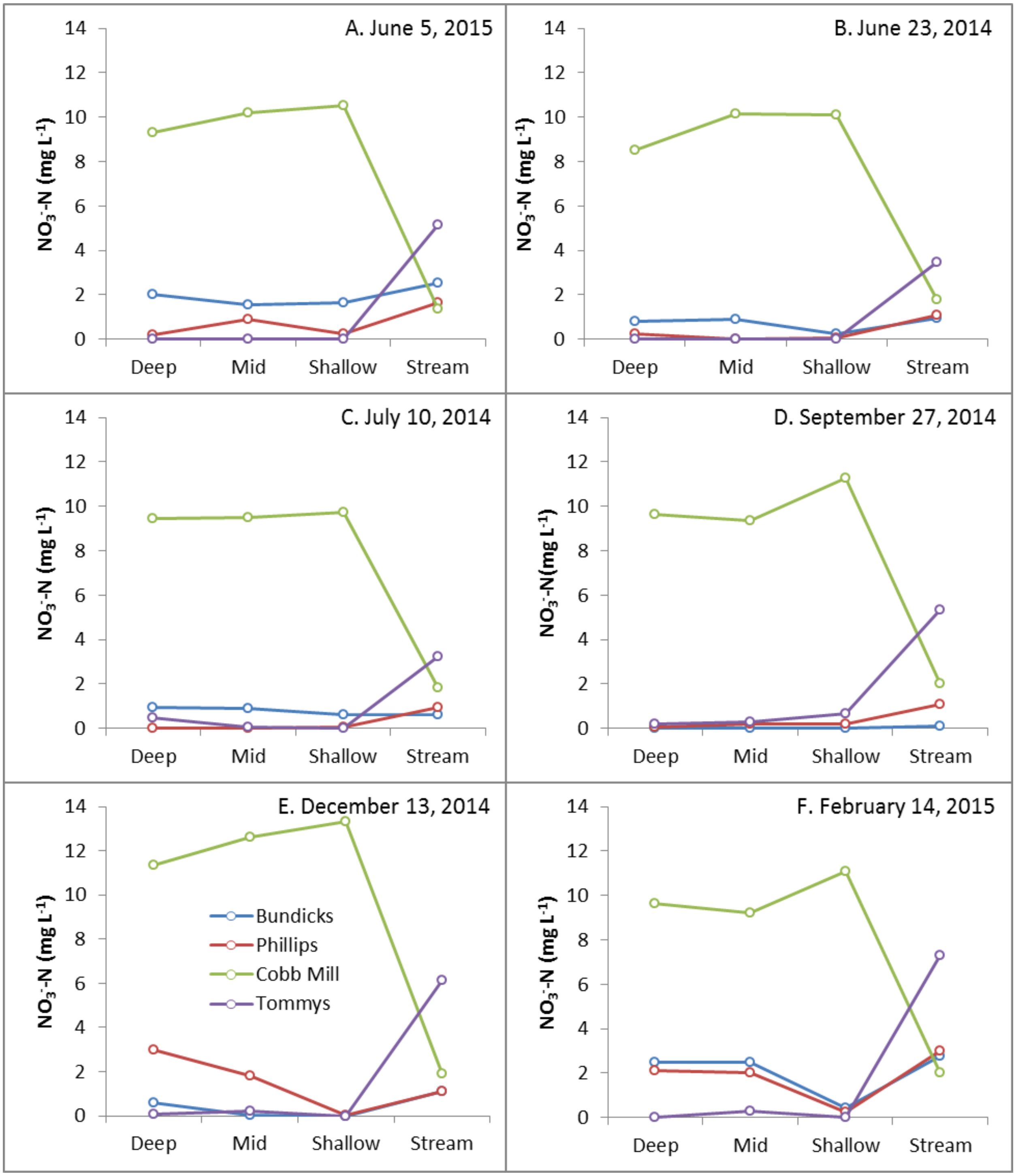

Figure 3: N concentrations in stream and groundwater samples at ~150, 100, and 60 cm below the streambed at four stream study sites for each sampling date.

