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# The impact of stream-groundwater exchange on seasonal nitrate loads in an urban stream

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## Abstract

Urbanization negatively impacts water quality in streams by reducing stream-groundwater interactions, which reduces the stream's ability to naturally attenuate nitrate. Meadowbrook Creek, a first order urban stream in Syracuse, New York, has a negative urbanization gradient that results in urbanized headwaters that are disconnected from the floodplain, and downstream reaches that have intact riparian floodplains and connection to riparian aquifers. This system allows us to assess how stream-aquifer interactions in urban streams impact the net sources and sinks of nitrate at the reach scale. We used continuous (15-minute) streamflow measurements, along with weekly grab samples at three gauging stations positioned longitudinally along the creek to develop continuous nitrate load estimates at the inlet and outlet of two contrasting reaches. Nitrate load estimates were determined using a USGS linear regression model, RLOADEST, and differences between loads at the inlet and outlet of contrasting reaches were used to quantify nitrate sink and source behavior year-round. In water year 2018, the outlet of the disconnected reach exported 13.1 x $10^5$ kg $NO_3^-$, while nitrate export at the outlet of the connected reach in the same year was 9.8 x $10^5$ kg $NO_3^-$. We found the hydrologically disconnected reach was a net source of nitrate regardless of season and stream-groundwater exchange allowed the hydrologically connected reach to be both a source and sink. Both reaches alter nitrate source and sink behavior at various spatiotemporal scales. Groundwater connection in urban streams reduces annual nitrate loads and provides more opportunities for sources and sinks of nitrate year-round than hydrologically disconnected streams, including groundwater discharge into the stream with variable nitrate concentrations, surface-water groundwater interactions that foster denitrification, and stream load loss to surrounding near-stream aquifers. This study empathizes how loads are important in understanding how stream-groundwater interactions impact reach scale nitrate export in urban streams.

# The impact of stream-groundwater exchange on seasonal nitrate loads in an urban stream

by

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B.S., New Mexico State University, 2017

Thesis
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## 1. Introduction

Increases in anthropogenic nitrogen delivered to streams, coupled with the urbanization of watersheds, has had detrimental effects on water quality and stream ecosystem health (Paul & Meyer, 2001; Bouwman, Van Drecht, Knoop, Beusen, & Meinardi, 2005; Meyer, Paul, &Taulbee, 2005; Newcomer, Kaushal, Mayer, Smith, & Sivirichi, 2016). Primary sources of nitrogen to urban streams are lawn fertilizer, wet and dry atmospheric deposition, and leaky wastewater systems including septic and sewer (Groffman, Law, Belt, Band, & Fisher, 2004). Increasing nitrogen loads, including nitrate from wastewater and fertilizer use in urban areas, can contribute to eutrophication and hypoxia of downstream receiving waters, decreased plant diversity, the formation of harmful algal blooms, and fish kills (Walsh et al., 2005). Headwater streams play a critical role in mitigating elevated nitrogen loads as they retain and transform more than 50% of inorganic nitrogen from their contributing watersheds (Peterson et al., 2001). Yet, urbanized headwaters are often vastly modified by human-made drainage networks and channelization; as a result, these alterations impact headwaters as essential transporters and transformers of energy and nutrients (Roy, Dybas, Fritz, & Lubbers, 2009; Kaushal & Belt, 2012).

Nitrate is typically the largest pool of inorganic nitrogen in many streams (Howarth et al., 1996; Groffman et al.,2004; Mayer, Reynolds, McCutchen, & Canfield, 2007) and is retained in streams through several mechanisms, including temporary assimilation by plants and algae (i.e. primary productivity), sorption to sediments, deposition of particulate organic nitrogen, and denitrification. Denitrification is the only processes that results in the permanent loss of nitrogen in streams because the other processes are internal transformations that cycle nitrogen between different pools (e.g. organic and inorganic), resulting in temporary storage and subsequent release at a later time (Mulholland et al., 2004). Denitrification occurs at anoxic geochemical hotspots that foster high reaction rates, such as riparian zones, stream benthic areas with riffles and debris dams, where shallow flow paths into the subsurface are easily accessible and unobstructed (Vidon et al., 2010). Transformation, retention, and attenuation of inorganic nitrogen in streams is controlled by biotic activity, redox conditions involving electron donor acceptor availability and dynamics (i.e., $O_2$, $NO_3^-$, and organic carbon), hydrologic residence time, and temperature (Mulholland et al., 2002; Naiman, Decamps, & McClain, 2005; Kaushal, Groffman, Mater, & Striz, 2008; Vidon et al., 2010; Passeport et al.,2013).

The potential for a stream to attenuate, retain, and transform nitrogen is altered by surrounding land use change due to urbanization (Paul & Meyer 2001; Groffman et al., 2004; Carey et al., 2012). Impervious surface coverage (ISC) is often used as an indicator of urbanization (Newcomer et al., 2016) and streams in watersheds with high ISC are often straightened, channelized, buried, and have concrete lined banks (Pennino et al., 2014). These alterations increase the velocity at which water moves through streams and reduce surface-water groundwater interactions and associated residence times, thus inhibiting the processes that can lead to nitrogen removal. Reduced infiltration in watersheds due to a high ISC, including roadways and parking lots, can lower riparian water tables, which decreases hydrologic connectivity of streams and adjacent riparian zones such that nitrate-rich groundwater bypasses biogeochemical hotspots (Groffman et al., 2002; Walsh 2004; Kashual et al., 2008). Removal of riparian zones results in less riparian shading, which increases available solar radiation and stream temperatures, which in turn drive primary productivity and further alter nitrogen cycling in urban streams (Catford, Walsh, & Beardall, 2007; Ledford, Lautz, Vidon, & Stella, 2017).

Although the effects of urbanization on streams have been documented through observed changes in nitrate concentrations, hydrograph response, and changes in nitrogen dynamics, the change in the export of nitrate in headwater streams affected by urbanization remains understudied. We fill this current gap in knowledge by examining how nitrate loads change along a negative urbanization gradient where the stream transitions from an incised, highly channelized, concrete-lined channel to a reach with high sinuosity, hydrologic connection, and broad riparian zones. This study addresses three guiding questions: (1) How do nitrate loads in an urban stream differ between reaches with and without connection to groundwater?; (2) How does groundwater connection in urban streams drive source and sink behavior for nitrate seasonally?; and (3) What are the implications for watershed management to mitigate nitrate loads to downstream receiving waters?

## 2. Methods

### 2.1 Study Site

Meadowbrook Creek is a first-order urban stream that emerges from a retention basin in Syracuse and flows eastward through Dewitt, New York, ultimately discharging to an Erie Canal feeder channel (Figure 1). The watershed is 11.2 km$^2$ and is in a temperate climate with approximately 100 cm of precipitation annually, which includes total snow accumulation of 315 cm. Average monthly temperatures range from -4.6 °C in January to 21.8 °C in July (NOAA 2015a). The Meadowbrook catchment has a negative urbanization gradient where the upper

4.1 km of the stream is heavily impacted by urbanization (highly channelized with armored banks) and hydrologically disconnected with <0.01 l/s per m of groundwater inflow, and 28% medium/ high intensity urban land use. The most downstream 1.5 km of the stream is not armored, naturally meanders, and has a broad riparian floodplain which is hydrologically connected to the stream with 0.19 l/s per m of groundwater inflow and only 10% medium/ high intensity urban land use (Ledford and Lautz 2015). The disconnected reach has 13.6 km road/km$^2$ within 200 m of the stream, and the connected reach has 6.1 km road/km$^2$ within 200 m. Meadowbrook Creek overlays an evaporitic geologic unit that contains gypsum which enriches the groundwater in the area in sulfate (Winkley, 1989).

### *2.2 Sample collection and Analysis*

Sample sites used in this study are strategically located to bound the limits of the disconnected reach and the connected reach, such that differences in nitrate loads between sites reflect net production or uptake of nitrate along the reach (Figure 1). Stream water samples were collected once every week, and more frequently during high flow events, from September 2017 through September 2019, thereby spanning two complete water years. Two longitudinal stream chemistry surveys were performed on September 21, 2019 and September 22, 2019 with the locations of stream sample points shown in Figure 1, along with the locations of mini piezometers used to sample riparian groundwater in this study and in a prior study of Ledford & Lautz (2015). Riparian groundwater for this study was sampled in a section of stream that runs through a large cemetery within the drainage basin (approximately 4000 m to 4500 m downstream of the headwater), while riparian groundwater sampled by Ledford & Lautz (2015) was from a riparian floodplain in a suburban neighborhood along the most downstream reaches of the stream (approximately 4800 m downstream of the headwater). Stream samples were collected near the water surface in the middle of the channel in 60 ml high-density polyethylene bottles, filtered in the field with a 0.45 µm Millipore filter, and then refrigerated prior to analysis. Samples were analyzed using a Dionex ICS-2000 Ion Chromatograph for major and minor anion and cation chemistry. Five in house standards were used for instrument calibration and three US Geological Survey standards for calibration verification.

Three gauging stations located at the three sampling sites record continuous 15-minute data including stream stage, specific conductivity, and stream temperature. To construct rating curves for each gauging station, stream discharge was measured at each station using both an acoustic doppler velocimeter (ADV) and a SONTEK-IQ acoustic doppler profiler (ADP). Separate rating curves relating stream stage to stream discharge were constructed for each gauging station using these discrete discharge measurements and contemporaneous stage observations from the gauging stations. The rating curves were used to convert 15-minute stream stage records into 15-minute stream discharge hydrographs.

