ABSTRACT

Title of Thesis:	HYDROLOGICAL, BIOLOGICAL, AND GEOCHEMICAL RELATIONSHIPS AMONG CARBON, NITROGEN, AND BASE CATIONS IN RESTORED AND UNRESTORED URBAN STREAMS
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Urban infrastructure changes hydrologic flowpaths of water into streams and alters ecosystem function. Geomorphic stream restoration is commonly implemented to stabilize channels, while ecosystem function, and nutrient retention are of secondary concern. This research investigated whether restoration alone significantly influences N uptake in streams and if significant hydrological, biological, and geochemical relationships exist between coupled biogeochemical cycles that should be considered when evaluating restorations. Carbon, nitrogen, base cations, and stream metabolism dynamics were investigated in six urban streams in Baltimore,MD. Nitrate tracer injections were used to quantify nitrogen uptake dynamics. Results did not show significant differences in nitrogen uptake based on restoration. Organic carbon, inorganic carbon, and nitrogen each have distinct but interrelated hydrological, biological, and

geochemical relationships across all sites. These dynamic relationships may also significantly affect nitrogen uptake, but more spatiotemporal data are needed to quantify and understand variability among restored and unrestored sites.

HYDROLOGICAL, BIOLOGICAL, AND GEOCHEMICAL RELATIONSHIPS AMONG CARBON, NITROGEN, AND BASE CATIONS IN RESTORED AND UNRESTORED URBAN STREAMS

By

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Chapter 1: Introduction

1.1 Urbanized Streams

Urbanization has significantly changed the structure and function of watersheds and the transport and transformation of carbon and nitrogen (Walsh *et al.*, 2005a). Increased impervious surface coverage and extensive storm drain networks create surface and storm sewer pathways that can rapidly convey precipitation (runoff) and sewage inputs of carbon and nitrogen (Kaushal and Belt 2012). Furthermore, many low-order streams have been placed in concrete channels to protect urban infrastructure and decrease flooding (Elmore and Kaushal 2008). These practices significantly decrease infiltration and contribute to lower groundwater tables, which shift dominant carbon sources to shallow flowpaths (Walsh *et al.*, 2005a). Consequently, less water moves through stream riparian zones and the deeper groundwater bypasses biologically active subsurface soils (Figure 1.1), which contribute to carbon sources and nitrogen retention or removal (Addy *et al.*, 1999; Groffman *et al.*, 2002; Bohlke *et al.*, 2007). Stream hydrograph changes that lead to higher peak discharges and more bankfull events can also contribute to significant channel incision (Wolman and Schick 1967; Leopold 1968; Booth 1990; Paul and Meyer 2001; Walsh *et al.*, 2005b). The combination of channel incision and groundwater lowering hydrologically impacts sources and transformations of carbon and nitrogen (Mayer *et al.*, 2010; Kaushal and Belt 2012). Decreased hydrologic connectivity among stream channels, riparian areas, and hyporheic zones can impair the capacity of streams and rivers to retain and transform watershed nitrogen pollution (Walsh *et al.*, 2005; Kaushal and Belt 2012). Recent work suggests strong relationships between carbon and nitrogen in natural watersheds, and this may also be evident in urban watersheds (Duan *et al.*, 2014; Kaushal *et al.*, 2014). Here, I investigate relationships between carbon and nitrogen in urban restored and non-restored streams and explore potential factors contributing to this relationship/stoichiometry. Does stream restoration alter this stoichiometry by changing local hydrology and stream reach geomorphology? If hyporheic exchange and floodplain connection are re-established, will that make a decrease in nitrogen more rapid with increasing carbon inputs?

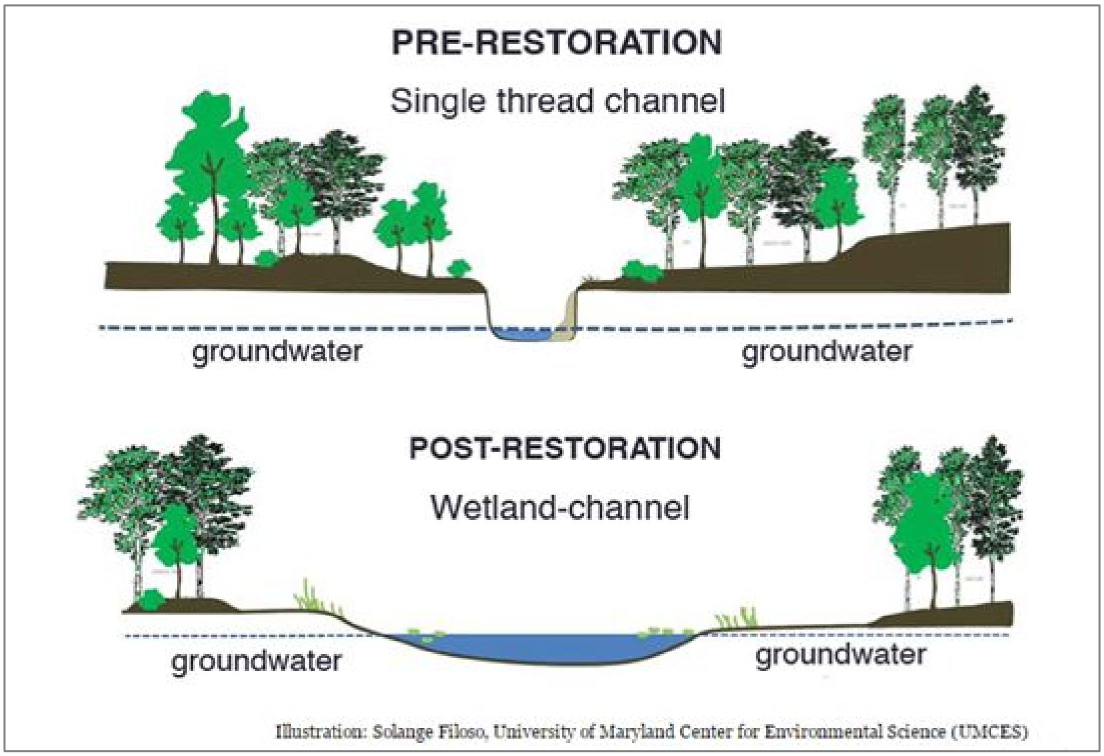

Figure 1.1: Conceptual diagram showing streams and associated riparian zones in restored and unrestored streams. High runoff during storms leads to incised stream channels in urban watersheds which, in combination with reduced infiltration in impervious urban uplands, can lead to reduced riparian groundwater levels. Restoration efforts (in this example, a wetland channel) may widen the channel and attempt to reconnect it with the adjacent riparian zone, thereby increasing groundwater levels..

Urban watersheds can transport significant nitrogen and carbon loads to streams from both nonpoint and point sources in watersheds (Carpenter *et al.*, 1998; Brett *et al.*, 2005; Carle *et al.*, 2005; Bernhardt *et al.*, 2008; Kaushal *et al.*, 2011). Significant work shows that base cations (K, Na, Ca, Mg), which are derived from weathering in non-urban streams can be elevated in urban streams due to fertilizer applications, leaky infrastructure,weathering of urban infrastructure, and road salt application (Rose 2002; Williams *et al.,* 2004; Kaushal *et al.,* 2005). Some urban watersheds are converted from agricultural lands and inherit groundwater nitrate contamination, although these watersheds may have lower or higher DOC than forests (Lewis *et al.*,, 2006). Increased urbanization and suburban sprawl has also stimulated the need for a broader sewer and septic infrastructure, which can age and leak C and N over time. Leaky and degrading sanitary sewer pipes can contribute nitrogen and carbon to groundwater and streams (Kaushal and Belt 2012). Fertilized lawns and golf courses can be a localized, yet important source of additional nitrogen and carbon (Law *et al.,* 2004; Raciti *et al.,* 2011). Increased vehicular traffic in urban areas can further contribute to additional NO_X due to vehicle emissions. As a result, increased transport of nitrogen from urban sources can contribute to algal blooms in coastal waters and carbon loading (Kaushal *et al.,* 2014), which create anoxic conditions that damage aquatic life and habitats. The Chesapeake Bay region has specific goals and regulations to reduce total maximum daily loads (TMDLs) of nitrogen to avoid these low oxygen conditions in coastal waters. Currently carbon is not managed but recent research suggests that dissolved organic carbon (DOC) dynamics may be important to best management practice considerations. Because DOC affects stream metabolism and wetland and riparian restoration projects alter fluvial DOC regimes, there is an increasing need to manage inputs (Stanley *et al.,* 2012). Nonpoint sources of N and C along the urban watershed continuum can contribute to cascading impacts along hydrologic flowpaths from headwaters to coastal zones (Kaushal *et al.,* 2014). The recognition that consequences of local impairments extend along river systems suggests a need to consider watersheds holistically (as opposed to the scale of individual reaches) and raises the question of how to focus restoration and management efforts within watershed systems.

1.2 Stream Restoration

In response to significant urban stream degradation, many cities have implemented stream restoration projects (Bernhardt *et al.*,, 2005a; Wohl *et al.*,, 2005). Frequently used restoration strategies implement the Natural Channel Design: geomorphic, aesthetic, and/or habitat-based designs, focusing on channel stability, flood prevention, and an emulation of a “natural” river channel (Rosgen, 2007). The primary purpose for many of these projects is infrastructure protection, preventing further erosion that may damage adjacent property or degrade sewer systems. Significant financial resources have been committed to geomorphic stream restoration projects.. More recent stream restorations incorporate a variety of different approaches and effectiveness, which may affect carbon and nitrogen (e.g., artificial wetland creation, woody debris structures, replacing riparian vegetation, “daylighting” streams). However, data on their effectiveness is mixed from project to project based on location, size, and type of restoration (Newcomer *et al.*,, 2014).

1.3 Nitrogen, Carbon, and Base Cations

There is a growing recognition that urban streams have a significant capacity to retain and transform nitrogen and carbon even due to their increased light availability, elevated temperature, and organic matter loading (Kaushal *et al.*, 2014). Both autotrophic and heterotrophic microbial communities remove N and increase carbon in streams. N uptake and carbon loading is primarily driven by ecosystem metabolism and biotic uptake in urban streams (Pennino *et al.*, 2014; Smith and Kaushal 2015). Most N uptake is temporary**,** but it can buffer timing of N export (i.e., lead to a delay in export). Conceptually, NH_4^+ and NO_3^- enter the stream reach via stream flow and lateral seepage (Peterson *et al.*,, 2001). NH_4^+ removal is due to uptake by primary producers, bacteria, and fungi plus direct nitrification. Indirect nitrification is the conversion of NH_4^+ mineralized from organic matter to NO_3^-. NO_3^- removal from the water is primarily via assimilation by biota and denitrification on the stream bottom. Regeneration is the release of NH_4^+ and NO_3^- from the stream bottom back to the water column and is the net result of several interacting processes, including mineralization, indirect nitrification, denitrification, and reuptake by organisms. NO_3^- and NH_4^+ remaining in the water are exported downstream (Figure 1.2).

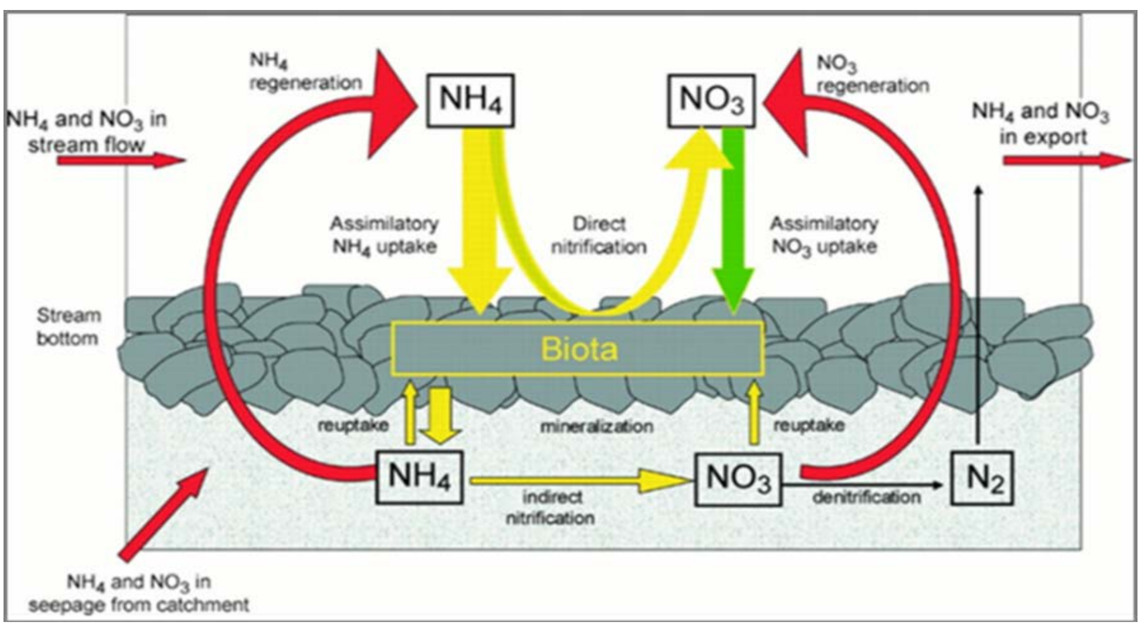

Figure 1.2: Conceptual model of dissolved inorganic nitrogen in headwater stream ecosystems (Peterson *et al.*,, 2001)

Coupled carbon, nitrogen and base cation dynamics are not as well-studied in urban streams; flashy discharges add significant difficulty to studying these streams. Recent work has shown that the dynamics of nitrogen and organic carbon can be strongly coupled in urban streams spatially and temporally (Mayer *et al.,* 2010, Kaushal *et al.,* 2014). Other work has shown that denitrification and nitrate uptake can be stimulated by labile organic matter sources in urban watersheds (Newcomer *et al.*, 2012; Duan *et al.,* 2014). Although organic matter is recognized to be important biologically in urban streams, few studies have explored the functions and management implications of organic matter in restored stream ecosystems. A major question is what effect does stream restoration have on nitrogen retention and export in urban streams? Directed efforts to reduce transport of nitrogen through surface waters use artificial wetland creation, stormwater best management practices (BMPs), and stormwater control measures (SCMs). Can stream restoration projects be effective methods for increased nitrogen retention, particularly during baseflow?

1.4 Hypotheses

In this study, the following hypotheses were evaluated:

1. Stream reaches with restoration attributes will have significantly shorter N uptake lengths than urban unrestored streams.
2. Stream reaches with restoration attributes will have significantly higher N uptake velocities than urban unrestored streams.
3. Stream reaches with restoration attributes will have significantly greater areal N uptake than urban unrestored streams.

Additional exploratory analyses were done to look at other factors that may influence carbon and nitrogen concentrations in urban streams. These hydrologic, biological, and geochemical factors were evaluated through stepwise multiple linear regression to explore whether similar factors controlled uptake and transport across streams. However, these factors go beyond the evaluation of how stream restoration may affect nitrogen uptake and were used to further understand the complex dynamics of urban streams.

Chapter 2: Study Sites

A set of six stream reaches chosen for this study are within four watersheds in the greater Baltimore region and are within the Baltimore Ecosystem Study LTER. The sites are located in in northeastern Baltimore County, northwestern Baltimore County and north Baltimore City, MD. They are part of the larger Chesapeake Bay Watershed (Figure 2.1)

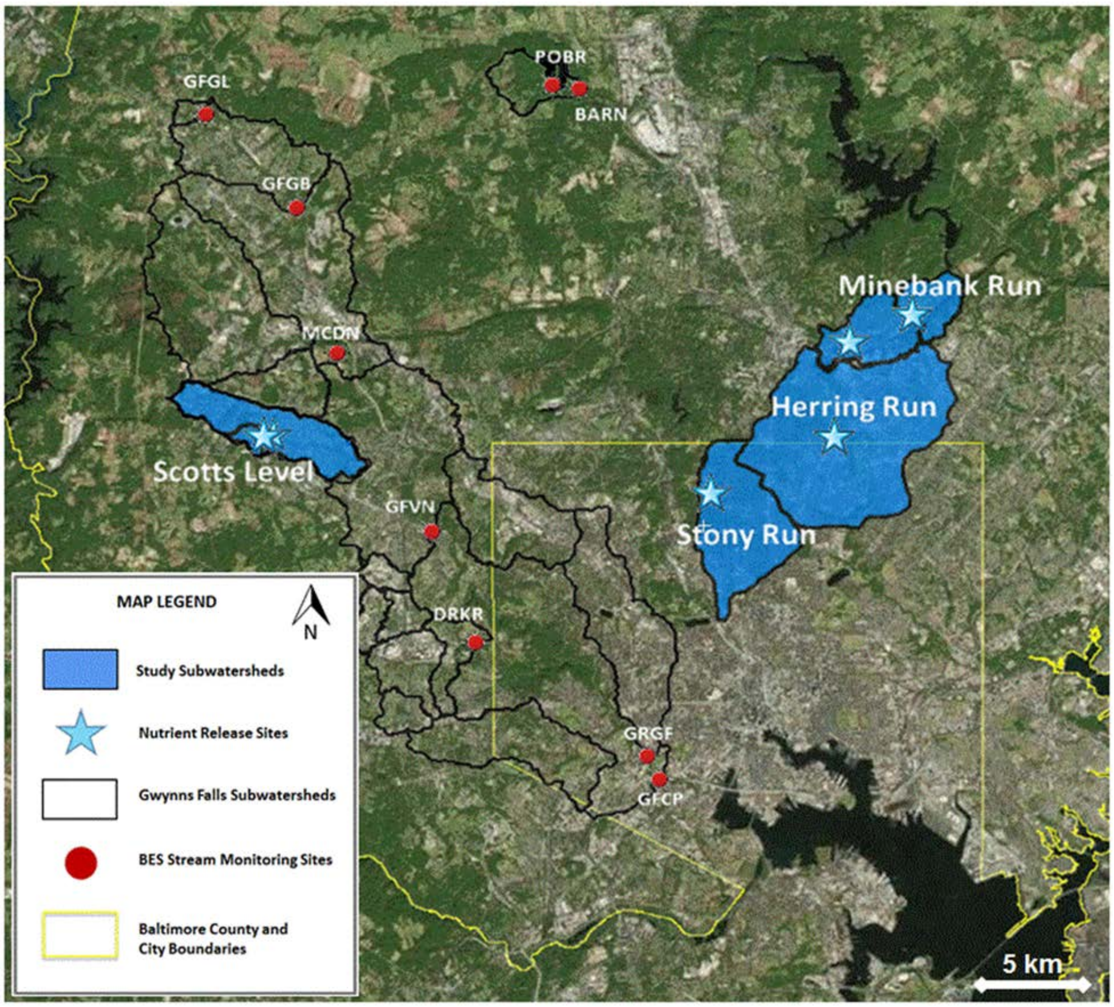

Figure 2.1: Six sites within four subwatersheds of the Chesapeake Bay watershed share similar land use characteristics and offer a variety of levels of degradation or restoration. Nutrient injection sites (blue stars) are also the positions of biweekly sampling conducted between May 2015 and August 2016. Baltimore Harbor and Chesapeake Bay are in the bottom right corner of the image *(image Tom Doody. GIS shape files courtesy of Dexter Locke, Clark University).*

Selected watersheds had similar drainage basin areas, intensity of development, and impervious surface coverage, but they had streams with different treatments, from unrestored to restored with different restoration features and a gradient of restoration ages (Table 2.1).

Table 2.1: Characteristics of watersheds containing reaches selected for this study

Site	Year Restored	% Developed	% Impervious	Basin Area (km^2)	Range of Discharge (L/s)	Stream Gradient	Average pH (±1σ)
Herring Run (HERR) 39°22'25.1"N, 76°35'03.6"W	n/a	91	25	5.5	10.2-14,781	0.016	7.71 (±0.21)
Minebank Run Upstream (MBRO) 39°24'43.0"N, 76°33'12.5"W	1999	82	23	1.1	0.65-381	0.007	7.63 (±0.20)
Minebank Run Downstream (MBRN) 39°24'34.6"N, 76°33'26.1"W	2004	73	21	5.3	14.7-2350	0.006	8.12 (±0.28)
Stony Run (STNY) 39°21'22.2"N, 76°37'49.3"W	2009	90	28	2	2.66-160	0.007	7.53 (±0.18)
Scotts Level Branch Restored (SLBR) 39°22'25.7"N, 76°47'41.5"W	2014	92	29	1	0.91-214	0.011	7.54 (±0.16)
Scotts Level Branch Unrestored (SLBU) 39°22'25.7"N, 76°47'41.5"W	n/a	92	29	< 1	0.90-195	0.003	7.49 (±0.15)

100-meter stream reaches were initially selected in each watershed for the study. Reach selection considerations included geomorphic and hydrological characteristics (the number of riffle-pool sequences, no significant inputs/outflows within the reach that would affect discharge, light availability and shading), location in the watershed (first or second order streams) and safety of access. They were also selected as representative of a gradient of restoration or degradation. The most degraded stream, Herring Run (HERR), serves as an endmember example of an unrestored reach. It is an engineered, trapezoidal, concrete-lined channel (Figure 2.2). The stream is a tributary near the northwestern headwaters of the larger Herring Run watershed, which discharges into the Back River in Baltimore, MD. Land use distribution is 60% residential, 31% commercial, 8% forested, and 1% water surface (Maryland Dept. of the Environment, 2007). The study reach is located at USGS gaging station 01585200 at Regester Avenue in Idlewylde, MD, 1.0 mi upstream from the mouth. Because it is completely engineered with an impervious concrete surface as its substrate, Herring Run is assumed to have zero hyporheic exchange and only interacts with the steep adjacent floodplain during overbank flow. It is considered one of the flashiest gaged streams in the nation with the potential for a three order of magnitude increase in discharge within 45-60 minutes during moderately intense precipitation events.

Figure 2.2: A view looking upstream in the concrete lined channel at Herring Run in Summer 2015, standing near the top of the study reach. USGS gage housing is behind the trees in the upper right corner of the photo. This trapezoidal concrete channel extends upstream for 300 meters before a bifurcation splits it into a degraded reach to the right, and a mix of concrete or stone and mortar lined channel to the left (*photo: Tom Doody)*

Two selected reaches within the Minebank Run watershed are in northeast Baltimore County near Towson, MD. The lithology of these sites differs from the other four because they drain a very small portion of the Cockeysville Marble and are the only watersheds in the study with any natural carbonate bedrock. Site designations refer to the age of restoration. The older restoration (MBRO, Figure 2.3) is an upstream reach draining 1.1 km^2 of the watershed, and was restored from 1998 to1999. The study reach is located in a small valley behind neighborhoods at Intervale Court and Cromwell Valley Elementary School. The newer restoration (MBRN, Figure 2.4) is the downstream reach draining 5.3 km^2 of the watershed, and was restored from 2004 to 2005. The study reach is located just below USGS gaging station 0158397967, 2.25 km upstream from the mouth. In both cases, the stream channels were reconstructed for purposes of improving stability and protecting nearby sewer infrastructure. Riffle and pool sequences were re-created by placement of rock weirs, which were also intended to control sediment supply. Where possible, flood plains were created to allow high discharge events to spread out and reduce the energy directed at the channel bed. Channel-bank slopes were reduced in many locations and natural vegetation was planted on the banks. Low to moderate channel sinuosity was maintained throughout the restored reaches to reduce the potential for lateral bank erosion and failure (Doheny *et al.*, 2007).

Figure 2.3: An upstream view of the Minebank Run reach restored in 1999 (MBRO). Several of the boulders used for stabilization of the stream bank (photo left) have failed and have fallen into the stream and altered flow and sediment dynamics. Further downstream, below our study reach, the channel widens and there is significant input from what appears to be residential drinking water pipes (*photo: Tom Doody*)

Figure 2.4: A downstream facing view of the Minebank Run reach restored in 2004 and 2005. The rip rap in photo left remain stable, but further downstream there is bank failure at an unstabilized portion of the reach on the opposite bank. Mixed sediment sizes ranging from sand to boulder are common in the reach and theses larger grain sizes have moved during high flow events. The USGS gage is approximately 100 meters upstream (*photo: Tom Doody*)

In the Scotts Level Branch watershed, two sites were selected (SLBU and SLBR), which are contiguous unrestored and a restored paired reaches on an unnamed headwater tributary of the Scotts Level Branch watershed. Scotts Level discharges into Gwynns Falls in southwestern Baltimore County, MD. Site designation names refer to the upstream unrestored reach (SLBU, Figure 2.5), which flows through a storm drain under Allenswood Rd. directly into a downstream, 500-foot restored reach (SLBR, Figure 2.6) in a residential area. Combined, these reaches drain a very small area (1 km^2). The restoration project was completed in 2014 on a 1420-foot corridor of the main stem and the 500-foot first order stream tributary, in which our reach is located. Typical of more recent stream restoration projects, the Scotts Level reaches include a variety of control structures. Four log cross vanes, six rock cross vanes, and five boulder j-hook vanes were installed and act as hydraulic features to help direct flow. 192 linear feet of rock toe protection were installed to prevent bank erosion. In order to control riffle grading, 13 log sills and 258 tons of boulders were installed. To further protect against erosion, 1085 live stakes and 646 linear feet of imbricated stone bank protection were installed, and three segments of the stream were re-aligned with clay cores. Woody debris was also scattered in the wetland areas to slow water down during overbank flow and to create wildlife habitat.

Figure 2.5: An upstream facing view of the unrestored reach at Scotts Level Branch (SLBU) taken summer 2016. This reach is very straight and is largely shaded. Most of the substrate is sand, silt, and some gravel. The slope of the bank in photo left is very steep, and 80 meters upstream both sides of the channel are nearly vertical, with the stream surface ~2m below the banks *(photo: Tom Doody).*

Figure 2.6: A downstream-facing view of the newly restored reach at Scotts Level Branch (SLBR), taken in summer 2015. Several large pools were included to increase residence time of water in the restoration, which receives water from the unrestored reach through a 2m diameter culvert that runs under the road. Not visible in the photo, approximately 120m downstream (below our study reach), is an early sign of some failure of rip rap on the right side of the stream. (*photo: A.J. Reisinger*).

In the restored reach the primary design includes rock walls along banks, bank re-grading, minor floodplain and channel bed re-grading, and outfall repairs with a series of rock step-pools. During baseflow conditions, no additional surface inputs contribute to discharge between the upstream and downstream reaches, allowing for better evaluation of the impact of the new restoration.

Stony Run (STNY, Figure 2.7) is a restored reach on the mainstem of the larger Stony Run Watershed. Land use in the watershed is approximately 73% residential, 17% commercial, 5% open, 1% transportation, and 1% forested, with an estimated 28%

imperviousness. The reach is located in a neighborhood park-like setting with an elevated walking trail, and is adjacent to the athletic fields of the Friends School of Baltimore. This segment of the upper portion of Stony Run drains approximately 2 km^2 of the watershed and was restored from 2008 to 2009. The restoration approach used step-pool sequences, mild stream meanders, and hardened stream banks to slow the flow of water in the stream to a baseflow discharge of 0.49 cubic feet per second. The restoration was designed to accommodate a 100-year discharge of 170 cubic feet per second.

Figure 2.7: An upstream facing view of the study reach at Stony Run (STNY). The reach is straight but the predominantly cobble-to-boulder sized substrate creates significant roughness in the channel. The adjacent floodplain in photo left is wider, more gently sloping and features wetland areas that receive water from neighborhood storm drains *(photo: Tom Doody)*.

Chapter 3: Methods

3.1 Biweekly Data Collection

Discharge and water quality parameters were measured in-situ, and water samples were collected biweekly for laboratory analyses between May 2015 and August 2016 (n=31 sampling dates). Samples of stream water were collected in acid-washed 250 mL HDPE bottles. Each sample bottle was rinsed five times with stream water prior to sampling in order to remove any residue in the bottle. Samples were collected in regions of significant flow velocity and bottles were capped underwater to minimize head space. After collection, the samples were stored immediately on ice and transported back to the lab for processing. Water samples were filtered in the lab through pre-combusted 0.45 micron Whatman glass fiber filters within 12 hours of collection and refrigerated at 4°C until further sample preparation for analyses were conducted.

Temperature (°C), pH, and specific conductance ($\mu S \cdot cm^{-1}$) data were also recorded at the time of each sample collection using a Hanna Instruments HI-98129 multiparameter tester (Hanna Inst, USA). At sites that were not gaged, discharge measurements were made when possible, taking into account safety and proper equipment calibration. For discharge, an appropriate transect was selected at the base of the reach and velocity was measured with a Marsh–McBirney 2000 flow meter (Hach Co., Loveland, CO, USA) using the 60 % depth method with a 5-s averaging interval (Sivirichi *et al.*, 2011). Stream depth measurements (~ 100) were made within each reach over a range of flow conditions in order to develop depth-to-discharge relationships and develop discharge relationships between the ungaged stream reaches and nearby

USGS gages.   For the older restored Minebank Run site (MBRO), discharge relationships were developed with USGS gage 0158397967 at Minebank Run (MBRN). Discharge relationships for both of the Scotts Level Branch sites (SLBR and SLBU) were developed with USGS gage 01589290 on the mainstem of Scotts Level Branch. A discharge relationship for Stony Run (STNY) was developed with nearby USGS gage 01589100 at Herbert Run.

In-situ instrumentation was also installed at each site to continuously measure dissolved oxygen saturation (PME miniDOT loggers, Vista, CA) and photosynthetic active radiation (PAR) to characterize light availability (Odyssey PAR loggers, Christchurch, New Zealand). These data were downloaded seasonally used for stream metabolism calculations of Gross Primary Production (GPP) and Ecosystem Respiration (ER). All metabolism calculations and model simulations were completed by Dr. A.J. Reisinger, a post-doctorate researcher at the Cary Institute, Millbrook, NY.

3.2 Stream Metabolism Data

A single-station open-channel O_2 exchange approach was used to estimate stream metabolism. This was a modification of the daytime regression approach (Atkinson *et al.,* 2008, Grace *et al.,* 2015) in which GPP and ER are modeled as:

$$[DO]_{t+1} = [DO]_t + AI_t^p - R\left(\theta^{(Tt-Tmean)}\right) + K_{DO} \text{ x } \left(1.024^{(Tt-Tmean)}\right) \text{ x } \left([DO]_{sat,t} - [DO]_{modeled,t}\right) \qquad \textit{(Equation 3.1)}$$

where t is the timestep; AIp is the primary production term (mg $O_2 \cdot L^{-1} \cdot d^{-1}$), where A is a constant, I is surface irradiance, and p is an exponent accounting for photo-saturation; R is respiration (mg $O_2 \cdot L^{-1} \cdot d^{-1}$); θ is the temperature dependence of respiration; T_t and T_{mean} are water temperature at time t and average daily water temperature; K_{DO} is the aeration coefficient (d^{-1}); and *sat* and *modeled* refer to dissolved oxygen [DO] at saturation and modeled concentrations, respectively. An updated version of the Bayesian single-station estimation (BASE) modeling approach (Grace *et al.*, 2015) was used to conduct the modeling, which has been modified based on recommendations of Song *et al.*, (2016) to estimate daily GPP and ER. The updated BASE approach employs *Equation 3.1* to use direct concentration of DO rather than a stepwise approach, and uses modeled DO concentration rather than measured concentration to estimate oxygen deficiency for aeration rates. The updated BASE model (BASE v2.0) can be accessed online (https://github.com/dgiling/BASE).

Due to large fluctuations in diel temperature we used BASE to simultaneously model GPP, ER, K,p, and θ. Output from BASE provides GPP and ER in volumetric units. To compare metabolic rates across sites and with previous literature values, we multiplied volumetric rates by mean daily stream depth to convert from volumetric to areal rates (g $O_2 \cdot m^{-2} \cdot d^{-1}$). We also calculated net ecosystem productivity (NEP; g $O_2 \cdot m^{-2} \cdot d^{-1}$) as

$$NEP = GPP + |ER| \qquad \textit{(Equation 3.2)}$$

where |ER| is the absolute value of ER, which is traditionally expressed as a negative value. For each site, we used daily discharge coupled with an empirically derived discharge–depth relationship (unique for each site; data not shown) to estimate mean daily stream depth (Reisinger *et al.*, 2017).

3.3 Nitrogen Uptake Experiments

Nitrogen uptake experiments were conducted in late June to early July 2015, mid November 2015, and late March 2016 in each of the six reaches. A winter series of N experiments were not feasible. In each of these experiments, a short-term addition of a concentrated N solution (with a conservative tracer) was dripped continuously into the stream to elevate concentrations of both N and the conservative tracer. When concentrations reached when in-stream concentrations reached a stable maximum (a plateau) near the input site, stream samples were collected at downstream stations set up at equidistant intervals downstream of the injection . These nitrogen uptake experiments are inexpensive, short-term analyses that can be used to compare N uptake between streams or at various times within one stream (Mulholland *et al.,* 2002, Tank *et al.*, 2006).

3.3.1 Uptake Calculation Methods

From the nutrient experiment data, a suite of nutrient uptake metrics were calculated in order to examine how the uptake rates, lengths, and velocities are related to restoration status, nutrient concentrations, and biological processes monitored with GPP and ER. The restored streams were expected to have reach characteristics that decreased stream velocities and therefore had longer residence times, which may alter nutrient uptake in the stream channel.

First, the N concentration data from the injections were plotted against stream distance and were fitted to an exponential decay model

$$\ln N_X = \ln N_0 - kx \qquad \textit{(Equation 3.3)}$$

where N_X is the background-corrected plateau N concentration at x meters downstream of the injection point, N_0 is the background-corrected N concentration at the site of injection (designated as 0m downstream), and k (m^{-1}) is the decay constant (Newbold *et al.,* 1981, Stream Solute Workshop 1990). A conservative tracer is added concurrently to account for dilution along the reach and N concentrations are divided by plateau background-corrected tracer concentrations at each sampling station. Linear regression is then used to calculate the decay constant (k) and test for significance of the relationship (Figure 3.1).