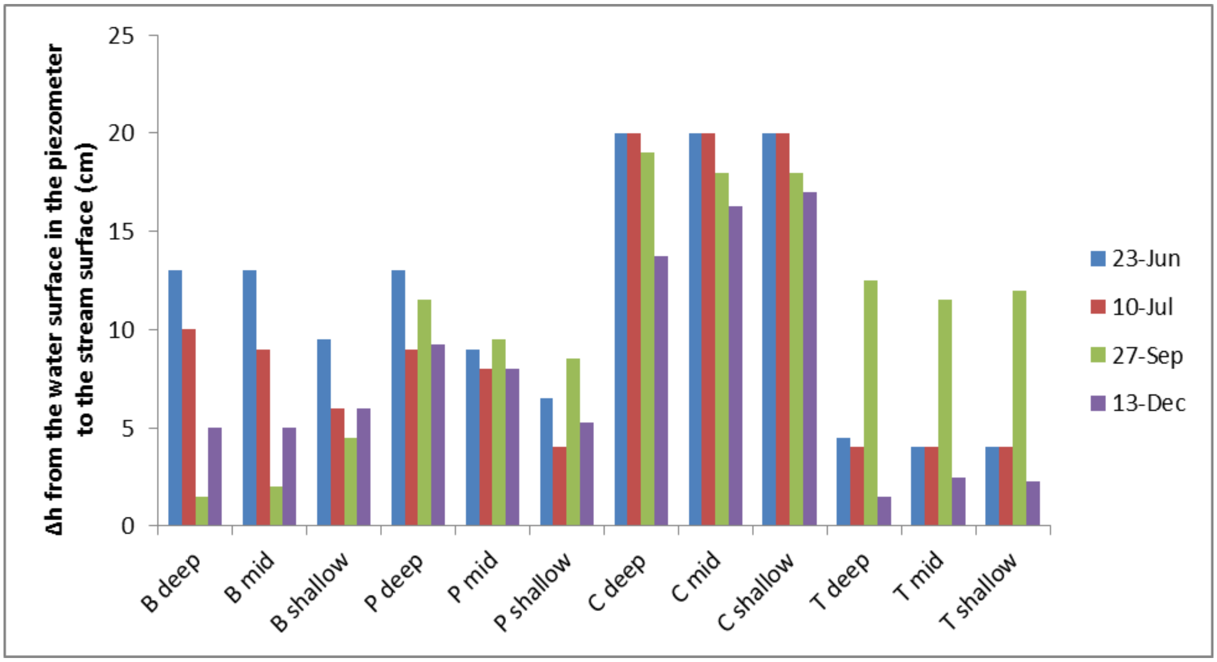

Figure 4: The vertical distance (Δh) between the equilibrium level of water in the piezometers and the stream-water surface level for four streams over sampling dates in June, July, September, and December (C = Cobb Mill Creek, T = Tommy's Ditch, B = Bundick's Creek, P = Phillip's Creek). The hydraulic gradient data from the June 5, 2014 and February 14, 2015 sample dates were not used because in early June the ground was disturbed by piezometer installation and in February the piezometers were iced over. The piezometers at each stream reach ~150, 100, 60 cm below the streambed surface.

Table 1: Saturated hydraulic conductivity (K_S) results for rising head tests performed in piezometers at all four streams in February 2015 and for two pilot tests in December 2014. In Bundick's and Phillip's rising head tests were not possible in the shallowest piezometer, because the water level recovered too slowly.

Piezometer	**K_s (cm/s)**	**Technique**	**Month**
Bundick's deep	0.0013	exponential fit	February
Bundick's middle	0.0033	exponential fit	February
Phillip's deep	0.0088	from data	February
Phillip's middle	0.0075	exponential fit	February
Tommy's deep	0.0067	from data	February
Tommy's middle	0.0022	exponential fit	February
Tommy's middle	0.0027	from data	December
Tommy's shallow	0.0060	exponential fit	February
Cobb Mill deep	0.0006	from data	February
Cobb Mill deep	0.0006	exponential fit	December
Cobb Mill middle	0.0052	exponential fit	February
Cobb Mill shallow	0.0032	exponential fit	February

Sediments from all of the streams show a large degree of variability in physical and chemical properties. Saturated hydraulic conductivity values obtained from streambed sediment cores using mini-permeameters ranged from less than 0.009 to 0.24 cm/sec, and organic matter values ranged from 0.3 to 42% (Figure 5). Saturated hydraulic condutivity values had a negative correlation to sediment percent organic matter (Figure 5). Samples with organic matter greater than 4% had conductivity values less than 0.1 cm/sec, and samples with organic matter greater than 12% had conductivity values too low to be measured using mini-permeameters (Figure 5). Similarly to the rising head test conductivity results, samples from Phillip's had some of the highest conductivity values, though low conductvity values also occurred in the sediments of Phillip's Creek (Figure 5).

Nitrogen concentrations in the porewater of the cores does not have an obvious relationship to either percent organic matter or conductivity under the conditions sampled (Figures 6-9). In most cases at Bundick's, Phillip's, and Tommy's, there is not much variability in N concentrations over the length of the core (Figures 6, 7, and 9). Cobb Mill Creek porewater does have a decrease in N concentrations with decreasing depth in two of the three sediment cores (Figures 8-A and 10-A). Core B from Cobb Mill Creek did not yield any water, potentially due to a poor seal causing loss of water (Figure 8-B). While N decreases along the Cobb Mill cores, chloride concentrations remain the same or increase with decreasing depth (Figure 10).