### *2.3 Modeling Approaches*

#### RLOADEST model calibration and evaluation

Solute load is defined as the total mass of the solute that is transported through a stream during a specific period of time. The total load (L, mass/time) of a solute at time t is found by multiplying the solute concentration $C_t$ (mass/volume) by the instantaneous discharge rate $Q_t$ (volume/time). The LOADEST model uses the linear relationship between the natural logarithm of discharge (ln Q) and the natural logarithm of observed loads (ln L) to construct a linear regression model that can be applied to continuous discharge records to estimate loads at times between observed values by using streamflow as the primary explanatory variable (Cohn 1995). Unit-value (15-min), daily, and monthly nitrate and sulfate loads were computed using the USGS R load Estimation (RLOADEST) package (R Development Core team, 2013; Lorenz, Runkel, & De Cicco, 2015), which is an implementation of the LOADEST program of Runkel, Crawford, and Cohn (2004) in the R computing language.

The RLOADEST model estimates regression coefficients ($a_n$) using an adjusted maximum likelihood estimator (ALME) which assumes a normal distribution of model residuals using discharge ($Q$), seasonality, long-term trends and any other continuous data (e.g. conductivity, temperature) as potential explanatory variables to estimate nitrate loads, as shown in Equation (1) (Hirsch 2014):

$$(1)\quad \ln(load) = a_0 + a_1 \ln(Q) + a_2 \ln(Q)^2 + a_3 \sin(dtime) + a_4 \cos(dtime) + a_5 \ln(surrogate) + \cdots$$

where $a_n$ are coefficients estimated by AMLE, $Q$ is discharge (expressed as the center of ln(Q) to minimize multicollinearity), *dtime* is a first-order Fourier series to account for seasonality, and *surrogate* represents other potential explanatory variables, such as conductivity and temperature. All coefficients for the predictive variables included in the regression models were statistically significant (p<0.05) unless otherwise stated. The final models selected from those considered in RLOADEST have the highest coefficient of determination ($R^2$) lowest potential bias percentage (BP) as shown in equation (2), and have statistically significant (p<0.05) coefficients.

$$(2)\qquad Bp = 100\left(\frac{\sum_{k=1}^{N}(\text{L}'-L)}{\sum_{k=1}^{N} L}\right)$$

Where $B_p$ is the bias percentage, $L'$ is the estimated load, L is the observed load and N is the number of observations in the calibration data set.

Hydrograph separation and Richards-Baker index

We used the hydrological separation model (HYSEP) (Sloto and Crouse 1996) to estimate the percentage of daily streamflow that is baseflow versus surface runoff at the gauging stations. The three hydrograph-separation techniques used in HYSEP (fixed interval, sliding interval, and local minimum) assume baseflow can be derived by systematically drawing connecting lines between selected low-flow points of a streamflow hydrograph and are averaged to give baseflow and storm runoff values. This analytical approach uses a parameter "2N" which is a time window assumed to be two times the number of days from the peak on the hydrograph of a runoff event after which surface runoff stops and all streamflow is now considered baseflow. N is calculated from Equation (3);

$$N = 0.83A^{0.2} \tag{3}$$

where N is the time, in days, after the peak discharge where all discharge is baseflow and A is basin area in $km^2$ (Linsley, Kohler, & Paulhus, 1949). In Meadowbrook Creek's 11.2 $km^2$ watershed, 2N is approximately 2.6 days, which means the minimum discharge to be used as baseflow occurs within 1.3 days before and after peak stream flow on any given day.

To quantitively evaluate stream flashiness we used Richards-Baker index (R-B index). R-B index is a dimensionless value that is positively correlated with increasing frequency and magnitude of storm events (Baker, Richards, Loftus, & Kramer, 2004). R-B index is calculated from Equation (4);

(4) $$R - B\ index = \frac{\sum_{i=1}^{n} |q_i - q_{i-1}|}{\sum_{i=1}^{n} q_i}$$

where $q_i$ is the daily mean discharge of the ith day ($m^3/s$) and n is the number of days in the study period.

## 3. Results

### *3.1 Physical hydrological response to urbanization*

Observed stream discharges at the “Disconnected Headwater” site, which is the most upstream station just downstream of the retention basin (Figure 1), showed minimal variability in streamflow seasonally compared to the other sites (Figure 2). The “Transition” site, which lies at the boundary between the disconnected and connected reaches, had the largest contrast in streamflow rates between seasons. The highest discharge rates occurred between December and June, which encompasses the period of spring snow melt, and lower discharge rates during summer months (June – October). The “Connected Outlet” site also had seasonal changes in streamflow, although less prominent and offset in timing relative to the transition site, with the highest discharge values in the summer months and lowest discharge generally in winter months (November – May) (Figure 2C). The disconnected headwater consistently had the smallest discharge rates across all seasons while the highest discharge rates varied between the transition site and the connected outlet. Table 1 shows on average that the stream is gaining along both the disconnected and connected reaches in the summer. In contrast, in winter, the disconnected reach is gaining, and the connected reach is losing.

Both the disconnected headwater and transition sites had more high frequency, short-duration high discharge events than the connected outlet (Figure 2C). R-B index decreased going downstream with values of 1.00 at the disconnected headwater, 0.76 at the transition site, and 0.57 at the connected outlet. This “flashiness” is attributed to their higher surrounding ISC and urbanization. The frequency of these events at the disconnected headwater and transition sites is consistent year-round, but the connected site has more frequent high discharge events in summer and fewer in winter (Figure 2C). In summer, the maximum discharge at the connected outlet was 5.31 $m^3/s$ but the maximum discharge observed at the same site in the winter was nearly half that value at 2.67 $m^3/s$. This is in contrast to the other two more urbanized gauging stations, where the maximum stream discharge in summer and winter is more similar. In contrast, the minimum stream discharges at the connected site were very similar in both winter and summer with a difference of only 0.0004 $m^3/s$, while the seasonal differences in minimum stream discharge at the more urbanized sites were larger at 0.005 $m^3/s$ and 0.023 $m^3/s$ for the disconnected headwater and transition site, respectively. The seasonal differences in minimum discharge rates suggest more consistent baseflow year-round at the connected outlet versus the more urbanized sites.

Stream temperatures show similar temporal patterns at all sites, where the stream is warmer in summer months and cooler in winter months but there are notable differences in magnitude of temperature change seasonally. The disconnected headwater and transition sites had similar mean steam temperatures during both summer (17.4°C) and winter (4.2°C) that were different from the connected outlet (15.0°C and 5.9°C in summer and winter, respectively; Table 1). Minimum stream temperatures show greater spatial variability, with values of -4.6°C at the disconnected headwater, -0.4°C at the transition site, and 0.0°C at the connected outlet.

All three gauging stations had similar temporal patterns in specific conductivity, where winter maximum values were higher than summer maximum values. Although maximum specific conductivity measurements were higher in winter versus summer at all sites, the mean specific conductivity values were not consistent across sites. The mean specific conductivity in winter was higher than the mean specific conductivity in summer at the disconnected headwater and transition sites, but the connected outlet had more similar mean specific conductivity in summer and winter, with mean values in summer slightly higher than in winter (Table 1).

### *3.2 Seasonal and spatial patterns in stream chemistry*

Nitrate concentrations show similar seasonal patterns across the urbanization gradient with concentrations higher during winter months and lower during summer months (Figure 2B). This seasonal pattern is more pronounced at the disconnected headwater and transition sites and less pronounced at the connected outlet site. The nitrate concentrations increased going downstream along an inverse urbanization gradient and were generally higher at the most downstream site during summer months. Nitrate concentrations during summer months at the disconnected headwater ranged from 0.01 ppm to 2.20 ppm with an average of 0.46 ppm, the transition site ranged from 0.02 ppm to 3.22 ppm with an average of 1.05 ppm, and the connected outlet ranged from 1.15 ppm to 6.62 ppm with an average of 3.45 ppm. Similar to patterns in summer, the nitrate concentrations increased going downstream in winter but at a slightly lower rate. Nitrate concentration during winter months at the disconnected headwater ranged from 0.03 ppm to 6.09 ppm with an average of 2.24 ppm, the transition site ranged from 0.03 ppm to 6.49 ppm with an average of 2.79 ppm, and the connected site ranged from 2.67 ppm to 5.79 ppm with an average of 4.60 ppm.

The stream longitudinal chemistry surveys show stream nitrate concentrations along the disconnected reach were fairly uniform spatially and ranged from 0.01 ppm to 0.18 ppm (Figure 3). In contrast, nitrate concentrations along the connected reach steadily increased going downstream and ranged from 0.23 ppm to 3.65 ppm. Nitrate concentrations in groundwater sampled adjacent to the connected reach in the cemetery show concentrations ranging from 4.98 ppm to 9.07 ppm. In contrast, nitrate concentrations in groundwater sampled adjacent to the connected reach in the suburban neighborhood show concentrations ranging from 0.02 ppm to 0.17 ppm. The riparian groundwater adjacent to the cemetery is elevated in both sulfate and nitrate concentrations compared to the stream, while the downstream suburban groundwater floodplain reported by Ledford and Lautz (2015) was lower in both nitrate and sulfate concentrations compared to the stream. The high nitrate and sulfate concentrations in groundwater sampled at the cemetery are spatially coincident with the sharp increases in nitrate and sulfate concentrations in stream water (Figure 3).