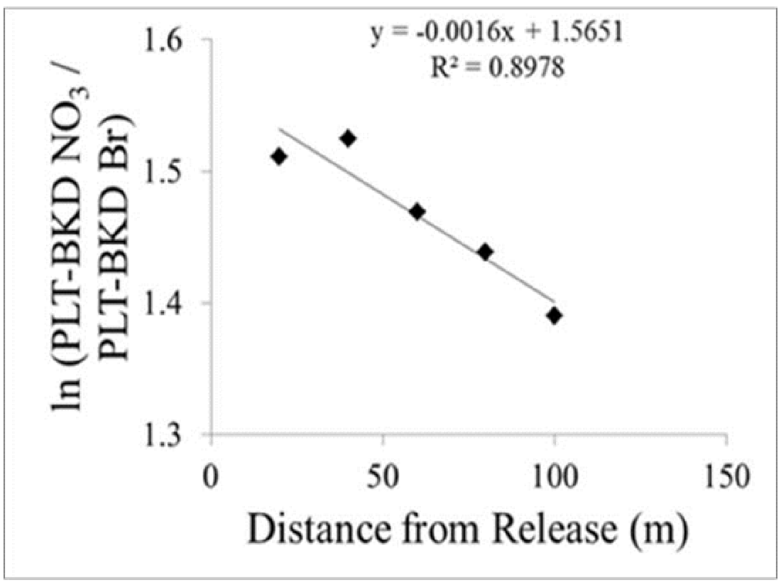

Figure 3.1: Sample regression results to calculate the decay constant *k.*

Uptake length (S_w) is calculated as the inverse of the decay constant:

$$S_w(\mathrm{m}) = k^{-1} \qquad \textit{(Equation 3.4)}$$

Uptake length can be considered the distance a single molecule of N would travel in the stream before it is either biologically removed or temporarily taken up before being regenerated and transported further downstream.

Because uptake length is strongly influenced by discharge (Q), which may vary among streams or within a stream over time, N uptake velocity (V_f, in mm·min^{-1}) was also calculated. N uptake velocity is the biotic demand for N relative to in-stream concentration, and is functionally the velocity at which N is vertically removed (drawn down) from the water column via biological consumption. This helps isolate the biological component of uptake despite hydrologic differences in streams and normalize S_w for effects of varying velocity (Runkel 2007). Uptake velocity is calculated as:

$$V_f(\text{mm}\cdot\text{min}^{-1}) = Qk/\text{w} \qquad \textit{(Equation 3.5)}$$

where Q (m^3·min^{-1}) is discharge, k (m^{-1}) is the decay constant, and w (m) is mean stream wetted width. Because the experiments are performed at constant Q, the uptake velocity is considered a constant linear rate.

Finally, the areal uptake rate (U, mgN·m^{-2}·min^{-1}) of N is calculated:

$$U = V_f N_b \qquad \textit{(Equation 3.6)}$$

in which V_f is uptake velocity and N_b is the background N concentration. This incorporates the availability of N already in the stream. When these parameters of N uptake (Sw, Vf, U) are used together, a greater understanding of the factors controlling uptake in stream ecosystems is possible, as uptake can then be understood relative to stream size, discharge, and nutrient availability.

3.3.2 Uptake Field Methods

First, the full length of the reach was measured from an appropriate point upstream in the reach from which the solution would be dripped when the injection began. This was considered the 0m position. Five equidistant stations were then marked in the reach as sampling points to collect water and measure RWT concentrations. The initial intent was to use 100m reaches at each site, with the five stations at 20m, 40m, 60m, 80m, and 100m downstream of the injection. However, after the first season of injections, times to plateau were much longer than anticipated in some of the reaches, hindering our ability to successfully complete a full experiment before dusk. Subsequently, some reaches were shortened to 75-80m and equidistant sampling stations were selected every 15-16 meters downstream. To establish baseline water chemistry, 60 mL of streamwater were sampled at each station before the nutrient injection. Samples were collected using acid-washed HDPE plastic syringes and filtered through 0.45 micron glass fiber filters. Separate syringe and filter housings were used at each sampling station. Syringes are sample-rinsed three times prior to sample collection. After collection, an aliquot of filtered sample water was used to sample rinse the collection container, a 60mL HDPE centrifuge tube. The remaining water was filtered into the centrifuge tube, capped and stored on ice in the field until it could be transported back to the lab.

The nutrient uptake experiments require constant discharge conditions, therefore, all the experiments were conducted during baseflow conditions. If rain events significantly altered discharge during the N injection period, the experiment was stopped and rescheduled for another date after the stream returned to baseflow conditions.

Discharge was measured just below the reach and/or the gaged discharge was recorded. The injection solution was prepared based on discharge, the desired drip rate into the stream, and the desired increase in background nitrate concentrations. During each injection, NO_3^- concentrations were increased by 0.2 mg NO_3^-/L. The increase in concentration (depending on the stream, 5-20% above baseline NO_3^- readings) was intentionally low to avoid over-saturating the stream, which may have yielded inaccurate measurements of uptake in the reach. Typically, 10L of streamwater was collected in a carboy or dark bucket. The solution is prepared from a nitrate salt ($NaNO_3$), a bromide salt (NaBr), and rhodamine WT. Due to the high specific conductance values and high chloride concentrations, the bromide was used as the conservative tracer. The (RWT) tracer was also added at non-toxic levels (generally in the 15-20 ppb range), to observe the location of the plume. Ambient levels of RWT were measured prior to the injections. Salts are pre-weighed and divided in vials/bags in 5L/s aliquots. For every 5 L/s of discharge, 36.36g of $NaNO_3$ and 7.73g of NaBr were added to the carboy. Once the solution had been fully mixed and all salts were in solution, a small volume of RWT (~1.5mL per 5 L/s of discharge) was added to the carboy and mixed (Figure 3.2a). Finally, an unfiltered 60 mL sample of the injection solution was collected and stored for later analysis.

The solution was pumped into the stream at a consistent drip rate of 50mL/min (Fig 3.2b). The rate was measured and confirmed twice before beginning the injection. Once the injection was started and the time noted, the drip rate was checked every 30-60 minutes to ensure consistency. Rising/plateau levels of RWT were monitored regularly during experiments using Hydrolab Water Quality Multiprobes fitted with RWT sensors

(Fig 3.2c) This monitoring was performed at each of the five stations as an in-situ indicator of when the stream was fully mixed and the stream had reached new NO_3^- plateau conditions. The time of plateau was recorded and water samples were collected in triplicate at each station from downstream to upstream using the same syringe-sampling method.   Samples were stored on ice while in the field. After all samples had been collected, the pump was turned off and the falling limb of the injection was monitored using the RWT probes until near-baseline conditions were reached.

Figure 3.2: Stages of setup/monitoring for nutrient addition experiments. Clockwise from top left: (a) shows the mixing of the solution and addition of RWT; (b) demonstrates the release of the solution at a constant rate with a visible plume being dipersed through the stream until fully mixed; (c) shows data sondes used to regularly monitor rising levels of RWT in the stream.

After all of the samples were collected and data recorded were made, 10 transects of the channel were taken (wetted width and 5-10 depths per transect) and substrate was characterized based on size class. These channel measurements were made after the injection because they required entering the stream and disturbing the substrate, albeit as minimally as possible. After all monitoring and data collection were completed, any remaining injection solution was pulsed into the stream and instruments were rinsed

3.4 Biweekly Sampling Analytical Methods

Biweekly water samples were prepared and analyzed for several water quality metrics. A Shimadzu Total Organic Carbon Analyzer (TOC-V CPH/CPN) was used to measure total dissolved nitrogen (TN), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC). UV absorption levels were measured with a Shimadzu UV-1800 Spectrophotometer. Nitrate concentrations were measured with a Lachat QuikChem® flow injection system. Base cation concentrations were measured with a Shimadzu 9820 ICP-ES Atomic Emission Spectrometer

3.4.1 Carbon and Nitrogen

Filtered samples are poured into acid-washed, ashed 24mL glass vials and capped with no head space. The vials are placed on the autosampler, along with premixed standards used to calibrate the instrument before each sample run. For DIC, the standard is a 100 mgC/L solution of sodium hydrogen carbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3) and milliQ water. For DOC and TN, a combined standard solution of 20mgC/L and 20mgN/L is prepared with potassium nitrate (KNO_3), potassium hydrogen phthalate ($C_8H_5KO_4$), 1M HCl, and milliQ water. All standards are internally diluted by the instrument to create a six-point calibration curve for DIC (100, 50, 20, 10, 5, and 0 mg/L) and a five point calibration curve for the combined DOC/TN (20, 10, 5, 2.5, and 0 mg/L). A blank sample of milliQ water is used as the 0 mg/L sample in the curves. Our lab practice is to calibrate and measure all samples first for DIC, then calibrate and measure for TN and DOC. Each sample is measured three times and a mean concentration is reported. Methods for all sample analyses are set to measure and report the best three of five injections (if necessary), with a maximum tolerance of a 2% coefficient of variation. If this level of dispersion is exceeded among the closest three measurements, an invalid reading is reported. For QA/QC purposes, standards and blanks are checked every 10 samples and at the end of each run. At least one random duplicate sample was also checked in each run. Ideally, checked standards measured throughout the run are within 5% of the concentration of the standard, but 10% would be considered acceptable. If a checked standard value differs from the standard concentration by more than 10%, all samples must be re-analyzed.

3.4.2 Ultraviolet Absorption

Measuring a water sample's absorbance of ultraviolet (UV) light at 254nm is of interest for the calculation of specific ultraviolet absorbance (SUVA,) a normalization of the UV 254nm value to dissolved organic carbon (DOC) in the sample. This is a potential indicator of the lability or recalcitrance of the carbon in the water. The spectrophotometer is calibrated using an empty quartz cuvette and a second cuvette of milliQ water to establish baseline conditions. All cuvettes must be completely clear of any residue, streaks, or condensation which could alter the accuracy of the analysis. Once calibrated, the instrument method is designed to analyze a single sample at a time for 1 minute across a 200nm to 900 nm spectrum. The blank cuvette is removed and a cuvette with an aliquot of filtered sample is placed in the instrument. Results are single numbers that report an absorbance per meter of path length at each wavelength. Duplicate samples and milliQ were analyzed after every 10 samples to ensure minimal instrument drift.

3.4.3 Nitrate

Filtered samples are poured into acid washed and ashed 10mL glass vials. Four reagents are prepared for use in the analysis: 15N sodium hydroxide (NaOH), an ammonium chloride buffer $(NH)_4Cl + Na_2EDTA*2H_20$) adjusted to pH 8.5, sulfaniliamide color reagent (H_3PO_4 + sulfanilamide + NED), and a diluted 0.2% sulfuric acid solution. Solutions are stable for one month. This method is a two-stage process, which measures first the nitrate+nitrite, then a reanalysis of only nitrite. The difference between the two yields the nitrate concentration.

Separate nitrate and nitrite working standards are made on the day of the analysis, beginning with the high range working standard of 20 mgN/L made with potassium nitrate (KNO_3) and sodium nitrite ($NaNO_2$), respectively. Additional working standards are made by dilution at the following concentrations (in mg N/L as NO_3^- or NO_2^-): 10, 5, 2.5, 1, 0.5, 0.25, 0.1, 0.05, and 0.025. Injected samples and reagents are merged in a manifold (reaction module). The nitrate is reduced to nitrite as the sample is passed through a copperized cadmium column. The reduced nitrate plus original nitrite is then determined by diazotizing with the sulfanilamide, followed by coupling with the NED. This creates a soluble magenta dye that is read at 520nm. Prior to analyzing for nitrite alone, the appropriate standards are replaced and flowpath of the samples through the manifold is switched by closing a valve, removing the cadmium column from the reaction. (Lachat Instruments, Milwaukee, WI). Each sample is injected and measured three times, generating concentrations for each and allowing for calculation of mean and RSD. Duplicate samples, blanks, and standard checks are measured every 10 to 20 samples, depending on the size of the run.

3.4.4 Base Cations

Samples must be acidified with nitric acid (HNO_3) to pH<2 prior to analysis to preserve the sample and prevent flocculation. Because Baltimore streams are known to have elevated chloride and base cation levels, analyses for Ca^{2+}, Mg^{2+}, Na^+, and K^+ were performed using the radial view of the ICP-OES, which is preferred for high concentration elements. Argon is used as the gas supply. Our method uses a set of standards diluted from a high concentration stock that contains 1000mgCa/L, 1000mgNa/L, 500mgMg/L, and 250mgK/L. Dilutions of the stock are made at six levels to create standards used in creating a calibration curve: 10:1, 13.33:1, 20:1, 40:1, 100:1, and 200:1. Once calibration curves have been examined and adjusted to achieve 0.999 R^2 for all elements, sample analysis can begin. Our method requires four measurements of each sample to avoid any dilution of the initial sample injection from milliQ water used to rinse in between samples (potential timing issue). For QA/QC, a subset of standards and blanks were checked every 10-20 samples depending on the length of the sample run. Post-run processing includes examination of all potential wavelengths and intensities for each element, including adjustment for baselines, integration range, and peak intensity. Output of all quantitative elemental concentration data from each injection is used to calculate a mean and RSD for each sample.

3.5 Data Synthesis and Statistical Methods

3.5.1 Nutrient Uptake

To evaluate hypotheses 1, 2 and 3 regarding areal uptake rates, uptake lengths, and uptake velocities between restored and unrestored streams preliminary Analyses of Variance (ANOVAs) were performed at α=0.05 and α=0.10. Uptake length (S_w) and uptake velocity (V_f) data were log transformed, and areal uptake rate (U) data square root transformed prior to analyses. Post-hoc analyses were then completed using a Fishers Least Significant Difference for ANOVA results that showed a significant result.

In addition to ANOVA, the three uptake metrics were independently evaluated with stepwise multiple linear regression in R version 3.3.2. These analyses were performed without the parameter of restoration status in order to determine if comparable independent variables comprised some of the best fit models across all sites. A suite of hydrological, biological, and geochemical explanatory variables were considered, but degrees of freedom were limited due to a small sample size (n=15). Therefore, subsets of the full suite of potential explanatory variables (Appendix II, Table A, B, C, D) were tested in multiple model runs.

First, the full model is defined using all possible parameters. Once the full model is defined, model residuals are inspected for assumptions of linearity by examining residual plots across multiple variables. Plots of residual vs. fitting parameters should be random and have a mean of approximately zero. Histograms of residuals are also plotted to determine whether or not their distributions are normal or skewed. The model is then iteratively tested for any variables that may be multi-collinear through the application of variance inflation factors (VIFs). The VIF quantifies how much the variance of a regression coefficient is increased because of collinearity. Predictor variables with high levels of multicollinearity should be removed from the regression to improve the assessment of the model for effects of independent variables on the variable of interest. The VIF function is repeated in each model run until all values for remaining predictors are ideally < 10.

After these criteria are met, the final model is run with the *'glmulti'* function in R, which evaluates every possible combination of the model and compares them based on the Akaike Information Criterion (AIC). The AIC evaluates the quality of the model relative to all other models given the available data, not the absolute quality of the model to support or refute a null hypothesis. The models with the lowest AIC numbers are considered the "best fit." A criterion of best fit models was set at those with a ΔAIC<2, meaning models with AIC values within 2 AIC of one another should be considered further. All model results are written with supporting information for consideration, including summary statistics of relative weight (proportional support), p-value, R^2, F-statistic, and degrees of freedom.

3.5.2 Biweekly Water Chemistry and Stream Metabolism

Bi-weekly sampling data and stream metabolism data were also evaluated through stepwise multiple linear regression.. Three response variables, nitrate (NO_3^-), dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC), were independently modeled using data across all sites and in each individual site to determine "best fit" models among our independent predictor variables. The full data set consists of six sites x 31 sampling dates x 20 variables: NO_3^-, DOC, DIC, total dissolved nitrogen (TN), calcium, potassium, magnesium, sodium, total cation concentration, specific conductance, discharge, temperature, dissolved oxygen, pH, UV absorption, SUVA, gross primary production (GPP), ecosystem respiration (ER), net ecosystem production (NEP), and production to respiration ratio (P:R). Sampling dates that did not have a full complement of data (due to instrument errors, contaminated samples, or unmodelable metabolism)were not included in model runs.

Chapter 4: Results

4.1 Seasonal Nitrogen Uptake

Of the 18 attempted nutrient uptake experiments (6 sites x 3 seasons), 15 were successful and yielded usable uptake data. The three failed injections were in the Minebank Run reaches: late June 2015 (MBRN), November 2015 (MBRO), and March 2016 (MBRO). Failure was not confirmed until post-run data were reviewed, but in all cases the problems were caused by technical glitches such as unexpected drops in pump rate or faulty sonde sensors that gave inaccurate readings when determining plateau conditions. Three other injections were stopped and rescheduled due to minor rain events.

4.1.1 ANOVA Results

ANOVA evaluation (α=0.05) of uptake lengths (S_w) between restored vs unrestored streams yielded a *p-value*=0.33 and F 1.02 < F_{crit} 4.67. Statistically, there was no significant difference between the mean N uptake lengths of restored vs unrestored urban streams (Figure 4.1). Data transformations did not yield different results. Because significance was not detected, no post-hoc test was performed. Hypothesis 1, stating that restored streams would have significantly lower uptake lengths, is therefore rejected.

ANOVA evaluation of uptake velocity (Vf) was performed twice at different confidence levels. At α=0.05 and 13 degrees of freedom there was no significant difference between the uptake velocities of restored and unrestored streams, with a *p-value*=0.086 and F 3.46 < F_{crit} 4.67. Based on this result, hypothesis 2 would also be rejected, citing no significant different in the mean uptake velocities based on restoration status. However, a retest at α=0.10, F 3.46 > Fcrit 3.14. Results of a post hoc Fisher's LSD test show that the difference in the mean uptake velocities (16.08) was greater than the least significant difference (15.09) and the null hypothesis is rejected. However, hypothesis 2 is not supported as stated, because the mean N uptake velocity was significantly greater in the unrestored reaches, which is opposite of what was hypothesized.

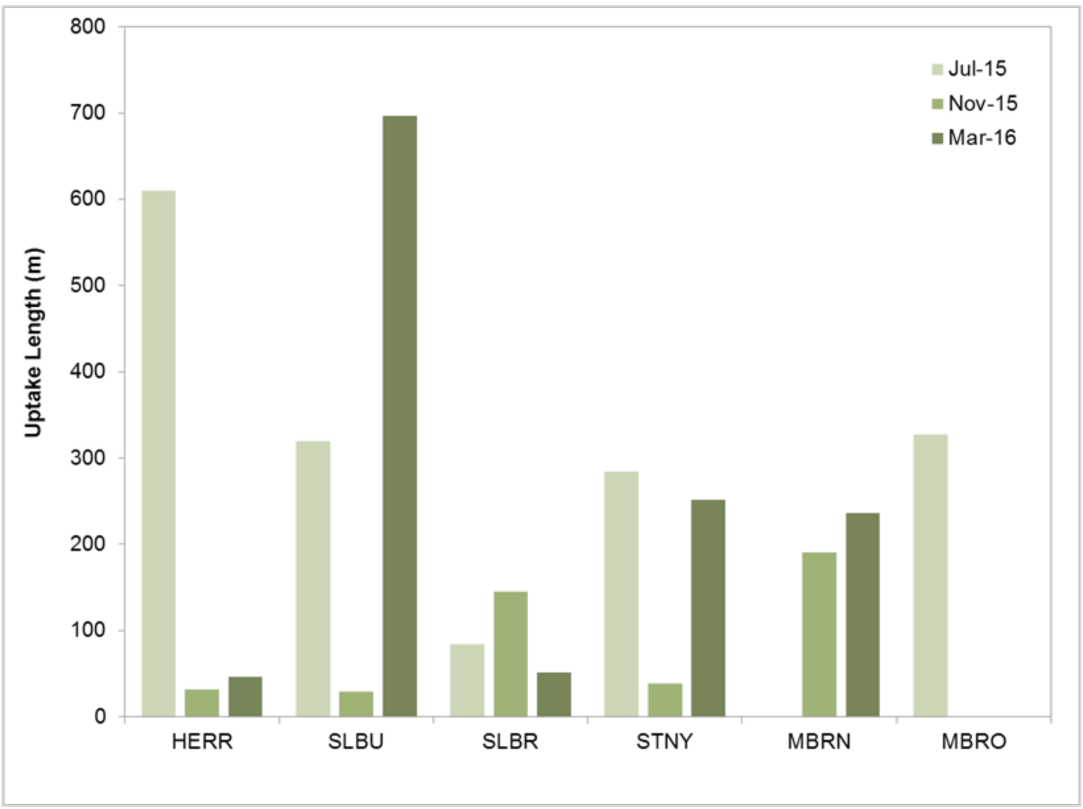

Figure 4.1: Uptake length across all 15 nutrient injections. Both unrestored reaches show the greatest variability in uptake length values, but no discernible seasonal pattern is evident across all sites.

ANOVA evaluation of areal uptake rate (U) was also performed twice at different confidence levels. Data we square root transformed. At α=0.05 and 13 degrees of freedom there was no significant difference between the uptake velocities of restored and unrestored streams, with a *p-value*=0.065 and F 4.06 < F_{crit} 4.67. Based on this result, hypothesis 3 would also be rejected, citing no significant different in the areal uptake rates based on restoration status (Figure 4.2).

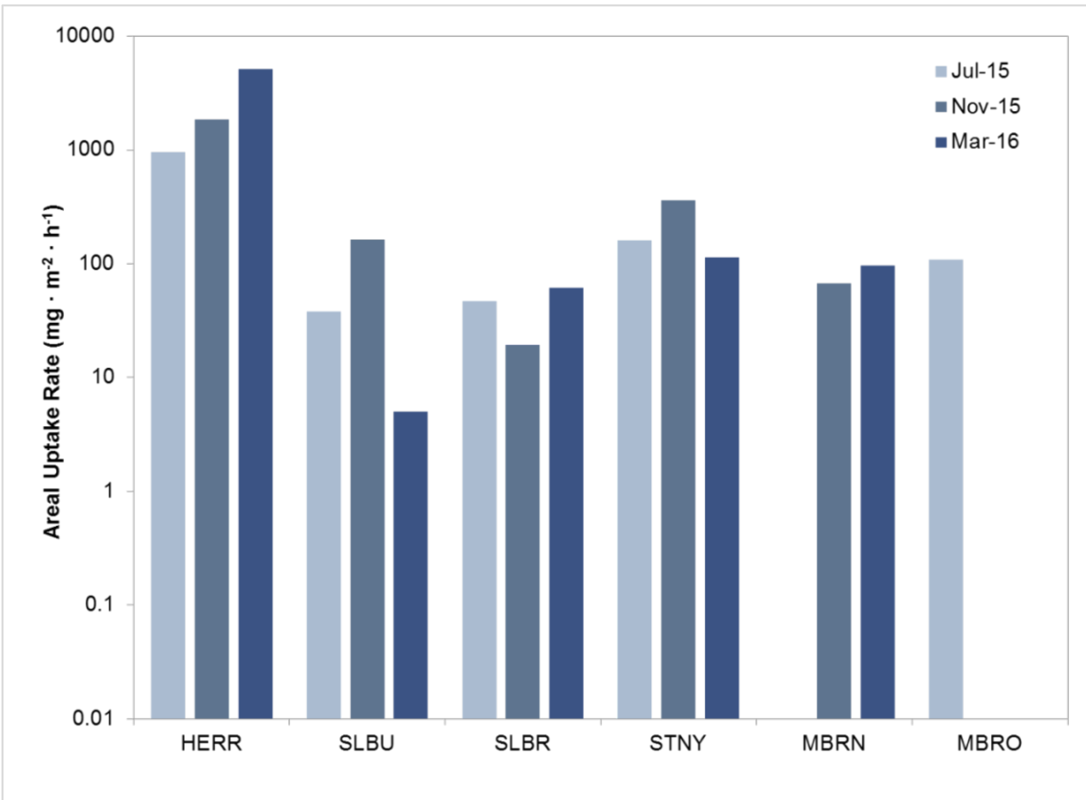

Figure 4.2: Areal uptake rate from all 15 nutrient injections. Unrestored reaches demonstrated the greatest relative variability across seasons (almost an order of magnitude at SLBU and HERR). No consistent relationship is seen when comparing restored vs unrestored reaches, or spring vs summer vs fall sampling dates.

However, a retest at α=0.10, F 4.06 > F_{crit} 3.14. Results of a post hoc Fisher's LSD test show that the difference in the means of the square roots of the areal uptake rates (17.77) was greater than the least significant difference (15.38) and the null hypothesis is rejected. However, hypothesis 3 is not supported as stated, because the mean N areal uptake rate was significantly greater in the unrestored reaches, which is opposite of what was hypothesized.

4.1.2 Multiple Linear Regression Results

Nitrate uptake experiments were conducted at baseflow conditions in each stream, but other conditions varied from reach to reach and in different seasons. In addition to watershed characteristics (Table 1.1) several hydrological, biological, and geochemical factors may also contribute to the results of the uptake experiments (Appendix Tables X,).   A subset of these data were used to attempt to individually model the uptake metrics with multiple linear regression. Because of the small dataset (n=15), a maximum of 10 explanatory variables were used in the full models in order to retain a few degrees of freedom. All combinations of the suite of variables were tried in order to include a balance of the hydrological, biological, and geochemical factors. The final full model selection included the following independent variables:

V_w: average stream velocity/wetted width

Q_BAV: discharge/(bed area*velocity)

Qmax_Qdays: 10 day antecedent discharge condition

D84: substrate 84th percentile grain size diameter (a roughness coefficient)

Cations: sum of base cation concentrations

NO_3^-: nitrate concentration

DOC: dissolved organic carbon

DIC: dissolved inorganic carbon

GPP: gross primary production

ER: ecosystem respiration

The ratio of stream velocity to wetted width of the channel is a parameter of the geomorphology of the stream and how it might accommodate increased flow. The 10-day antecedent discharge condition attempts to quantify the impact of recent storms on channel biogeochemical processes. This variable was calculated using the peak discharge from the 10 day period prior to each experiment, divided by the discharge on the day of the experiment. This Q ratio was then divided by the number of days that passed between the peak event and the day of the experiment. I incorporated the number of days between the two measurements to give some sort of weight to recovery time. For example, a very high Q one or two days before the experiment should affect uptake more than a moderate Q seven days before the experiment.

Uptake Metrics--Multiple Linear Regression Model Results

Rersponse Metric	Model	Rank	w_i	ΔAIC	R^2
Uptake length (S_w)	Y = 156.04 + 15.96*$Q_{max}Qdays$ + 153.95* D_{84}	1	0.21	0	0.17
	Y = **278.8** - 432.3*D_{84}	2	0.17	0.42	0.04
	Y = **426.25** - 579.2*V_w + **24.8* $Q_{max}Qdays$** - 1171.3* D_{84}	3	0.12	1.20	0.31
Uptake velocity (V_f)	Y = -3.23 + 78.09*V_w – **2.06* $Q_{max}Qdays$** + 21.03* D_{84}	1	0.29	0	0.89
	Y = 0.65 + **72.48*V_w – 2.02* $Q_{max}Qdays$**	2	0.26	0.18	0.90
Areal uptake rate (U)	Y = -363.5 +**5395*V_w – 138.2* $Q_{max}Qdays$** +2297* D_{84}	1	0.61	0	0.85

Table 4.1: Multiple linear regression models chosen with Akaike's Information Criterion predicting uptake metrics. Shown are up to three best-fit models (ΔAIC<2) for the response variable. Rank is the model rank relative to all possible models, w_i is the weighting evidence that an individual model is the best among all competing models, and R^2 is the coefficient of determination for each model. Variables in bold have coefficients that were statistically significant ($p<0.05$).

The uptake length regression did not yield statistically significant results in two of the three best fit models, in which the antecedent discharge condition and grain size data were considered the two variables in the best fit. However, neither of the coefficients for these were at an acceptable level of significance. The third best fit within the $\Delta AICc<2$ criterion included a third term, velocity/width, and did find a significant positive correlation with the antecedent discharge condition. This indicates that longer uptake lengths might be significantly related to higher maximum discharge events prior to the nutrient injection and/or fewer days after the maximum discharge event. The weighting assigned to any of the three models was relatively low, as were R^2 values. Additionally, the confidence in any of the three models is low, with $p>0.05$ in all cases.

Uptake velocity regressions yielded two best fit models that also included the same hydrologic variables of antecedent discharge conditions, velocity divided by width, and grain size. However, the relationship with antecedent discharge was inverse. Both models had low p-values $<<0.05$ and variables and coefficients that were significant. In this case, the correlation is very high ($R^2=0.90$) but the weights assigned to the best models are moderate (<0.30).

Areal uptake rate regressions yielded only one model fit and it had only hydrologic variables in the equation. There was a significant direct relationship with average stream velocity divided by wetted width of the channel (Figure 4.3), and a much weaker inverse relationship with antecedent discharge conditions. The is the only model among all three uptake metrics that has both high correlation and weight.

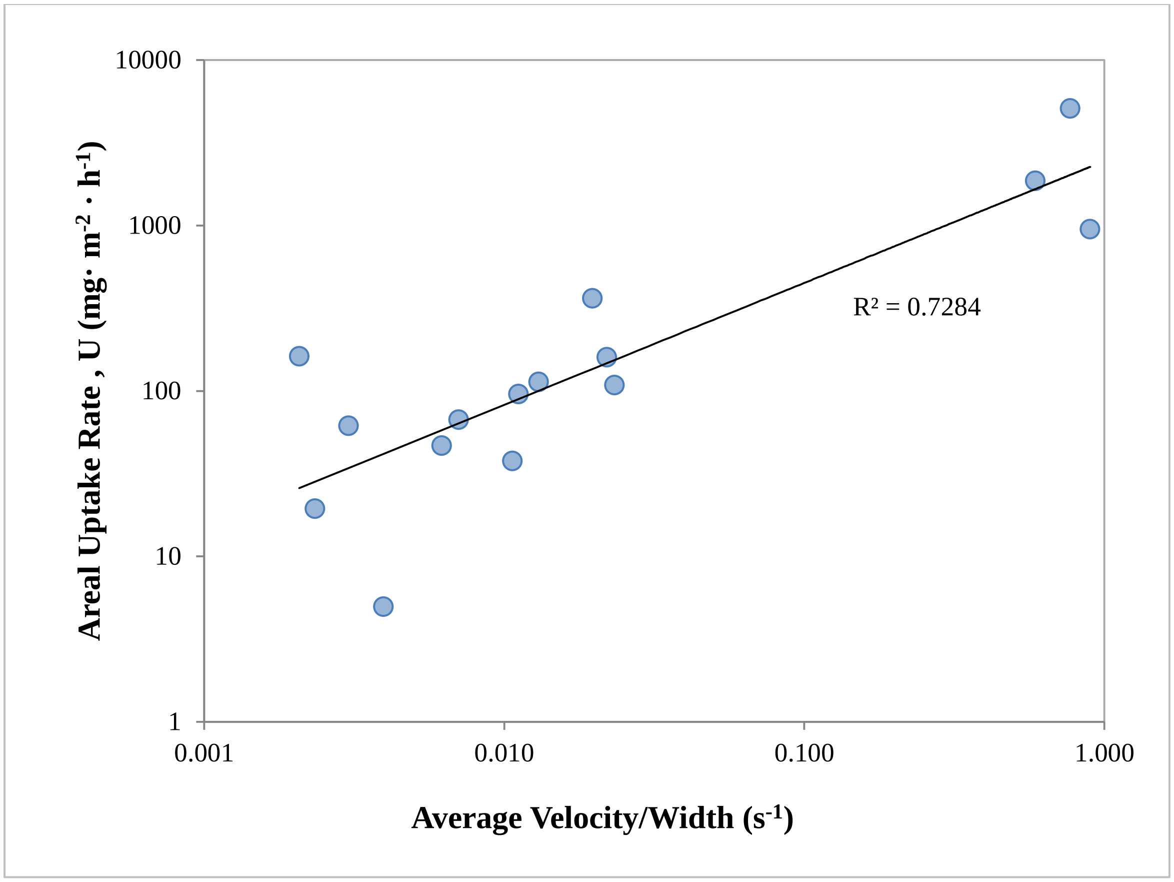

Figure 4.3: Of the hydrologic variables, only a velocity/width parameter had a significant direct relationship with areal uptake rate

Finally, cation data from background water chemistry analyses were also compared directly to uptake metrics to determine any relationship that may influence nitrogen uptake. This is a small part of the exploratory work done on the relationships between carbon, nitrogen, and several factors that may influence their concentrations and cycling through in-stream processes. Only potassium (K^+) showed a potentially significant direct power law relationship with individual areal uptake rate across all sites, with an R^2=0.40 (Figure 4.4).