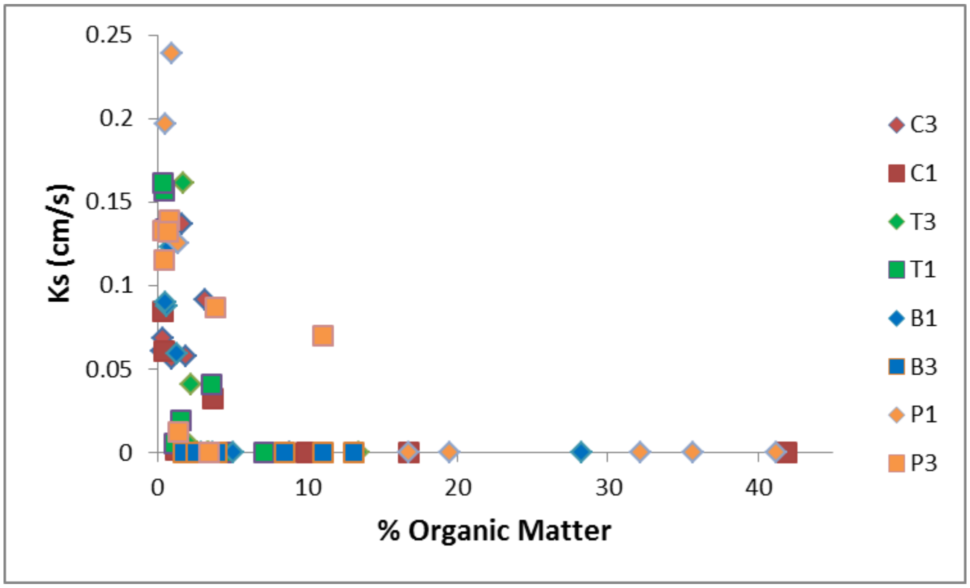

Figure 5: Saturated hydraulic conductivity (K_S) determined with mini-permeameters plotted against percent organic matter in sediment samples from all four streams. (C = Cobb Mill Creek, T = Tommy's Ditch, B = Bundick's Creek, P = Phillip's Creek). K_s values below about 0.009 cm/s were too low for measurement and were approximated as 0.00 cm/s for all sediment core samples.

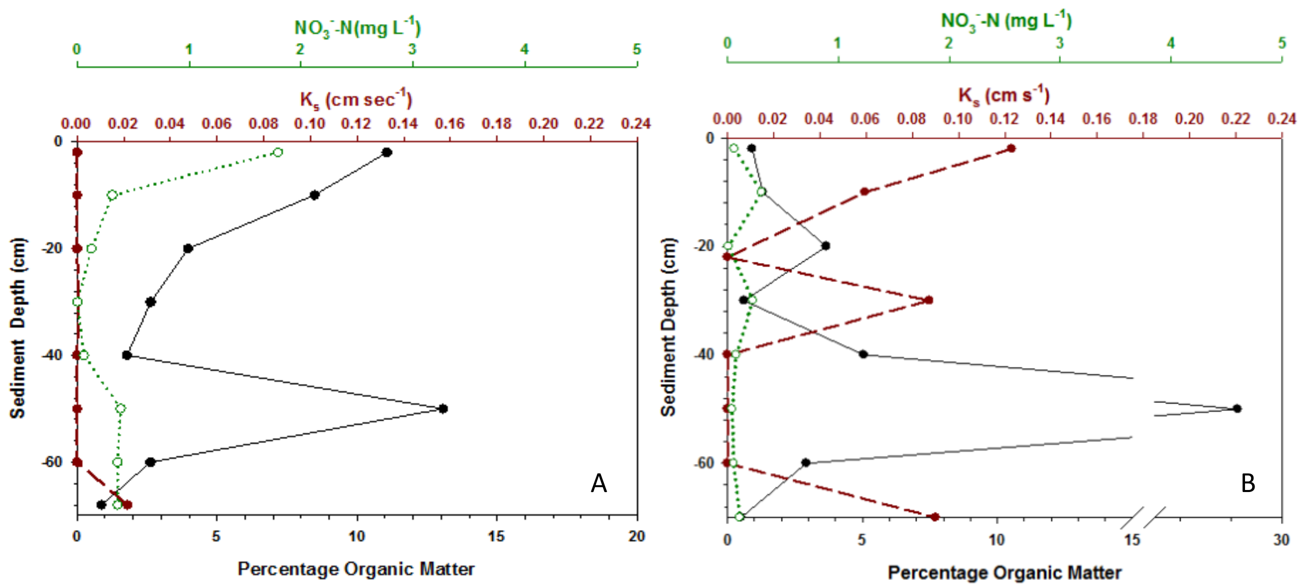

Figure 6: Nitrogen concentration, hydraulic conductivity (K_s), and percent organic matter at 10 cm intervals along sediment cores from Bundick's Creek. Note that in Figures 6-9, the percent organic matter axes have different scales.