### *3.3 LOADEST modeling of solute loads*

The optimized LOADEST models were selected based on goodness of fit parameters that included the highest $R^2$, p-values <0.05 for regression coefficients, and lowest bias percentage (BP) (Table 2). Visual inspection of Figure 4 shows the model at the disconnected headwater performs well except at extremely low values. The transition site model estimates loads accurately across the full range of values and the model at the connected outlet has a small negative bias when estimating loads (Table 2). Goodness of fit parameters, accuracy of observed values compared to estimated values shown in Figure 2D, and visual inspection of the cluster of values along a 1:1 line in Figure 4 show that these models are effective for estimating continuous loads over the two-year period. We were able to achieve similar goodness of fit and accuracy for simulations of sulfate loads, as shown in the Supplementary Information (Appendix).

### *3.4 Spatiotemporal patterns in stream solute loads*

Seasonal patterns and trends in streamflow and nitrate concentrations manifested themselves in the patterns and trends in the nitrate load estimations. The same seasonal pattern of relatively high nitrate loads in winter and low nitrate loads in summer are present at all sites and are similar to the nitrate concentration seasonal pattern at the disconnected headwater and transition sites (Figure 2D). Flashy hydrographs influence spatiotemporal patterns in loads, such that the disconnected headwater and transition site have very flashy nitrate loads while the connected site is less flashy. Nitrate loads at the disconnected headwater generally ranged from 0.1 kg/day to 1000 kg/day, nitrate loads at the transition site range from 0.06 kg/day to 2080 kg/day, and nitrate loads at the connected outlet ranged from 15.1 kg/day to 542 kg/day (Figure 2D).

To assess whether the disconnected and connected reaches were sources or sinks for nitrate throughout the year, we calculated the differences between nitrate loads at the upstream and downstream ends of the reaches monthly. If nitrate loads at the outlet of the reach exceed those at the inlet, the reach is a net source and if the nitrate loads at the outlet are less than those at the inlet, the reach is a net sink. Differences in cumulative monthly loads show whether the disconnected and connected reaches act as sources or sinks during different seasons of the year (Figure 5). The more heavily urbanized reach is always a net source of nitrate, while the connected reach oscillates seasonally between being a source and sink for nitrate. The monthly differences in nitrate loads between the connected outlet and the transition site show that the connected reach of the watershed is a sink for nitrate during winter months and a net source of nitrate during summer months. Patterns in cumulative monthly sulfate loads have similar temporal patterns to nitrate loading, but different relative magnitudes across seasons. The disconnected reach is always a net source of sulfate, with smaller seasonal variability in sulfate loads compared to nitrate loads. The connected reach is a small net sink of sulfate in the winter, which reflects the fact that this reach is a losing stream during that time. Summer sulfate loads are much higher than winter losses in the connected reach.

### *3.5 Nitrate load response to urbanization and storm runoff*

To assess how nitrate loads are impacted by baseflow versus surface runoff, we compared cumulative daily nitrate loads at the transition site and the connected outlet to the percentage of stream discharge from surface runoff at those locations each day. The relationship between percentage surface runoff and nitrate loads is shown in Figure 6. We observe that the transition site has a greater range of nitrate loads across varying surface runoff percentages, while the connected site has fewer days with large percentages of surface runoff and a smaller range of estimated daily nitrate loads. We see a weak positive correlation between nitrate load and percentage surface runoff at both sites with Pearson correlation coefficients of 0.41 at the transition site and 0.54 at the connected site with p-values<0.05. Winter nitrate loads at the connected outlet tend to be lower than summer loads with consistently lower surface runoff percentage. Unlike the connected outlet, the transition site has large winter nitrate loads regardless of surface runoff percentage and summer nitrate loads are largely variable but are lower than nitrate loads at the connected outlet.

## 4. Discussion

### *4.1 How do nitrate loads in an urban stream differ between reaches with and without connection to groundwater?*

Our results indicate that flashy hydrographs characteristic of urban streams result in urban stream loads where short high flow events export large amounts of nitrate downstream (Figure 2). Stream flashiness is prominent at our disconnected headwater and transition sites as indicated by larger R-B indices, which bracket the upstream, degraded reach with the most impervious cover and least connection to groundwater. Flashiness is a result of poor infiltration and higher surface runoff which leads to more direct runoff to the stream, increased water velocity, and decreased water residence time (Walsh et al., 2005). When coupled with the short, variable groundwater flow pathways characteristic of urban catchments (Lawrence et al., 2013), this leads to minimal interaction of stream water with zones of nitrate attenuation. Eimers and McDonald's (2015) multi-basin analysis of seasonally snow-covered catchments similarly found that urban land cover is a driver of hydrologic differences and alters seasonality in hydrographs where high flow event frequency, flow variability, and percent quick flow increase with increasing urbanization. Nitrate loads at the transition site and connected outlet are positively correlated with the percentage of streamflow from surface runoff, supporting the assertion that high nitrate loads are driven by short high flow events and can be exacerbated by stream flashiness. The higher correlation at the connected reach suggests less variable nitrate loads are likely due to relatively consistent baseflow throughout the year (Figure 6). The transition site had 201 days of flow events with >25% surface runoff whereas the connected outlet had only 90 days of flow events with >25% surface runoff. The numerous short-duration high flow events with high nitrate loads at the transition site culminate in a higher cumulative nitrate export from the disconnected reach compared to the connected reach. For example, annual nitrate export rates at the transition site in water year 2018 and 2019 were $13.1 \times 10^5$ kg $NO_3^-$ and $13.7 \times 10^5$ kg $NO_3^-$ respectively, while nitrate export at the connected site in water year 2018 and 2019 were $9.78 \times 10^5$ kg $NO_3^-$ and $11.1 \times 10^5$ kg $NO_3^-$ respectively (Figure 2).

Although stream flashiness is an important driver of large annual exports of nitrate, we also observed important seasonal differences in nitrate loads. The largest nitrate loads at the disconnected headwater and transition sites occurred during winter months, regardless of whether during flashy storm events or periods of baseflow (Figure 2). These upstream sites have more seasonal variation than the connected outlet, which has a more consistent hydrograph due to groundwater discharge (Eimers & McDonald, 2015). Similar to the impact of flashiness on nitrate loads in urban streams, the seasonal changes in groundwater contributions influences urban stream nitrate loads. At the transition site, nitrate loads are positively correlated with percentage surface runoff year-round, but nitrate loads are also consistently higher in winter months than in summer months at the same percentage of surface runoff (Figure 6). In contrast to the transition site’s more variable relation to percent surface runoff, particularly in summer months, the connected outlet had more consistent nitrate loads with less variation across both seasons and percent surface runoff.

The seasonal patterns in nitrate concentrations we observed are consistent with previous studies (Ledford and Lautz 2015; Duncan, Welty, Kemper, Groffman, & Band, 2017), where nitrate uptake mechanisms, such as permanent removal via denitrification and temporary storage through primary assimilation by plants and algae in streams, were hypothesized to decrease nitrate concentrations in the summer. These uptake mechanisms are greatly reduced during colder months resulting in higher nitrate concentrations in winter relative to summer. In urban streams, where shading from riparian zones is removed and no hydrologic connection to riparian groundwater is present, the contrast in seasonality is intensified by increased stream temperatures, which amplify algae's ability to temporally strip nitrate from the water column, coupled with no additional source of nitrate from groundwater discharge (Figure 2B) (Ledford et al., 2017). This seasonality pattern in nitrate concentrations is also seen in nitrate loads with lower nitrate export during summer months and high nitrate export during winter months. Lin, Böhlke, Haung, Gonzalez-Meler, and Sturchio (2019) reported similar seasonal patterns in urban streams with lower nitrate export at an urban site in the summer, while Kaushal et al., (2014) report no clear seasonal patterns in nitrate in an urban stream. Ledford and Lautz (2015) hypothesized that floodplain and groundwater connection buffered solute concentrations, and our analysis of nitrate loads confirms that the connection to floodplains and groundwater mutes nitrate loads during storm events and seasonality (Figure 2D).

By combining nitrate concentrations and streamflow to determine nitrate loads, we directly quantify the amount of nitrate exported by stream reaches, rather than relying on concentrations alone, which are impacted by dilution or enrichment. Nitrate concentrations alone show the connected reach is enriched in nitrate across all seasons relative to the disconnected reach, but nitrate loads show the connected reach actually has smaller annual exports of nitrate due to seasonal changes in streamflow and groundwater exchange. Our results show that the connected reach it is not a year-round source of nitrate export and that internal nitrate cycling within urban watersheds can be more complicated than loads at the outlet alone may suggest (Figure 5). Both nitrate concentrations and loads at the disconnected headwater and transition site have seasonal extremes, but nitrate concentrations and loads at the connected outlet show different temporal patterns. Generally, nitrate concentrations at the connected outlet are higher than the other sites regardless of season and are less variable (Figure 2). In contrast, nitrate loads at the connected outlet are not always higher than the other sites and the annual nitrate loads are lower at the connected outlet than the other two sites. Nitrate loads at streams with connection to groundwater are more consistent, have smaller seasonal shifts, have less numerous short-duration high flow events with high nitrate loads, and smaller overall nitrate export than reaches without connection to groundwater.