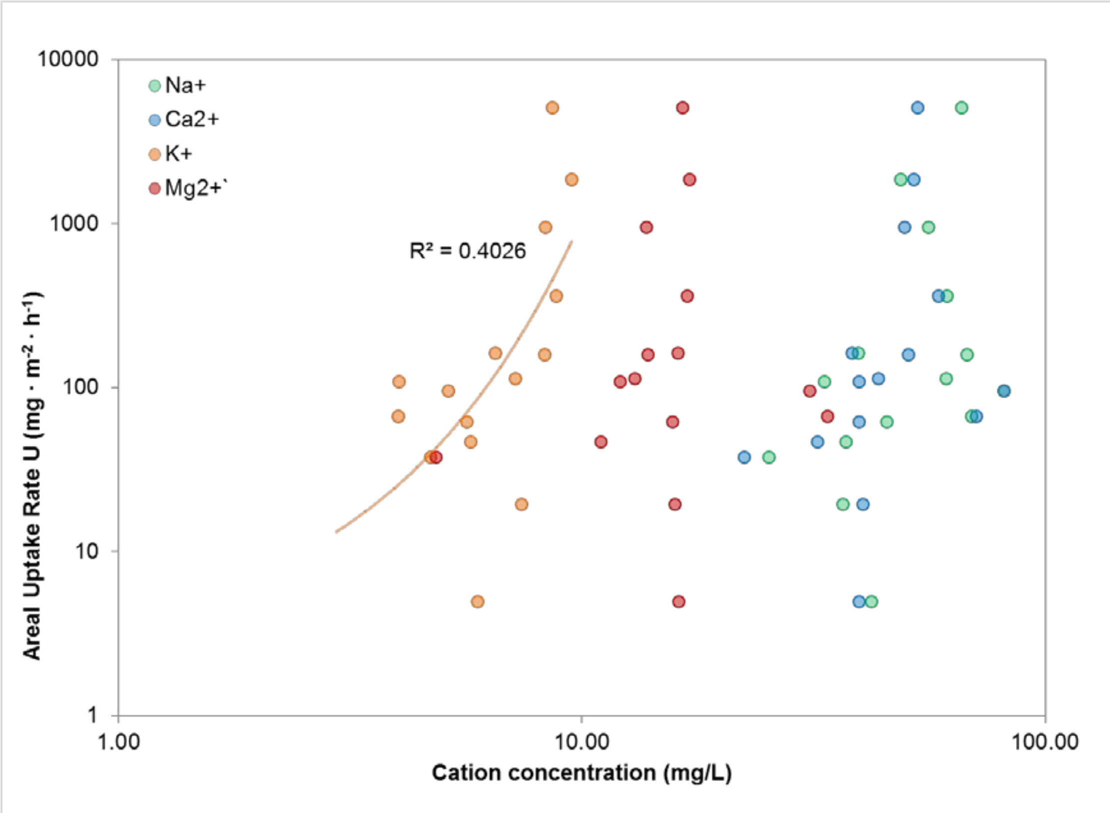

Figure 4.4: Areal uptake rate of NO_3^- across all sites has a significant power law relationship with K^+ concentrations but not with other base cations on dates of nutrient injections. K^+ is a significant biological factor in regulating nitrate uptake in plants and soils.

4.2 Relationships between Nitrate Concentrations and Geochemical, Hydrological, and Biological Factors

Statistical analyses indicates that nitrate concentrations were explained by geochemical, hydrological, and biological factors in the streams, but the relative importance of these factors varied by site. For example, the sum of base cations, dissolved inorganic carbon, and dissolved oxygen were typically significant components of the AIC model with the greatest weights (Table 4.2). The sum of base cations was used as a predictor variable in order to eliminate multicollinearity among individual base cations without sacrificing the potential influence of the cations in the model runs. The number of potential best-fit models for nitrate across all sites ranged from one (SLBU, MBRN) to three (HERR), but the weight associated with the best fits were variable across sites. Generally, those models that may overfit by including a larger number of significant explanatory variables in the final model have the highest weighting. Modeling the sites individually was done to attempt to determine if nitrate concentrations were explained by different predictors at certain sites with different levels of significance.

Nitrate (NO_3^-) response variable					
Site	Model	Rank	w_i	ΔAIC	R^2
HERR	Y = 0.31 + **0.09*DIC** – 0.15*ER	1	0.15	0.00	0.63
	Y = -0.14 + **0.11*DIC** + 0.002*GPP	2	0.10	0.85	0.61
	Y = 5.46 – 0.66*pH + **0.09*DIC** - 0.23* ER	3	0.06	1.79	0.64
MBRN	Y = 0.33 + **0.006*CationSum** + 0.002*DO	1	0.36	0.00	0.72
MBRO	Y = **-0.48** + **0.01*CationSum** + **0.05*DO** + **0.02*DIC** – **0.16*GPP** + 0.03*ER	1	0.50	0.00	0.94
	Y = **-0.79 + 0.01*CationSum + 0.06*DO + 0.03*DOC + 0.02*DIC – 0.19*GPP + 0.05*ER**	2	0.40	0.45	0.95
SLBR	Y = -1.59 + **0.04*CationSum** + 0.05*DO - 0.06*GPP	1	0.23	0.00	0.73
	Y = -1.49 + **0.04*CationSum** + 0.05*DO – 0.08*ER	2	0.20	0.30	0.72
SLBU	Y = **4.03 – 0.06*Q – 0.03*DO - 0.19*DOC – 0.22*GPP**	1	0.76	0.00	0.98
STNY	Y = **-1.01 + 0.04*CationSum** + 0.04*DO – 0.11*GPP	1	0.31	0.00	0.92
	Y = **-1.18 + 0.04*CationSum** + 0.03*DO - 0.07*ER	2	0.25	0.46	0.91

Table 4.2: Stepwise multiple linear regression models chosen with Akaike's Information Criterion predicting nitrate concentrations. Shown are up to three best-fit models (ΔAIC<2) for the response variable. Rank is model rank relative to all possible models, w_i is the weighting evidence that an individual model is the best among all competing models, and R^2 is the coefficient of determination for each model. Predictor variables and their coefficients in bold are those which are statistically significant in the model.

Although data show that nitrate was consistently the highest fraction of total dissolved nitrogen (TDN) in the streams, the same stepwise multiple linear regression models were run with TDN as the response variable (Table 4.3). In all cases the basic structure of the best fit models was almost identical to those for nitrate. Primary explanatory variables were related with the same directionality, but exceptions were at MBRO and SLBU, in which nitrate models were more complex and/or more heavily weighted.

Total Dissolved Nitrogen (TDN) response variable					
Site	Model	Rank	w_i	ΔAIC	R^2
HERR	Y = 0.82 + **0.07*DIC** – 0.12*ER	1	0.12	0.00	0.52
	Y = 0.46 + **0.08*DIC** + 0.005*GPP	2	0.09	0.53	0.50
	Y = -0.02 + 0.07*DO + **0.08*DIC** - 0.10* ER	3	0.05	1.74	0.54
MBRN	Y = **0.74** + **0.005*CationSum** - 0.003*DO	1	0.39	0.00	0.64
MBRO	Y = **0.69 + 0.006*CationSum +** 0.006*DO	1	0.19	0.00	0.48
	Y = **1.35** + **0.0005*CationSum – 0.002* Q**	2	0.17	0.13	0.37
	Y = **0.81 + 0.004*CationSum** – 0.0005*Q + 0.005*DO	3	0.10	1.24	0.51
SLBR	Y = -1.16 + **0.03*CationSum** + 0.07*DO - 0.06*GPP	1	0.18	0.00	0.57
	Y = -1.07 + **0.03*CationSum** + 0.07*DO – 0.08*ER	2	0.16	0.27	0.56
SLBU	Y = **3.85 – 0.06*Q –** 0.009*DO - **0.13*DOC –** 0.16*GPP	1	0.33	0.00	0.92
	Y = **3.83 – 0.05*Q** – 0.003* DO – **0.13*DOC** - 0.10*ER	2	0.28	0.31	0.92
STNY	Y = **-**1.03 **+ 0.03*CationSum** + 0.07*DO – 0.09*GPP	1	0.25	0.00	0.86
	Y = -0.91+ **0.03*CationSum** + 0.06*DO - 0.06*ER	2	0.23	0.45	0.86

Table 4.3: Stepwise multiple linear regression models chosen with Akaike's Information Criterion predicting total dissolved nitrogen concentrations. Shown are up to three best-fit models (ΔAIC<2) for the response variable. Rank is the model rank relative to all possible models, w_i is the weighting evidence that an individual model is the best among all competing models, and R^2 is the coefficient of determination for each model. Predictor variables and their coefficients in bold are those which are statistically significant in the model.

Across all sites, nitrate concentrations showed significant linear relationships with Ca^{2+} and Mg^{2+} concentrations, but the linear relationships were distinctly different for sites draining carbonate *vs.* non-carbonate lithology (Figures 4.5 and 4.6).

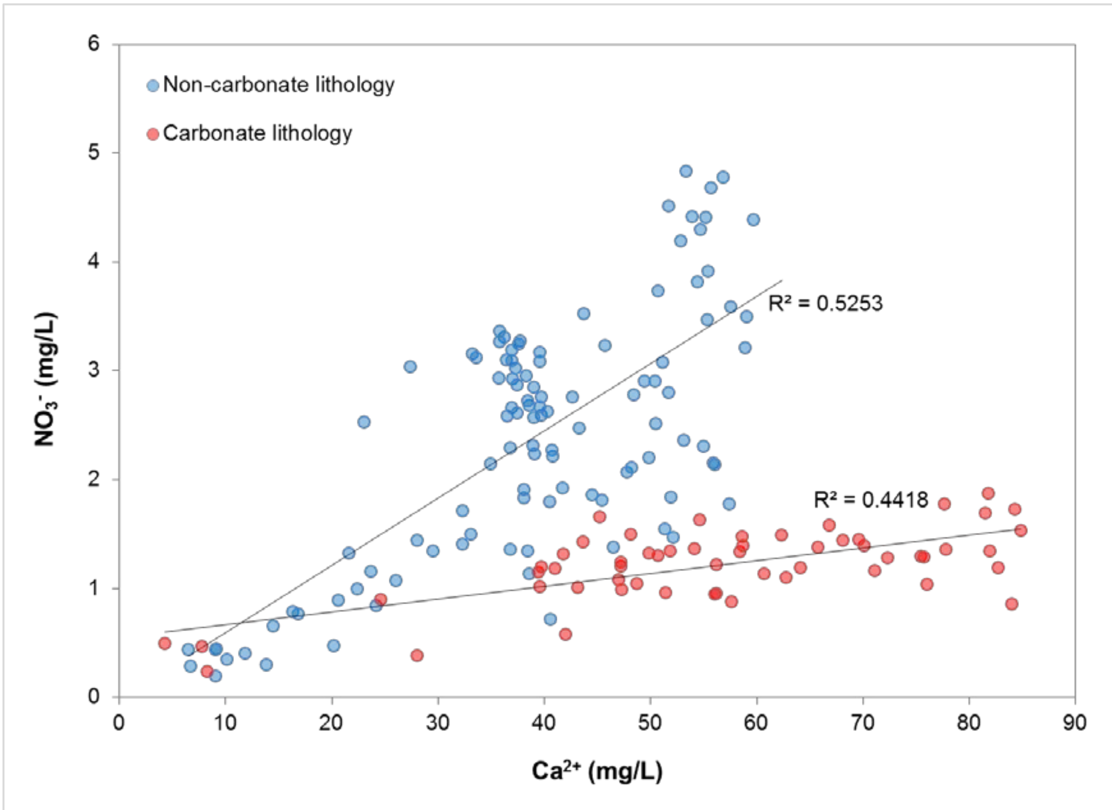

Figure 4.5: The significant linear relationship between NO_3^- and Ca^{2+}concentrations is distinctly different in study sites based on lithology. The increased natural availability of Ca^{2+} as $CaCO_3$ in the Minebank Run sites (MBRN and MBRO) that drain the Cockeysville Marble correlates with significantly lower nitrate levels. Data near the origin are generally from storm events in which both NO_3^- and Ca^{2+} are significantly diluted by precipitation and subsequent runoff. Higher concentrations of both Ca^{2+} and nitrate are from baseflow conditions.

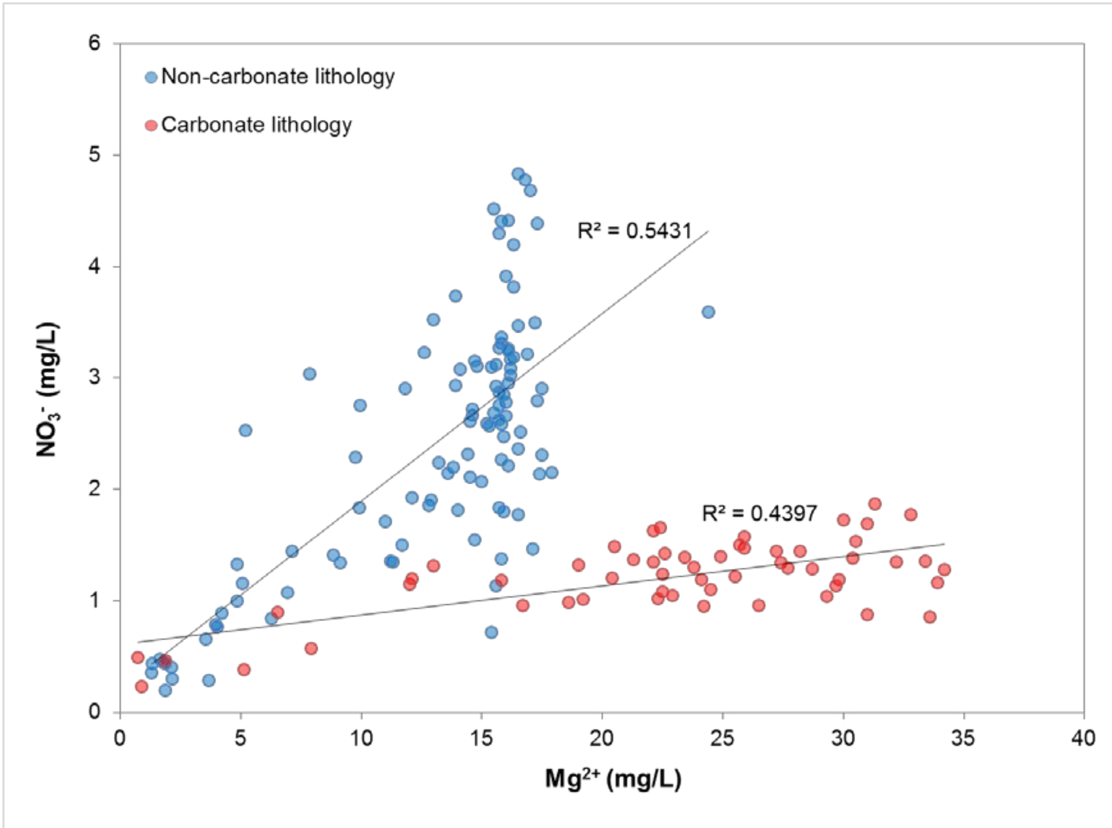

Figure 4.6: The significant linear relationship between NO_3^- and Mg^{2+}concentrations is also distinctly different in study sites based on lithology. Data near the origin are generally from storrm events in which both NO_3^- and Mg^{2+} are significantly diluted by precipitation and subsequent runoff.

Similarly, nitrate concentrations showed linear relationships with DIC concentrations, but the linear relationships were distinctly different for sites draining carbonate *vs.* non-carbonate lithology (Figure 4.7).

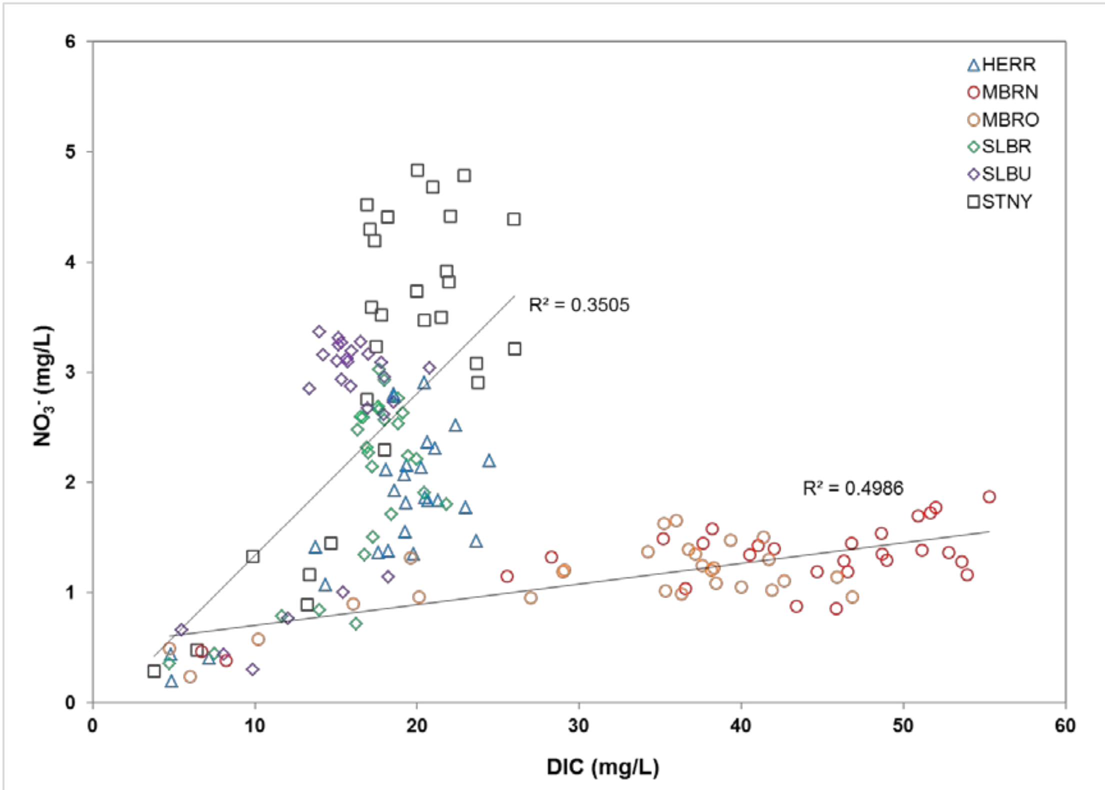

Figure 4.7: DIC and nitrate also have a significant linear relationship among all sites, but is lithologically distinct. Carbonate lithology is drained by sites MBRN and MBRO. Data indicate an upper limit of DIC available for the noncarbonate streams at ~25mg/L.

Hydrologically, nitrate concentrations showed significant and distinct inverse relationships with discharge across all sites (Figure 4.8). Although stream nitrate concentrations dilute during storm events as discharge increases, there is a limit to dilution that can be equated to the mean NO_3^--N concentration in rainfall in the greater Baltimore area of ~0.4-0.5 mg/L (NADP, 2015).

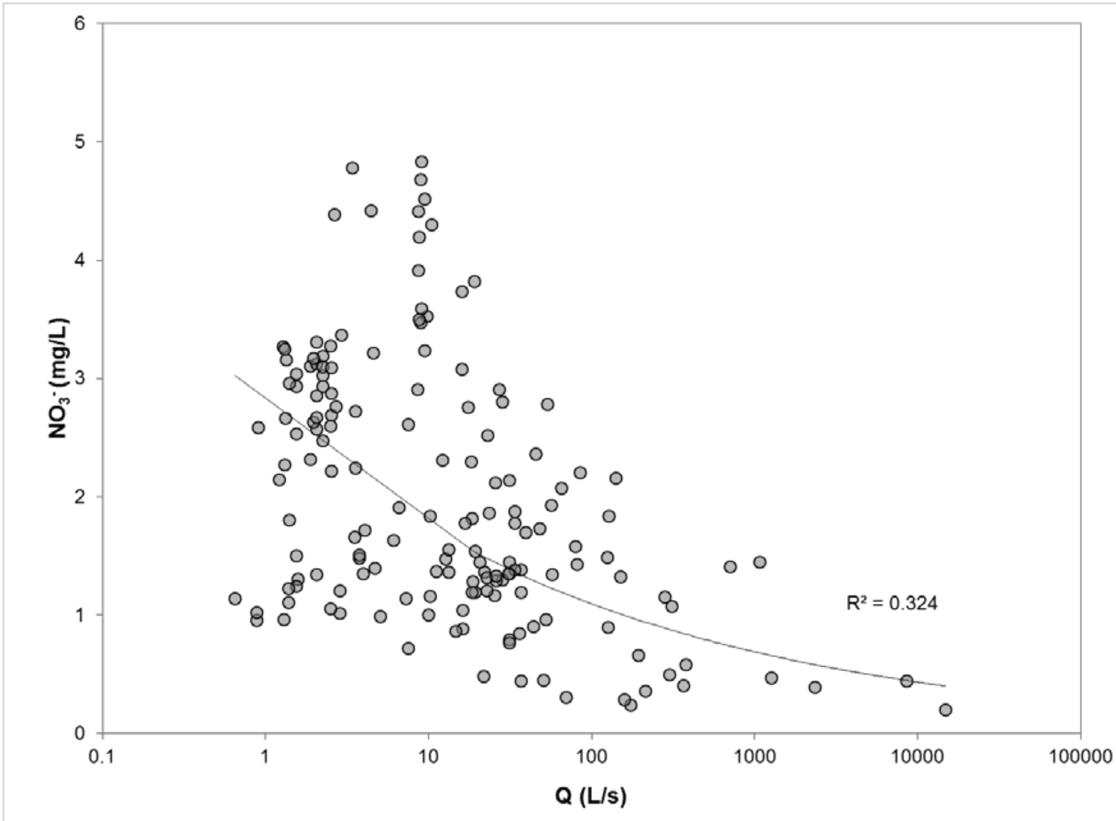

Figure 4.8: A significant inverse power law relationship exists as NO_3^- concentrations are diluted with rising discharge.

Sites draining carbonate lithology (Minebank Run) were the only sites with strong inverse linear relationships between nitrate concentrations and discharge for the best fit. For all other sites draining non-carbonate lithology, power law relationships between nitrate concentrations and discharge were the best fit and showed dilution as discharge increased (Figure 4.9).

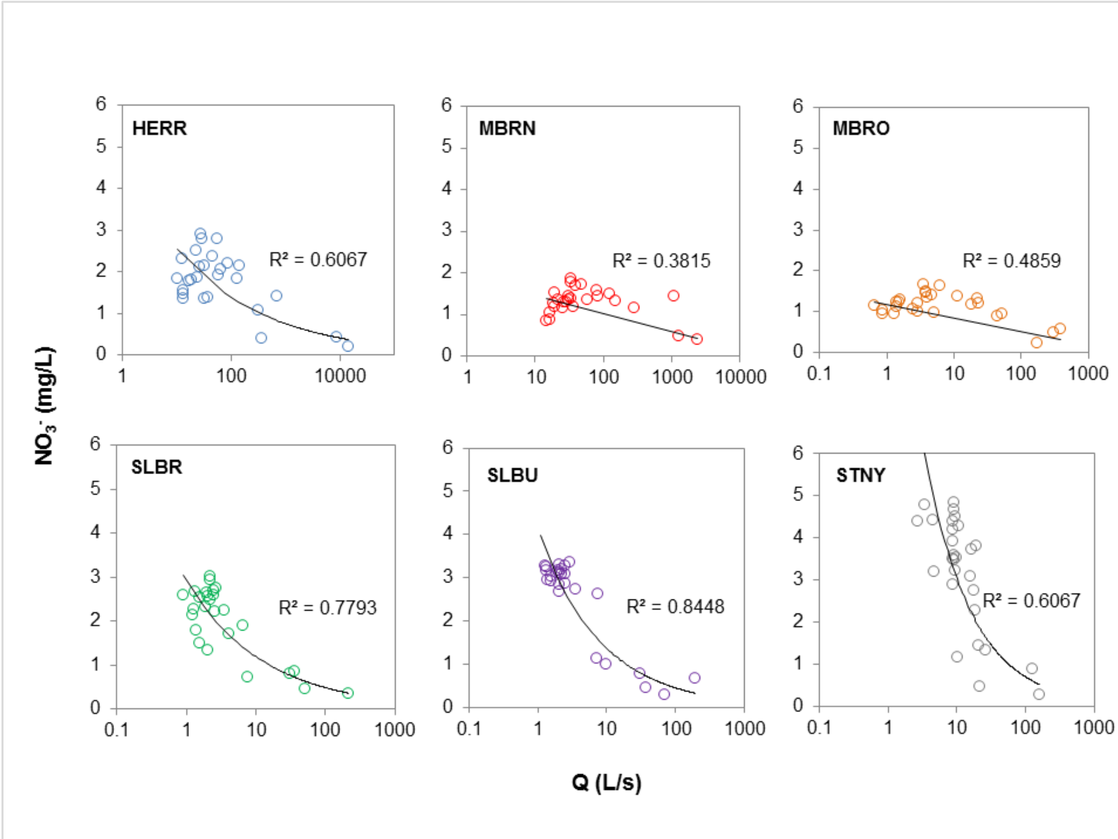

Figure 4.9: A semi-log plot of NO_3^- *vs* discharge relationships demonstrates the distinct differences among the sites, but common general trends. Nitrate supply at each site varies, but has the same limit to dilution during high flow events. Note that the ranges on the logarithmic x-axes vary.

Across all sites, Ca^{2+} concentrations and Mg^{2+} concentrations showed inverse relationships with discharge (similar to nitrate) and were diluted at higher streamflow whereas Na^+ and K^+ showed no significant relationships with streamflow (Figure 4.10).

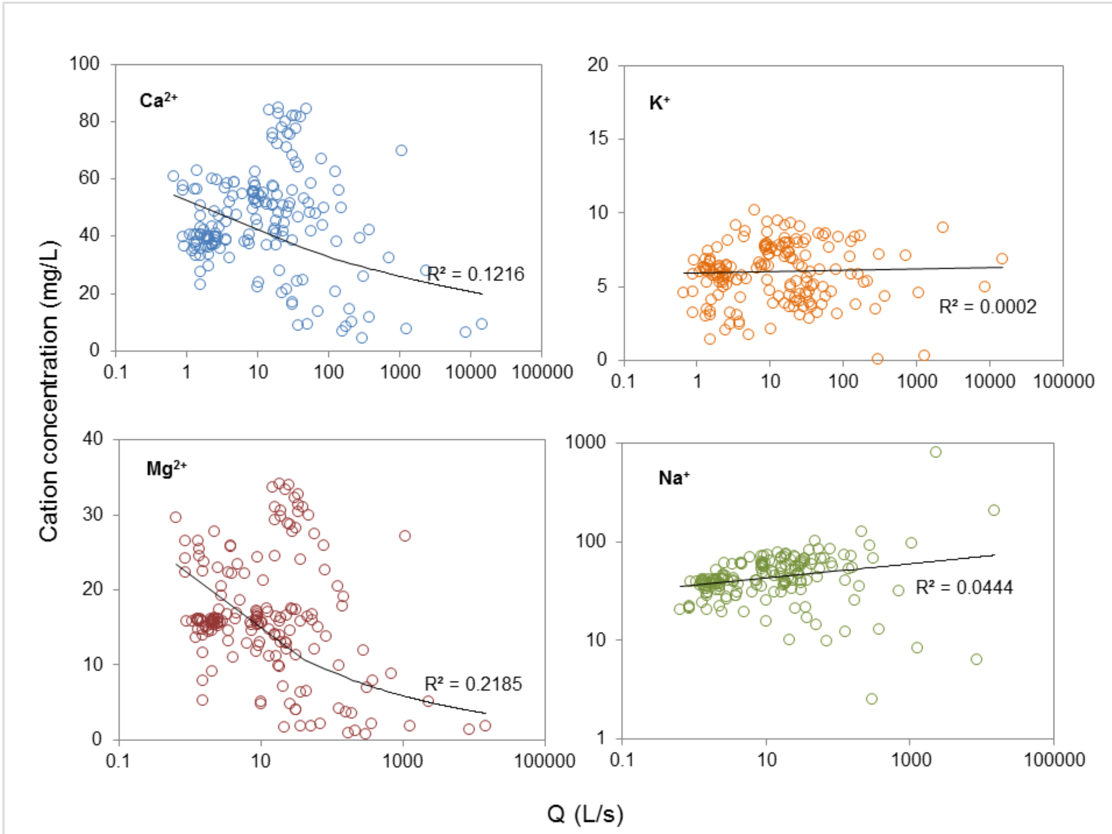

Figure 4.10: The divalent atomic cations Ca^{2+} and Mg^{2+} shift in similar patterns across all sites as discharge increases. A distinct pattern is not evident with the monovalent atomic cations Na^{+} and K^{+}. This plot includes high concentrations of Na^{+} (206 and 795 mg/L) measured in samples during February 2016 after a major winter storm and as discharge was high from snow melt.

Biologically there was markedly greater variability in the range of GPP and ER at lower concentrations of nitrate across all sites (Figure 4.11), but with no discernible patterns on a site-specific basis (Figure 4.12). Across all sites, there was a significant relationship between nitrate concentrations and dissolved organic carbon concentrations (Figure 4.13), which may have been due to biological factors or differences in sources and hydrologic flowpaths for DOC and nitrate.

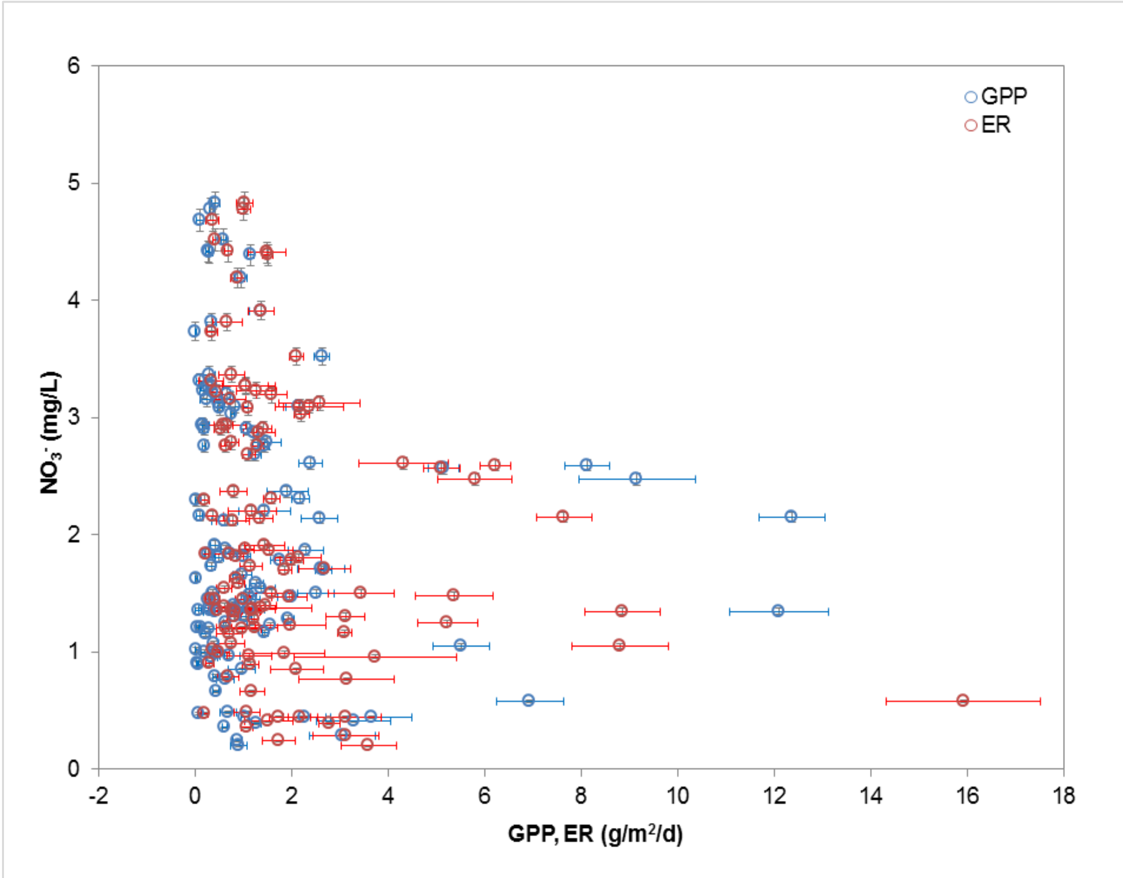

Figure 4.11: Biological activity indicators Gross Primary Production (GPP) and Ecosystem Respiration (ER) vary across all sites. Large horizontal error bars in some measurements result from modeled results of metabolism with greater uncertainty due to oversaturated oxygen results in some sensors. Note that the size of the sampled data is smaller than the full set of biweekly data. Several of the days were not able to be modeled as a result of missing PAR or DO data due to sensor tempering or being washed out of the stream channel during storm flow.