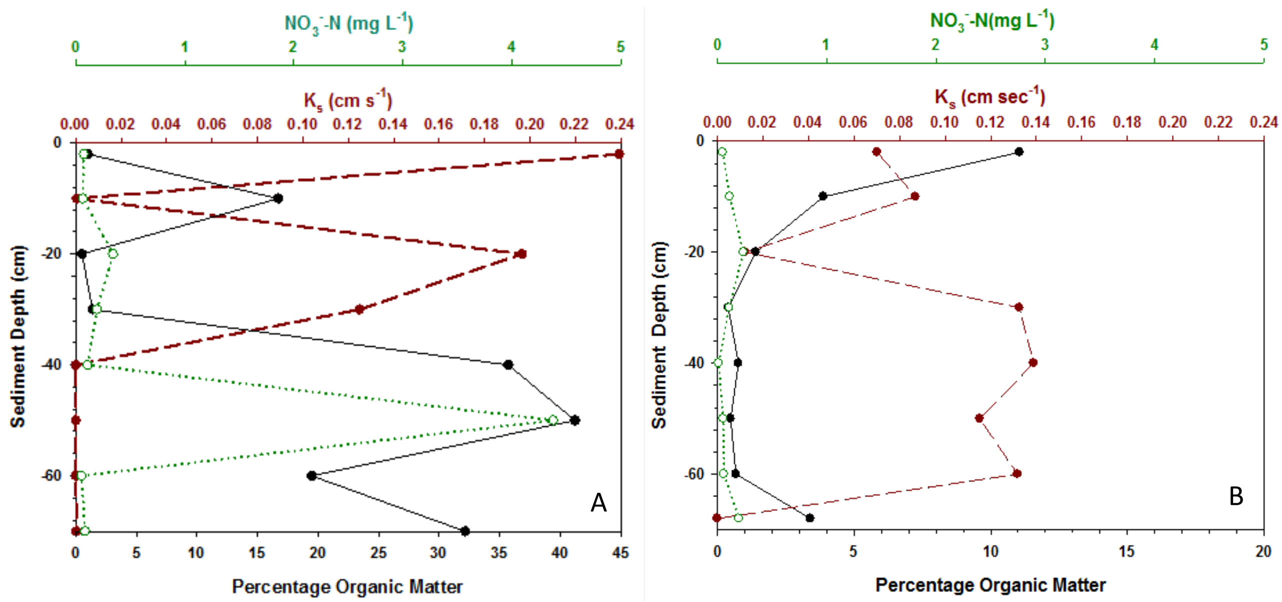

Figure 7: Nitrogen concentration, hydraulic conductivity (K_s), and percent organic matter results at 10 cm intervals along sediment cores from Phillip's Creek.

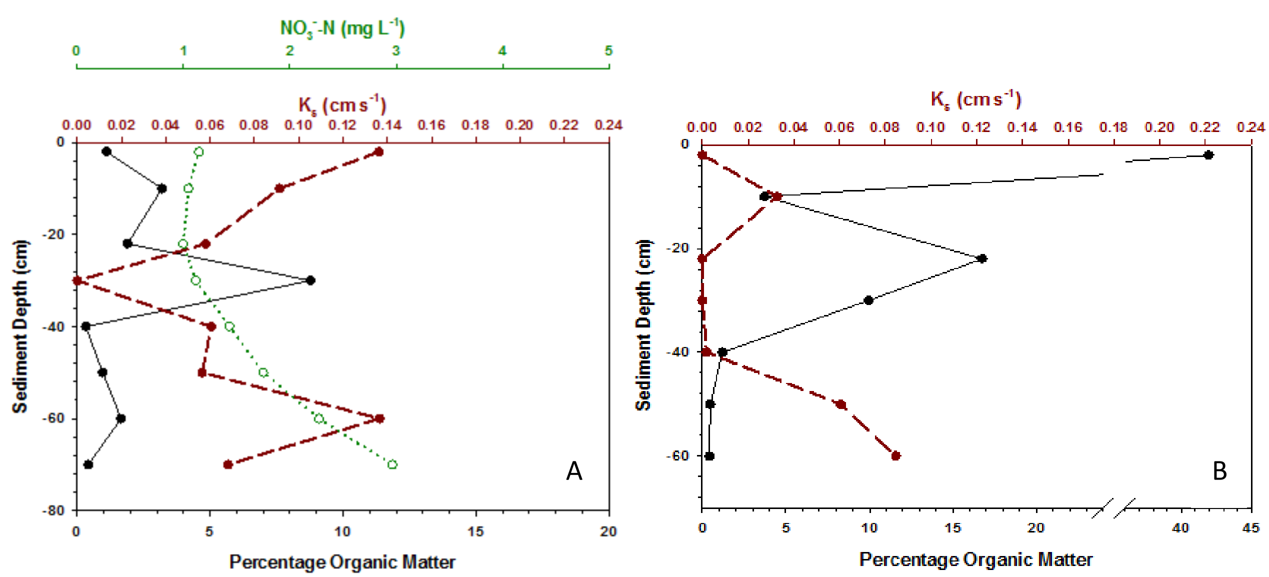

Figure 8: Nitrogen concentratoin, hydrualic conductivity (K_s), and percent organic matter at 10 cm intervals along sediment cores from Cobb Mill Creek Creek.