### *4.2 How does groundwater connection in urban streams drive source-sink behavior for nitrate seasonally?*

The disconnected reach is always a net source of nitrate loading to downstream waters (Figure 5), even in summer months when nitrate uptake is very high and nitrate export rates are very low. In winter months, nitrate export from the disconnected reach is a large source of nitrate, but the connected reach retains an equal or larger amount while acting as a net sink for nitrate. Nitrate uptake mechanisms, such as assimilation by primary production or denitrification, are at a minimum during winter months. As a result, nitrate moves relatively conservatively through the stream system in the winter and the only sources and sinks for nitrate are groundwater dynamics. This adds a seasonal component to the preceding conclusion that streams act as both transporters and transformers of N (Sivirichi et al., 2011; Kaushal & Belt 2012). Previous studies report that urban streams are a consistent net export of nitrate (Sivirichi et al., 2011; Kaushal et al., 2014), but emphasize that there is substantial variability and fine-scale spatial heterogeneity that is also shown by our high resolution load estimates at three sites throughout our watershed.

Instream algae that incorporated nitrate into their biomass during summer months can be buried in benthic sediments along the disconnected reach and later released to downstream waters following scouring events (Sobota, Johnson, Gregory, & Ashkenas, 2012 ; Beaulieu et al., 2015) during winter months, thereby acting as a source of nitrate export. Duan and Kaushal (2013) similarly reported increases in nutrient fluxes from sediments in urban streams with increased stream water temperatures. In addition to nitrogen temporarily stored in the summer and released in the winter, groundwater can also be a source and sink of nitrate. Groundwater nitrate concentrations can be highly variable spatially (Figure 5), acting either as a large or small source of nitrate in instances of groundwater discharge. In contrast, loss of stream water to groundwater is a large sink of nitrate during winter months along the connected reach. Sulfate, which is a relatively conservative and abundant ion in Meadowbrook Creek, reveals the important role of groundwater in source-sink behavior in this system during winter months (Figure 4B). The connected reach is a losing stream in the winter, as confirmed by decreases in discharge and declines in sulfate loads from the transition site to the connected outlet site during winter months (Table 1).

Recent research in stream restoration emphasizes the importance of light availability as early drivers in nitrate metabolism and nutrient dynamics, but also indicates that over longer periods of time the heterotrophic and dissimilatory processes resulting from longer water residence times and increased hydrologic connectivity that foster denitrification may be more significant (Reisinger, Doody, Groffman, Kaushal, & Rosi, 2019). Although previous studies have shown that autotrophic uptake is the primary way that nitrogen is retained in urban streams (Beaulieu et al., 2014; Arango, James, & Hatch, 2015; Ledford et al., 2017), we observed that autotrophic uptake is likely only a temporary summer storage process. Due to the flashiness and high frequency of high flow events that scour urban streams, accumulated algae and other biomass later release nitrate to urban systems in winter months and thus can be large sources of nitrate that can be difficult to manage. As observed in other studies, our results show that both in stream biological processes and stream-groundwater interactions in combination regulate nitrate loads (Klein & Toran, 2016). Here, groundwater loss serves as an important sink for nitrate export to downstream waters in winter.

The seasonal patterns of source-sink behavior in urban watersheds are summed in Figure 7. Nitrate load sources in the urban watershed are atmospheric deposition, surface runoff containing lawn fertilizer, and aging sanitary sewer systems (Groffman et al., 2004). During the summer in the disconnected reach, higher stream temperatures from lack of riparian shading and minimal groundwater discharge cause primary assimilation to be a dominant sink for nitrate and export downstream is very small (Catford et al., 2007; Ledford et al., 2017). During winter months in the disconnected reach, primary assimilation is minimized and inorganic nitrate is released by organic matter decomposition and leaky sanitary sewer systems, followed by high discharge scouring events, resulting in large export rates of nitrate downstream with little to no nitrate uptake. Seasonal patterns in temporary nitrate uptake are exacerbated in urbanized catchments, causing the system to retain large amounts of nitrate in summer that is later released to downstream receiving waters in the winter.

The connected reach receives a small nitrate load in the summer from the disconnected reach and nitrate loads increase going downstream so that the connected reach acts as a source of nitrate. Sources of nitrate in the connected reach are similar to the disconnected reach but also include variable groundwater inputs given the high rates of groundwater discharge in summer. Primary assimilation and stream-groundwater interactions that foster denitrification may reduce and regulate high nitrate loads from groundwater discharge in the summer, but groundwater discharge is a dominate source of nitrate to the system. Assimilation of nitrate, denitrification, and groundwater discharge are greatly reduced or cease in the winter, and groundwater loss reduces high nitrate loads received from upstream waters. Without connection to groundwater, urbanized streams transport large amounts of nitrate to downstream receiving waters with little to no possibilities for nitrate removal in winter. Seasonal groundwater connection drives nitrate load source and sink behavior by acting as either a source, or a large enough sink, that groundwater exchange attenuates seasonal changes in nitrate loads received from upstream waters. Groundwater connection in urban streams provides more opportunities for sources and sinks of nitrate year-round than hydrologically disconnected streams, including groundwater discharge into the stream with variable nitrate concentrations, surface-water groundwater interactions that foster denitrification, and stream load loss to surrounding near-stream aquifers.

### *4.3 What are the implications for watershed management to mitigate nitrate loads to downstream receiving waters?*

The key findings of this study are that urban streams that lack a strong groundwater connection have increased annual nitrate loading rates, are generally a source of nitrate across all seasons, and amplify winter nitrate loading rates. In contrast, urban streams with connection to groundwater alter nitrate delivery in space and time such that they have seasonally variable source and sink behavior. Hydrologic disconnection and urbanization cause streams to be constant sources of nitrate across all seasons and flashiness in hydrographs results in short, high nitrate loading rates that culminate in larger annual nitrate loads than in streams that are hydrologically connected. Hydrologically connected streams can both be a source and sink of nitrate depending on the season and export less nitrate annually than a hydrologically disconnected stream. This study demonstrates how loads reveal a more complicated nitrate uptake and export dynamic in urban streams than concentration data alone, and how groundwater can be a driving factor in source and sink behavior. Both hydrologic connection and disconnection alter nitrate dynamics in space and at both seasonal and smaller time scales.

Our high-resolution continuous measurements of streamflow and estimations of nitrate loads through time capture how the flashiness in urban streams increases nitrate exports on both a small single storm event and on a larger annual basis. This stresses the importance of using smaller time steps in nutrient monitoring programs because daily estimates of nutrient loads in urban watersheds can underestimate loads up to 60% (Horowitz, Kent, & Smith, 2008; Hopkins, Loperfido, Craig, Noe, & Hogan, 2017). This study and previous research suggest that due to variable groundwater inputs throughout urban watersheds, water quality monitoring programs should do intensive surveys to determine baseflow stream water chemistry and longitudinal variability (Likens & Buso 2006; Sivirichi et al., 2011). This spatial heterogeneity can result from altered geohydrologic conditions, sewer and drinking water supply infrastructure, and proximity to various non-point sources of contamination including impervious surface runoff and possibly cemeteries.

This work demonstrates that connection to groundwater can decrease extreme seasonal exports of nitrate from urban watersheds that are disconnected to groundwater. Using stream loads to evaluate solute mass balance will better inform best management practices and provide a complete picture when examining complex nitrate loading patterns in urban watersheds. Urban water quality can improve through increasing water residence time, reconnecting streams to aquifers to foster permanent removal of nitrate, and riparian shading that reduces autotroph uptake in the summer and subsequent release in the winter. These effects can be achieved through the application of urban stream restoration and this work has implications for the management of urban water quality.

## 5. Conclusion

The impact of urbanization and the resulting disconnection between streams and groundwater have focused on changes in nitrate concentrations, hydrographs, and nitrate dynamics but do not include reach scale mass balances that inform processes happening within a watershed. We used a USGS linear regression program, RLOADEST, to estimate nitrate loads from weekly stream chemistry samples and continuous (15-minute) streamflow measurements to quantify reach scale nitrate export within a watershed containing a negative urbanization gradient. The nitrate loads were used to compare nitrate export in stream reaches that are disconnected and connected to groundwater, identify how groundwater connection in urban stream drive source sink behavior, and inform best management practices in mitigating nitrate loads.

We found the hydrologically disconnected reach was a net source of nitrate regardless of season and stream-groundwater exchange allowed the hydrologically connected reach to be both a source and sink. Both reaches alter nitrate source and sink behavior at various spatiotemporal scales. Groundwater connection in urban streams reduces annual nitrate loads and provides more opportunities for sources and sinks of nitrate year-round than hydrologically disconnected streams, including groundwater discharge into the stream with variable nitrate concentrations, surface-water groundwater interactions that foster denitrification, and stream load loss to surrounding near-stream aquifers. This study's two years of nitrate loads along a negative urbanization gradient empathizes that connection to groundwater can alter source and sink behavior to reduce annual nitrate loads and a streams seasonal connection to groundwater is an important factor when considering nitrate management.