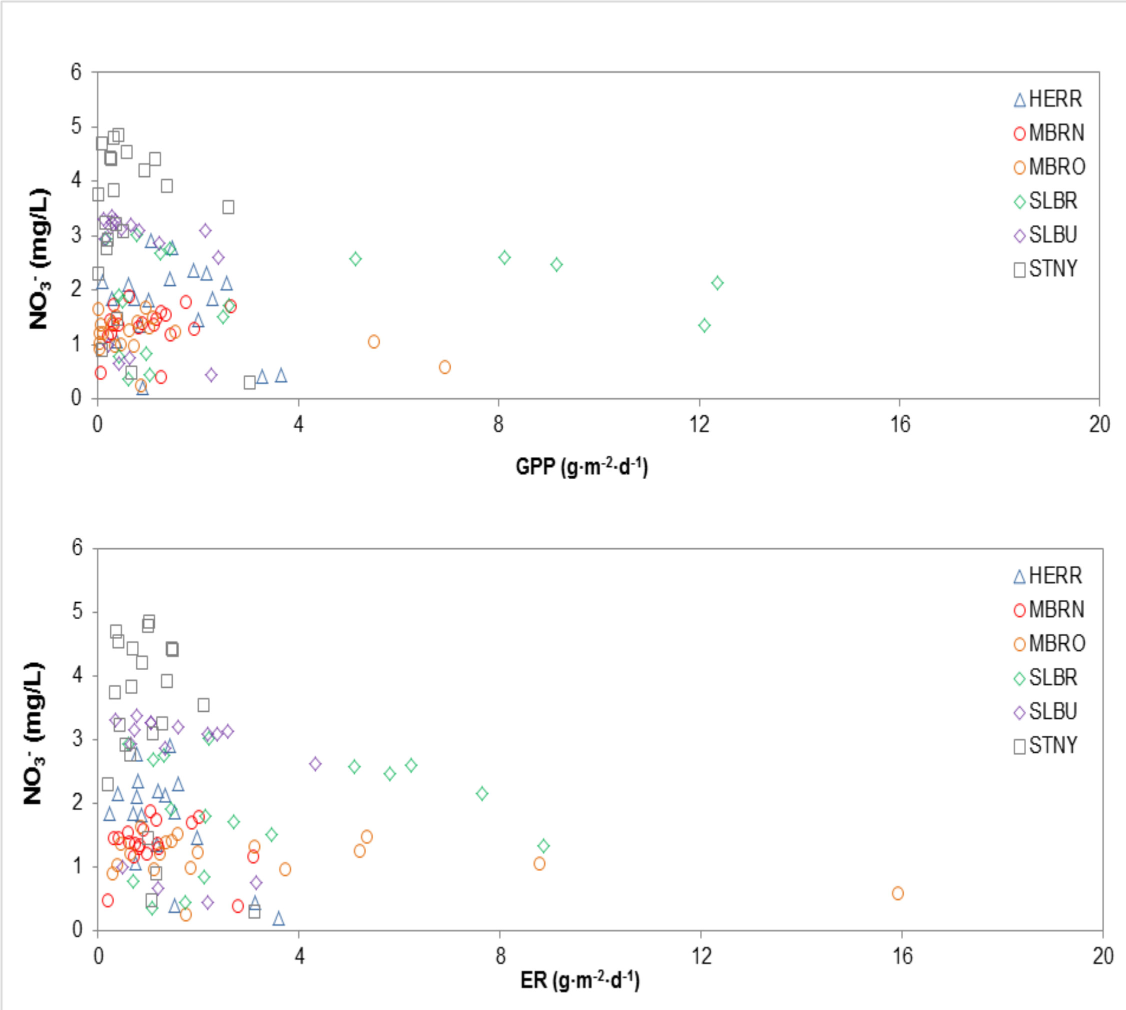

Figure 4.12: By site, GPP and ER each varied widely by site and the restored reaches are not distinctly different than the unrestored group. The highest levels of GPP and ER at SLBR generally correspond with warmer spring and summer sampling dates, but the peak data at MBRO are from February 2016 on a date with elevated discharge and high turbidity.

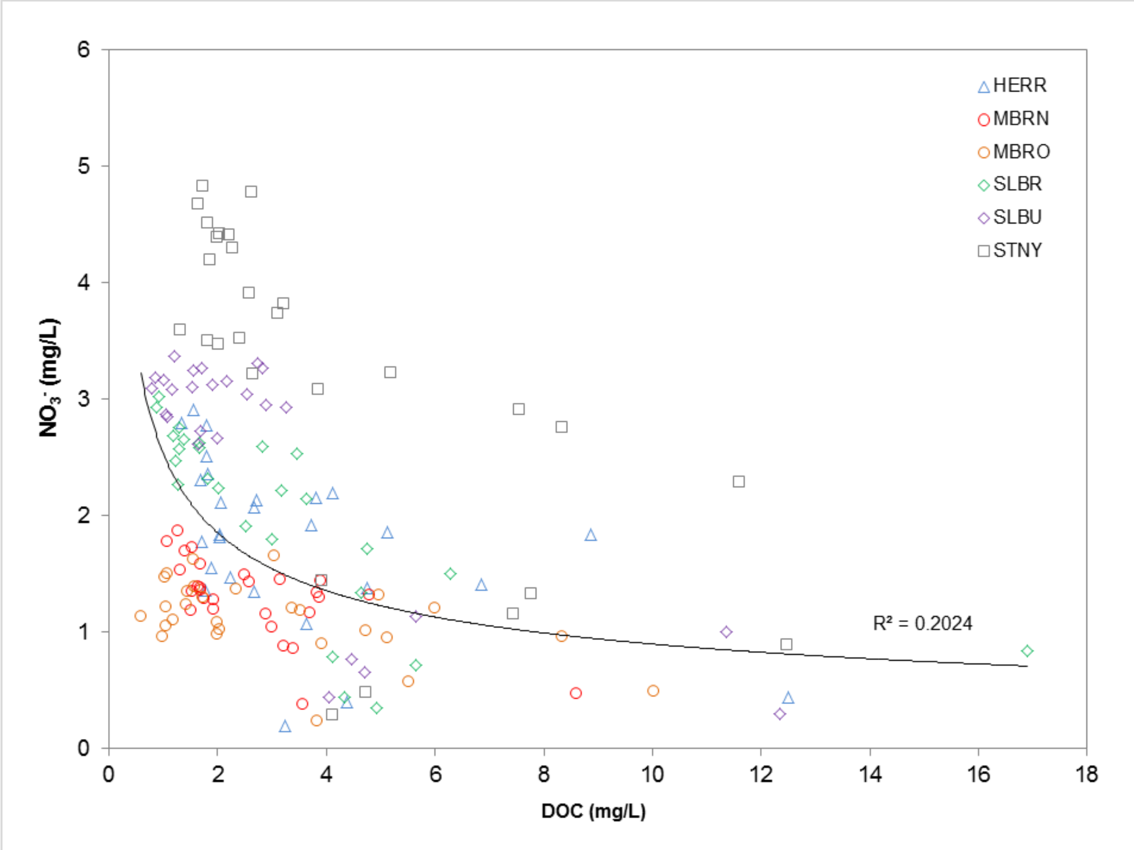

Figure 4.13: All sites display an inverse power law relationship between DOC and NO_3^- concentrations. Hydrologically, a few storm flow events that tended to dilute nitrate were also accompanied by larger flushes of DOC

4.3 Relationships between DIC Concentrations and Geochemical, Hydrological, and Biological Factors

DIC concentrations are explained by geochemical, hydrological, and biological factors in all streams, but the relative importance of these factors varied site by site. For example, the sum of base cations, discharge, and dissolved organic carbon were typically significant components of the AIC model with the greatest weights (Table 4.4).

DIC response variable					
Site	Model	Rank	w_i	ΔAIC_c	R^2
HERR	Y = 5.45 + **0.08*CationSum – 0.002*Q** + 0.19*Temp + 2.02*ER	1	0.21	0.00	0.79
	Y = -33.23 + **0.12*CationSum** – **0.003*Q** + 4.20*pH + 0.98*DOC + 3.12*ER	2	0.08	1.82	0.82
MBRN	Y = 2.84 +1.52*Temp + 3.43*DO – **7.14*DOC** + 2.46*ER	1	0.24	0.00	0.80
	Y = 3.43 + 1.53*Temp + 3.67*DO – **7.44*DOC** – 0.07*GPP	2	0.19	0.51	0.80
MBRO	Y = 35.26 – **0.17*Q** + 0.44*Temp + 0.10*DO – 1.69*DOC + 0.59*ER	1	0.22	0.00	0.89
	Y = 44.23 – **0.17*Q** + 0.55*DO – 1.38*DOC + 0.70*ER	2	0.18	0.41	0.88
	Y = 48.13 - **0.20*Q** – 1.26*pH – 0.41*DO + 1.15*ER	3	0.13	1.07	0.80
SLBR	Y = **19.54 – 0.20*Q** – 0.02*DO – 0.21*GPP	1	0.30	0.00	0.82
	Y = **19.67 – 0.20*Q** – 0.02*DO – 0.28*ER	2	0.16	1.22	0.81
	Y = **18.77 – 0.23*Q** + 0.01*DO + 0.20*DOC – 0.24*GPP	3	0.15	1.40	0.86
SLBU	Y = -1.28 + **0.15*CationSum – 0.03*Q** + **0.68*DOC** + 0.78*GPP + 0.62*ER	1	0.31	0.00	0.97
	Y = 3.07 + 0.10*CationSum – 0.12*Q + 0.05*DO + **0.62*DOC** + 0.81*GPP + 0.81*ER	2	0.13	1.71	0.96
	Y = 0.42 + **0.14*CationSu**m – **0.04*Q** – 0.08*Temp + **0.72*DOC** + 1.12*GPP	3	0.12	1.88	0.96
STNY	Y = -57.62 + **0.10*CationSum** + 8.59*pH -0.05*DO – 1.13*GPP	1	0.18	0.00	0.66
	Y = -51.20 + **0.10*CationSum** + 8.59*pH – 0.04*DO – 0.97*ER	2	0.15	0.36	0.65
	Y = -51.30 + 8.43*pH – 0.30*DO + **2.97*TN** – 1.00*ER	3	0.10	1.07	0.64

Table 4.4: Multiple linear regression models chosen with Akaike's Information Criterion predicting DIC concentrations. Shown are up to three best-fit models ($\Delta AIC<2$) for the response variable. Rank is the model rank relative to all possible models, w_i is the weighting evidence that an individual model is the best among all competing models, and R^2 is the coefficient of determination for each model. Note that predictor variables and their coefficients in bold are those which are statistically significant in the model.

Across all sites, DIC concentrations showed significant positive linear relationships with Ca^{2+} and Mg^{2+} concentrations (Figure 4.14).

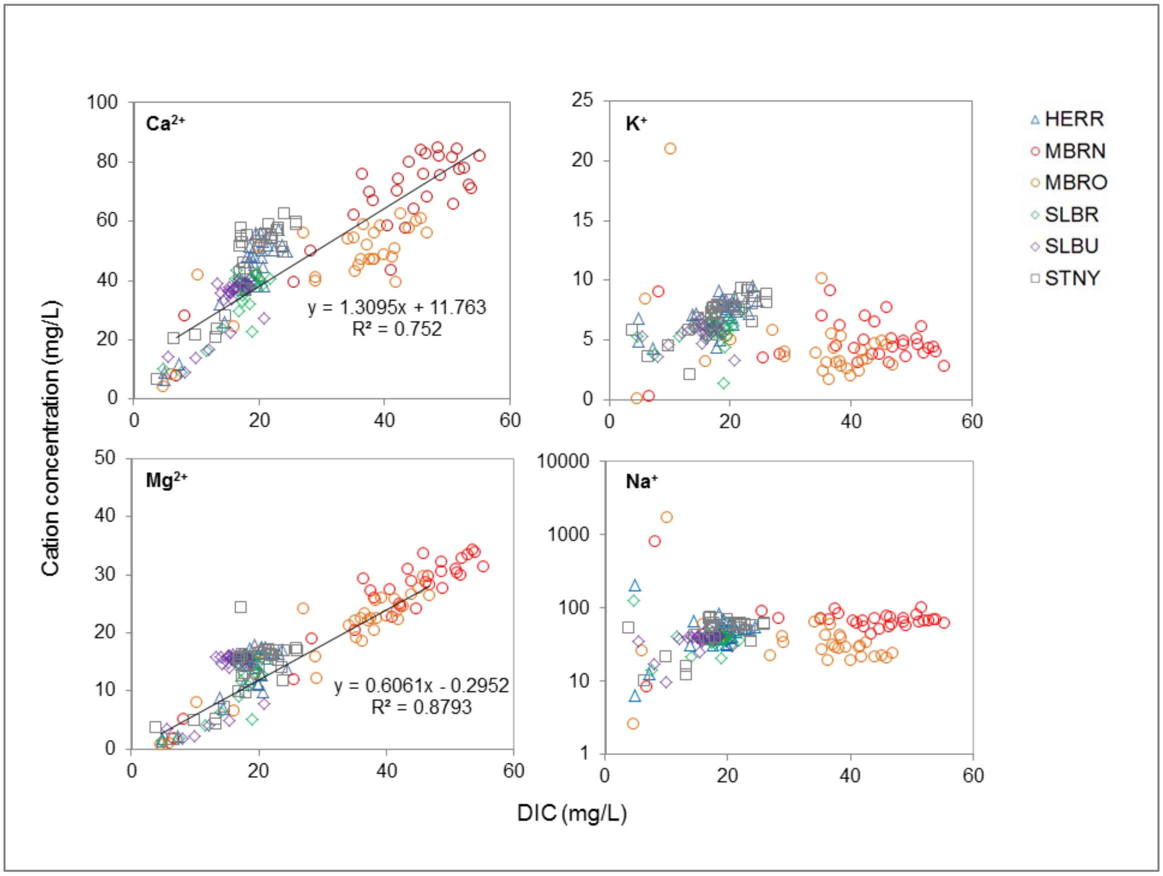

Figure 4.14: An examination of cation concentration relative to DIC shows highly significant relationships between DIC and Ca^{2+} and Mg^{2+}. Unlike relationships between base cations and nitrate concentrations, the relationships between Ca^{2+} and Mg^{2+} and DIC did not appear to be different for sites draining carbonate *vs.* non-carbonate lithology aside from the magnitudes of the both variables, which are elevated in carbonate watershed

Interestingly, there was also a statistically significant positive relationship between Na^{+} and DIC concentrations, particularly when a few high Na^{+} values above 100 mg/L from road salting were excluded. The true significance of the relationship between Na^{+} and DIC is more apparent when separating the carbonate and non-carbonate lithology (Figure 4.15).

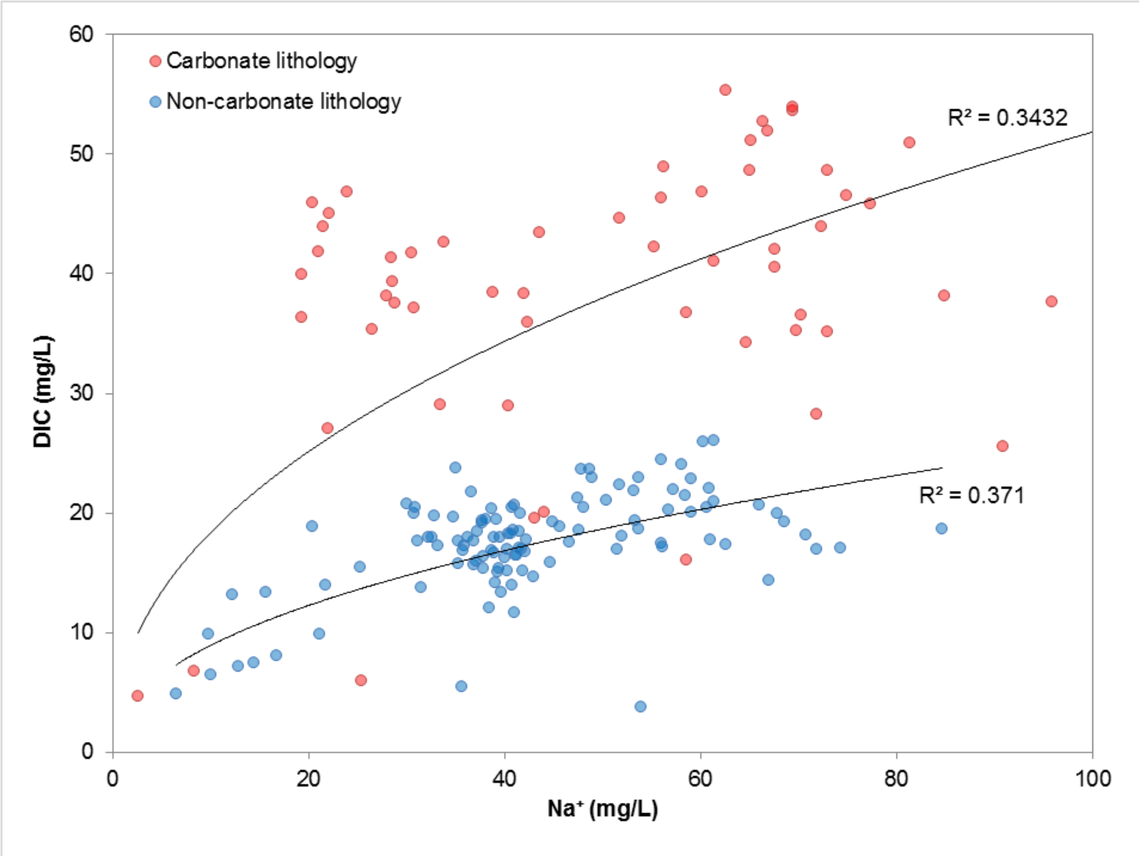

Figure 4.15: The relationships between DIC and Na^+ strengthen when separating sites by underlying lithology. However, Na^+ varies widely across all watersheds r and is not entirely seasonal. Although concentrations spike due to salting and snow events, levels remain elevated in urban streams throughout the year.

From a hydrologic perspective, all sites showed strong significant inverse relationships with discharge indicating dilution at higher streamflow similar to nitrate, Ca^{2+}, and Mg^{2+} concentrations (Figure 4.16).

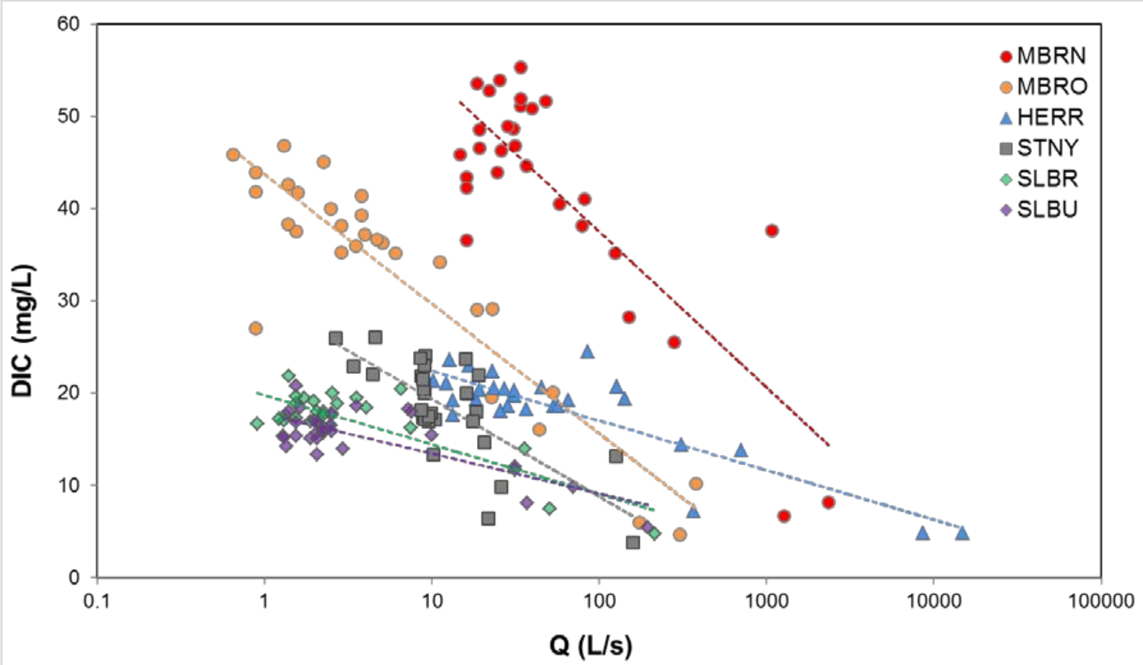

Figure 4.16: Data demonstrate strong inverse relationships between DIC and discharge at all sites due to dilution at higher flows. R^2 values by site: MBRN 0.6764; MBRO 0.8351; HERR 0.7343; STNY 0.5457; SLBR 0.6935; SLBU 0.5769

Biologically, there was markedly greater variability in the range of GPP and ER at lower concentrations of DIC across all sites similar to the pattern observed for nitrate concentrations. Specifically, some of the GPP and ER data from the older Minebank Run site (MBRO) and newest restoration at Scotts Level Branch (SLBR) consistently demonstrate the greatest range of variability (Figure 4.17).

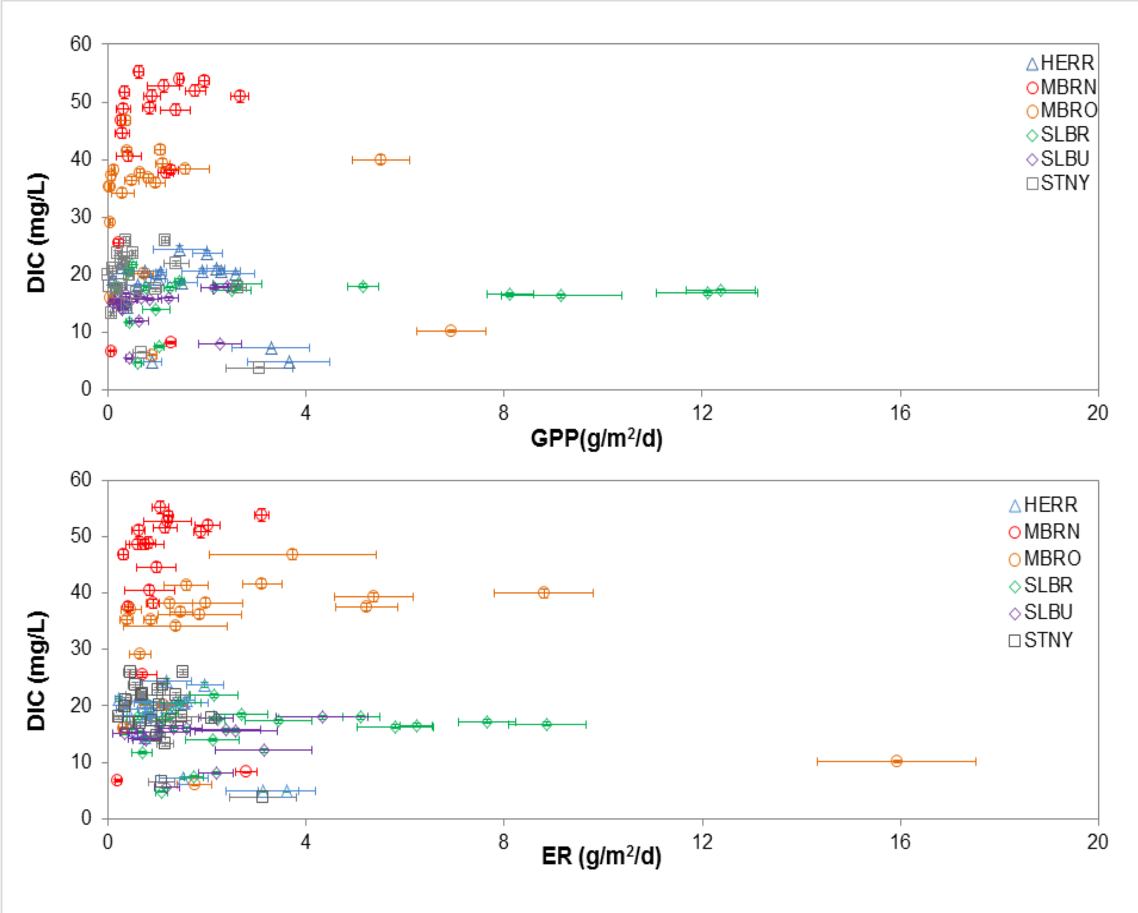

Figure 4.17: C metabolism data are more variable at low concentrations of DIC.

4.4 Relationships between DOC Concentrations and Geochemical, Hydrological, and Biological Factors

DOC concentrations were also explained by geochemical, hydrological, and biological factors in all streams, but there was greater complexity compared to nitrate and DIC with lower AIC weights in the models. For example, the sum of base cations, discharge, dissolved oxygen, and temperature were typically significant components of the AIC model with the greatest weights (4.5).

DOC response variable					
Site	Model	Rank	w_i	ΔAIC_c	R^2
HERR	Y = **6.04** – **0.04*CationSum** + **0.0005*Q** + **0.16*Temp** – 0.67*ER	1	0.13	0.00	0.71
	Y = **5.97** – **0.04*CationSum** + **0.0004*Q** + **0.17*Temp** – 0.35*GPP	2	0.12	0.13	0.71
	Y = **14.72** – **0.04*CationSum** + **0.0005*Q** – **0.56*DO** – 0.72*ER	3	0.08	0.99	0.73
MBRN	Y = 2.72 - **0.02*CationSum** + **0.002* Q** + **0.12*Temp** + 0.06*DO – 0.18*GPP	1	0.14	0.00	0.91
	Y = 3.80 **– 0.02*CationSum** +**0.002*Q** + **0.11*Temp** + 0.02*DO + 0.08*ER	2	0.09	0.82	0.90
	Y = 0.23+ **0.20*Temp** + 0.41*DO **– 0.11*DIC –** 0.15*GPP	3	0.09	0.96	0.87
MBRO	Y = **5.39** + **0.20*Temp – 0.15*DIC** + 0.05*ER	1	0.08	0.00	0.53
	Y = **4.78** + 0.20*Temp + 0.01*DO – **0.13*DIC** – 0.11*ER	2	0.08	0.07	0.44
	Y = **9.45** – 0.24*DO **– 0.13*DIC** – 0.07*ER	3	0.06	0.72	0.39
SLBR	Y = 205.24 – 25.42*pH – 0.98*DO + 1.26*ER	1	0.21	0.00	-0.11
	Y = 148.59 - 18.13*pH – 0.70*DO + 0.54*GPP	2	0.12	1.19	-0.22
SLBU	Y = 1.84 **– 0.21*CationSum** + **0.14*Tem**p + 0.15*DO + **1.12*DIC – 0.98*GPP**	1	0.37	0.00	0.92
	Y = 1.26 **– 0.19*CationSum + 0.04*Q + 0.10*Temp + 1.15*DIC – 1.44*GPP**	2	0.20	1.27	0.91
	Y = 3.55 **– 0.20*CationSum + 0.04*Q + 1.23*DIC – 1.10*GPP – 0.83*ER**	3	0.18	1.40	0.91
STNY	Y = 12.55 – **0.06*CationSum** + 0.72*pH – **0.52*DO** – 1.20*ER	1	0.08	0.00	0.61
	Y = **18.21 – 0.06*CationSum – 0.53*DO** - 1.17*ER	2	0.06	0.81	0.67
	Y = 9.77 – **0.06*CationSum** + 0.20*Temp – 0.007*DO – 1.01*ER	3	0.05	0.93	0.67

Table 4.5: Multiple linear regression models chosen with Akaike's Information Criterion predicting DOC concentrations. Shown are up to three best-fit models ($\Delta AIC<2$) for the response variable. Rank is the model rank relative to all possible models, w_i is the weighting evidence that an individual model is the best among all competing models, and R^2 is the coefficient of determination for each model. Note that predictor variables and their coefficients in bold are those which are statistically significant in the model.

DOC model results from SLBR were not resolvable and were the only scenario among all model runs that did not have a best fit based on the AIC value and yielded negative adjusted R^2. The negative adjusted value can be considered zero (the regular R^2 approached zero) and this result indicates that my data are not a However, beyond ΔAIC>2 results, the fourth best fit actually yielded a potentially viable equation, but was not used in this evaluation because it did not meet the criterion for model acceptance. Full model runs and supplementary tables are available in the appendix.

From a hydrologic perspective, there was a significant positive relationship between discharge and DOC concentrations indicating flushing at higher streamflow, unlike nitrate, Ca^{2+}, and Mg^{2+} concentrations (Figure 4.18). By site, there were variable but distinct relationships between DOC and discharge that may be indicative of differences in sources or stormflow response (Figure 4.19).

Biologically, there was markedly greater variability in the range of GPP and ER at lower concentrations of DOC across all sites similar to the pattern observed for nitrate and DIC concentrations. High discharge events with DOC concentrations > 7 mg/L have been removed to examine the larger body of data at baseflow conditions (Figure 4.20).

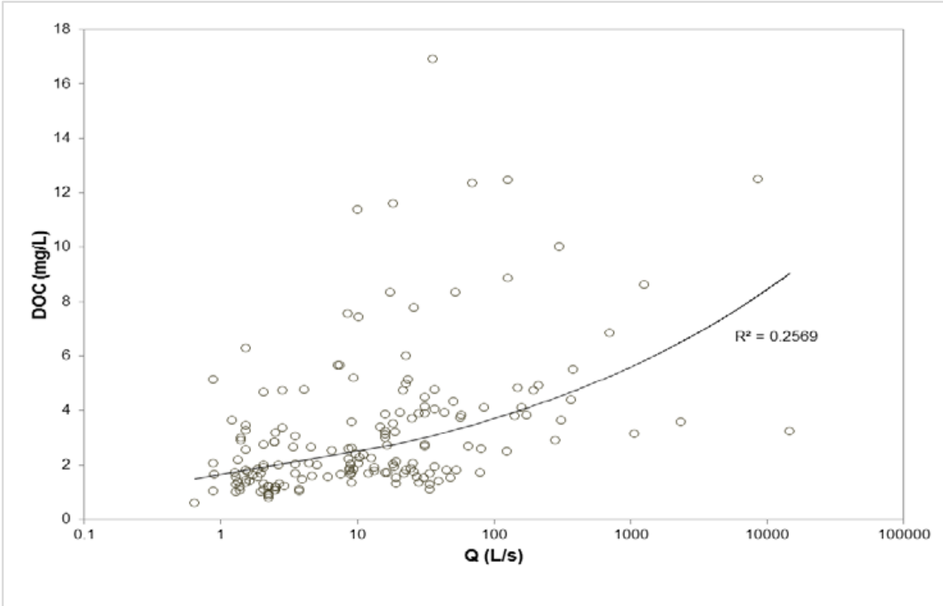

Figure 4.18: A significant power law relationship exists between DOC concentration and discharge. Storms can mobilize excess carbon in the form of soil, leaf litter, and substrate material.

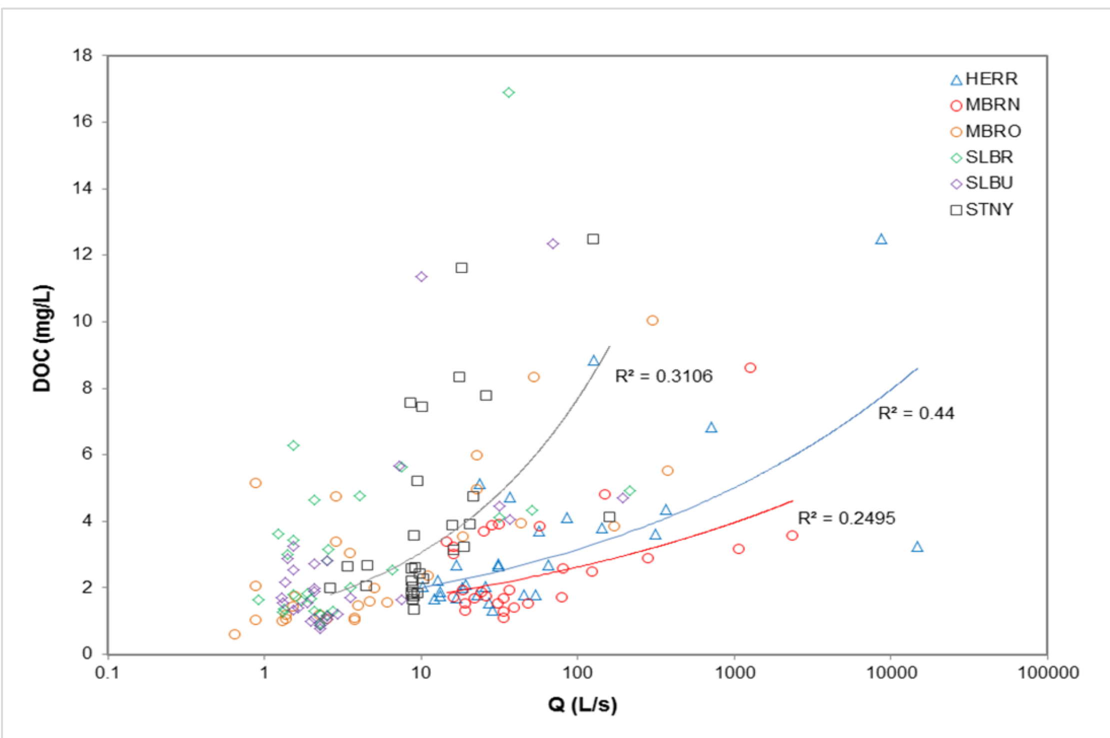

Figure 4.19: The response of DOC to elevated discharge was more apparent in three sites (HERR, MBRO, STNY), but is not related directly to restoration status. Availability and source of carbon in these sites may differ. The highest DOC levels were recorded when discharge was at least an order of magnitude above baseflow conditions.

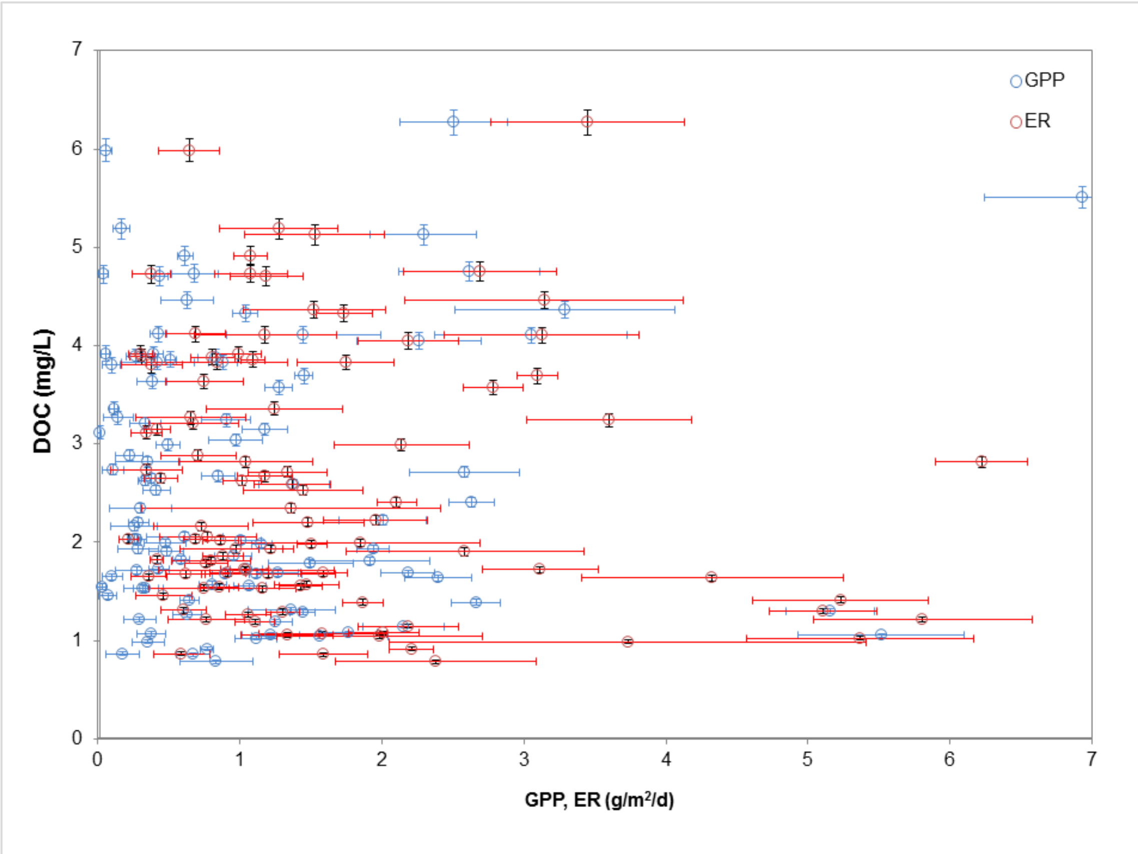

Figure 4.20: Increased variablity in C metabolism metrics at low DOC concentrations

Across all sites, there was a significant inverse relationship between DIC concentrations and DOC concentrations (similar to the inverse relationship observed for nitrate and DIC), which may have been due to biological factors or differences in sources and hydrologic flowpaths for DOC and DIC (Figure 4.21). During baseflow conditions, most delivery of water to the stream is likely through shallow groundwater sources, especially in the carbonate watersheds in Minebank Run. DOC tends to flush into the stream during rain events, either through stormwater conveyance or particulate matter that is alongside the stream in the immedite floodplain.