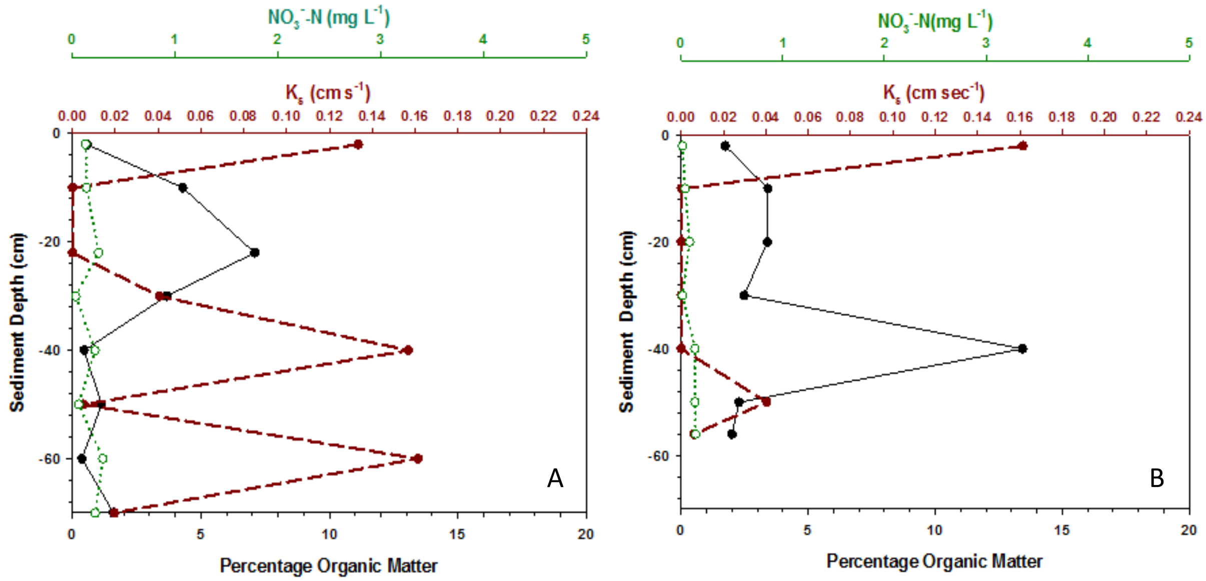

Figure 9: Nitrogen concentration, hydraulic conductivity (K_s), and percent organic matter at 10 cm intervals along sediment cores from Tommy's Ditch.

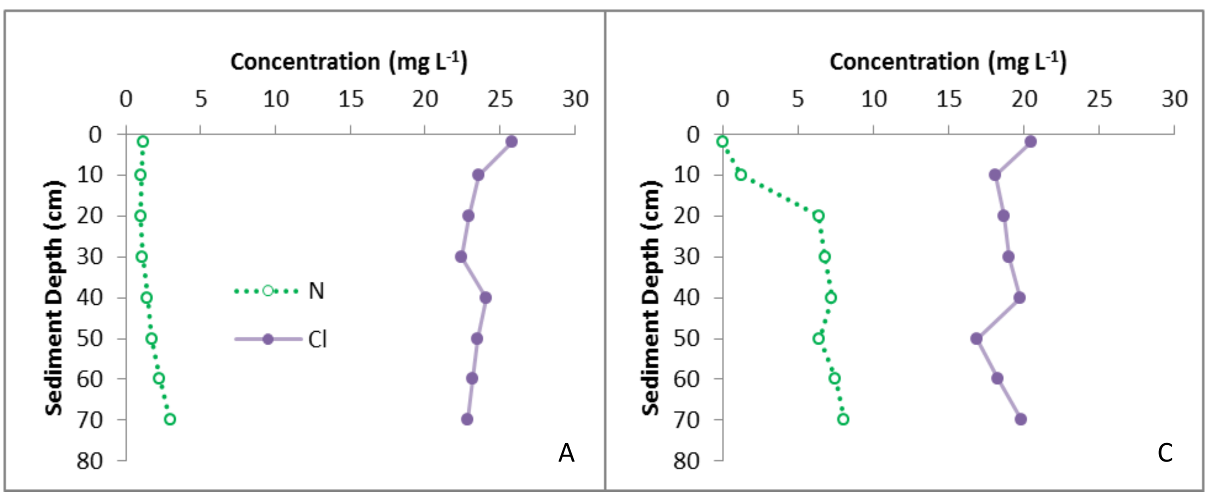

Figure 10: Nitrogen and chloride concentrations at 10 cm intervals along sediment cores from Cobb Mill Creek.

DISCUSSION

. One of the most striking results is the difference in hydrologic and geochemical characteristics between Cobb Mill Creek and the other three streams. Concentrations of N in Cobb Mill groundwater were higher at all depths than in the groundwater at any other study site. With the high N at all depths, a clear decrease in N from groundwater to the gaining stream occurs (Figures 3, 8 A, and 10). Chloride is considered to be an unreactive conservative solute that traces mixing and flowpaths of water in the environment (Eby, 2004). Since chloride concentrations are not similarly decreased along the upward flowpath (Appendix A), at least some of the reduction in N can be attributed to denitrification. However N remains high in all three depths of groundwater sampled at Cobb Mill, so any denitrification occurs more shallowly than 60 cm below the streambed (Figure 3), a result consistent with the field studies of Gu et al. (2007) who concluded that denitrification occurred over the final 40 cm of the upward flowpath. In the present study, the porewater in this shallow interval was sampled from sediment cores and does indeed show a reduction in N at increasingly shallow depths in Cobb Mill Creek sediments (Figure 10). The near-surface sediments underlying the streambed are highly heterogeneous in their distribution of organic matter and hydraulic conductivity (Figure 8). Heterogeneous sediments have been shown to create particularly favorable denitrification zones (Sawyer, 2015). There does not appear to be a precise portion of this shallow zone that is most favorable for denitrification, because one sediment core (A) shows reduction in N between 70 and 40 cm below the streambed while another core (B) has the greatest loss of N concentration from 20 cm to 2 cm below the streambed (Figure 10).