## 6. Figures

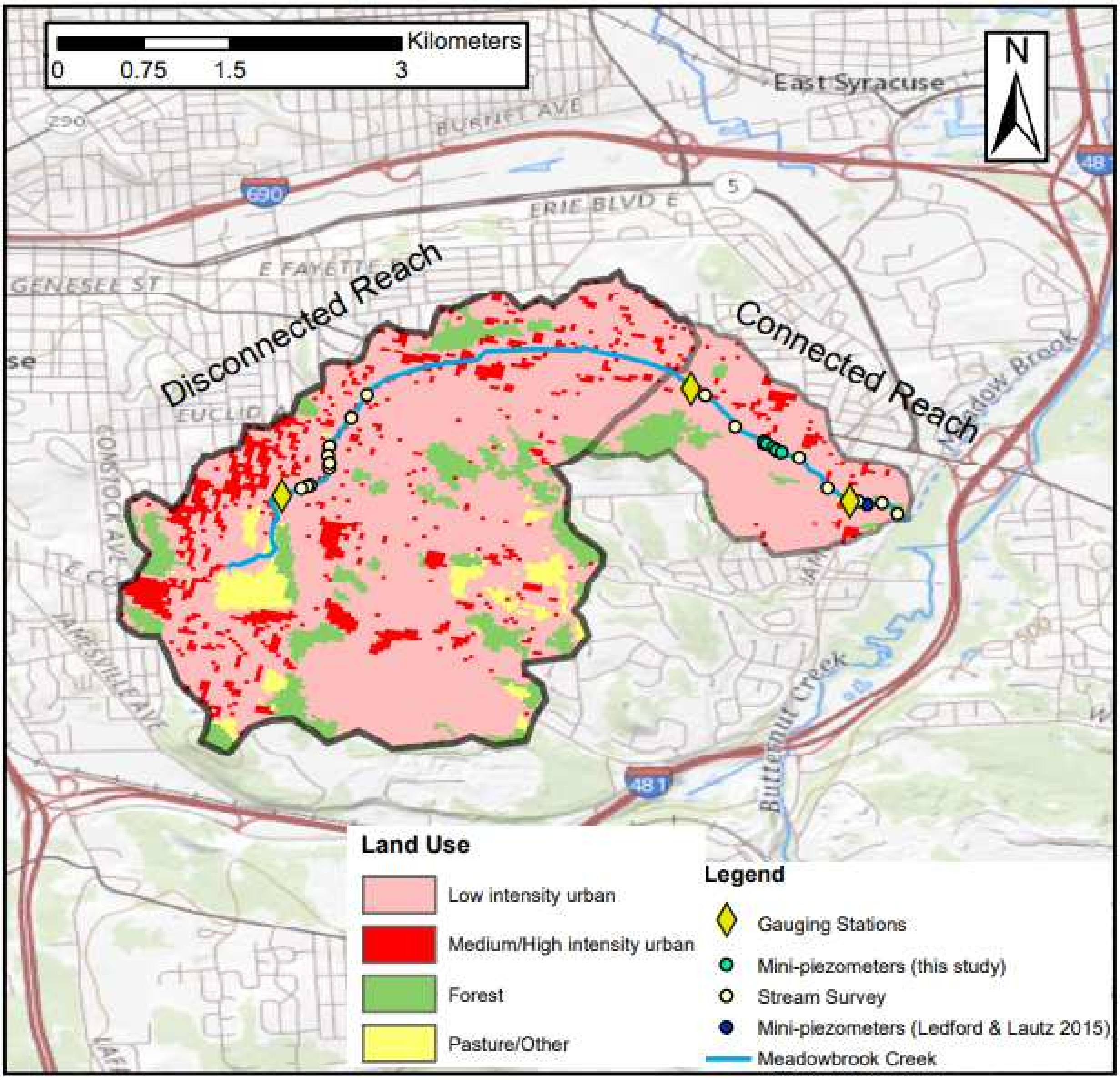


Figure 1. Meadowbrook Creek watershed located in Onondaga County, in New York State. Land cover data is from the National Land Cover Database (NLCD, CONUS), 2016.

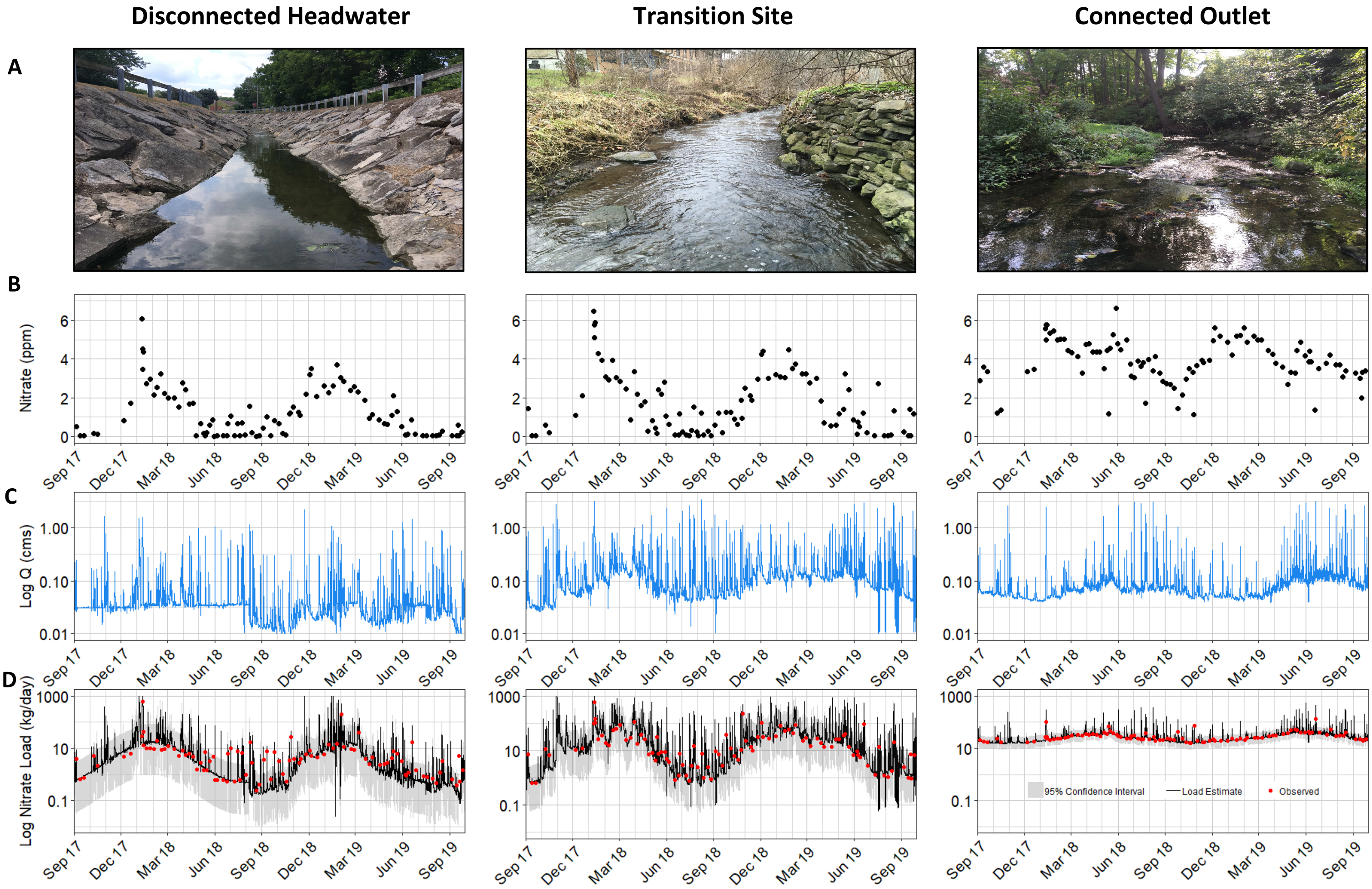


Figure 2. Study results for the disconnected headwater, transition, and connected outlet gauging stations, showing: (A) Photographs of the sampling sites; (B) Concentrations of nitrate in stream grab samples; (C) Continuous (15-minute interval) streamflow at sampling sites (note y-axis is in a log scale); and (D) Continuous (15-minute interval) nitrate loads estimated from LOADEST models. In D, the black line is the nitrate load estimate, gray band is a 95% confidence interval, and red circles indicate discrete observed loads. Note the y-axis is in log scale.