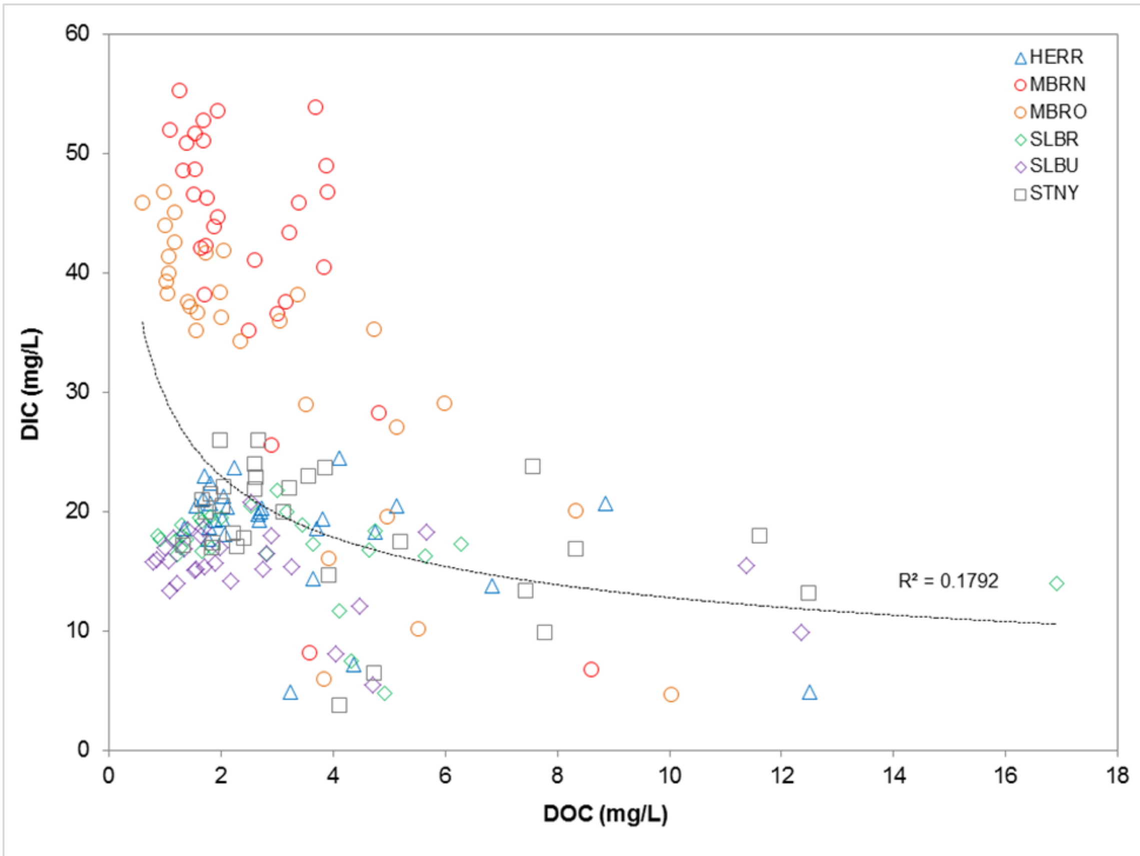

Figure 4.21: A weak inverse power law relationship exists between inorganic and organic carbon in all sites. During high flow events increased turbidity in streams corresponds to higher rates of flushing organic carbon and a dilution of inorganic carbon.

Chapter 5: Discussion

5.1 Effects of Stream Restoration on N Uptake in Urban Streams

Results from nutrient uptake studies and data analyses were largely inconclusive. Comparing the reaches based on a single factor of "restoration" is not definitive, but it is still helpful in a preliminary test of significance. Restored reaches, although partially degraded over time, do have some common characteristics that set them apart relative to unrestored and more degraded urban streams. For example, control measures designed to slow water velocity such as riffle and pool sequences should create a significant difference for in-stream uptake length, which is usually dependent on increased residence time of the water in the channel (Buckaveckas 2007; Klocker *et al*., 2009). However the result was the exact opposite in two cases (Herring Run Fall 2015 and Spring 2016). The increased variability in uptake in the unrestored reaches relative to the restored reaches is an important factor in the statistical analyses. These wide swings in uptake length and uptake velocity may be related to characteristics of the unrestored reaches that may be more sensitive to flow conditions and movement of the substrate. None one of the three hypotheses about the restored reaches was supported, but what is confounding is the possibility that uptake velocity and areal uptake rate were higher in the unrestored reaches. Although confidence in those statements is statistically lower than ideal (90% confidence interval), they was an interesting results that further guided analysis of data by evaluating additional hydrologic variables that were not initially considered.

Adding relationships such as grain size, normalization of flow to basin area or bed area, and 10-day antecedent discharge better constrain the conditions in the channel on the days of the nitrate injections. Of greatest interest washow preceding storm events may have affected the results of the uptake experients. The best example is the June 29, 2015 experiment in Herring Run. A very high discharge event was recorded in the days leading up to our injection period. (Figure 5.1). Our data show that N-uptake length on this date was significantly longer (610m) relative to the other two injections in November 2015 (31m) and March 2016 (46m). However, the uptake velocity (7.1 mm/min) and areal uptake rate (952 mg/m^2/h) were both significantly higher than values in the restored reaches. These results are the opposite of what is seen in the literature when evaluating restoration projects (Newcomer *et al.*, 2016) in which a "positive" result for a stream restoration is usually a decreased uptake length and increased uptake velocity and areal uptake rate. Although this finding cannot be considered a direct assessment of the four restored reaches in this study because pre-restoration uptake data was not considered, it does offer a comparison to a channelized, engineered reach in an urban setting.

At least three other significant rain events occurred within the 10 day period preceding nutrient injections (Appendix II, Table B). If heightened storm flow did scour the substrate enough to remove most or all active biota, results might be misleading and would make seasonal or cross-site comparisons very difficult. Adding representative measurements of the biota on a day of the injection or considering these antecedent flow conditions may have adequately addressed that. The results of the regressions on the uptake metrics do indicate some influence of the antecedent discharge.. Recent studies show recovery periods of GPP and ER of 7-14 days after storm events, even after almost complete removal of active biota (Reisinger *et al.*, 2017).

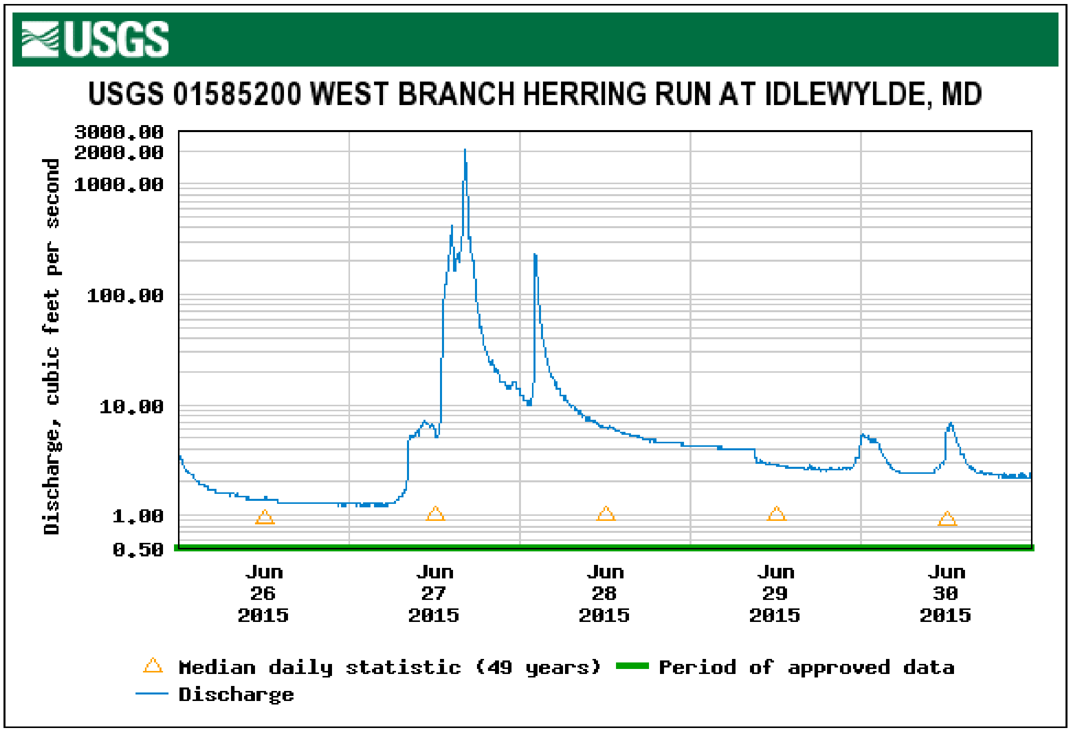

Figure 5.1: Our summer 2015 injection was completed two days after the peak discharge at Herring Run on June 27. Because of the high velocity and rapid mixing in this reach, it reaches plateau nutrient conditions quickly during a release (minutes). Despite the fact that we were on the falling limb of the storm, Q was constant during the release.

Increased areal uptake rates in an unrestored reach like Herring Run may also be due to increased primary production in the channel (Reisinger 2017, unpublished results) as a reach with full sunlight in the regularly wetted channel, despite having negligible (if any) connection to a hyporheic zone. Urban streams can show significantly higher primary production due to increased light availability, nutrient enrichment, and elevated temperatures (Kaushal *et al.*, 2014; Pennino *et al.*, 2014; Smith and Kaushal 2015). Although the concrete channel at Herring Run showed the highest uptake rates, there was considerable seasonal variability at this site and in all of the other reaches in the study. The high level of seasonal variability may be due in part to seasonal change in light availability (Smith and Kaushal 2015; Kaushal *et al.*, 2014), but other hydrologic factors and scouring of the benthos by storms may also be important (Beaulieu *et al.*, 2014).

The multiple linear regression data were unexpected because anticipated relationships between biological factors succh as GPP and ER did not appear in the best fit uptake metric models and neither did any relationship between DOC and ambient nitrate levels. The results were dominated by a few hydrologic variables. A possible explanation may be small sample size and the nature of the data, especially for the uptake length values. The extreme values (high and low) in the unrestored reaches added skewness to the distribution. Despite having a large set of potential explanatory variables that include hydrological, biological, and geochemical data, degrees of freedom were low because of the number of releases. Further investigation of all possible combinations of the candidate variables might yield different results. Overall studies evaluating the effects of stream restoration need to measure ecosystem scale N-uptake at a higher frequency to capture temporal variability (Newcomer-Johnson *et al.*, 2014) and beyond the reach scale when possible to capture longitudinal variability.

5.2 Hydrological, Geochemical, and Biological Controls on NO_3^-

The concentration of nitrogen in the urban streams was significantly related to hydrological, geochemical and biological factors. From a hydrological perspective, nitrate concentrations were highest at baseflow, which suggested the importance of groundwater inputs. Previous work at these study sites has shown that groundwater concentrations of nitrate and total dissolved nitrogen are significantly higher than surface waters (Mayer *et al.,* 2010; Sivirichi *et al.,* 2011; Newcomer-Johnson *et al.,* 2014).

During storms, nitrate is diluted from atmospheric sources and surface runoff from impervious surfaces.

Interestingly, there were strong relationships between base cations and both nitrate and total dissolved nitrogen. These relationships could have been due to similarities in: (1) hydrologic flowpaths (2) anthropogenic sources and inputs and (3) geochemical processes contributing to transport. Both base cations and nitrate concentrations are typically higher in ground water as compared to surface waters. In fact, base cations are sometimes used as hydrologic tracers of groundwater contributions. Thus, the strong positive correlation between Ca^{2+} and Mg^{2+} could have been driven by similarities in hydrologic flowpaths. However, there are considerable inputs of sewage and road salts in these streams, which can contribute to Na^{+} and K^{+} pollution (in addition to Ca^{2+} and Mg^{2+}). So, a similarity in anthropogenic sources and inputs can't be ruled out. Furthermore, the elevated levels of Na^{+} and Cl^{-} in these watersheds due to road salt inputs could enhance ion exchange and displace Mg^{2+} and Ca^{2+} from exchange sites on sediments and soils. The study reaches were not uniformly distributed by distance from road or bridge crossings, so proximity to major roadways may partially influence certain areas of a catchment (Löfgren 2001). Previous work at these study sites has shown that experimental salt additions can enhance the mobilization of carbon and nitrogen from soils and stream sediments to stream water (Duan and Kaushal 2015). More experimental work is necessary to investigate the relative importance of hydrological vs. geochemical controls on nitrogen in urban streams, as most research has focused on biological controls (discussed below).

Finally, ecosystem metabolism can also influence N concentrations in streams. Ecosystem metabolism was a significant explanatory variable in the AIC models and there appeared to be a pattern in which nitrate concentrations became more stable and decreased at higher levels of ecosystem respiration and gross primary production. Previous work has demonstrated biological controls on nitrogen in urban streams in a variety of ways. For example, there are diurnal patterns in N concentrations associated with denitrification and ecosystem metabolism in urban rivers (McCutchan *et al.,* 2003). Other studies have shown significant relationships between stream metabolism and N uptake in urban streams (Pennino *et al.,* 2014; Beaulieu *et al.,* 2014). An inverse relationship between ecosystem respiration and areal uptake rate was seen in this study, but only on a site-by-site basis (three data points per relationship). No pattern was evident with gross primary production.

5.3 Hydrological, Geochemical, and Biological Controls on DIC

The concentration of carbonates in urban waters is a function of dissolved CO_2, temperature, pH, cations, and dissolved salts. There were strong relationships between base cations and DIC in all watersheds. Further, DIC was strongly related to specific conductance across all sites. In addition, DIC concentrations were related to pH across all sites (Appendix I, Figure A). These relationships were widespread and interesting given that the study watershed were underlain by both carbonate and non-carbonated lithology. The fact that base cations (particularly calcium and magnesium) showed relationships with DIC in watersheds draining non-carbonated lithology suggests anthropogenic inputs. These anthropogenic inputs are likely weathering of concrete roadways and sidewalks. Previous work in nearby watersheds suggests that chemical weathering of impervious surfaces can enhance concentrations of base cations and bicarbonate in urban streams (Kaushal *et al.*, 2017). The concentrations of base cations in urban streams of the present study are significantly elevated compared to nearby forest watersheds (Kaushal *et al.*, 2017). There were also strong relationships between sodium and DIC in watersheds draining both carbonate and non-carbonated lithology. These relationships across sites may have been influenced by the effects of road salts on base cation exchange and leaching of Ca^{2+} and Mg^{2+} in soils. For example previous work at the Minebank Run site showed that there was evidence of Na^{+} exchanging Ca^{2+} and Mg^{2+} in soils (Cooper, Mayer *et al.*, 2014). Other work across a land use gradient in Baltimore has also shown that these ion exchange processes can occur (Kaushal *et al.*, 2017), and that there can be variability in concentrations of Ca^{2+} and Mg^{2+} along stream networks influenced by proximity to roadways (Sivirichi *et al.*, 2011).

Hydrological and biological factors can also influence DIC in urban streams. For example, DIC concentrations dilute with increasing streamflow during storm events, especially in urban areas when flashy streams are receiving significant overland or pipe flow. Although the storm water may include some DIC from weathered infrastructure, other flowpaths may be dominant in seasonal baseflow conditions. DIC may originate from deeper groundwater flowpaths as water comes into contact with weathered bedrock and peak seasonally as the shallow groundwater is pushed into the stream. Groundwater concentrations of bicarbonate are typically greater than surface waters. However, biological factors can also influence DIC concentrations in streams via ecosystem metabolism. For example, photosynthesis can take up CO_2 and this reduction in CO_2 can result in precipitation of carbonate in streams. Given that gross primary production is significantly elevated in urban streams compared to forest streams (Kaushal *et al.*, 2014), it may have some influence on precipitation of calcium carbonate during certain times of day or during certain seasons when there is increased light availability. This is also dependent upon dissolved CO_2, temperature, pH, cations, and dissolved salts. Previous work has shown that day length and light availability significantly influence metabolism in urban streams (Smith and Kaushal 2015). Both discharge and light availability are important controls on DIC in urban streams over diurnal and annual time scales (Smith and Kaushal 2015).

5.4 Hydrological, Geochemical, and Biological Controls on DOC

Dissolved organic carbon showed an inverse relationship with base cations, particularly calcium and magnesium. This could be due to a difference in hydrologic flowpaths. DOC has been shown to originate from flushing of upper soil horizons. DOC is primarily concentrated in hydrophobic fractions such as humic and fulvic acids, which are rich in carbon. Another explanation for the inverse relationship between DOC and base cations is the loss of cations in solution by base cation exchange with organic matter.

DOC also showed an inverse relationship with both NO_3^- and total dissolved nitrogen (TDN). Although data from TDN analyses were not presented graphically here, the majority of the nitrogen in the streams was in the form of nitrate and their concentrations were directly linearly related (R^2=0.95). Mean NO_3^-:TN was 0.83±0.16. Multiple linear regression results also demonstrated that controls on TDN and NO_3^- were the same in almost all sites. Much previous work has documented the inverse relationship between DOC and nitrate at global scales and across biomes (Kaushal *et al.,* 2005; Goodale *et al.,* 2005; Bernhardt *et al.,* 2005b; Taylor and Townsend 2010). Typically, a biological explanation is invoked to explain these patterns (e.g., organic carbon is used as a substrate for enhancing denitrification). However, others have pointed out that there can also be differences in DOC or NO_3^- due to differences in origin in shallow vs. deep hydrologic flowpaths (Mulholland *et al.*, 1990; Hinton *et al.*, 1998; Böhlke *et al.*, 2007).

Interestingly, there were also strong inverse relationships between DOC and DIC across all streams. This could have also been due to differences in shallow vs. deep hydrologic flowpaths (as discussed earlier) rather than just discharge Another possibility is that this also could have been due to mineralization of DOC to DIC in the stream. For example, the AIC model also suggested that suppressed ecosystem metabolism was also a explaining increases in DOC concentrations in streams. Previous work at these sites has shown that there can be significant retention and release of DOC at a stream reach scale (Sivirichi *et al.*, 2011, Kaushal *et al.*, 2014). Recent work also suggests that DOC uptake along stream networks can be important (Mineau *et al.*, 2016), especially if carbon regulation becomes part of the Chesapeake Bay TMDL program. An investigation of the hydrologic, geochemical, and biological factors influencing the relationship between DOC and DIC warrant further study in urban streams.

Chapter 6: Conclusions and Broader Implications

6.1 Primary Conclusions

The status of a stream as restored or unrestored is not enough to determine how well a stream functions regarding uptake or buffering of nitrogen. Shorter nitrogen uptake lengths were anticipated in restored streams where flow is slowed and residence time increases, but the data do not support this. Uptake velocity and areal uptake rates are also known in the literature to be greater in restored reaches, but these were variable in this study. Additional variables such as style of restoration, light availability, and sources and amounts of nutrient inputs make evaluation across all sites of different restoration age and status difficult. Additionally, seasonal changes in carbon inputs and light reaching the channel add to the complexity of the system. Many of the previous studies using short-term nutrient uptake experiments as an evaluative tool have been performed in forested or agricultural headwater streams in which nutrient sources and flowpaths may be more predictable. The watersheds studied here add a layer of unpredictability because of nonpoint sources of pollution and altered hydrology from urbanization. Although some nutrient uptake studies have been completed in restored urban streams, the results are mixed.

Additional consideration was given to potential hydrological, biological, and geochemical factors that may affect nitrogen uptake. Through stepwise multiple linear regression, results indicate that some of the same predictor variables appear in models across all sites. Two variables of interest that show some significant correlation are the ratio of velocity to wetted width of the stream and the antecedent conditions under which experiments were conducted. There is a moderately significant relationship between uptake and the width metric in the channel, which can indicate how the stream responds to increased discharge. The capacity of a channel to accomondate flow by increasing wetted bed area as opposed to significant depth or velocity changes may be of interest in future studies. Regarding antecedent conditions, significant storm events that increase discharge prior to uptake measurements may also play a role in changing nitrogen uptake. In more than one case, uptake experiments performed shortly after a large storm event show significantly increased nitrogen uptake lengths. If this resulted in a reduction of normal function of the stream to buffer nitrogen then the experimental results may be skewed.

Finally, significant realtionships between additional hyrdrological, biological, and geochemical factors may predictors of nitrogen and carbon concentrations in urban streas. Nitrate concentration was significantly correlated with base cations and dissolved inorganic carbon.   Dissolved inorganic carbon was significantly correlated with base cations and discharge, suggesting sources from shallow groundwater flowpaths in addition to surface inputs. Dissolved organic carbon was significantly correlated with base cations, discharge, and temperature, the last of which may be a seasonal variation. Overall, these relationships and more simple measurements may be useful as predictors in evaluating stream restoration practices and in guiding best management practices.

6.2 Monitoring and Management Implications

Evaluation of stream restoration projects is difficult because of the variety in type and scope of restoration, as well as the general lack of pre-restoration water chemistry data. This practice is changing and newer projects include not only baseline measurements of basic water chemistry metrics (pH, conductance, nitrate), but also post-restoration monitoring. However, with regard to nutrient uptake, some additional complications have become apparent throughout this research. A few factors were not taken into account in these one-day nutrient injections that may significantly affect the uptake results and subsequent recommendations for best management practices.

First, the selection of a reach may be representative of the larger stream network in a particular watershed, but it is difficult to determine if nearby there may be different conditions that negatively impact the performance of the restored reach. For example, if downstream of a 100 meter study site there is significant input from a leaky sewer the study misses a potential impact on the effectiveness of the restoration project. Therefore, it might be more appropriate to perform additional uptake studies longitudinally, to pinpoint a few specific places of interest (headwaters, after major tributary inputs, and at major outflow points).

As mentioned in discussion of the uptake results, setting a criterion for performing these injections after storm events should be considered and studied. The function of the stream changes and its ability to take up or transiently store nitrogen is altered. In areas with frequent, flashy storms, this may now define “normal” functioning and there is regular turnover of the biota. In urban streams in the Baltimore, this may or may not be the case, but it is important to understand uptake and the relationships between carbon and nitrogen in different flow regimes. Current and future work by members of the Baltimore Ecosystem Study will attempt to model this by understanding if there is a threshold discharge for a stream when N uptake essentially shuts off, and how

N uptake then changes in overbank flow conditions when the channel interacts with the floodplain.

More frequent temporal data regarding nitrogen uptake and N-C-cation dynamics is beneficial to fully characterize a stream network. Bi-weekly sampling partially achieves that, but more frequent N-uptake studies would make results more conclusive. This may sacrifice studying multiple restored and unrestored reaches broadly for the benefit of studying an important reach more intensely. This approach may be helpful in determining where the "best place" would be to not only study a stream reach, but also where in a watershed a BMP might be most effective and how large or small it should be.

Finally, design of restoration projects regarding nitrogen uptake should continue to include hydrological/geomorphic factors, but perhaps in a different way. Features that reduce water velocity and increase residence time may work well in baseflow conditions and in moderate storm events, but their effectiveness is limited in high discharge events. For example, some restorations are designed to accommodate a 100-year storm (Stony Run) but this relates to the ability manage the discharge and not necessarily managing nutrient uptake. If high flow events scour the benthic layer regularly and reset the clock on in-stream nitrogen buffering, then a preferable design would both accommodate high flows and minimize scouring. This might be accomplished through flow redirection (multiple channels) or targeting areas with the capacity for wide riparian buffers and wetlands.

Appendix I: Supplemental Figures

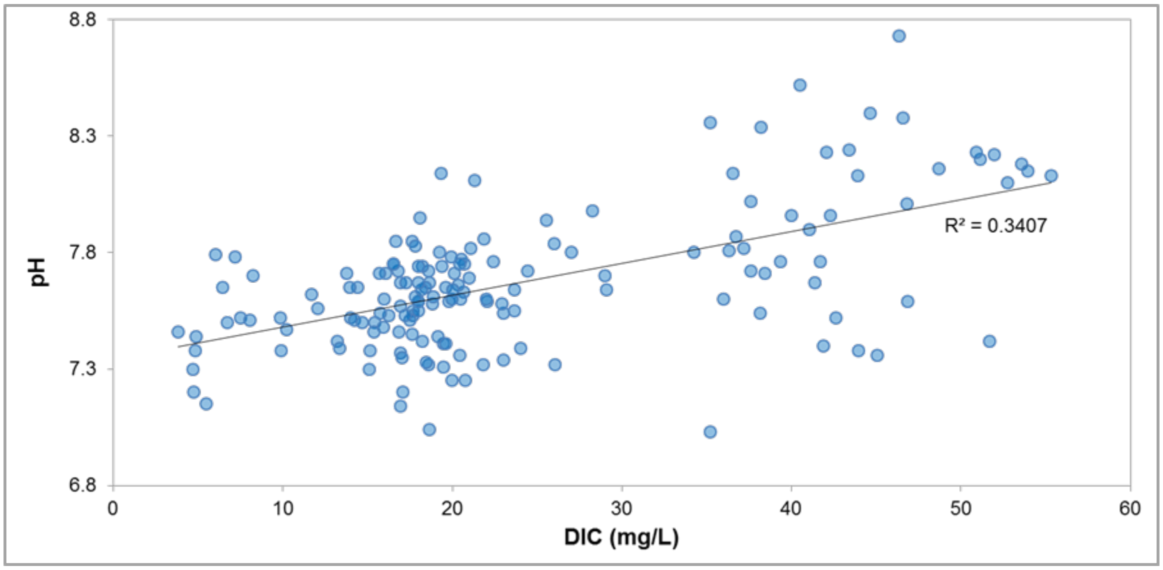

Figure A: All sites have a significant direct linear relationship between pH and DIC concentrations. This is in agreement with previous studies that have traced alkalinization in urban watersheds due to changes in land use and weathering of infrastructure.

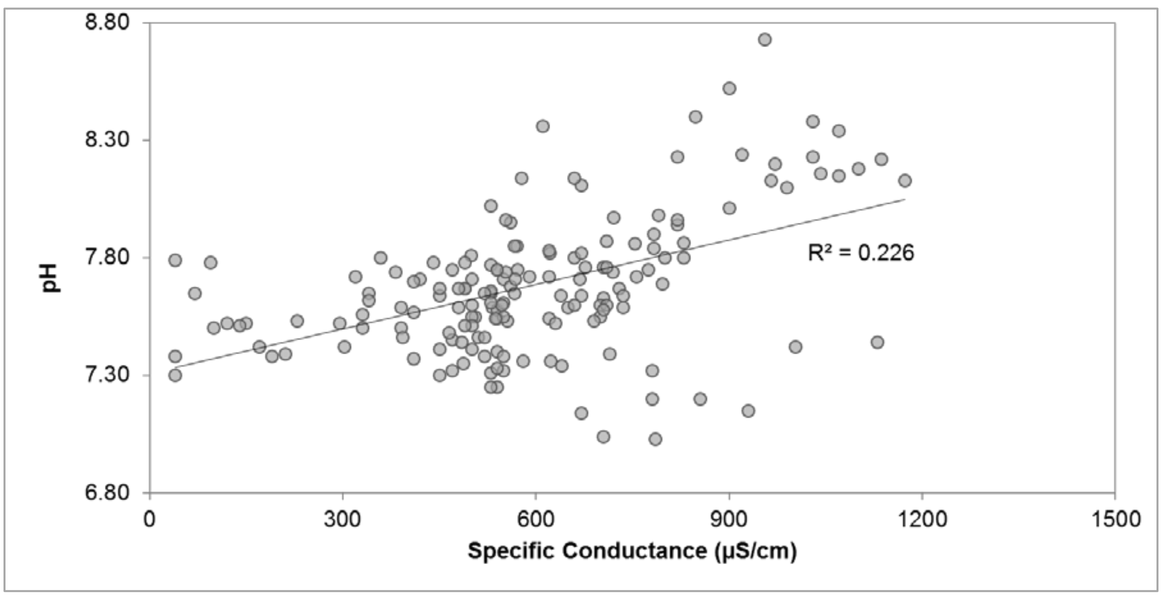

Figure B: Factors that contribute to alkalinization are consistent with elevated specific conductance, measuring a potential combined impact of base cations and carbonate from natural and anthropogenic sources.

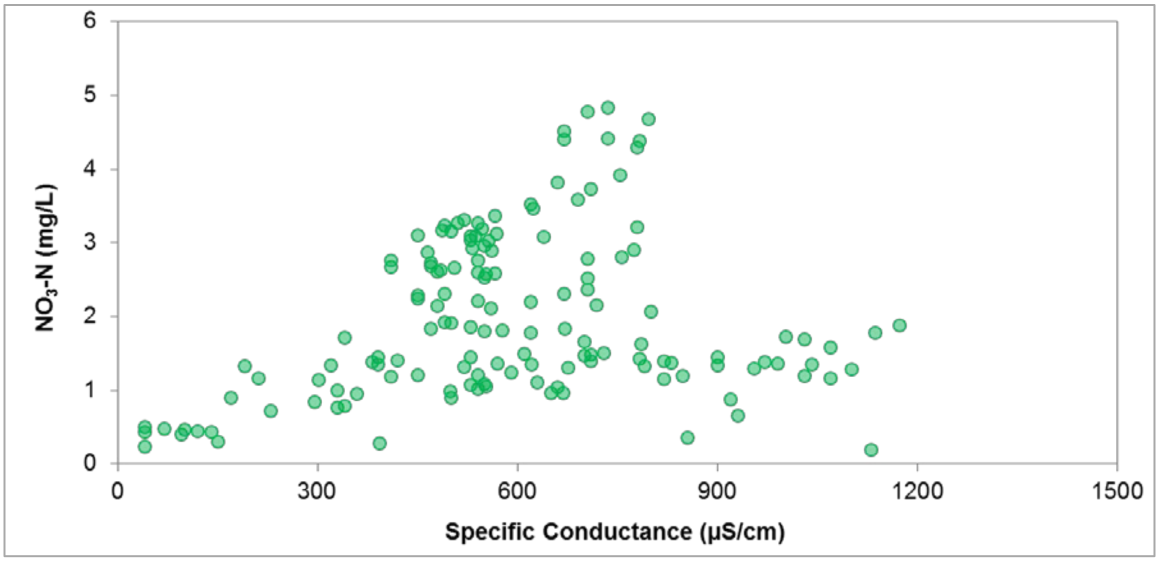

Figure C: As a basic water quality measurement, conductance is useful in confirming elevated nitrate concentrations.

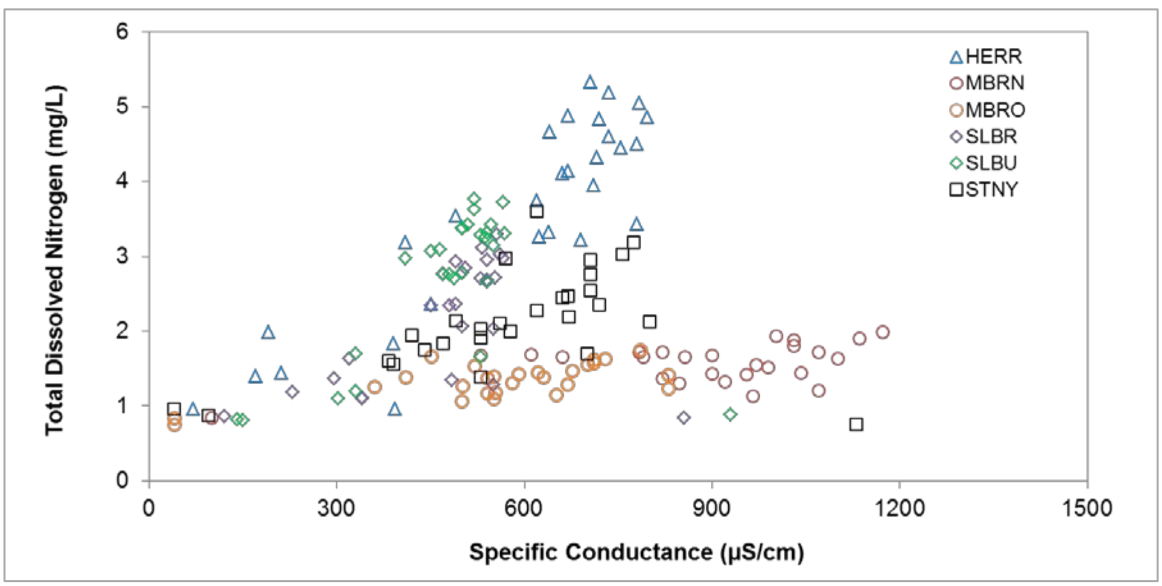

Figure D: By site, variability in TDN with specific conductance. Significant linear relationships persist by lithology type, as expected considering other measurements such as DIC and its role in conductance.