Bundick's Creek, Phillip's Creek, and Tommy's Ditch often have groundwater with N concentrations too low for denitrification to be readily detectible (Figures 3, 6, 7, and 9). In the winter, Phillip's and Bundick's groundwater N concentrations are higher than in other seasons, and the N concentration appears to decrease along the flowpath from deep to shallow groundwater samples (Figure 3, Appendix A). The reduction in N concentration is at a much smaller scale than at Cobb Mill Creek and occurs deeper in the sediments (Figure 3). Tommy's Ditch streamwater also has its highest N concentration in the winter, though the groundwater N concentration remains low (Figure 3). Since these higher N concentrations occur during cold months, they are unlikely to be caused by greater agricultural N inputs that tend to be concentrated with spring and summer fertilizer applications (Maguire et al., 2009). Colder temperatures slow microbial denitrification (Kadlec and Reddy, 2001), so it is possible that in warmer months most N is removed earlier along the flowpath of groundwater from the agricultural fields to the streams.

Similarly to Cobb Mill Creek, Bundick's, Phillip's, and Tommy's all have variable sediment organic matter content and saturated hydraulic conductivity (Table 1, Figures 6-9). Organic content has a strong inverse relationship to saturated hydraulic conductivity (Figure 5). Since most of the sediments on the Eastern Shore of Virginia are fine sand, which should have fairly consistent K_s values, it is likely that organic content variability is driving the measured K_s variability. Percent organic content varied greatly along the vertical profiles of individual sediment cores from each stream (Figures 6-9). The duplicate sediment cores tested for conductivity at each stream generally differed as much between cores for the same stream as between separate streams (Figures 6-9). Since the organic content and saturated hydraulic conductivity are similarly variable in all four streambeds, these sediment properties are unlikely to be responsible for inter-stream groundwater and streamwater N concentration differences.

Though all four streams are in the same agricultural area, Cobb Mill Creek is located at the bottom of a hillslope and has much greater topographic relief than the other three streams. Since the shape of the water table mimics the topography in an unconfined aquifer, this higher relief at Cobb Mill Creek causes a larger difference in elevation potential than can be achieved at the other three streams located in relatively flat areas (Hornberger et al., 1998). This larger difference in elevation potential gives rise to a higher gradient that would force deeper circulation of groundwater underneath the riparian zone before rising under the stream channel. Indeed, measured hydraulic gradients are larger at Cobb Mill Creek (Figure 4). The topography may cause a unique flowpath for Cobb Mill Creek groundwater compared to the other streams. Steep slopes adjacent to streams have been found to be unfavorable for denitrifcation since the water table is deeper (Burt et al., 2002). Deeper groundwater entering Cobb Mill Creek may have bypassed shallow denitrification zones with adequate organic material, leading to the higher concentrations of nitrogen in groundwater beneath the stream despite the relatively wide forested riparian buffer. Thus, at Cobb Mill Creek, denitrification is observed at the very last stage of the subsurface flowpath (Figure 10). This finding is consistent with Gu et al. (2007) who demonstrated with column experiments the nearly complete N removal in the 40 cm of streambed sediments immediately underlying the sediment-water interface.

Tommy’s Ditch conversely often has the lowest groundwater N concentrations, which may be because it is the only site bounded by land that is not currently being farmed (Figure 3). Despite the lack of active adjacent farming, Tommy’s consistently has the highest streamwater N concentrations which must be the result of upstream contributions. Upstream conditions may include land use in the catchment that loads Tommy’s more heavily with N than the other streams. Examples of upstream conditions include a larger agricultural area within Tommy’s watershed or greater rates of fertilizer application due to soil conditions or crop type. Aerial photos of the upstream areas of the four streams indicate that the contributing area of Tommy's may be larger and more intensively farmed closer to the stream.

Previous monthly measurement of stream N concentrations from October 2010 to September 2011 only found Tommy's to have the highest streamwater concentrations in the five months of October, December, February, March, and April (Cosans et al., 2014). During other months, Phillip's Creek or Cobb Mill Creek had higher stream-water N concentrations. For the time periods sampled, Bundicks Creek consistently had relatively low stream N concentrations. Bundicks has the smallest watershed area of the four streams, reinforcing the possibility that land-use N contributions are a big factor influencing stream N concentration (Cosans et al., 2014). A survey of land use in the catchments upstream of the study sites might be useful in understanding the observed differences in chemical characteristics between the streams, but such an analysis is beyond the scope of this project.