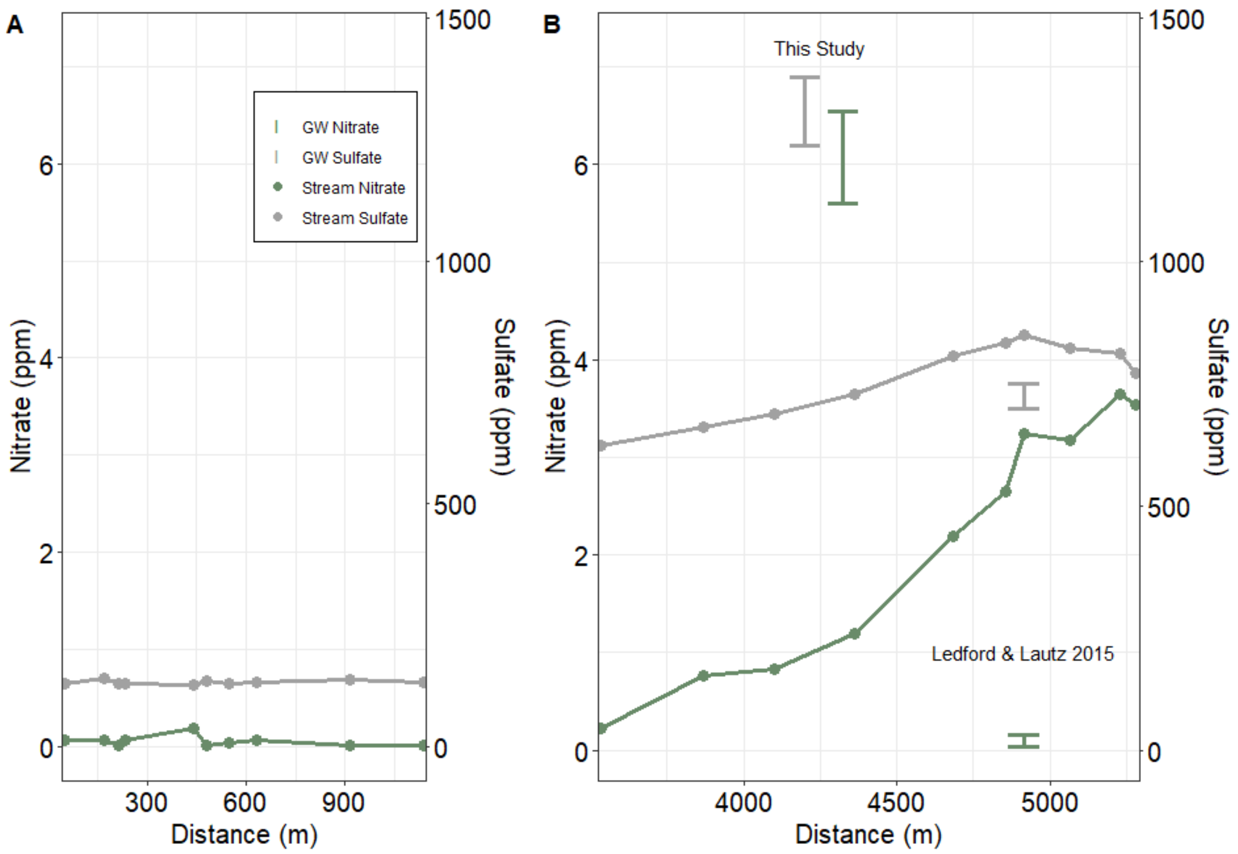


Figure 3. Stream chemistry surveys done September 22, 2019 (**A**) and September 21, 2019 (**B**). Ranges of riparian groundwater concentrations adjacent to cemetery at 4250 m are from mini-piezometers. Ranges of suburban groundwater floodplain concentration samples at 4800 m are from Ledford and Lautz (2015).

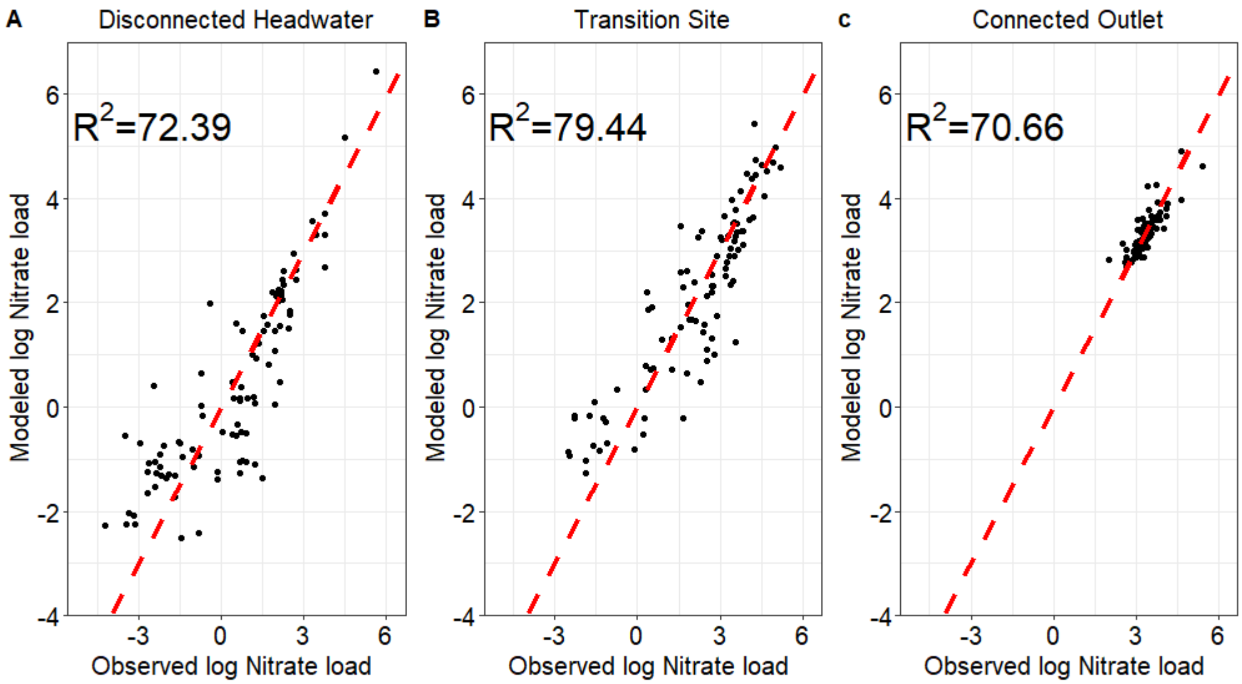


Figure 4. Model goodness of fit shown as modeled versus observed nitrate loads relative to a one to one line, shown as a dashed red line, at the: (A) Disconnected Headwater, (B) Transition site; and (C) Connected Outlet.

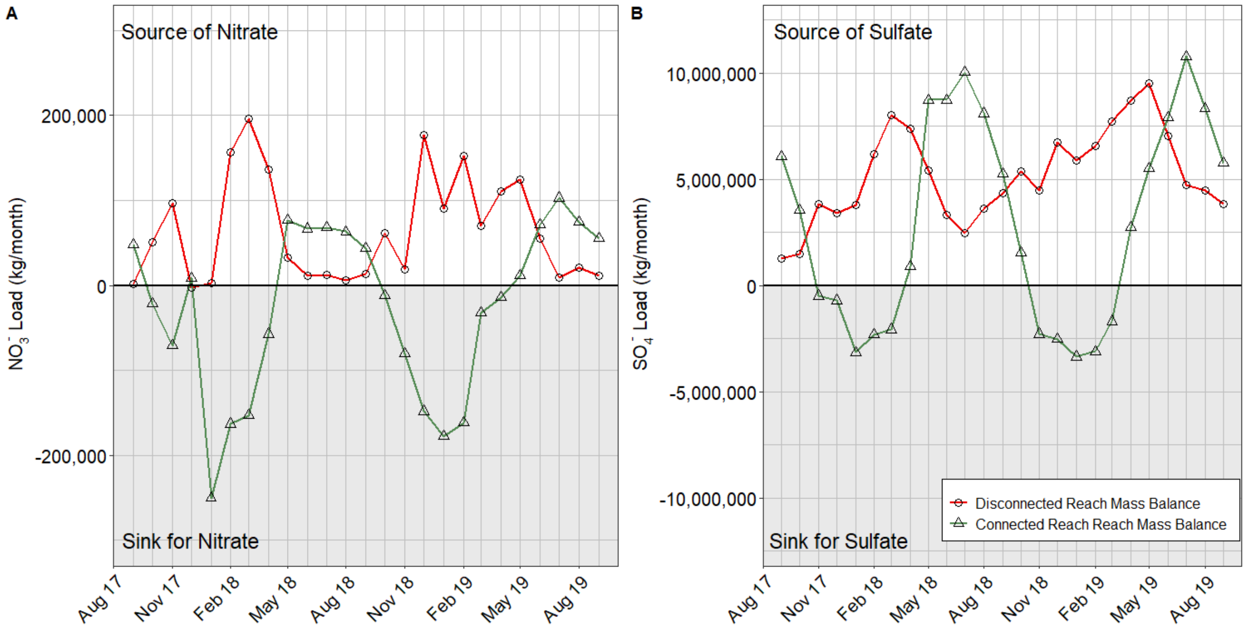


Figure 5. Differences in cumulative monthly load estimates between gauging stations from September 2017 through September 2019 for nitrate (**A**) and sulfate (**B**). Open circles indicate the difference in load between the most upstream sampling station in the disconnected reach and the transition sampling station located at the outlet of the disconnected reach; Open triangles indicate the difference between the transition sampling site and the connected outlet sampling site.