Appendix II: Supplementary Tables

Table A: Hydrological site characteristics of stream reaches used in nutrient uptake experiments

Site and Season	Date	Q (m^3/s)	Avg width (m)	Avg depth (m)	Reach length (m)	Bed Area (m^2)	basin area (ha)	Gradient	Average Velocity (m/s)	V/depth (s^{-1})
HERR Summer	6/29/15	0.0827	1.14	0.071	100	114.00	550	0.016	1.022	14.4
HERR Fall	11/7/15	0.0116	0.79	0.032	100	79.09	550	0.016	0.466	14.8
HERR Spring	3/20/16	0.0510	1.00	0.067	100	99.82	550	0.016	0.768	11.5
MBRN Fall	11/5/15	0.0253	6.17	0.094	100	617.10	530	0.006	0.044	0.5
MBRN Spring	3/23/16	0.0566	6.83	0.109	100	682.92	530	0.006	0.076	0.7
MBRO Summer	6/28/15	0.0229	2.57	0.148	88	226.16	110	0.007	0.060	0.4
SLBR Summer	7/1/15	0.0041	2.83	0.082	96	271.68	100	0.011	0.018	0.2
SLBR Fall	11/8/15	0.0014	2.69	0.082	61	163.83	100	0.011	0.006	0.1
SLBR Spring	3/21/16	0.0014	2.76	0.061	62	171.28	100	0.011	0.008	0.1
SLBU Summer	7/2/15	0.0100	2.25	0.186	97	218.25	90	0.003	0.024	0.1
SLBU Fall	11/9/15	0.0014	2.40	0.116	65	156.00	90	0.003	0.005	0.0

SLBU Spring	3/22/16	0.0014	2.15	0.077	75	161.59	90	0.003	0.009	0.1
STNY Summer	6/29/15	0.0161	2.79	0.094	75	209.25	200	0.007	0.061	0.7
STNY Fall	11/7/15	0.0045	2.54	0.090	75	190.31	200	0.007	0.050	0.6
STNY Spring	3/20/16	0.0088	2.66	0.095	70	186.33	200	0.007	0.035	0.4

Table B: Additional hydrological characteristics of stream reaches used in nutrient uptake studies, including calculation of an antecedent flow condition (Qmax/Qday/recovery days).

Site and Season	Date	V/depth (s^{-1})	Q/ba ($L \cdot s^{-1} \cdot ha^{-1}$)	Q/ (BA*V)	10 day Max Q (l/s)	Recovery Days	(Qmax/ Qday)/ recovery days	D_{50} (mm)	D_{84} (mm)	depth/ D_{84}
HERR Summer	6/29/15	14.4	0.2	0.00071	57482	2	348	1	1	71.00
HERR Fall	11/7/15	14.8	0.0	0.00031	1133	9	10.8	1	1	31.52
HERR Spring	3/20/16	11.5	0.1	0.00066	4502	6	14.7	1	1	66.53
MBRN Fall	11/5/15	0.5	0.0	0.00094	991	8	4.9	60.4	148.5	0.64
MBRN Spring	3/23/16	0.7	0.1	0.00109	2124	9	4.2	55.6	145.7	0.75
MBRO Summer	6/28/15	0.4	0.2	0.00169	2170	1	94.9	100.5	196.7	0.75
SLBR Summer	7/1/15	0.2	0.0	0.00085	723	4	44.4	159.4	247	0.33
SLBR Fall	11/8/15	0.1	0.0	0.00135	37.3	9	3	98.2	203.8	0.40
SLBR Spring	3/21/16	0.1	0.0	0.00099	61.4	7	6.1	50.7	131.1	0.47
SLBU Summer	7/2/15	0.1	0.1	0.00191	723	5	14.4	NA	NA	NA
SLBU Fall	11/9/15	0.0	0.0	0.00179	37.3	10	2.7	50.9	135.4	0.86
SLBU Spring	3/22/16	0.1	0.0	0.00103	61.4	8	5.4	32.3	97.9	0.79
STNY Summer	6/29/15	0.7	0.1	0.00126	806	2	25	144.2	250.7	0.38
STNY Fall	11/7/15	0.6	0.0	0.00047	41.98	9	1.04	159.3	267.8	0.34
STNY Spring	3/20/16	0.4	0.0	0.00136	158.46	6	3.00	98.3	211.2	0.45

Table C: Biological variables that characterize stream reaches on the dates of nutrient uptake experiments

Site and Season	Date	Dissolved Oxygen (mg/L)	DOC (mg/L)	GPP (g per m^2 per d)	ER (g per m^2 per d)	NEP (g $O^2/m^2/d$)	P:R
HERR Summer	6/29/15	8.94	4.11	0.964	1.178	0.270	1.229
HERR Fall	11/7/15	10.49	2.22	2.007	1.956	0.051	1.026
HERR Spring	3/20/16	11.04	1.81	1.913	0.797	1.116	2.400
MBRN Fall	11/5/15	11.53	3.69	1.451	3.095	-1.644	0.469
MBRN Spring	3/23/16	11.84	1.39	2.663	1.868	0.795	1.426
MBRO Summer	6/28/15	8.82	5.99	0.057	0.643	-0.587	0.088
SLBR Summer	7/1/15	10.09	4.75	2.614	2.688	-0.074	0.973
SLBR Fall	11/8/15	8.55	2.99	0.494	2.139	-1.645	0.231
SLBR Spring	3/21/16	10.99	1.29	1.444	1.304	0.140	1.108
SLBU Summer	7/2/15	7.35	11.37	0.201	0.478	-0.277	0.422
SLBU Fall	11/9/15	7.92	2.89	0.124	0.496	-0.372	0.250
SLBU Spring	3/22/16	9.37	1.15	2.153	2.183	-0.031	0.986
STNY Summer	6/29/15	8.48	3.12	0.011	0.345	-0.334	0.033

STNY Fall	11/7/15	8.15	2.65	0.372	0.444	-0.072	0.838
STNY Spring	3/20/16	13.24	2.40	2.630	2.103	0.527	1.251

Table D: Geochemical variables characterizing the stream reaches on dates of nutrient uptake releases.

Site and Season	NO3 (mg/L)	DOC (mg/L)	DIC (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Sum cations (mg/L)	Conductance (uS/cm)	Temp (^{0}C)	pH
HERR Summer	2.20	4.11	24.45	49.80	8.36	13.80	56.00	127.96	620	17.8	7.72
HERR Fall	1.47	2.22	23.64	52.10	9.50	17.10	48.70	127.40	700	15.8	7.55
HERR Spring	2.36	1.81	20.64	53.10	8.63	16.50	65.93	144.16	705	8.8	7.63
MBRN Fall	1.16	3.69	53.93	71.10	4.01	33.90	69.40	178.41	1070	13.3	8.15
MBRN Spring	1.69	1.39	50.90	81.50	5.16	31.00	81.33	198.99	1030	8	8.23
MBRO Summer	1.20	5.99	29.10	39.70	4.03	12.10	33.40	89.23	450	19.4	7.64
SLBR Summer	1.71	4.75	18.42	32.30	5.75	11.00	37.20	86.25	340	21.5	7.65
SLBR Fall	1.80	2.99	21.81	40.50	7.43	15.90	36.63	100.46	550	11.2	7.32
SLBR Spring	2.76	1.29	18.83	39.70	5.65	15.70	45.57	106.61	540	6.3	7.58
SLBU Summer	1.00	11.37	15.43	22.40	4.72	4.85	25.30	57.27	330	20.2	7.5
SLBU Fall	2.96	2.89	17.99	38.30	6.50	16.10	39.47	100.37	550	10.9	7.55
SLBU Spring	3.09	1.15	17.79	39.60	5.95	16.20	42.17	103.92	530	6.9	7.61
STNY Summer	3.74	3.12	19.98	50.70	8.31	13.90	67.77	140.68	710	20.2	7.6
STNY Fall	3.21	2.65	26.02	58.90	8.80	16.90	61.30	145.90	780	16.2	7.32
STNY Spring	3.52	2.40	17.79	43.70	7.19	13.00	61.03	124.92	620	7.2	7.83

Table E: Nitrogen uptake metrics for all successful nutrient uptake experiments

Site and Season	**Date**	**k (m^{-1})**	**Sw (m)**	**Vf (mm·min^{-1})**	**U (mg·m^{-2}·h^{-1})**
HERR Summer	6/29/15	-0.002	609.6	7.1	952.0
HERR Fall	11/7/15	-0.032	31.1	28.3	1859.8
HERR Spring	3/20/16	-0.022	45.9	66.7	5098.2
MBRN Fall	11/5/15	-0.005	190.5	1.3	66.9
MBRN Spring	3/23/16	-0.004	236.3	2.1	95.7
MBRO Summer	6/28/15	-0.003	326.9	1.6	108.7
SLBR Summer	7/1/15	-0.012	83.8	1.0	46.8
SLBR Fall	11/8/15	-0.007	144.9	0.2	19.5
SLBR Spring	3/21/16	-0.019	51.7	0.6	61.7
SLBU Summer	7/2/15	-0.003	319.5	0.8	37.8
SLBU Fall	11/9/15	-0.034	29.4	1.2	162.4
SLBU Spring	3/22/16	-0.001	697.0	0.1	5.0
STNY Summer	6/29/15	-0.004	283.9	1.2	159.6
STNY Fall	11/7/15	-0.026	38.8	2.7	362.9
STNY Spring	3/20/16	-0.004	252.0	0.8	113.2

Table F: Dissolved inorganic carbon multiple linear regression model runs

Site	Cation	Fit #	Model	AICC	Weight	ΔAIC	RSE	Model DF	Adj R^2	F stat	Deg of Freedom	P
All Sites	Sum	1	DIC ~ 1 + CationSum + Q + pH + DO + TN + GPP + ER	609.3077	0.5000	0.0000	6.448	83	0.7511	39.8	7 , 83	2.2E-16
All Sites	Sum	2	DIC ~ 1 + CationSum + Q + Temp + pH + DO + TN + GPP + ER	610.7238	0.2463	1.4161	6.448	83	0.7511	34.95	8 , 82	2.2E-16
All Sites	Paired	1	DIC ~ 1 + CaMg + NaK + pH + DO + TN + GPP + ER	506.7998	0.2707	0.0000	3.671	83	0.9193	147.5	7 , 83	2.2E-16
All Sites	Paired	2	DIC ~ 1 + CaMg + pH + DO + TN + GPP + ER	508.3175	0.1268	1.5176	3.73	84	0.9167	166.1	6 , 84	2.2E-16
HERR	Sum	1	DIC ~ 1 + CationSum + Q + Temp + ER	98.1171	0.2093	0.0000	2.832	12	0.7864	15.73	4 , 12	0.000102
HERR	Sum	2	DIC ~ 1 + CationSum + Q + pH + DOC + ER	99.9330	0.0844	1.8159	2.612	11	0.8183	15.41	5 , 11	0.001197
HERR	Paired	1	DIC ~ 1 + CaMg + Temp + ER	89.6634	0.0791	0.0000	2.454	13	0.8396	28.92	3 , 13	5.06E-06
HERR	Paired	2	DIC ~ 1 + CaMg + Temp + GPP	89.8702	0.0713	0.2068	2.469	13	0.8376	28.52	3 , 13	5.48E-06
HERR	Paired	3	DIC ~ 1 + CaMg + pH + ER	90.3941	0.0549	0.7306	2.508	13	0.8326	27.52	3 , 13	6.68E-06
HERR	Paired	4	DIC ~ 1 + CaMg + ER	90.6465	0.0484	0.9831	2.417	15	0.8365	44.49	2 , 15	4.94E-07
HERR	Paired	5	DIC ~ 1 + CaMg + pH + GPP	90.7254	0.0465	1.0620	2.532	13	0.8293	26.9	3 , 13	7.57E-06
HERR	Paired	6	DIC ~ 1 + CaMg + Q + GPP	91.0277	0.0400	1.3643	2.267	14	0.8561	34.72	3 , 14	9.75E-07
HERR	Paired	7	DIC ~ 1 + CaMg + GPP	91.2518	0.0357	1.5884						

HERR	Paired	8	DIC ~ 1 + CaMg + Q + Temp + GPP	91.5775	0.0304	1.9140						
HERR	Paired	9	DIC ~ 1 + CaMg + Q + ER	91.6273	0.0296	1.9639						
MBRN	Sum	1	DIC ~ 1 + Temp + DO + DOC + ER	115.8336	0.2405	0.0000	5.593	11	0.8 035	16.33	4 , 11	0.00013 5
MBRN	Sum	2	DIC ~ 1 + Temp + DO + DOC + GPP	116.3434	0.1864	0.5098	5.683	11	0.7 971	15.73	4 , 11	0.00016
MBRN	Paired	1	DIC ~ 1 + CaMg + Q + Temp + DO + ER	94.7008	0.3172	0.0000	2.461	10	0.9 62	76.87	5 , 10	1.19E-07
MBRN	Paired	2	DIC ~ 1 + CaMg + Q + Temp + DO + GPP	94.7674	0.3068	0.0666	2.466	10	0.9 618	76.54	5 , 10	1.22E-07
MBRO	Sum	1	DIC ~ 1 + Q + Temp + DO + DOC + ER	104.5032	0.2200	0.0000	3.43	10	0.8 907	25.44	5 , 10	2.2E-05
MBRO	Sum	2	DIC ~ 1 + Q + DO + DOC + ER	104.9103	0.1794	0.4071	3.458	12	0.8 775	29.65	4 , 12	3.88E-06
MBRO	Sum	3	DIC ~ 1 + Q + pH + DO + ER	105.5731	0.1288	1.0699	4.725	10	0.7 952	14.59	4 , 10	0.00035 3
MBRO	Sum	4	DIC ~ 1 + Q + pH + DO + DOC + ER	105.9127	0.1087	1.4095	3.923	9	0.8 588	18.03	5 , 9	0.00018 8
MBRO	Paired	1	DIC ~ 1 + CaMg + NaK + Q + Temp + DO + DOC + GPP	103.2386	0.1432	0.0000	1.915	9	0.9 62	58.81	7 , 9	8.49E-07
MBRO	Paired	2	DIC ~ 1 + CaMg + NaK + Q + DO + DOC + ER	103.6458	0.1168	0.4072	2.447	10	0.9 387	41.82	6 , 10	1.63E-06
MBRO	Paired	3	DIC ~ 1 + CaMg + NaK + Q + Temp + DO + DOC + ER	104.3888	0.0806	1.1502	1.993	8	0.9 611	53.98	7 , 8	4.16E-06
MBRO	Paired	4	DIC ~ 1 + Q + Temp + DO + DOC + ER	104.5032	0.0761	1.2646	3.343	10	0.8 907	25.44	5 , 10	2.2E-05
MBRO	Paired	5	DIC ~ 1 + Q + DO + DOC + ER	104.9103	0.0621	1.6717	3.458	12	0.8 775	29.65	4 , 12	3.88E-06
MBRO	Paired	6	DIC ~ 1 + CaMg + NaK + Q + DO + DOC + GPP	105.2018	0.0537	1.9632	2.365	11	0.9 394	44.96	6 , 11	4.17E-07

SLBR	Sum	1	DIC ~ 1 + Q + DO + GPP	61.8925	0.2984	0.0000	1.398	10	0.8 224	21.07	3 , 10	0.00012 1
SLBR	Sum	2	DIC ~ 1 + Q + DO + ER	63.1115	0.1622	1.2190	1.46	10	0.8 063	19.04	3 , 10	0.00018 6
SLBR	Sum	3	DIC ~ 1 + Q + DO + DOC + GPP	63.2894	0.1484	1.3970	1.228	9	0.8 63	21.47	4 , 9	0.00012 7
SLBR	Sum	4	DIC ~ 1 + Q + DO + DOC + ER	63.6324	0.1250	1.7399	1.243	9	0.8 596	20.9	4 , 9	0.00014 1
SLBR	Paired	1	DIC ~ 1 + CaMg + Q + Temp + TN + ER	60.5378	0.2040	0.0000	0.8461	10	0.9 65	83.76	5 , 10	7.86E-08
SLBR	Paired	2	DIC ~ 1 + CaMg + Q + Temp + TN + GPP	60.5554	0.2022	0.0176	0.8466	10	0.9 65	83.67	5 , 10	7.9E-08
SLBR	Paired	3	DIC ~ 1 + Q + DO + GPP	61.8925	0.1036	1.3547	1.398	10	0.8 224	21.07	3 , 10	0.00012 1
SLBU	Sum	1	DIC ~ 1 + CationSum + Q + DOC + GPP + ER	48.8081	0.3101	0.0000	0.5864	10	0.9 688	94.22	5 , 10	4.43E-08
SLBU	Sum	2	DIC ~ 1 + CationSum + Q + DO + DOC + GPP + ER	50.5158	0.1320	1.7077	0.4704	8	0.9 615	59.31	6 , 8	3.38E-06
SLBU	Sum	3	DIC ~ 1 + CationSum + Q + Temp + DOC + GPP	50.6845	0.1213	1.8765	0.6219	10	0.9 649	83.58	5 , 10	7.94E-08
SLBU	Paired	1	DIC ~ 1 + CaMg + DO + DOC + GPP + ER	32.8609	0.3583	0.0000	0.3436	9	0.9 795	134.6	5 , 9	3.55E-08
SLBU	Paired	2	DIC ~ 1 + CaMg + DO + DOC + ER	33.7019	0.2353	0.8410	0.4305	10	0.9 678	106.1	4 , 10	3.8E-08
STNY	Sum	1	DIC ~ 1 + CationSum + pH + DO + GPP	99.5064	0.1775	0.0000	2.618	13	0.6 592	9.221	4 , 13	0.00928 6
STNY	Sum	2	DIC ~ 1 + CationSum + pH + DO + ER	99.8656	0.1483	0.3592	2.644	13	0.6 523	8.974	4 , 13	0.00105 1
STNY	Sum	3	DIC ~ 1 + pH + DO + TN + ER	100.5756	0.1040	1.0693	2.697	13	0.6 383	8.501	4 , 13	0.00134 2

STNY	Sum	4	DIC ~ 1 + pH + DO + TN + GPP	100.6106	0.1022	1.1042	2.699	13	0.6 376	8.479	4 , 13	0.00135 8
STNY	Sum	5	DIC ~ 1 + CationSum + pH + DO + DOC + GPP	101.0536	0.0819	1.5473	2.437	12	0.7 046	9.111	5 , 12	0.00089 7
STNY	Sum	6	DIC ~ 1 + CationSum + Q + pH + DO + GPP	101.2820	0.0731	1.7756	2.453	12	0.7 009	8.966	5 , 12	0.00096 4
STNY	Sum	7	DIC ~ 1 + CationSum + Q + pH + DO + ER	101.3247	0.0715	1.8183						
STNY	Paired	1	DIC ~ 1 + CaMg + pH + DO + GPP	94.5949	0.1463	0.0000	2.284	13	0.7 406	13.13	4 , 13	0.00016 9
STNY	Paired	2	DIC ~ 1 + CaMg + pH + DO + ER	94.6444	0.1427	0.0495	2.287	13	0.7 399	13.09	4 , 13	0.00017 2
STNY	Paired	3	DIC ~ 1 + CaMg + pH + DO + DOC + GPP	95.1961	0.1083	0.6013	2.071	12	0.7 867	13.54	5 , 12	0.00013 9
STNY	Paired	4	DIC ~ 1 + CaMg + pH + DO + DOC + ER	95.2382	0.1061	0.6433	2.074	12	0.7 862	13.5	5 , 12	0.00014 1
STNY	Paired	5	DIC ~ 1 + CaMg + Q + pH + DO + ER	96.1110	0.0686	1.5161	2.125	12	0.7 756	12.75	5 , 12	0.00018 6
STNY	Paired	6	DIC ~ 1 + CaMg + Q + pH + DO + GPP	96.4572	0.0577	1.8623	2.145	12	0.7 712	12.46	5 , 12	0.00020 8

Table G: Dissolved organic carbon multiple linear regression model runs

Site	Cation	Fit #	Model	AICC	Weight	ΔAIC	RSE	Model DF	Adj R^2	F stat	Deg of Freedom	P
All Sites	Sum	1	DOC ~ 1 + CationSum + Q + Temp + pH + DO + TN + ER	413.9187	0.3207	0.0000	2.204	83	0.4398	11.09	7 , 83	8.01E-10
All Sites	Sum	2	DOC ~ 1 + CationSum + Q + Temp + pH + DO + ER	415.6298	0.1363	1.7111	2.242	84	0.4205	11.68	6 , 84	1.3E-09
All Sites	Paired	1	DOC ~ 1 + CaMg + Temp + pH + DO + TN + ER	414.1450	0.1369	0.0000	2.223	84	0.4298	12.31	6 , 84	6.8E-10
All Sites	Paired	2	DOC ~ 1 + CaMg + Temp + pH + DO + DIC + ER	414.8128	0.0981	0.6678	2.232	84	0.4256	12.12	6 , 84	9.1E-10
All Sites	Paired	3	DOC ~ 1 + CaMg + Temp + pH + DO + TN + DIC + ER	415.9785	0.0547	1.8336	2.229	93	0.427	10.58	7 , 83	1.93E-09
All Sites	Paired	4	DOC ~ 1 + CaMg + NaK + Temp + pH + DO + TN + ER	416.0685	0.0523	1.9235	2.23	83	0.4264	10.56	7 , 83	2.01E-09
HERR	Sum	1	DOC ~ 1 + CationSum + Q + Temp + ER	77.8230	0.1300	0.0000	1.559	12	0.7105	10.82	4 ,12	0.000597
HERR	Sum	2	DOC ~ 1 + CationSum + Q + Temp + GPP	77.9552	0.1217	0.1322	1.565	12	0.7082	10.71	4 , 12	0.000625
HERR	Sum	3	DOC ~ 1 + CationSum + Q + DO + ER	78.8124	0.0793	0.9894	1.473	13	0.7273	12.33	4 , 13	0.000231
HERR	Sum	4	DOC ~ 1 + CationSum + Q + DO + GPP	79.5420	0.0551	1.7190	1.504	13	0.716	11.71	4 , 13	0.000298

HERR	Sum	5	DOC ~ 1 + CationSum + Q + pH + DO + GPP	79.6321	0.0526	1.8091	1.438	11	0.7538	10.8	5 , 11	0.000597
HERR	Paired	1	DOC ~ 1 + CaMg + Temp + GPP	78.4859	0.0999	0.0000	1.767	13	0.6283	10.01	3 ,13	0.001089
HERR	Paired	2	DOC ~ 1 + CaMg + Temp + ER	78.5188	0.0983	0.0329	1.768	13	0.6276	9.987	3 , 13	0.00102
HERR	Paired	3	DOC ~ 1 + NaK + Q + DO + ER	79.8030	0.0517	1.3172	1.514	13	0.7118	11.5	4 , 13	0.000326
HERR	Paired	4	DOC ~ 1 + NaK + Q + Temp + ER	80.1087	0.0444	1.6228	1.668	12	0.6688	9.078	4 , 12	0.001294
MBRN	Sum	1	DOC ~ 1 + CationSum + Q + Temp + DO + GPP	47.5300	0.1419	0.0000	0.5635	10	0.9093	31.08	5 , 10	8.77E-06
MBRN	Sum	2	DOC ~ 1 + CationSum + Q + Temp + DO + ER	48.3535	0.0940	0.8234	0.5782	10	0.9045	29.42	5 , 10	1.13E-05
MBRN	Sum	3	DOC ~ 1 + Temp + DO + DIC + GPP	48.4866	0.0880	0.9566	0.6818	11	0.8672	25.5	4 , 11	1.63E-05
MBRN	Sum	4	DOC ~ 1 + CationSum + Q + Temp + GPP + ER	48.8037	0.0751	1.2736	0.5709	12	0.8981	30.95	5 , 12	1.85E-06
MBRN	Sum	5	DOC ~ 1 + Temp + DO + DIC + ER	48.9132	0.0711	1.3832	0.6909	11	0.8637	24.75	4 , 11	1.88E-05
MBRN	Paired	1	DOC ~ 1 + Temp + DO + DIC + GPP	48.4866	0.1259	0.0000	0.6818	11	0.8672	25.5	4 , 11	1.63E-05
MBRN	Paired	2	DOC ~ 1 + Temp + DO + DIC + ER	48.9132	0.1017	0.4266	0.6909	11	0.8637	24.75	4 , 11	1.88E-05
MBRN	Paired	3	DOC ~ 1 + CaMg + NaK + Q + Temp + ER	49.5294	0.0748	1.0427	0.5825	12	0.8939	29.63	5 , 12	2.35E-06
MBRN	Paired	4	DOC ~ 1 + NaK + Temp + pH + DO + DIC	50.2096	0.0532	1.7230	0.5936	12	0.8939	29.66	5 , 12	2.34E-06
MBRN	Paired	5	DOC ~ 1 + CaMg + NaK + Q + Temp + GPP + ER	50.4744	0.0466	1.9878	0.5171	11	0.9164	32.04	6 , 11	2.4E-06
MBRO	Sum	1	DOC ~ 1 + Temp + DIC + ER	74.7637	0.0794	0.0000	1.443	14	0.5316	7.432	3 , 14	0.003246

MBRO	Sum	2	DOC ~ 1 + Temp + DO + DIC + ER	74.8299	0.0768	0.0662	1.553	11	0.444	3.995	4 , 11	0.03062
MBRO	Sum	3	DOC ~ 1 + DO + DIC + ER	75.4817	0.0554	0.7180	1.617	13	0.3855	4.345	3 , 13	0.02503
MBRO	Sum	4	DOC ~ 1 + pH + DIC + ER	75.7228	0.0491	0.9591	1.629	13	0.4104	4.713	3 , 13	0.01942
MBRO	Sum	5	DOC ~ 1 + pH + DO + DIC + ER	75.9411	0.0441	1.1774	1.76	10	0.2923	2.445	4 , 10	0.1147
MBRO	Sum	6	DOC ~ 1 + Q + Temp + DO + DIC + ER	76.4446	0.0343	1.6809	1.391	10	0.554	4.727	5 , 10	0.0178
MBRO	Sum	7	DOC ~ 1 + Temp + DIC + GPP	76.6634	0.0307	1.8997						
MBRO	Sum	8	DOC ~ 1 + pH + DO + DIC + GPP	76.6727	0.0306	1.9090						
MBRO	Sum	9	DOC ~ 1 + Temp + DO + DIC + GPP	76.7197	0.0299	1.9560						
MBRO	Paired	1	DOC ~ 1 + CaMg + Temp + DIC + ER	72.8332	0.1278	0.0000	1.248	13	0.6498	8.886	4 , 13	0.001099
MBRO	Paired	2	DOC ~ 1 + CaMg + Temp + DIC + GPP	74.2702	0.0623	1.4370	1.207	14	0.6531	9.474	4 , 14	0.000636
MBRO	Paired	3	DOC ~ 1 + Temp + DIC + GPP	74.7637	0.0487	1.9305	1.443	14	0.5316	7.432	3 , 14	0.003246
MBRO	Paired	4	DOC ~ 1 + Temp + DO + DIC + ER	74.8299	0.0471	1.9966	1.553	11	0.444	3.995	4 , 11	0.03062
SLBR	Sum	1	DOC ~ 1 + pH + DO + ER	85.9682	0.2144	0.0000	4.63	8	-0.1081	0.6422	3 , 8	0.6091
SLBR	Sum	2	DOC ~ 1 + pH + DO + GPP	87.1584	0.1182	1.1902	4.865	8	-0.2237	0.3298	3 , 8	0.8042
SLBR	Paired	1	DOC ~ 1 + pH + DO + ER	85.9682	0.2080	0.0000	4.63	8	-0.1081	0.6422	3 , 8	0.6091
SLBR	Paired	2	DOC ~ 1 + pH + DO + GPP	87.1584	0.1147	1.1902	4.865	8	-0.2237	0.3298	3 , 8	0.8042
SLBU	Sum	1	DOC ~ 1 + CationSum + Temp + DO + DIC + GPP	56.6901	0.3714	0.0000	0.7604	9	0.9172	32.03	5 , 9	1.79E-05
SLBU	Sum	2	DOC ~ 1 + CationSum + Q + Temp + DIC + GPP	57.9599	0.1968	1.2698	0.7806	10	0.9099	31.29	5 , 10	8.5E-06

SLBU	Sum	3	DOC ~ 1 + CationSum + Q + DIC + GPP + ER	58.0863	0.1848	1.3962	0.7837	10	0.9092	31.03	5 , 10	8.84E-06
SLBU	Paired	1	DOC ~ 1 + CaMg + DO + DIC + GPP + ER	41.3477	0.4060	0.0000	0.456	9	0.9702	92.28	5 , 9	1.87E-07
SLBU	Paired	2	DOC ~ 1 + CaMg + Q + DO + DIC + ER	42.1763	0.2683	0.8286	0.4688	9	0.9685	97.22	5 , 9	2.4E-07
SLBU	Paired	3	DOC ~ 1 + CaMg + DO + DIC + ER	43.2678	0.1554	1.9202	0.5922	10	0.9498	67.23	4 , 10	3.45E-07
STNY	Sum	1	DOC ~ 1 + CationSum + pH + DO + ER	90.5794	0.0824	0.0000	2.043	13	0.6148	7.783	4 , 13	0.001981
STNY	Sum	2	DOC ~ 1 + CationSum + DO + ER	91.3881	0.0550	0.8087	1.859	16	0.6731	14.04	3 , 16	9.57E-05
STNY	Sum	3	DOC ~ 1 + CationSum + Temp + DO + ER	91.5139	0.0517	0.9345	1.9	14	0.6666	9.995	4 , 14	0.000488
STNY	Sum	4	DOC ~ 1 + CationSum + pH + DO + GPP	91.9292	0.0420	1.3498	2.121	13	0.5848	6.986	4 , 13	0.003139
STNY	Sum	5	DOC ~ 1 + CationSum + DO + DIC + ER	92.1271	0.0380	1.5477	1.762	15	0.7064	12.43	4 , 15	0.000117
STNY	Sum	6	DOC ~ 1 + CationSum + Temp + DO + GPP	92.2118	0.0364	1.6324	1.936	14	0.6541	9.509	4 , 14	0.000624
STNY	Sum	7	DOC ~ 1 + CationSum + pH + DO + DIC + ER	92.5426	0.0309	1.9632						
STNY	Paired	1	DOC ~ 1 + NaK + pH + DO + ER	90.9767	0.0560	0.0000	2.066	13	0.6062	7.542	4 , 13	0.002269
STNY	Paired	2	DOC ~ 1 + NaK + DO + ER	91.5266	0.0425	0.5498	1.866	16	0.6708	13.91	3 , 16	0.000101
STNY	Paired	3	DOC ~ 1 + NaK + Temp + DO + ER	91.6881	0.0392	0.7114	1.909	14	0.6635	9.872	4 , 14	0.000519
STNY	Paired	4	DOC ~ 1 + NaK + pH + DO + GPP	91.9507	0.0344	0.9740	2.122	13	0.5843	6.973	4 , 13	0.003162

STNY	Paired	5	DOC ~ 1 + NaK + Temp + DO + GPP	92.2964	0.0289	1.3197	1.94	14		0.6525	9.451	4 , 14	0.000643
STNY	Paired	6	DOC ~ 1 + CaMg + pH + DO + ER	92.4479	0.0268	1.4712	2.152	13		0.5726	6.695	4 , 13	0.003744
STNY	Paired	7	DOC ~ 1 + CaMg + DO + DIC + ER	92.5563	0.0254	1.5796							
STNY	Paired	8	DOC ~ 1 + NaK + Q + DO + ER	92.8302	0.0222	1.8535							

Table H: Nitrate multiple linear regression model runs

Site	Cation	fit #	Model	AICC	Weight	ΔAIC	RSE	Model DF	Adj. R^2	F stat	Deg. of Freedom	P
All Sites	Sum	1	NO3 ~ 1 + CationSum + Q + pH + DO + DOC + DIC + ER	241.5353	0.247437	0	0.8548	83	0.4708	12.44	7 , 83	8.64E-11
All Sites	Sum	2	NO3 ~ 1 + CationSum + Q + Temp + pH + DO + DOC + DIC + ER	242.339	0.165554	0.803715	0.8519	82	0.4744	11.15	8 , 82	1.55E-10
All Sites	Sum	3	NO3 ~ 1 + CationSum + Q + pH + DO + DOC + DIC + GPP	243.1435	0.110724	1.608232	0.8506	84	0.4709	12.57	7 , 84	6.42E-11
All Sites	Sum	4	NO3 ~ 1 + CationSum + Q + Temp + pH + DO + DOC + DIC + GPP + ER	243.3339	0.100672	1.798575	0.8496	81	0.4772	10.13	9 , 81	2.81E-10
All Sites	Paired	1	NO3 ~ 1 + CaMg + Q + pH + DO + DOC + DIC + ER	199.0129	0.073941	0	0.6941	83	0.6684	26.91	7 , 83	2.2E-16
All Sites	Paired	2	NO3 ~ 1 + CaMg + Q + pH + DO + DIC + GPP + ER	199.2376	0.066083	0.224696	0.6775	83	0.6675	23.81	7 , 83	2.2E-16
All Sites	Paired	3	NO3 ~ 1 + CaMg + Q + pH + DO + DOC + DIC + GPP + ER	199.3378	0.062855	0.324881	0.6726	82	0.6723	24.08	8 , 82	2.2E-16
All Sites	Paired	4	NO3 ~ 1 + CaMg + NaK + pH + DO + DOC + DIC + ER	199.6385	0.05408	0.625587	0.679	83	0.6661	26.64	7 , 83	2.2E-16
All Sites	Paired	5	NO3 ~ 1 + CaMg + pH + DO + DOC + DIC + ER	199.928	0.046792	0.915092	0.6852	84	0.6599	30.1	6 , 84	2.2E-16