CONCLUSION

The primary controls of N concentration in the streams of the Delmarva Peninsula in Virginia appear to be the land use and contributing area that determine N input to the watershed, that is then moderated by groundwater flowpaths that govern the length of time water spends in denitrifying zones in the subsurface. All shallow streambed sediments analyzed here have sufficient organic content to support denitrification. Zones of low hydraulic conductivity slow groundwater movement, allowing for enough residence time for denitrification to proceed (Flewelling et al., 2012). Relatively topographically flat stream sites have lower hydraulic gradients that increase residence time to create more favorable conditions for denitrification (Vidon and Hill, 2004). Given that this study establishes the existence of sufficient subsurface zones favorable for denitrification at all the studied streams, the N concentration in streamwater indicates that groundwater bypassing these zones is a large contributing source of N to at least some streams of the Eastern Shore. In future studies, tools such as GIS could be used to compare the contributing area, land use, and topographic gradients to stream N concentration in order to discern how much of the variability in N flux can be accounted for by these factors.

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APPENDIX A

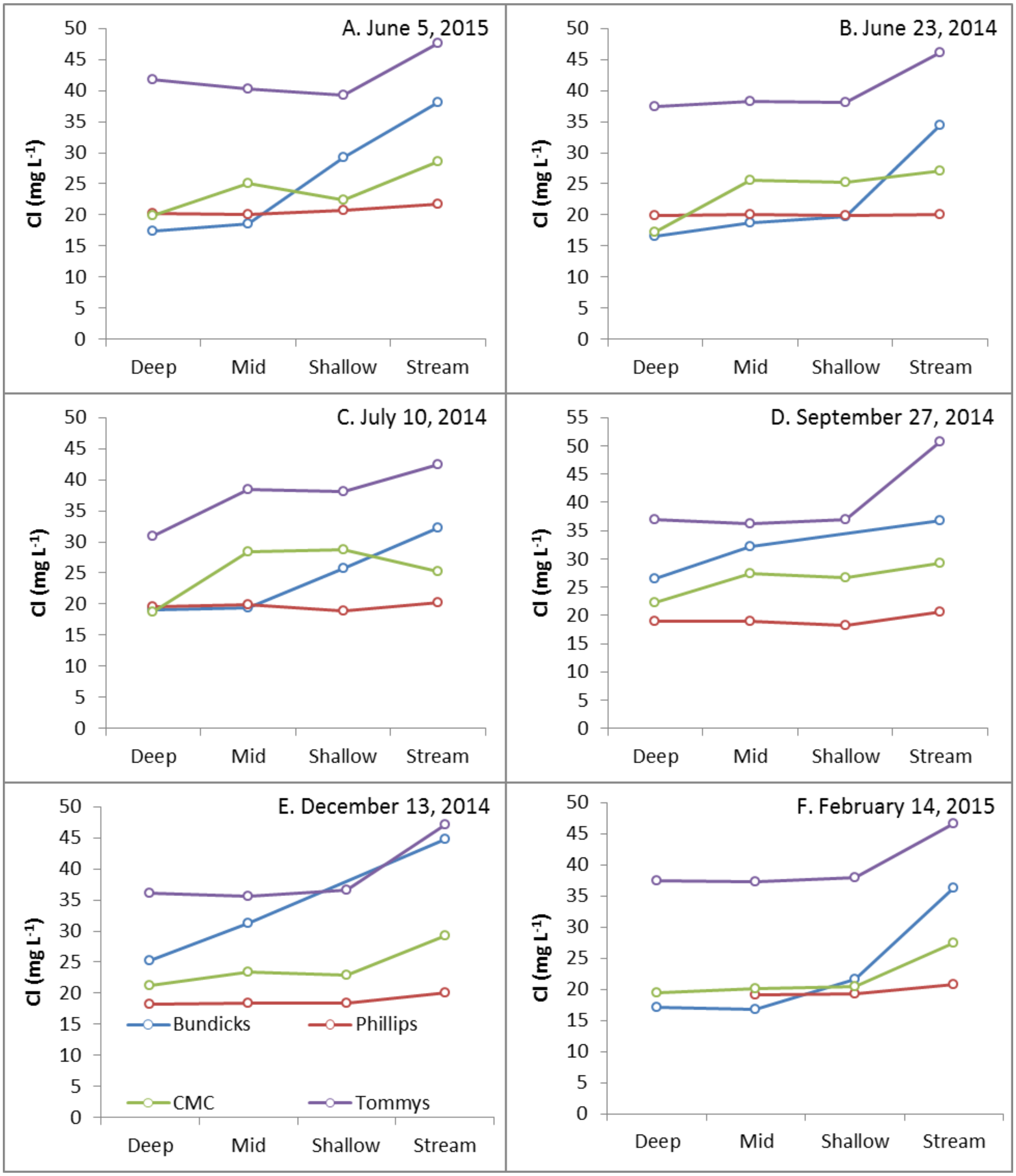

Figure 1: Chloride concentrations in stream and groundwater at ~150, 100, and 60 cm below the streambed at the four stream study sites for each sampling date.

APPENDIX B

Table 1: Nitrogen and chloride concentrations at 10 cm intervals along sediment cores from Bundick's Creek, Phillip's Creek, Cobb Mill Creek, and Tommy's Ditch. Three cores were collected from each stream and designated A, B, and C. Some cores and depths did not yield pore water.