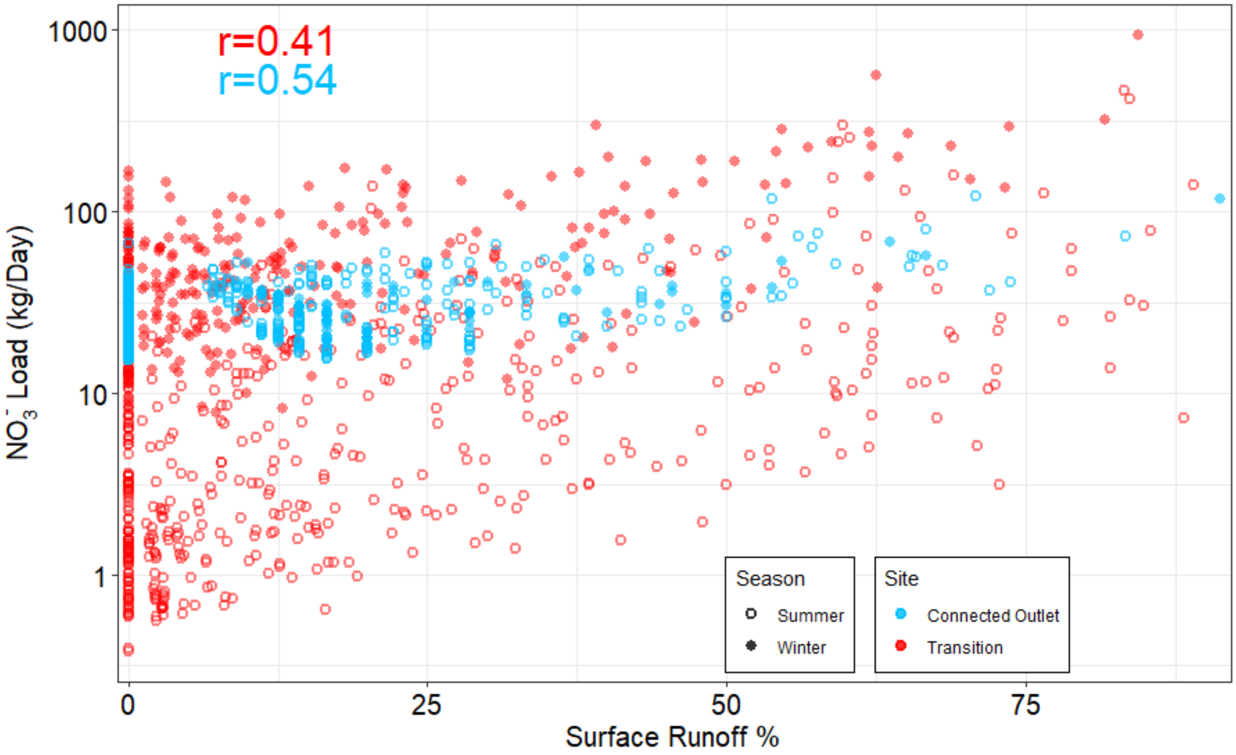


Figure 6. The relationship between daily averaged surface runoff % from HYSEP and daily cumulative load at the connected outlet and transition site. Pearson correlation coefficient (r) between surface runoff % and both the transition site (red) and connected outlet (blue) have p-values <0.05.

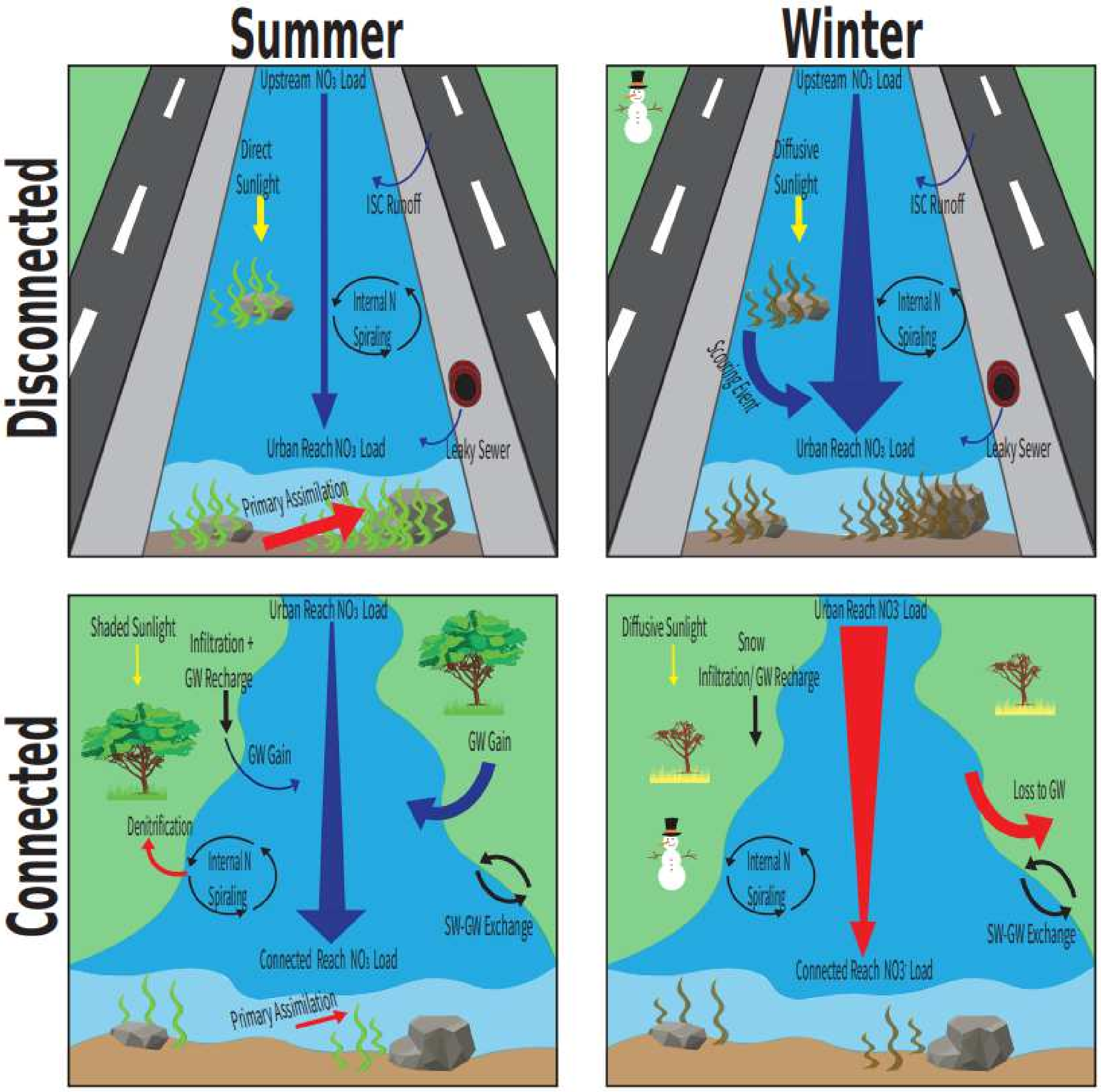


Figure 7. Conceptual diagram showing the processes affecting nitrate load from a degraded urbanized reach to a more natural meandering reach. Size of arrow represents the magnitude of that process, red arrows are nitrate sinks, blue arrows are nitrate sources, and black or yellow arrows are factors that influence nitrate dynamics.

## 7. Tables

| Site | Season | Flow (m$^3$/s) | | | Stream Temperature (°C) | | | Specific Conductivity (µS/cm) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean |
| Disconnected Headwater | Summer | 0.005 | 1.63 | 0.042 | 4.7 | 29.9 | 19.7 | 418 | 2034 | 865 |
| | Winter | <0.001 | 2.24 | 0.056 | -4.6 | 24.7 | 6.6 | 9 | 4106 | 1414 |
| Transition Site | Summer | 0.007 | 4.74 | 0.106 | 6.7 | 31.0 | 19.6 | 348 | 1156 | 794 |
| | Winter | 0.030 | 3.15 | 0.157 | -0.4 | 26.6 | 6.2 | 442 | 3353 | 1278 |
| Connected Outlet | Summer | 0.039 | 5.31 | 0.107 | 7.2 | 28.4 | 16.5 | 118 | 2804 | 2126 |
| | Winter | 0.039 | 2.67 | 0.076 | 0.0 | 20.3 | 7.3 | 162 | 13802 | 1932 |