All Sites	Paired	6	NO3 ~ 1 + CaMg + Q + pH + DO + DOC + DIC + ER	200.0567	0.043875	1.043821	0.6857	84	0.6594	30.04	6 , 84	2.2E-16
HERR	Sum	1	NO3 ~ 1 + DIC + ER	32.3019	0.15324	0	0.478	15	0.627	15.29	2 , 15	0.00024
HERR	Sum	2	NO3 ~ 1 + DIC + GPP	33.15608	0.099975	0.854184	0.4895	15	0.6089	14.23	2 , 15	0.003424
HERR	Sum	3	NO3 ~ 1 + pH + DIC + ER	34.09215	0.062607	1.79025	0.4787	13	0.642	10.57	3 , 13	0.000858
HERR	Paired	1	NO3 ~ 1 + CaMg + ER	22.81697	0.167149	0	0.3673	15	0.7798	31.1	2 , 15	4.61E-06
HERR	Paired	2	NO3 ~ 1 + CaMg + GPP	23.26803	0.133401	0.451062	0.3719	15	0.7742	30.14	2 , 15	5.56E-06
HERR	Paired	3	NO3 ~ 1 + CaMg + pH + ER	24.50303	0.071942	1.686066	0.3611	13	0.7964	21.86	3 , 13	2.35E-05
MBRN	Sum	1	NO3 ~ 1 + CationSum + DO	-10.0031	0.35673	0	0.1565	17	0.7178	25.16	2 , 17	8.31E-06
MBRN	Paired	1	NO3 ~ 1 + CaMg + NaK + DO	-6.75327	0.15929	0	0.1599	16	0.7056	16.18	3 , 16	4.2E-05
MBRN	Paired	2	NO3 ~ 1 + CaMg + Temp + DO	-6.15594	0.118163	0.597329	0.1577	15	0.7256	16.87	3 , 15	4.53E-05
MBRN	Paired	3	NO3 ~ 1 + NaK + DO + DIC	-5.57777	0.088498	1.1755	0.1646	16	0.6878	14.95	3 , 16	6.67E-05
MBRN	Paired	4	NO3 ~ 1 + CaMg + NaK + Temp + DO	-4.84462	0.061338	1.908651	0.1505	14	0.7499	14.49	4 , 14	6.99E-05
MBRO	Sum	1	NO3 ~ 1 + CationSum + DO + DIC + GPP + ER	-18.1603	0.496562	0	0.08101	11	0.9354	47.3	5 , 11	4.54E-07
MBRO	Sum	2	NO3 ~ 1 + CationSum + DO + DOC + DIC + GPP + ER	-17.7138	0.397208	0.446496	0.06893	10	0.9532	55.31	6 , 10	4.28E-07
MBRO	Paired	1	NO3 ~ 1 + NaK + DO + DOC + DIC + GPP + ER	-17.2691	0.821247	0	0.06984	10	0.952	53.84	6 , 10	4.87E-07
SLBR	Sum	1	NO3 ~ 1 + CationSum + DO + GPP	30.37069	0.234133	0	0.4534	10	0.7285	12.63	3 , 10	0.000977

SLBR	Sum	2	NO3 ~ 1 + CationSum + DO + ER	30.673	0.201288	0.302307	0.4583	10	0.7226	12.29	3 , 10	0.001086
SLBR	Paired	1	NO3 ~ 1 + CaMg + pH + DIC + ER	15.25951	0.190338	0	0.2328	10	0.936	52.2	4 , 10	1.15E-06
SLBR	Paired	2	NO3 ~ 1 + CaMg + DO + DIC + ER	16.17187	0.120617	0.912363	0.2282	9	0.9312	45.01	4 , 9	5.93E-06
SLBR	Paired	3	NO3 ~ 1 + CaMg + Q + Temp + DIC + ER	16.70573	0.09236	1.446219	0.2151	10	0.9421	49.81	5 , 10	9.58E-07
SLBR	Paired	4	NO3 ~ 1 + CaMg + Q + Temp + DIC + GPP	17.14924	0.07399	1.889733	0.2181	10	0.9405	48.39	5 , 10	1.1E-06
SLBU	Sum	1	NO3 ~ 1 + Q + DO + DOC + GPP	0.611969	0.764879	0	0.1429	10	0.9798	171	4 , 10	3.68E-09
SLBU	Paired	1	NO3 ~ 1 + CaMg + DO + DIC + GPP	-5.94146	0.380033	0	0.1148	10	0.987	266.1	4 , 10	4.16E-10
SLBU	Paired	2	NO3 ~ 1 + CaMg + Q + DIC + GPP	-5.71841	0.339927	0.223056	0.1253	11	0.9868	280.9	4 , 11	5.43E-11
STNY	Sum	1	NO3 ~ 1 + CationSum + DO + GPP	27.37733	0.313	0	0.3753	16	0.9156	69.74	3 , 16	2.1E-09
STNY	Sum	2	NO3 ~ 1 + CationSum + DO + ER	27.83642	0.248802	0.459092	0.3796	16	0.9137	68.03	3 , 16	2.52E-09
STNY	Paired	1	NO3 ~ 1 + CaMg + DO + DIC + GPP	24.268	0.159673	0	0.3231	15	0.9375	72.23	4 , 15	1.29E-09
STNY	Paired	2	NO3 ~ 1 + CaMg + DO + DIC + ER	24.56593	0.137575	0.297922	0.3255	15	0.9365	71.1	4 , 15	1.44E-09
STNY	Paired	3	NO3 ~ 1 + CaMg + NaK + DO + GPP	26.15996	0.062001	1.891954	0.3387	15	0.9313	65.37	4 , 15	2.61E-09

Table I: Total dissolved nitrogen multiple linear regression model runs

Site	Cation	fit #	Model	AICC	Weight	ΔAIC	RSE	Model DF	Adj. R^2	F stat	Deg. of Freedom	P
All Sites	Sum	1	TDN ~ 1 + CationSum + Q + pH + DO + DOC + DIC + ER	244.7755	0.212929	0	0.8701	83	0.4383	11.03	7 , 83	8.85E-10
All Sites	Sum	2	TDN ~ 1 + CationSum + Q + pH + DO + DOC + DIC + ER	245.2192	0.170559	0.4437	0.8789	84	0.427	12.18	6, 84	8.29E-10
All Sites	Sum	3	TDN ~ 1 + CationSum + Q + pH + DO + DOC + DIC + GPP	246.1254	0.108422	1.3499	0.8645	84	0.4419	11.29	7 , 84	5.29E-10
All Sites	Sum	4	TDN ~ 1 + CationSum + Q + pH + DO + DIC + GPP + ER	246.5344	0.088367	1.7589	0.8786	83	0.4274	10.6	7 , 83	1.88E-09
All Sites	Paired	1	TDN ~ 1 + CaMg + Q + pH + DO + DIC + GPP + ER	205.8606	0.064608	0	0.7026	83	0.6338	23.25	7 , 83	2.2E-16
All Sites	Paired	2	TDN ~ 1 + CaMg + pH + DO + DIC + GPP + ER	206.3577	0.050389	0.4972	0.7099	84	0.6262	26.12	6, 84	2.2E-16
All Sites	Paired	3	TDN ~ 1 + CaMg + pH + DO + DIC + ER	206.3754	0.049944	0.5149	0.7152	85	0.6206	30.44	5 , 85	2.2E-16
All Sites	Paired	4	TDN ~ 1 + CaMg + q+ pH + DO + DIC + ER	206.4640	0.04778	0.6035	0.7103	84	0.625	26.08	6, 84	2.2E-16
All Sites	Paired	5	TDN ~ 1 + CaMg + pH + DO + DIC + GPP	206.6715	0.043072	0.8110	0.708	86	0.6257	31.43	5 , 86	2.2E-16

All Sites	Paired	6	TDN ~ 1 + CaMg + Q + pH + DO + DIC + GPP	206.6957	0.042555	0.8352	0.703	85	0.631	26.93	6 , 85	2.2E-16
HERR	Sum	1	TDN ~ 1 + DIC + ER	0.1159	0	31.5723	0.4684	15	0.5172	10.11	2 , 15	0.0017
HERR	Sum	2	TDN ~ 1 + DIC + GPP	0.0891	0.5274	32.0996	0.4753	15	0.5029	9.599	2 , 15	0.00207
HERR	Sum	3	TDN ~ 1 + DO + DIC + ER	0.0487	1.7352	33.3075	0.4562	14	0.542	7.705	3 , 14	0.00279
HERR	Sum	4	TDN ~ 1 + pH + DIC + ER	0.0436	1.9542	33.5264	0.4708	13	0.5335	7.098	3, 13	0.004547
HERR	Sum	5	TDN ~ 1 + DO + DIC + GPP	0.0433	1.9687	33.5409	0.4592	14	0.4592	7.546	3, 14	0.003049
HERR	Paired	1	TDN ~ 1 + CaMg + ER	21.8980	0.1327	0	0.358	15	0.718	22.64	2 , 15	2.949E-05
HERR	Paired	2	TDN ~ 1 + CaMg + GPP	21.9124	0.1318	0.0144	0.3582	15	0.7177	22.61	2 , 15	2.966E-05
HERR	Paired	3	TDN ~ 1 + CaMg + pH + ER	23.6059	0.0565	1.7079	0.3517	13	0.7397	16.16	3 , 13	0.000113
MBRN	Sum	1	TDN ~ 1 + CationSum + DO	-10.66142004	0.3909	0	0.154	17	0.6416	18	2 , 17	6.335E-05
MBRN	Paired	1	TDN ~ 1 + CaMg + NaK + DO	-7.0286	0.1772	0	0.1588	16	0.6189	11.29	3 , 16	0.0003174
MBRN	Paired	2	TDN ~ 1 + NaK + DO + DIC	-6.8764	0.1642	0.1522	0.1594	16	0.616	11.16	3, 16	0.0003368
MBRO	Sum	1	TDN ~ 1 + CationSum + DO	-10.8085	0.1866	0	0.1727	23	0.4841	12.73	2, 23	0.0001897
MBRO	Sum	2	TDN ~ 1 + CationSum + Q	-10.6763	0.1747	0.1322	0.1799	23	0.3672	9.125	2, 26	0.000995

MBRO	Sum	3	TDN ~ 1 + CationSum + Q + DO	-9.5668	0.1003	1.2416	0.1676	21	0.5126	9.412	3, 21	0.0003846
MBRO	Sum	4	TDN ~ 1 + CationSum + Q + DOC	-8.8089	0.0687	1.9996	0.1801	25	0.3659	6.385	3, 25	0.002312
MBRO	Paired	1	TDN ~ 1 + NaK + Q	-10.5905	0.1622	0	0.1802	26	0.3654	9.059	2, 26	0.001034
MBRO	Paired	2	TDN ~ 1 + NaK + Q + DOC	-8.5944	0.0598	1.9961	0.1808	25	0.3611	6.276	3, 25	0.002526
SLBR	Sum	1	TDN ~ 1 + CationSum + DO + GPP	35.3817	0.1831	0	0.5422	10	0.5687	6.713	3 , 10	0.009252
SLBR	Sum	2	TDN ~ 1 + CationSum + DO + ER	35.6521	0.1599	0.2704	0.5475	10	0.5603	6.521	3 , 10	0.01015
SLBR	Paired	1	TDN ~ 1 + CaMg + Q + Temp + DIC + GPP	18.0701	0.2966	0	0.2244	10	0.926	38.53	5, 10	3.225E-06
SLBR	Paired	2	TDN ~ 1 + CaMg + Q + Temp + DIC + ER	18.1550	0.2842	0.0849	0.225	10	0.9256	38.31	5, 10	3.31E-06
SLBR	Paired	3	TDN ~ 1 + CaMg + NaK + Temp + DIC + ER	19.7990	0.1249	1.7290	0.2369	10	0.9175	34.37	5 , 10	5.495E-06
SLBU	Sum	1	TDN ~ 1 + Q + DO + DOC + GPP	17.3074	0.3275	0	0.2493	10	0.9224	42.61	4 , 10	2.992E-06
SLBU	Sum	2	TDN ~ 1 + Q + DO + DOC + ER	17.6206	0.2800	0.3132	0.2519	10	0.9208	41.68		3.318E-06
SLBU	Paired	1	TDN ~ 1 + CaMg + ER	16.3813	0.1066	0	0.3113	13	0.9019	69.93	2, 13	1.103E-07
SLBU	Paired	2	TDN ~ 1 + CaMg + Q + DIC + GPP	16.4033	0.1054	0.0221	0.2502	11	0.9367	56.45	4 , 11	2.912E-07
SLBU	Paired	3	TDN ~ 1 + CaMg + GPP	16.6718	0.0922	0.2905	0.3142	13	0.9001	68.56	2, 13	1.241E-07
SLBU	Paired	4	TDN ~ 1 + Q + DO + DOC + GPP	17.3074	0.0671	0.9261	0.2493	10	0.9224	42.61	4, 10	2.992E-06

STNY	Sum	1	TDN ~ 1 + CationSum + DO + GPP	36.5130	0.2499	0	0.4716	16	0.8622	40.63	3 , 16	1.04E-07
STNY	Sum	2	TDN ~ 1 + CationSum + DO + ER	36.6623	0.2319	0.1493	0.4733	16	0.8612	40.28	3 , 16	1.103E-07
STNY	Paired	1	TDN ~ 1 + CaMg + DO GPP	27.5506	0.1539	0	0.3769	16	0.912	66.61	3, 16	2.943E-09
STNY	Paired	2	TDN ~ 1 + CaMg + DO + ER	27.6758	0.1446	0.1253	0.3781	16	0.9114	66.16	3, 16	3.093E-09
STNY	Paired	3	TDN ~ 1 + CaMg + DIC + DO + GPP	29.0856	0.0715	1.5351	0.3644	15	0.9177	53.98	4, 15	9.971E-09
STNY	Paired	4	TDN ~ 1 + CaMg + DIC + DO + ER	29.1972	0.0676	1.6467	0.3654	15	0.9173	53.65	4, 15	1.039e-08

Table J: All site data—multiple linear regression best fit models variable coefficient data

Model fit #	*Variable*	*Coeff Estimate*	*Std. Error t*	*t value*	*Pr(>|t|)*
		DIC Cation Sum			
1	(Intercept)	-6.66E+01	2.39E+01	-2.786	0.006611
	CationSum	2.21E-01	1.96E-02	11.287	< 2e-16
	Q	-2.67E-03	4.25E-04	-6.268	1.56E-08
	pH	9.80E+00	3.14E+00	3.121	0.002482
	DO	-2.69E-01	2.86E-01	-0.942	0.348798
	TN	-3.76E+00	6.92E-01	-5.43	5.48E-07
	GPP	-1.92E+00	6.68E-01	-2.877	0.005102
	ER	2.64E+00	7.09E-01	3.722	0.000359
2	(Intercept)	-6.92E+01	2.41E+01	-2.878	0.005098
	CationSum	2.22E-01	1.96E-02	11.33	< 2e-16
	Q	-2.69E-03	4.26E-04	-6.314	1.32E-08
	Temp	1.40E-01	1.40E-01	1.004	0.318363
	pH	9.58E+00	3.15E+00	3.041	0.003163
	DO	-4.39E-02	3.63E-01	-0.121	0.90417
	TN	-3.75E+00	6.92E-01	-5.417	5.93E-07
	GPP	-2.23E+00	7.35E-01	-3.034	0.003237
	ER	2.89E+00	7.52E-01	3.843	0.000238
		DIC Paired Cations			
1	(Intercept)	-0.98477	-14.50035	0.068	0.94602
	CaMg	0.48928	0.02073	23.604	< 2e-16
	NaK	-0.03173	-0.01647	1.927	0.05737 .
	pH	0.66663	1.91835	0.348	0.72909
	DO	0.03675	0.16401	0.224	0.82324
	TN	-3.85379	0.38218	-10.084	4.49E-16
	GPP	-1.12409	-0.38117	2.949	0.00414
	ER	1.20599	0.40316	2.991	0.00366
2	(Intercept)	-4.65297	-14.60529	0.319	0.75083
	CaMg	0.47629	0.01992	23.914	< 2e-16
	pH	1.10832	1.93514	0.573	0.56836
	DO	-0.04012	-0.16163	0.248	0.80456
	TN	-3.86649	-0.38825	9.959	7.03E-16
	GPP	-1.12103	-0.38727	2.895	0.00484
	ER	1.29142	0.40714	3.172	0.00211
		DOC Cation Sum			
1	(Intercept)	10.7243685	8.0978025	1.324	0.189
	CationSum	-0.0275639	0.0066955	-4.117	9.02E-05

	Q	0.0003585	0.0001452	2.469	0.0156
	Temp	0.1918366	0.0433235	4.428	2.88E-05
	pH	-0.8342739	1.0735254	-0.777	0.4393
	DO	0.1247904	0.1119906	1.114	0.2684
	TN	-0.4664166	0.2362143	-1.975	0.0516
	ER	-0.3704839	0.1562357	-2.371	0.02
2	(Intercept)	3.2599677	7.283782	0.448	0.65562
	CationSum	-0.0325746	0.006302	-5.169	1.57E-06
	Q	0.0004552	0.000139	3.275	0.00154
	Temp	0.1910376	0.0440628	4.336	4.02E-05
	pH	0.0795188	0.985224	0.081	0.93586
	DO	0.1104373	0.1136664	0.972	0.33404
	ER	-0.3447158	0.1583534	-2.177	0.0323
		DOC Paired Cations			
1	(Intercept)	8.77272	8.55181	1.026	0.30792
	CaMg	-0.04677	-0.01178	3.971	0.00015
	Temp	0.19911	0.04357	4.57	1.66E-05
	pH	-0.57631	-1.14299	0.504	0.61543
	DO	0.09491	0.11216	0.846	0.39985
	TN	-0.55971	-0.23044	2.429	0.01728
	ER	-0.26969	-0.15424	1.748	0.08404
2	(Intercept)	5.45978	8.09929	0.674	0.5021
	CaMg	-0.09723	-0.02051	4.741	8.58E-07
	Temp	0.20657	0.04383	4.713	9.57E-06
	pH	-0.25648	-1.10497	0.232	0.817
	DO	0.11259	0.11356	0.991	0.3243
	DIC	0.09761	0.04263	2.29	0.0246
	ER	-0.28864	-0.15667	1.842	0.0689
3	(Intercept)	8.57479	8.57727	1	0.3204
	CaMg	-0.06975	-0.03243	2.151	0.0344
	Temp	0.20265	0.04392	4.614	1.42E-05
	pH	-0.59412	-1.14611	0.518	0.6056
	DO	0.10694	0.11355	0.942	0.349
	TN	-0.37073	-0.33919	1.093	0.2776
	DIC	0.04757	0.06252	0.761	0.4489
	ER	-0.28797	-0.15649	1.84	0.0693
4	(Intercept)	9.616727	8.660808	1.11	0.270045
	CaMg	-0.043907	0.01249	-3.515	0.000714
	NaK	-0.007069	0.010033	-0.705	0.483059
	Temp	0.196693	0.043832	4.487	2.30E-05
	pH	-0.66919	1.153989	-0.58	0.563558
	DO	0.10855	0.114154	0.951	0.344415
	TN	-0.557021	0.231162	-2.41	0.018179

	ER	-0.289183	0.157162	-1.84	0.069338
		NO3 Cation Sum			
1	(Intercept)	7.99E+00	3.13E+00	2.554	0.0125
	CationSum	2.14E-02	3.58E-03	5.978	5.46E-08
	Q	-3.18E-04	6.04E-05	-5.276	1.03E-06
	pH	-7.90E-01	4.21E-01	-1.876	0.0642
	DO	-3.75E-02	3.77E-02	-0.996	0.3224
	DOC	-7.89E-02	3.77E-02	-2.093	0.0394
	DIC	-6.51E-02	1.20E-02	-5.42	5.72E-07
	ER	2.70E-02	6.39E-02	0.423	0.6735
2	(Intercept)	8.03E+00	3.12E+00	2.574	0.0118
	CationSum	2.08E-02	3.60E-03	5.762	1.41E-07
	Q	-3.08E-04	6.07E-05	-5.07	2.42E-06
	Temp	2.33E-02	1.86E-02	1.252	0.214
	pH	-8.55E-01	4.23E-01	-2.022	0.0464
	DO	-8.28E-03	4.42E-02	-0.187	0.8517
	DOC	-1.01E-01	4.16E-02	-2.435	0.0171
	DIC	-6.41E-02	1.20E-02	-5.343	8.03E-07
	ER	1.84E-02	6.41E-02	0.287	0.7745
3	(Intercept)	8.11E+00	3.10E+00	2.612	0.0107
	CationSum	2.07E-02	3.31E-03	6.256	1.59E-08
	Q	-3.10E-04	5.74E-05	-5.402	6.04E-07
	pH	-7.98E-01	4.19E-01	-1.904	0.0603
	DO	-3.33E-02	3.84E-02	-0.867	0.3885
	DOC	-8.26E-02	3.66E-02	-2.257	0.0266
	DIC	-6.36E-02	1.14E-02	-5.586	2.81E-07
	GPP	-2.23E-03	5.69E-02	-0.039	0.9688
4	(Intercept)	6.90E+00	3.25E+00	2.12	0.037
	CationSum	2.15E-02	3.65E-03	5.898	8.15E-08
	Q	-3.23E-04	6.19E-05	-5.221	1.35E-06
	Temp	3.24E-02	2.00E-02	1.618	0.1096
	pH	-7.56E-01	4.30E-01	-1.757	0.0827
	DO	1.47E-02	4.81E-02	0.306	0.7604
	DOC	-9.99E-02	4.15E-02	-2.404	0.0185
	DIC	-6.86E-02	1.25E-02	-5.469	4.90E-07
	GPP	-1.22E-01	1.01E-01	-1.197	0.2346
	ER	1.23E-01	1.08E-01	1.137	0.2589
		NO3 Paired Cations			
1	(Intercept)	8.20E+00	2.47E+00	3.323	0.00133
	CaMg	7.13E-02	6.91E-03	10.318	< 2e-16
	Q	-7.56E-05	4.27E-05	-1.773	0.07997
	pH	-8.88E-01	3.33E-01	-2.664	0.00928
	DO	-2.09E-02	2.94E-02	-0.71	0.47956

	DOC	-5.33E-02	2.95E-02	-1.807	0.07444
	DIC	-1.32E-01	1.32E-02	-10.034	5.63E-16
	ER	1.52E-02	4.83E-02	0.314	0.75417
2	(Intercept)	6.77E+00	2.54E+00	2.663	0.0093
	CaMg	7.79E-02	6.44E-03	12.095	<2e-16
	Q	-8.92E-05	4.28E-05	-2.082	0.0404
	pH	-7.79E-01	3.42E-01	-2.281	0.0251
	DO	6.21E-04	2.96E-02	0.021	0.9833
	DIC	-1.43E-01	1.34E-02	-10.612	<2e-16
	GPP	-1.28E-01	7.32E-02	-1.747	0.0844
	ER	1.38E-01	7.83E-02	1.769	0.0806
3	(Intercept)	7.24E+00	2.54E+00	2.844	0.00563
	CaMg	7.35E-02	7.04E-03	10.439	< 2e-16
	Q	-8.30E-05	4.27E-05	-1.943	0.05541
	pH	-7.83E-01	3.39E-01	-2.309	0.02348
	DO	-9.90E-03	3.02E-02	-0.328	0.74373
	DOC	-4.46E-02	3.00E-02	-1.489	0.14034
	DIC	-1.38E-01	1.37E-02	-10.058	5.73E-16
	GPP	-1.05E-01	7.42E-02	-1.417	0.16013
	ER	1.07E-01	8.05E-02	1.326	0.18846
4	(Intercept)	8.366926	2.485797	3.366	0.00116
	CaMg	0.076265	0.007087	10.762	< 2e-16
	NaK	-0.004933	0.003088	-1.597	0.11397
	pH	-0.900817	0.335031	-2.689	0.00867
	DO	-0.016348	0.029981	-0.545	0.58702
	DOC	-0.060934	0.029617	-2.057	0.04279
	DIC	-0.136725	-0.013289	10.288	< 2e-16
	ER	-0.00472	0.048931	-0.096	0.92339
5	(Intercept)	7.931845	2.49355	3.181	0.00206
	CaMg	0.073313	0.006904	10.619	< 2e-16
	pH	-0.85509	0.336876	-2.538	0.01298
	DO	-0.026672	0.029545	-0.903	0.36925
	DOC	-0.05717	0.029795	-1.919	0.05841
	DIC	-0.133973	-0.013298	10.075	4.12E-16
	ER	0.007682	0.048755	0.158	0.87518
6	(Intercept)	7.88E+00	2.49E+00	3.16	0.00219
	CaMg	7.62E-02	6.44E-03	11.825	< 2e-16
	Q	-8.13E-05	4.31E-05	-1.886	0.06272
	pH	-9.11E-01	3.37E-01	-2.699	0.0084
	DO	-1.07E-02	2.92E-02	-0.365	0.71586
	DIC	-1.37E-01	1.31E-02	-10.397	< 2e-16
	ER	3.00E-02	4.83E-02	0.622	0.53558

Table K: Herring Run (HERR)—multiple linear regression best fit models variable coefficient data

Model fit #	*Variable*	*Coeff Estimate*	*Std. Error*	*t value*	*Pr(>|t|)*
		DIC Cation Sum			
1	(Intercept)	5.4500297	3.8663534	1.41	0.184043
	CationSum	0.081254	0.0187316	4.338	0.000965
	Q	-0.001734	0.0003686	-4.704	0.00051
	Temp	0.1948125	0.1062126	1.834	0.091531
	ER	2.0206348	1.5920043	1.269	0.228421
2	(Intercept)	-3.32E+01	2.40E+01	-1.382	0.194267
	CationSum	1.21E-01	2.58E-02	4.687	0.000664
	Q	-2.26E-03	4.05E-04	-5.583	0.000164
	pH	4.20E+00	2.83E+00	1.484	0.165989
	DOC	9.82E-01	3.90E-01	2.514	0.028789
	ER	3.12E+00	1.55E+00	2.008	0.069819
		DIC Paired Cations			
1	(Intercept)	4.89826	3.18317	1.539	0.148
	CaMg	0.238	0.03675	6.476	2.08E-05
	Temp	0.07396	0.0836	0.885	0.392
	ER	-0.57966	-0.91283	0.635	0.536
2	(Intercept)	3.9293	2.32412	1.691	0.115
	CaMg	0.2469	0.03075	8.03	2.15E-06
	Temp	0.09098	0.08776	1.037	0.319
	GPP	-0.34182	-0.69603	0.491	0.632
3	(Intercept)	-3.04764	-20.33729	0.15	0.883
	CaMg	0.23726	0.03754	6.321	2.66E-05
	pH	1.15158	2.55699	0.45	0.66
	ER	-0.50108	-0.98281	0.51	0.619
4	(Intercept)	6.60205	2.80142	2.357	0.0325
	CaMg	0.22768	0.03456	6.588	8.62E-06
	ER	-0.80357	-0.87799	0.915	0.3745
5	(Intercept)	-7.25554	-19.21384	0.378	0.712
	CaMg	0.24856	0.03162	7.86	2.71E-06
	pH	1.54375	2.49042	0.62	0.546
	GPP	-0.04407	-0.69526	0.063	0.95
6	(Intercept)	8.6175674	2.6241129	3.284	0.005433
	CaMg	0.1934372	0.0368977	5.243	0.000125
	Q	-0.0003819	0.0002005	-1.905	0.077589
	GPP	-0.4789656	0.572292	-0.837	0.416693
		DOC Cation Sum			
1	(Intercept)	6.0438753	2.1285184	2.839	0.01491
	CationSum	-0.0379321	0.0103122	-3.678	0.00316
	Q	0.0005485	0.0002029	2.703	0.0192

	Temp	0.1626736	0.0584725	2.782	0.01659
	ER	-0.6691604	0.8764358	-0.764	0.45991
2	(Intercept)	5.9667199	2.1465716	2.78	0.01666
	CationSum	-0.0398983	0.0118375	-3.37	0.00557
	Q	0.0004438	0.0001097	4.045	0.00162
	Temp	0.1680911	0.0586702	2.865	0.01422
	GPP	-0.3474043	0.4986172	-0.697	0.49924
3	(Intercept)	14.7230657	2.2899235	6.43	2.24E-05
	CationSum	-0.0374065	0.0094386	-3.963	0.00162
	Q	0.000522	0.0001863	2.802	0.01498
	DO	-0.5648949	0.1838305	-3.073	0.0089
	ER	-0.7242775	0.8086133	-0.896	0.3867
4	(Intercept)	14.3510467	2.4161456	5.94	4.91E-05
	CationSum	-0.0375177	0.0106098	-3.536	0.00365
	Q	0.000394	0.0001013	3.887	0.00187
	DO	-0.5709353	0.187898	-3.039	0.00951
	GPP	-0.2171512	0.4308645	-0.504	0.6227
5	(Intercept)	30.2278691	13.323981	2.269	0.04441
	CationSum	-0.0467012	0.011446	-4.08	0.00182
	Q	0.0004063	0.0001033	3.934	0.00234
	pH	-1.772974	1.6150849	-1.098	0.29576
	DO	-0.6191219	0.1857869	-3.332	0.00668
	GPP	-0.7340352	0.5034821	-1.458	0.17282
		DOC Paired Cations			
1	(Intercept)	4.57322	1.66281	2.75	0.01653
	CaMg	-0.07725	-0.022	3.511	0.00383
	Temp	0.2264	0.06279	3.606	0.00320
	GPP	0.13525	0.49798	0.272	0.7902
2	(Intercept)	4.42741	2.29354	1.93	0.07567
	CaMg	-0.07598	-0.02648	2.869	0.01316
	Temp	0.23251	0.06023	3.86	0.00197
	ER	0.14482	0.65771	0.22	0.82915
3	(Intercept)	13.0043883	2.287418	5.685	7.48E-05
	NaK	-0.0501986	0.0133358	-3.764	0.00236
	Q	0.0007866	0.0002287	3.439	0.0044
	DO	-0.5328579	0.1929957	-2.761	0.01619
	ER	-0.8776769	0.8466341	-1.037	0.31879
4	(Intercept)	4.7715367	2.0620406	2.314	0.03919
	NaK	-0.0494654	0.015399	-3.212	0.00746
	Q	0.0007875	0.0002601	3.027	0.01052
	Temp	0.1460588	0.065582	2.227	0.04585
	ER	-0.7533847	0.9559411	-0.788	0.44592
		NO3 Cation Sum			

1	(Intercept)	0.31434	0.64782	0.485	0.63452
	DIC	0.09132	0.02588	3.529	0.00304
	ER	-0.15126	-0.17713	0.854	0.40657
2	(Intercept)	-0.139682	0.487967	-0.286	0.7786
	DIC	0.105846	0.021222	4.988	0.000162
	GPP	-0.001815	0.123881	-0.015	0.988503
3	(Intercept)	5.4612	3.86417	1.413	0.18107
	pH	-0.65771	-0.48898	1.345	0.2016
	DIC	0.09194	0.02624	3.504	0.00388
	ER	-0.23008	-0.18617	1.236	0.23839
		NO3 Paired Cations			
1	(Intercept)	0.264861	0.425698	0.622	0.543
	CaMg	0.029475	0.005252	5.612	4.95E-05
	ER	-0.082456	0.133417	-0.618	0.546
2	(Intercept)	0.03657	0.31751	0.115	0.91
	CaMg	0.03162	0.0043	7.353	2.39E-06
	GPP	0.00335	0.09316	0.036	0.9
3	(Intercept)	4.532492	2.928483	1.548	0.146
	CaMg	0.030306	0.005405	5.607	8.53E-05
	pH	-0.549283	0.368196	-1.492	0.16
	ER	-0.13649	0.141521	-0.964	0.352

Table L: Minebank Run New (MBRN)—multiple linear regression best fit models variable coefficient data

Model , fit #	***Variable***	***Coeff Estimate***	***Std. Error***	***t value***	***Pr(>|t|)***
		DIC Cation Sum			
1	(Intercept)	2.8374	20.6302	0.138	0.89309
	Temp	1.5243	0.4212	3.619	0.00404
	DO	3.4286	1.5497	2.212	0.04901
	DOC	-7.1367	1.152	-6.195	6.76E-05
	ER	2.4673	4.1289	0.598	0.56223
2	(Intercept)	3.42742	21.06193	0.163	0.87368
	Temp	1.5228	0.43575	3.495	0.00502
	DO	3.67181	1.57692	2.328	0.03998
	DOC	-7.4442	1.13075	-6.583	3.95E-05
	GPP	-0.07034	2.30906	-0.03	0.97624
		DIC Paired Cations			
1	(Intercept)	-16.647334	9.722415	-1.712	0.1176
	CaMg	0.364232	0.034383	10.593	9.35E-07
	Q	-0.007456	0.002401	-3.105	0.0112
	Temp	0.425096	0.170903	2.487	0.0321
	DO	2.132321	0.678197	3.144	0.0104
	ER	-0.803742	1.92104	-0.418	0.6845
2	(Intercept)	-17.749294	10.002814	-1.774	0.1064
	CaMg	0.367288	0.037079	9.906	1.73E-06
	Q	-0.00699	0.002334	-2.995	0.0135
	Temp	0.446522	0.167227	2.67	0.0235
	DO	2.133327	0.683917	3.119	0.0109
	GPP	-0.375383	1.030204	-0.364	0.7232
		DOC Cation Sum			
1	(Intercept)	2.7200123	7.7343877	0.352	0.7394
	CationSum	-0.0184845	0.0049464	-3.737	0.00387
	Q	0.0018264	0.0004824	3.786	0.00356
	Temp	0.1150843	0.0414225	2.778	0.01951
	DO	0.0625765	0.1621275	0.386	0.7076
	GPP	-0.1763033	0.2344522	-0.752	0.46939
2	(Intercept)	3.8043005	2.5311175	1.503	0.16374
	CationSum	-0.0200156	0.0046916	-4.266	0.00165
	Q	0.0018151	0.0005308	3.42	0.00655
	Temp	0.1110843	0.0426737	2.603	0.02635
	DO	0.0191155	0.1619984	0.118	0.90841
	ER	0.0842383	0.4471793	0.188	0.85435
3	(Intercept)	0.23397	2.52883	0.093	0.92795
	Temp	0.20106	0.04574	4.396	0.00107
	DO	0.41933	0.19351	2.167	0.05305