Stream	**Core Sample (cm below streambed)**	**Chloride (mg/ L)**	**Nitrogen (NO3-N mg/L)**
Bundick's Creek	B 2cm	33.49	0.06
Bundick's Creek	B 10cm	17.04	0.31
Bundick's Creek	B 20cm	16.40	0.01
Bundick's Creek	B 30cm	20.83	0.23
Bundick's Creek	B 40cm	20.01	0.08
Bundick's Creek	B 50cm	18.80	0.04
Bundick's Creek	B 60cm	19.10	0.06
Bundick's Creek	B 70cm	17.05	0.11
Bundick's Creek	B 80cm	15.72	0.21
Bundick's Creek	C 2cm	28.84	2.83
Bundick's Creek	C 10cm	20.88	0.01
Bundick's Creek	C 20cm	14.52	0.03
Bundick's Creek	A 2cm	25.61	1.79
Bundick's Creek	A 10cm	19.30	0.31
Bundick's Creek	A 20cm	17.29	0.13
Bundick's Creek	A 30cm	14.92	0.00
Bundick's Creek	A 40cm	17.86	0.06
Bundick's Creek	A50cm	18.67	0.39
Bundick's Creek	A 60cm	18.47	0.36
Bundick's Creek	A 70cm	17.76	0.36
Bundick's Creek	A 75cm	17.81	0.28
Phillip's Creek	A 2cm	21.46	0.07
Phillip's Creek	A 10cm	24.68	0.06
Phillip's Creek	A 20cm	22.61	0.34
Phillip's Creek	A 30cm	20.27	0.19
Phillip's Creek	A 40cm	18.46	0.11
Phillip's Creek	A 50cm	17.05	4.38
Phillip's Creek	A 60cm	8.03	0.05
Phillip's Creek	A 70cm	9.96	0.08
Phillip's Creek	C 2cm	21.87	0.41
Phillip's Creek	C 10cm	20.23	0.15
Phillip's Creek	C 20cm	20.58	0.07
Phillip's Creek	C 30cm	21.88	0.05

Stream	**Core Sample (cm below streambed)**	**Chloride (mg/ L)**	**Nitrogen (NO3-N mg/L)**
Phillip's Creek	C 40cm	21.55	0.08
Phillip's Creek	C 50cm	34.35	1.11
Phillip's Creek	C 55cm	31.44	0.84
Phillip's Creek	B 2cm	23.73	0.05
Phillip's Creek	B 10cm	22.87	0.11
Phillip's Creek	B 20cm	21.04	0.24
Phillip's Creek	B 30cm	20.72	0.11
Phillip's Creek	B 40cm	19.67	0.01
Phillip's Creek	B 50cm	19.25	0.05
Phillip's Creek	B 60cm	18.40	0.06
Phillip's Creek	B 70cm	17.02	0.20
Cobb Mill Creek	B 60cm	19.37	3.39
Cobb Mill Creek	C 2cm	20.48	0.02
Cobb Mill Creek	C 10cm	18.17	1.24
Cobb Mill Creek	C 20cm	18.74	6.39
Cobb Mill Creek	C 30cm	19.06	6.82
Cobb Mill Creek	C 40cm	19.76	7.26
Cobb Mill Creek	C 50cm	16.93	6.45
Cobb Mill Creek	C 60cm	18.28	7.51
Cobb Mill Creek	C 70cm	19.89	8.08
Cobb Mill Creek	A 2cm	25.86	1.14
Cobb Mill Creek	A 10cm	23.60	1.05
Cobb Mill Creek	A 20cm	22.93	1.00
Cobb Mill Creek	A 30cm	22.45	1.11
Cobb Mill Creek	A 40cm	24.08	1.43
Cobb Mill Creek	A 50cm	23.55	1.75
Cobb Mill Creek	A 60cm	23.22	2.27
Cobb Mill Creek	A 70cm	22.83	2.97
Tommy's Ditch	A 2cm	41.43	0.13
Tommy's Ditch	A 10cm	38.64	0.14
Tommy's Ditch	A 20cm	38.70	0.25
Tommy's Ditch	A 30cm	37.64	0.03
Tommy's Ditch	A 40cm	36.74	0.22
Tommy's Ditch	A 50cm	35.43	0.06
Tommy's Ditch	A 60cm	40.08	0.30
Tommy's Ditch	A 65cm	33.33	0.22
Tommy's Ditch	C 2cm	45.78	0.49

Stream	**Core Sample (cm below streambed)**	**Chloride (mg/ L)**	**Nitrogen (NO3-N mg/L)**
Tommy's Ditch	C 10cm	44.02	0.01
Tommy's Ditch	C 20cm	44.78	0.08
Tommy's Ditch	C 40cm	41.82	0.16
Tommy's Ditch	C 50cm	43.76	0.25
Tommy's Ditch	C 60cm	44.27	0.15
Tommy's Ditch	C 70cm	40.53	0.22
Tommy's Ditch	B 2cm	41.75	0.01
Tommy's Ditch	B 10cm	40.72	0.04
Tommy's Ditch	B 20cm	41.18	0.08
Tommy's Ditch	B 30cm	38.52	0.01
Tommy's Ditch	B 40cm	37.24	0.14
Tommy's Ditch	B 50cm	37.11	0.14
Tommy's Ditch	B 55cm	43.77	0.14