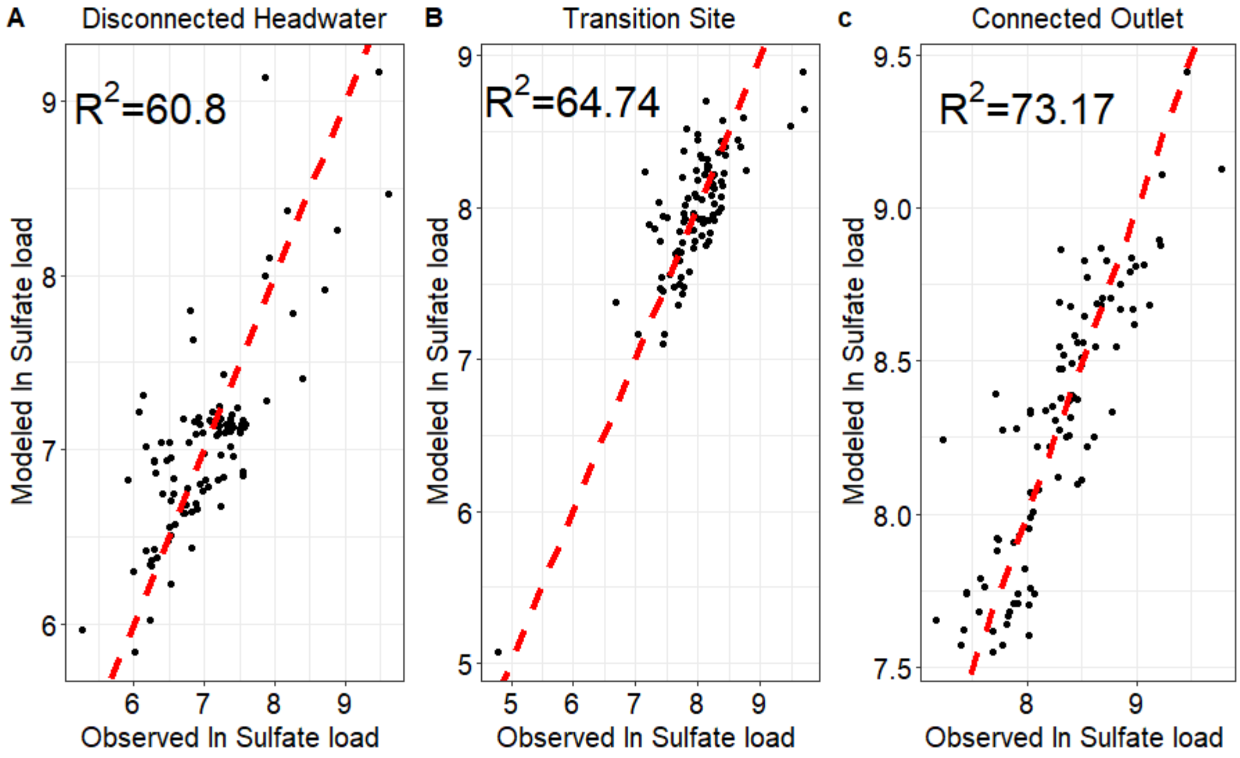
Table 1. Minimum, maximum, and mean values of flow, stream temperature, and specific conductivity for the three study reaches from 15-minute interval data. Seasons where divided by the seasonal nitrate signal where summer is June through October and winter is November through May.

| Site | $R^2$ (%) | $B_P$ (%) | Coefficients for stated variables in the selected LOADEST models | | | | |
|---|---|---|---|---|---|---|---|
| | | | a0 (intercept) | a1 (ln Q) | a2 (sine Dtime) | a3 (cosine Dtime) | a4 (ln SC or ln T) |
| Disconnected | 72.4 | 140.3 | 1.35* | 1.29* | 0.75 | 1.63* | N/A |
| Transition | 79.4 | 48.3 | 11.8* | 1.40* | 1.01* | 1.53* | -1.41* |
| Connected | 70.7 | -1.5 | 6.44* | 0.70* | 0.16* | -0.14 | -0.72 |

Table 2. Goodness of fit parameters for LOADEST nitrate models. Dtime is adjusted decimal time (dtime= decimal time – center of decimal time). The a4 coefficient in the transition site model is for the log of specific conductivity and for the connected site model is for log temperature.

***** Indicates p-value <0.05

## 8. Appendix



Supplementary Figure 1. Model goodness of fit shown as modeled versus observed sulfate loads relative to a one to one line, shown as a dashed red line, at the: (A) Disconnected Headwater, (B) Transition site; and (C) Connected Outlet.

| Site | $R^2$ (%) | $B_P$ (%) | Coefficients for stated variables in the selected LOADEST models | | | | |
|---|---|---|---|---|---|---|---|
| | | | a0 (intercept) | a1 (ln Q) | a2 (sine Dtime) | a3 (cosine Dtime) | a4 (ln $Q^2$ or ln T) |
| Disconnected | 60.8 | -3.18 | 7.46* | 0.71* | 0.07 | -0.18* | N/A |
| Transition | 64.7 | -1.72 | 7.97* | 0.55* | 0.14* | -0.11* | -0.09* |
| Connected | 73.2 | -0.58 | 4.92* | 0.30* | 0.19* | -0.24* | 0.88* |

Supplementary Table 1. Goodness of fit parameters for LOADEST sulfate models. Dtime is adjusted decimal time (dtime= decimal time – center of decimal time). The a4 coefficient in the transition site model is for the log of $Q^2$ and for the connected site model is for log temperature.

***** Indicates p-value <0.05

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# JULIO BELTRAN

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## KEY SKILLS

- Collected and analyzed two years of hydrologic data such as streamflow using various methods, stream chemistry, and nitrogen uptake length in streams for publication.
- Constructed various linear regression models of stream solute loads using streamflow and stream chemistry data to assess water quality in an urban stream.
- Managed, planned, and taught session on stream addition techniques and assisted in teaching streamflow gauging techniques to 20 master/PhD students in the EMPOWER 2019 Summer Domestic Field Course.

## EDUCATION

**Syracuse University** – Syracuse, NY **August 2020**
*Master of Science in Earth Science*, hydrology emphasis

**New Mexico State University** – Las Cruces, NM **August 2017**
*Bachelor of Science in Geology*

## RESEARCH EXPERIENCE

***Masters Thesis Research*****,** Syracuse University **August 2018 - Summer 2020**
Advisor: Dr. Laura Lautz, Department of Earth Sciences

- Collected, filtered, and analyzed two years of stream water samples using graphical methods, summary statistics, and linear regression to identify seasonality, sources, and sinks along an urban stream
- Prepared laboratory standards and analyzed major cations and anions in water samples using Dionex ICS-2000 Ion Chromatograph
- Measured stream discharge using acoustic doppler velocimeter and installed/programmed Sontek IQ for continuous hour measurements of stream discharge in an urban stream
- Constructed, budgeted, and implemented isotopically labeled and unlabeled stream nitrate addition experiment to estimate nitrogen cycling in an urban stream
- Surveyed land points to help estimate steam degradation and aggradation near man made beaver dam analogs
- Built and deployed mini-piezometers with iButton temperature loggers to sample stream benthic water and measure benthic stream temperature
- EMPOWER fellow: Interdisciplinary group focused on professional development and issues at the water-energy nexus. Collaborate with disciplines outside hydrology on current water-energy issues. Participate in science communication workshops such as Alan Alda Center for Communicating Science and Josh Henkin professional development workshops.

***Hydrogeologist Intern*** **June 2018-August 2018**
**The South Florida Water Management District-** West Palm Beach, FL

- Characterized hydraulic conductivity of the Surficial Floridian Aquifer system through grain size analysis

- Assisted in groundwater sampling, supervision of well construction, slug and pump tests, and plugging and abandoning monitoring wells
- Compiled and evaluated water quality data for quality control using AquaChem software and produced a map in ArcGIS of usable well data

***Wellsite Geologist*** **August 2017 – May 2018**
**Selman and Associates** – Midland, TX

- Collected, processed, logged and analyzed geological samples
- Determined and demarcated critical stratigraphic geological units to assist in drilling conventional oil and gas, horizontal oil and gas, and salt water disposal wells
- Calibrated, maintained, and troubleshot gas chromatograph (FID and TCD) and gas monitoring systems
- Prepared reports for drill site supervisor, senior geologist, and client
- Implemented and followed safety regulations

## TECHNICAL SKILLS

**Software:** ArcGIS, Visual MODFLOW, MATLAB, ModelMuse (MODFLOW GUI), AquaChem, AQTESOLV, Microsoft Office Suite, R statistical software, SAS

**Laboratory Skills:** ICS 2000 Ion Chromatograph (IC)

**Field Equipment:** Marsh-McBirney Flow Meter, FLowTracker Handheld Acoustic Doppler Velocimeter, Total Station, HOBO Water Level Data Loggers, iButton Temperature Loggers, YSI pH/conductivity multi-meter, Sontek IQ velocity profiler

## HONORS AND FELLOWSHIPS

| | |
|---|---|
| Energy Model Program on Water-Energy Research, NSF NRT Program | August 2018-Present |
| Charles & Parker Gunn Memorial Scholarship | May 2017 |

## GRANTS

| | |
|---|---|
| EMPOWER Seed grant (~$3000) | May 2019 |
| Geological Society of America Student Research grant (~$2000) | February 2019 |
| Syracuse University Earth Sciences Merriam grant (~$2000) | January 2019 |

## PRESENTATIONS

**Poster Presentations:**

**Beltran**, J., L.K. Lautz, and J.R. Slossan. The impact of stream-groundwater exchange on seasonal nitrate uptake dynamics in an urban stream. Proceeding of the America Geophysical Union Annual Meeting, December 9-13, 2019: San Francisco, California H13N-1936

J.R. Slossan, L.K. Lautz, and **Beltran**,J. Groundwater Storage of Seasonally-Applied Road Salt in an Urban Watershed. Proceeding of the America Geophysical Union Annual Meeting, December 9-13, 2019: San Francisco, California H33J-2060

## PUBLICATIONS

Richardson, E., Janzen, J. and **Beltran**, J. 2020. Hydrogeologic Investigation at the S61 Locks for the Central Florida Water Initiative. Technical Publication WS-50, South Florida Water Management Distract, West Palm Beach, FL. Available online at https://www.sfwmd.gov/sites/default/files/documents/s61_locks_hydro_investigation_rpt_ws-50.pdf

## SERVICE AND LEADERSHIP

Syracuse University Earth Sciences August 2019 – May 2020
Graduate Student Seminar coordinator (WAGGS)

- Organize and manage student speakers for graduate student seminar
- Budget and purchase snacks for department graduate events
- Invited and organized the arrival of guest speaker for the student symposium.