	DIC	-0.10714	0.01627	-6.583	3.95E-05
	GPP	-0.15403	0.27311	-0.564	0.58407
4	(Intercept)	1.0942928	0.545525	2.006	0.067942
	CationSum	-0.0084295	0.0015682	-5.375	0.000167
	Q	0.0030129	0.0003295	9.144	9.34E-07
	Temp	0.1439139	0.0243765	5.904	7.21E-05
	GPP	-0.7113412	0.246935	-2.881	0.013813
	ER	1.079707	0.2749832	3.926	0.002012
5	(Intercept)	0.41659	2.54757	0.164	0.87307
	Temp	0.19903	0.04826	4.124	0.00169
	DO	0.40588	0.19488	2.083	0.06141
	DIC	-0.10891	0.01758	-6.195	6.76E-05
	ER	-0.07376	0.51778	-0.142	0.88929
6	(Intercept)	0.23397	2.52883	0.093	0.92795
	Temp	0.20106	0.04574	4.396	0.00107
	DO	0.41933	0.19351	2.167	0.05305
	DIC	-0.10714	0.01627	-6.583	3.95E-05
	GPP	-0.15403	0.27311	-0.564	0.58407
		DOC Paired Cations			
1	(Intercept)	0.41659	2.54757	0.164	0.87307
	Temp	0.19903	0.04826	4.124	0.00169
	DO	0.40588	0.19488	2.083	0.06141
	DIC	-0.10891	0.01758	-6.195	6.76E-05
	ER	-0.07376	0.51778	-0.142	0.88929
2	(Intercept)	3.0805329	1.0076999	3.057	0.009954
	CaMg	-0.0301246	0.0081889	-3.679	0.003156
	NaK	-0.0063163	0.0017293	-3.653	0.003311
	Q	0.0018893	0.0005525	3.419	0.005084
	Temp	0.135873	0.0252041	5.391	0.000162
	ER	0.6743326	0.242202	2.784	0.016522
2	(Intercept)	16.216906	4.134095	3.923	0.00203
	NaK	-0.021289	0.008039	-2.648	0.02125
	Temp	0.095655	0.032987	2.9	0.01333
	pH	-1.24494	0.544074	-2.288	0.04107
	DO	0.038967	0.052226	0.746	0.46996
	DIC	-0.084412	0.013945	-6.053	5.73E-05
3	(Intercept)	2.58578	0.9263175	2.791	0.017541
	CaMg	-0.0233717	0.0079766	-2.93	0.013689
	NaK	-0.0071046	0.0015822	-4.49	0.000916
	Q	0.0022137	0.0005152	4.297	0.001263
	Temp	0.1369612	0.0223797	6.12	7.52E-05
	GPP	-0.509208	0.2476284	-2.056	0.06427
	ER	0.9624199	0.2566173	3.75	0.003208

		NO3 Cation Sum			
1	(Intercept)	0.330096	0.17795	1.855	0.081
	CationSum	0.006295	0.000898	7.01	2.10E-06
	DO	0.001969	0.009642	0.204	0.841
		NO3 Paired Cations			
1	(Intercept)	0.3499959	0.185412	1.888	0.077346
	CaMg	0.0071038	0.0017272	4.113	0.000814
	NaK	0.0052511	0.0021055	2.494	0.023962
	DO	0.0002456	0.0103302	0.024	0.981329
2	(Intercept)	1.145263	0.259681	4.41	0.000506
	CaMg	0.008304	0.001541	5.389	7.52E-05
	Temp	-0.019978	0.007228	-2.764	0.014478
	DO	-0.022111	0.011587	-1.908	0.075691
3	(Intercept)	0.28662	0.195756	1.464	0.16252
	NaK	0.006799	0.001999	3.402	0.00365
	DO	0.002451	0.010498	0.233	0.81836
	DIC	0.01369	0.00353	3.878	0.00133
4	(Intercept)	0.855448	0.309244	2.766	0.015153
	CaMg	0.007084	0.001664	4.257	0.000797
	NaK	0.003419	0.002181	1.568	0.139249
	Temp	-0.015069	0.007578	-1.988	0.06667
	DO	-0.014323	0.012126	-1.181	0.257201

Table M: Minebank Run Old (MBRO)—multiple linear regression best fit models variable coefficient data

Model , fit #	***Variable***	***Coeff Estimate***	***Std. Error***	***t value***	***Pr(>|t|)***
		DIC Cation Sum			
1	(Intercept)	35.26169	6.8297	5.163	0.000423
	Q	-0.16557	0.02321	-7.132	3.17E-05
	Temp	0.4433	0.26557	1.669	0.126024
	DO	-0.10011	0.51006	-0.196	0.848332
	DOC	-1.68653	0.54142	-3.115	0.010966
	ER	0.58552	0.48589	1.205	0.25593
2	(Intercept)	44.22546	4.3224	10.232	2.79E-07
	Q	-0.17288	0.02353	-7.347	8.88E-06
	DO	-0.55362	0.42554	-1.301	0.2177
	DOC	-1.38425	0.51499	-2.688	0.0197
	ER	0.70016	0.48209	1.452	0.172
3	(Intercept)	48.1321	51.241	0.939	0.37
	Q	-0.1951	0.0307	-6.354	8.31E-05
	pH	-1.2648	6.6223	-0.191	0.852
	DO	-0.4142	0.6015	-0.689	0.507
	ER	1.1512	0.7155	1.609	0.139
4	(Intercept)	50.53947	42.55641	1.188	0.265392
	Q	-0.16882	0.02783	-6.066	0.000187
	pH	-0.85475	5.50113	-0.155	0.879953
	DO	-0.55852	0.50316	-1.11	0.295767
	DOC	-1.43004	0.60942	-2.347	0.04355
	ER	0.77872	0.6149	1.266	0.237158
		DIC Paired Cations			
1	(Intercept)	20.93465	6.94146	3.016	0.014576
	CaMg	0.22211	0.05331	4.166	0.002425
	NaK	-0.10927	0.03238	-3.375	0.008193
	Q	-0.09128	0.02312	-3.949	0.003361
	Temp	0.43464	0.159	2.734	0.023088
	DO	0.33334	0.39144	0.852	0.416534
	DOC	-1.56881	0.29948	-5.239	0.000536
	GPP	-0.38127	0.65847	-0.579	0.576771
2	(Intercept)	33.08026	5.77842	5.725	0.000192
	CaMg	0.202	0.06624	3.05	0.012262
	NaK	-0.13221	0.04374	-3.023	0.01283
	Q	-0.10543	0.02868	-3.676	0.004274
	DO	-0.1783	0.31948	-0.558	0.589062
	DOC	-1.31554	0.36882	-3.567	0.005122
	ER	-0.14778	0.42025	-0.352	0.732406
3	(Intercept)	21.90347	6.31196	3.47	0.00844

	CaMg	0.22578	0.05619	4.018	0.00385
	NaK	-0.11466	0.03669	-3.125	0.01412
	Q	-0.09072	0.02413	-3.76	0.00555
	Temp	0.42385	0.16462	2.575	0.03288
	DO	0.29416	0.31674	0.929	0.38021
	DOC	-1.62886	0.32315	-5.041	0.001
	ER	-0.26423	0.3573	-0.74	0.48072
4	(Intercept)	35.26169	6.8297	5.163	0.000423
	Q	-0.16557	0.02321	-7.132	3.17E-05
	Temp	0.4433	0.26557	1.669	0.126024
	DO	-0.10011	0.51006	-0.196	0.848332
	DOC	-1.68653	0.54142	-3.115	0.010966
	ER	0.58552	0.48589	1.205	0.25593
5	(Intercept)	44.22546	4.3224	10.232	2.79E-07
	Q	-0.17288	0.02353	-7.347	8.88E-06
	DO	-0.55362	0.42554	-1.301	0.2177
	DOC	-1.38425	0.51499	-2.688	0.0197
	ER	0.70016	0.48209	1.452	0.172
6	(Intercept)	34.67569	6.03394	5.747	0.000129
	CaMg	0.18549	0.06324	2.933	0.013608
	NaK	-0.11613	0.03984	-2.915	0.014063
	Q	-0.11	0.02727	-4.033	0.001971
	DO	-0.34293	0.37892	-0.905	0.384849
	DOC	-1.29472	0.34925	-3.707	0.003458
	GPP	0.2399	0.7637	0.314	0.759298
			DOC Cation Sum		
1	(Intercept)	5.39011	1.45046	3.716	0.002303
	Temp	0.19601	0.08896	2.203	0.04481
	DIC	-0.15494	0.03314	-4.675	0.000358
	ER	0.05466	0.11003	0.497	0.627032
2	(Intercept)	4.781944	3.579564	1.336	0.2086
	Temp	0.197044	0.115549	1.705	0.1162
	DO	0.007482	0.237403	0.032	0.9754
	DIC	-0.129001	0.045092	-2.861	0.0155
	ER	-0.106409	0.229602	-0.463	0.6521
3	(Intercept)	9.45009	2.50299	3.776	0.00231
	DO	-0.24115	0.19735	-1.222	0.24342
	DIC	-0.12722	0.04548	-2.797	0.01511
	ER	-0.07179	0.23254	-0.309	0.76242
4	(Intercept)	12.37097	15.10443	0.819	0.42753
	pH	-0.67777	1.96744	-0.344	0.73599
	DIC	-0.13088	0.03531	-3.706	0.00264
	ER	-0.05803	0.10483	-0.554	0.58926

5	(Intercept)	10.32418	19.65256	0.525	0.6108
	pH	-0.18693	2.46852	-0.076	0.9411
	DO	-0.19024	0.22871	-0.832	0.4249
	DIC	-0.12808	0.05247	-2.441	0.0348
	ER	-0.05683	0.28855	-0.197	0.8478
6	(Intercept)	10.401666	4.334095	2.4	0.0373
	Q	-0.039213	0.020351	-1.927	0.0829
	Temp	0.218589	0.104093	2.1	0.0621
	DO	0.008299	0.212627	0.039	0.9696
	DIC	-0.292004	0.09374	-3.115	0.011
	ER	0.022479	0.216246	0.104	0.9193
		DOC Paired Cations			
1	(Intercept)	3.84986	1.40983	2.731	0.017158
	CaMg	0.07872	0.03291	2.392	0.032547
	Temp	0.23772	0.07887	3.014	0.009968
	DIC	-0.2771	0.05856	-4.732	0.000392
	ER	0.01242	0.09677	0.128	0.899839
2	(Intercept)	3.81954	1.34105	2.848	0.012897
	CaMg	0.0775	0.03164	2.45	0.02806
	Temp	0.23402	0.07093	3.299	0.00527
	DIC	-0.27388	0.05682	-4.82	0.000272
	GPP	0.05403	0.1856	0.291	0.775222
3	(Intercept)	5.39011	1.45046	3.716	0.002303
	Temp	0.19601	0.08896	2.203	0.04481
	DIC	-0.15494	0.03314	-4.675	0.000358
	ER	0.05466	0.11003	0.497	0.627032
4					
	(Intercept)	4.781944	3.579564	1.336	0.2086
	Temp	0.197044	0.115549	1.705	0.1162
	DO	0.007482	0.237403	0.032	0.9754
	DIC	-0.129001	0.045092	-2.861	0.0155
	ER	-0.106409	0.229602	-0.463	0.6521
		NO3 Cation Sum			
1	(Intercept)	-0.478391	0.145885	-3.279	0.00734
	CationSum	0.0055136	0.000937	5.88	0.00016
	DO	0.0461089	0.012308	3.746	0.003232
	DIC	0.0203011	0.002822	7.192	1.77-E05
	GPP	-0.1637879	0.036111	-4.536	0.00085
	ER	0.034291	0.018231	1.881	0.086717
2	(Intercept)	-0.793832	0.185943	-4.269	0.001639
	CationSum	0.005494	0.000798	6.885	4.27E-05
	DO	0.057825	0.011668	4.956	0.000574
	DOC	0.028584	0.012545	2.279	0.045896

	DIC	0.023948	0.002887	8.297	8.55E-06
	GPP	-0.188636	0.032606	-5.785	0.000176
	ER	0.045494	0.016274	2.795	0.018941
		NO3 Paired Cations			
1	(Intercept)	-0.957163	0.193337	-4.951	0.000578
	NaK	0.008027	0.001185	6.776	4.88E-05
	DO	0.056446	0.011861	4.759	0.00077
	DOC	0.042186	0.012846	3.284	0.008234
	DIC	0.035283	0.002547	13.855	7.48E-08
	GPP	-0.187765	0.033042	-5.683	0.000203
	ER	0.054694	0.016827	3.25	0.008715

Table N: Scotts Level Restored (SLBR)—multiple linear regression best fit models variable coefficient data

Model , fit #	*Variable*	*Coeff Estimate*	*Std. Error*	*t value*	*Pr(>|t|)*
		DIC Cation Sum			
1	(Intercept)	19.54043	2.25438	8.668	5.80E-06
	Q	-0.20386	0.02585	-7.885	1.34E-05
	DO	-0.02689	0.19506	-0.138	0.8931
	GPP	-0.21242	0.11474	-1.851	0.0939 .
2	(Intercept)	19.66727	2.35063	8.367	7.93E-06
	Q	-0.20089	0.02684	-7.486	2.10E-05
	DO	-0.02489	0.20816	-0.12	0.907
	ER	-0.28497	0.1876	-1.519	0.16
3	(Intercept)	18.77232	2.017695	9.304	6.50E-06
	Q	-0.232409	0.026866	-8.651	1.18E-05
	DO	0.009514	0.172331	0.055	0.9572
	DOC	0.195273	0.098151	1.99	0.0779
	GPP	-0.240254	0.101766	-2.361	0.0425
4	(Intercept)	18.74117	2.04556	9.162	7.38E-06
	Q	-0.23511	0.02768	-8.493	1.37E-05
	DO	0.03807	0.17955	0.212	0.8368
	DOC	0.22292	0.1018	2.19	0.0563
	ER	-0.37751	0.16522	-2.285	0.0482
		DIC Paired Cations			
1	(Intercept)	9.827295	1.16239	8.454	7.23E-06
	CaMg	0.345245	0.033942	10.172	1.36E-06
	Q	-0.028805	0.006388	-4.509	0.001127
	Temp	-0.091044	0.039854	-2.284	0.045444
	TN	-3.245802	0.600298	-5.407	0.000298
	ER	-0.022096	0.10752	-0.206	0.841302
2	(Intercept)	9.806865	1.177046	8.332	8.23E-06
	CaMg	0.344841	0.034202	10.082	1.47E-06
	Q	-0.028782	0.006396	-4.5	0.001143
	Temp	-0.091454	0.040554	-2.255	0.047765
	TN	-3.239627	0.611107	-5.301	0.000347
	GPP	-0.011823	0.066933	-0.177	0.863324
3	(Intercept)	19.54043	2.25438	8.668	5.80E-06
	Q	-0.20386	0.02585	-7.885	1.34E-05
	DO	-0.02689	0.19506	-0.138	0.8931
	GPP	-0.21242	0.11474	-1.851	0.0939 .
		DOC Cation Sum			
1	(Intercept)	205.2418	173.6213	1.182	0.271
	pH	-25.4157	22.7207	-1.119	0.296
	DO	-0.9755	0.9184	-1.062	0.319

	ER	1.26	1.0312	1.222	0.257
	pH	-18.1377	23.3729	-0.776	0.46
	DO	-0.7006	0.9298	-0.753	0.473
	GPP	0.5473	0.7086	0.772	0.462
		DOC Paired Cations			
1	(Intercept)	205.2418	173.6213	1.182	0.271
	pH	-25.4157	22.7207	-1.119	0.296
	DO	-0.9755	0.9184	-1.062	0.319
	ER	1.26	1.0312	1.222	0.257
2	(Intercept)	148.5916	178.7549	0.831	0.43
	pH	-18.1377	23.3729	-0.776	0.46
	DO	-0.7006	0.9298	-0.753	0.473
	GPP	0.5473	0.7086	0.772	0.462
		NO3 Cation Sum			
1	(Intercept)	-1.58674	0.827768	-1.917	0.084241
	CationSum	0.037146	0.006205	5.986	0.000135
	DO	0.048874	0.063334	0.772	0.458149
	GPP	-0.055389	0.036541	-1.516	0.160523
2	(Intercept)	-1.496213	0.822489	-1.819	0.098917
	CationSum	0.036292	0.006164	5.888	0.000154
	DO	0.053378	0.06558	0.814	0.434635
	ER	-0.081561	0.057175	-1.427	0.184186
		NO3 Paired Cations			
1	(Intercept)	-10.29337	3.95661	-2.602	0.02642
	CaMg	0.09189	0.01009	9.111	3.71E-06
	pH	1.46038	0.54014	2.704	0.02217
	DIC	-0.16009	0.03586	-4.464	0.00121
	ER	-0.07819	0.02926	-2.672	0.02341
2	(Intercept)	-0.553682	0.481662	-1.15	0.27997
	CaMg	0.078536	0.009065	8.663	1.17E-05
	DO	0.097099	0.032563	2.982	0.0154
	DIC	-0.108383	0.039307	-2.757	0.02221
	ER	-0.105458	0.028929	-3.645	0.00536
3	(Intercept)	1.634128	0.442416	3.694	0.00415
	CaMg	0.091854	0.00963	9.538	2.45E-06
	Q	-0.006279	0.001978	-3.175	0.00991
	Temp	-0.020397	0.00873	-2.336	0.0416
	DIC	-0.203767	0.040577	-5.022	0.00052
	ER	-0.014565	0.027376	-0.532	0.60633
4	(Intercept)	1.6077947	0.4482387	3.587	0.00495
	CaMg	0.0908688	0.0098793	9.198	3.40E-06
	Q	-0.0061952	0.0020099	-3.082	0.01159

Temp	-0.0227428	0.0088056	-2.583	0.02729
DIC	-0.2004362	0.0417277	-4.803	0.00072
GPP	-0.0007528	0.0172152	-0.044	0.96598

Table O: Scotts Level Unrestored (SLBU)—multiple linear regression best fit models variable coefficient data

Model , fit #	*Variable*	*Coeff Estimate*	*Std. Error*	*t value*	*Pr(>|t|)*
		DIC Cation Sum			
1	(Intercept)	-1.283322	1.475742	-0.87	0.4049
	CationSum	0.147373	0.012683	11.62	3.95E-07
	Q	-0.032527	0.003831	-8.491	6.96E-06
	DOC	0.689524	0.091933	7.5	2.06E-05
	GPP	0.777197	0.288685	2.692	0.0226
	ER	0.628695	0.196116	3.206	0.0094
2	(Intercept)	3.07241	2.08013	1.477	0.17792
	CationSum	0.09946	0.02029	4.902	0.00119
	Q	-0.12003	0.03219	-3.728	0.0058
	DO	0.0455	0.0461	0.987	0.35248
	DOC	0.61746	0.08032	7.687	5.81E-05
	GPP	0.80982	0.24383	3.321	0.01052
	ER	0.80608	0.17017	4.737	0.00147
3	(Intercept)	0.420462	1.543119	0.272	0.7908
	CationSum	0.148068	0.013484	10.981	6.70E-07
	Q	-0.037948	0.004471	-8.489	6.98E-06
	Temp	-0.079007	0.027876	-2.834	0.01772
	DOC	0.729601	0.10115	7.213	2.88E-05
	GPP	1.121323	0.255403	4.39	0.00136
		DIC Paired Cations			
1	(Intercept)	-0.608424	0.769867	-0.79	0.4497
	CaMg	0.244937	0.009838	24.896	1.31E-09
	DO	0.092341	0.032791	2.816	0.0202
	DOC	0.735929	0.054083	13.607	2.62E-07
	GPP	0.449116	0.173584	2.587	0.0293
	ER	0.826562	0.116658	7.085	5.76E-05
2	(Intercept)	0.10153	0.90112	0.113	0.913
	CaMg	0.23884	0.01197	19.959	2.19E-09
	DO	0.06278	0.03851	1.63	0.134
	DOC	0.69721	0.06511	10.708	8.46E-07
	ER	0.99589	0.12098	8.232	9.16E-06
		DOC Cation Sum			
1	(Intercept)	1.83987	1.93208	0.952	0.36583
	CationSum	-0.20693	0.01835	-11.275	1.31E-06
	Temp	0.13644	0.04036	3.381	0.00812
	DO	0.14967	0.09032	1.657	0.13186
	DIC	1.12177	0.1491	7.523	3.60E-05
	GPP	-0.97896	0.36705	-2.667	0.02574
2	(Intercept)	1.266474	1.902522	0.666	0.520673

	CationSum	-0.185781	0.01702	-10.916	7.08E-07
	Q	0.043174	0.008486	5.088	0.000472
	Temp	0.104675	0.033352	3.138	0.010537
	DIC	1.149645	0.159384	7.213	2.88E-05
	GPP	-1.438785	0.306432	-4.695	0.000848
3	(Intercept)	3.549292	1.709852	2.076	0.064653
	CationSum	-0.196678	0.017253	-11.4	4.73E-07
	Q	0.038651	0.008109	4.766	0.000761
	DIC	1.23138	0.164178	7.5	2.06E-05
	GPP	-1.098025	0.368965	-2.976	0.013903
	ER	-0.827973	0.265929	-3.114	0.010995
		DOC Paired Cations			
1	(Intercept)	1.32875	0.9591	1.385	0.1993
	CaMg	-0.32348	0.01679	-19.266	1.26E-08
	DO	-0.12772	0.04182	-3.054	0.0137
	DIC	1.29584	0.09523	13.607	2.62E-07
	GPP	-0.62315	0.2222	-2.804	0.0206
	ER	-1.0944	0.15669	-6.985	6.43E-05
2	(Intercept)	7.0745	2.58154	2.74	0.022832
	CaMg	-0.39607	0.03185	-12.434	5.69E-07
	Q	-0.13642	0.05171	-2.638	0.027007
	DO	-0.07961	0.04136	-1.925	0.086379
	DIC	1.12575	0.12203	9.225	6.97E-06
	ER	-0.97637	0.19661	-4.966	0.000774
3	(Intercept)	0.75663	1.21704	0.622	0.548
	CaMg	-0.32542	0.02179	-14.937	3.64E-08
	DO	-0.09285	0.05186	-1.79	0.104
	DIC	1.31924	0.1232	10.708	8.46E-07
	ER	-1.38659	0.15198	-9.124	3.66E-06
		NO3 Cation Sum			
1	(Intercept)	4.028812	0.162381	24.811	2.59E-10
	Q	-0.06082	0.004347	-13.991	6.82E-08
	DO	-0.032757	0.013637	-2.402	0.03719
	DOC	-0.185656	0.018128	-10.241	1.28E-06
	GPP	-0.21948	0.063115	-3.477	0.00595
		NO3 Paired Cations			
1	(Intercept)	1.03384	0.240659	4.296	0.00157
	CaMg	0.091351	0.004084	22.366	7.18E-10
	DO	-0.020274	0.010514	-1.928	0.08267
	DIC	-0.151165	0.023041	-6.561	6.39E-05
	GPP	-0.140447	0.041795	-3.36	0.00724
2	(Intercept)	1.120417	0.285049	3.931	0.00235
	CaMg	0.087044	0.004215	20.649	3.79E-10

Q	-0.005873	0.001221	-4.81	0.000545
DIC	-0.154611	0.025874	-5.976	9.25E-05
GPP	-0.092143	0.042893	-2.148	0.054817

Table P: Stony Run (STNY)—multiple linear regression best fit models variable coefficient data

Model , fit #	***Variable***	***Coeff Estimate***	***Std. Error***	***t value***	***Pr(>|t|)***
		DIC Cation Sum			
1	(Intercept)	-57.61663	34.84009	-1.654	0.12211
	CationSum	0.10287	0.01893	5.435	0.000114
	pH	8.58881	4.56153	1.883	0.082285
	DO	-0.04686	0.31789	-0.147	0.885078
	GPP	-1.13192	1.3566	-0.834	0.419134
2	(Intercept)	-51.20183	32.86567	-1.558	0.14326
	CationSum	0.10221	0.01923	5.316	0.00014
	pH	7.95886	4.44357	1.791	0.09658
	DO	-0.16463	0.27411	-0.601	0.55842
	ER	-0.96964	1.48636	-0.652	0.52554
3	(Intercept)	-51.2984	33.5221	-1.53	0.14991
	pH	8.4334	4.5189	1.866	0.084725
	DO	-0.3027	0.286	-1.059	0.309056
	TN	2.6967	0.5222	5.164	0.000182
	ER	-1.0006	1.5155	-0.66	0.520597
4	(Intercept)	-54.2546	35.9898	-1.508	0.155594
	pH	8.6329	4.7037	1.835	0.089428
	DO	-0.2144	0.3352	-0.64	0.533467
	TN	2.7083	0.5211	5.197	0.000172
	GPP	-0.8976	1.402	-0.64	0.533148
5	(Intercept)	-68.42181	33.02907	-2.072	0.06052
	CationSum	0.13635	0.02615	5.213	0.000217
	pH	8.79003	4.24816	2.069	0.060781
	DO	0.23731	0.33838	0.701	0.496487
	DOC	0.55197	0.31869	1.732	0.108873
	GPP	-0.95986	1.26683	-0.758	0.463259
6	(Intercept)	-80.22027	35.3158	-2.272	0.042322
	CationSum	0.12801	0.02322	5.513	0.000134
	Q	0.05351	0.03192	1.677	0.119471
	pH	10.8262	4.47712	2.418	0.032429
	DO	0.12619	0.31521	0.4	0.695946
	GPP	-1.41233	1.28193	-1.102	0.292187
		DIC Paired Cations			
1	(Intercept)	-32.93993	30.91671	-1.065	0.306
	CaMg	0.22521	0.03439	6.549	1.86E-05
	pH	5.20621	4.07435	1.278	0.224
	DO	-0.0907	0.27814	-0.326	0.75
	GPP	-0.54761	1.19117	-0.46	0.653
2	(Intercept)	-30.51736	28.91748	-1.055	0.31

	CaMg	0.22482	0.03463	6.492	2.03E-05
	pH	4.99672	3.93506	1.27	0.226
	DO	-0.14661	0.23618	-0.621	0.546
	ER	-0.5413	1.29381	-0.418	0.6
3	(Intercept)	-36.57961	28.09755	-1.302	0.2174
	CaMg	0.28565	0.04395	6.5	2.94E-05
	pH	4.57238	3.7089	1.233	0.2413
	DO	0.16428	0.28405	0.578	0.5737
	DOC	0.50187	0.25714	1.952	0.0747
	GPP	-0.24485	1.09124	-0.224	0.8262
4	(Intercept)	-31.66271	26.22377	-1.207	0.2505
	CaMg	0.28971	0.04571	6.338	3.73E-05
	pH	3.87488	3.61354	1.072	0.3047
	DO	0.14052	0.25973	0.541	0.5984
	DOC	0.52209	0.26727	1.953	0.0745
	ER	0.18342	1.23027	0.149	0.884
5	(Intercept)	-48.098799	28.67525	-1.677	0.119
	CaMg	0.265694	0.039742	6.685	2.24E-05
	Q	0.046774	0.026707	1.751	0.105
	pH	6.736218	3.787712	1.778	0.101
	DO	-0.003624	0.234084	-0.015	0.988
	ER	-0.958919	1.225215	-0.783	0.449
6	(Intercept)	-47.5402	30.34546	-1.567	0.143
	CaMg	0.26479	0.04018	6.589	2.58E-05
	Q	0.0439	0.02652	1.655	0.124
	pH	6.52906	3.90895	1.67	0.121
	DO	0.05108	0.2749	0.186	0.856
	GPP	-0.6844	1.12172	-0.61	0.553
		DOC Cation Sum			
1	(Intercept)	12.54537	25.39315	0.494	0.62952
	CationSum	-0.06226	0.01485	-4.192	0.00106
	pH	0.72896	3.43325	0.212	0.83515
	DO	-0.52452	0.21179	-2.477	0.02778
	ER	-1.20393	1.14841	-1.048	0.31358
2	(Intercept)	18.21345	2.27134	8.019	5.38E-07
	CationSum	-0.06226	0.01323	-4.706	0.000238
	DO	-0.5341	0.1871	-2.855	0.011472
	ER	-1.17639	0.91543	-1.285	0.217058
3	(Intercept)	9.769451	7.733792	1.263	0.2271
	CationSum	-0.061255	0.013616	-4.499	0.0005
	Temp	0.197958	0.172536	1.147	0.2705
	DO	-0.006917	0.499866	-0.014	0.9892
	ER	-1.007585	0.949245	-1.061	0.3064

4	(Intercept)	19.57571	28.22736	0.694	0.5002
	CationSum	-0.06065	0.01533	-3.955	0.00165
	pH	-0.36454	3.69574	-0.099	0.92293
	DO	-0.51482	0.25756	-1.999	0.06698
	GPP	-0.31173	1.09911	-0.284	0.78117
5	(Intercept)	15.86249	2.56893	6.175	1.78E-05
	CationSum	-0.08603	0.01892	-4.546	0.000386
	DO	-0.46568	0.18196	-2.559	0.021795
	DIC	0.23297	0.13892	1.677	0.114256
	ER	-1.13313	0.86799	-1.305	0.211405
6	(Intercept)	6.04456	8.09136	0.747	0.467402
	CationSum	-0.06021	0.01386	-4.343	0.000675
	Temp	0.25693	0.17828	1.441	0.171517
	DO	0.20568	0.55836	0.368	0.718117
	GPP	-0.6749	0.88528	-0.762	0.458497
		DOC Paired Cations			
1	(Intercept)	23.08173	25.52017	0.904	0.38221
	NaK	-0.11341	0.02759	-4.111	0.00123
	pH	-0.78492	3.4306	-0.229	0.82259
	DO	-0.51614	0.2146	-2.405	0.03178
	ER	-0.98319	1.15612	-0.85	0.41048
2	(Intercept)	17.2556	2.1835	7.903	6.50E-07
	NaK	-0.1137	0.0243	-4.678	0.000252
	DO	-0.5179	0.1886	-2.746	0.014359
	ER	-1.0994	0.918	-1.198	0.248526
3	(Intercept)	8.894396	7.729731	1.151	0.269142
	NaK	-0.111784	0.025041	-4.464	0.000535
	Temp	0.196295	0.173356	1.132	0.276519
	DO	0.004505	0.502223	0.009	0.992969
	ER	-0.933289	0.952982	-0.979	0.344036
4	(Intercept)	31.84189	28.15404	1.131	0.27849
	NaK	-0.11168	0.02827	-3.951	0.00166
	pH	-2.04614	3.66553	-0.558	0.58619
	DO	-0.53624	0.25682	-2.088	0.05704
	GPP	-0.02084	1.09843	-0.019	0.98515
5	(Intercept)	5.48015	8.08294	0.678	0.508829
	NaK	-0.11018	0.02547	-4.326	0.000697
	Temp	0.25067	0.17878	1.402	0.182646
	DO	0.20004	0.5596	0.357	0.726078
	GPP	-0.62002	0.8878	-0.698	0.496383
6	(Intercept)	2.19378	27.20585	0.081	0.93696
	CaMg	-0.1243	0.03258	-3.815	0.00215

	pH	2.14874	3.70215	0.58	0.57157
	DO	-0.54996	0.2222	-2.475	0.02787
	ER	-1.38812	1.21723	-1.14	0.2747
		NO3 Cation Sum			
1	(Intercept)	-1.342299	0.470925	-2.85	0.0116
	CationSum	0.037093	0.002668	13.901	2.38E-10
	DO	0.041017	0.043938	0.934	0.3644
	GPP	-0.118468	0.167027	-0.709	0.4884
2	(Intercept)	-1.186455	0.463745	-2.558	0.021
	CationSum	0.037001	0.002701	13.699	2.95E-10
	DO	0.02685	0.038201	0.703	0.492
	ER	-0.067016	0.186905	-0.359	0.725
		NO3 Paired Cations			
1	(Intercept)	-1.01327	0.48404	-2.093	0.0537
	CaMg	0.094967	0.008787	10.808	1.78E-08
	DO	0.033428	0.038765	0.862	0.4021
	DIC	-0.082657	0.031644	-2.612	0.0196
	GPP	-0.072177	0.143785	-0.502	0.623
2	(Intercept)	-0.925242	0.478872	-1.932	0.0725
	CaMg	0.094994	0.008856	10.727	1.97E-08
	DO	0.024077	0.033642	0.716	0.4852
	DIC	-0.083067	0.03187	-2.606	0.0198
	ER	-0.026094	0.160384	-0.163	0.8729
3	(Intercept)	-1.566746	0.4378	-3.579	0.00274
	CaMg	0.057199	0.009664	5.919	2.82E-05
	NaK	0.019147	0.008691	2.203	0.04364
	DO	0.047078	0.039759	1.184	0.2548
	GPP	-0.101137	0.150965	-0.67	0.51308

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