A Longitudinal Study of Redox Sensitive Elements Along a Regenerative Stormwater Conveyance (RSC) System

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Abstract

A Regenerative Stormwater Conveyance (RSC) system is a stream restoration technique that creates a series of step pools and cascades along part of a stream. The goal of this restoration process is to decrease bank erosion and improve water quality in the stream and surrounding floodplain. However, this technique is relatively new, and more research needs to be completed in order to understand how effective it is at achieving these goals. This study examines how redox sensitive element (RSE) concentration change over the length of an RSC system and how concentrations are impacted by seasonal changes. Samples were collected seasonally from Campus Creek, a stream located on the University of Maryland's campus, where an RSC system was constructed in 2019. Samples were collected from six step pools along the conveyance system and five points downstream not included in the conveyance system as a comparison Samples were analyzed to determine RSE (Fe, Mn, N) concentrations as well as base cation concentrations (Na, Cl, Mg, K). Measurements of specific conductance, salinity, pH, temperature, and total dissolved solids (TDS) were taken as proxies for water quality. Seasonal variations in temperature and organic content were compared to assess the impact of seasonal variation as well as longitudinal variation in RSE concentrations in the RSC system. Velocity, width, and depth measurements were taken at sampling sites during the spring collection and used to calculate discharge in order to the assess total load of analyzed elements. It was found that RSE elements, Fe and Mn, existed in elevated concentrations in the RSC to those downstream and had an overall decreasing trend along campus creek. Inversely, N concentrations were lowered in the conveyance system and increased downstream. A dependent relationship was observed in nitrogen concentrations with seasonal factors of temperature and organic carbon concentrations.

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Chapter 1: Introduction

1.1: Urbanization and Stream Quality

As land is increasingly developed and urbanized, the streams located in these areas face bank erosion from surface runoff and decreasing water quality. Conventional water drainage relies on sewers and drains to convey surface runoff from paved surfaces to streams. These type of systems increase surface water velocity, leading to enhanced stream bank and channel erosion and instability (Booth et al., 2005). Urban surface runoff also carries a variety of pollutants into streams, and with climate change projections indicating an increase in the likelihood of larger-volume storms, larger pollutant loads are likely to more negatively impact these streams (Williams et al., 2017).

An increase in impervious land cover, stream channelization, and degradation of riparian zones has led to an increase in nutrient concentrations in streams (Collins et al., 2010). Excess loading of nutrients such as nitrogen and phosphorous in urban streams and watersheds is one of the leading causes of eutrophication (Smith, 2003). Sources of nitrogen in urban streams include fertilizer applications, motorized vehicle combustion, septic and sewage leaks, and animal waste (Groffman et al., 2005). Additionally, stormwater runoff from roadways and other impervious surfaces serves as a source for heavy metals such as copper, lead, and zinc (Burton, 2001). With the increase in impervious surfaces that comes with urbanization, there has been a significant increase in concentrations of dissolved inorganic carbon (DIC) and major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) in streams (Kaushal et al., 2017). Urbanization also contributes to the formation of elemental combinations in watersheds known as ‘chemical cocktails’ that can originate from sources such as sewage, automobiles, and weathering of impervious surfaces (Kaushal et al., 2020).

Increasing stormwater runoff and water pollution in urban streams pose a threat to both the communities and ecosystems that they encompass. More stormwater runoff increases the likelihood of flooding events surrounding floodplain of the stream threating the people and buildings that are located within the floodplain of the stream. Additionally, water pollution may cause detrimental health effects to people if it were to contaminate drinking water supplies and also may harm the organisms in the stream’s ecosystem.

1.2: Regenerative Stormwater Conveyance Systems

A solution to the issues of streambank erosion and water pollution in urban streams may be the construction of a Regenerative Stormwater Conveyance (RSC) System. An RSC is a relatively new stormwater control measure (SCM) and stream restoration practice that is intended to decrease streambank erosion and increase nutrient reduction by slowing the flow of water in a stream. This design aims to increase the residence time of water and encourage frequent flooding of the floodplain, increasing sediment deposition and nutrient removal (Thompson et al., 2018). This is accomplished through the construction of a series of step pools that are connected by boulder cascades (Fig. 1) that have a sand and woodchip bed composition. The water is retained within these step pools for long periods of time, converting stormwater to groundwater through filtration as the water percolates through the sand bottom (Koryto et al., 2017; Brown et al., 2010). The longer residence time of water within these step pools decreases the velocity of the water, leading to a decrease in bank erosion in the stream. Optimal storm mitigation performance of an RSC is expected when it includes: a minimum of three pool/riffles, established vegetation, and exfiltration trenches (Cizek et al., 2018).

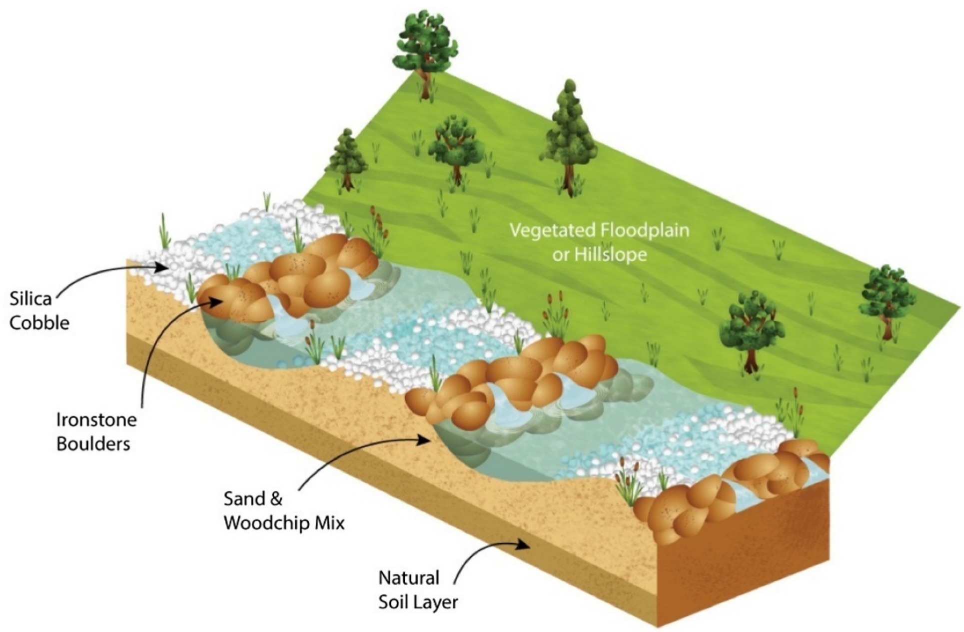

Figure 1: Diagram of RSC system. Step pools are separated by rock weirs constructed of ironstone boulders and silica cobble and have a sand and woodchip mixture bed composition. Source: Williams et al. (2016)

1.3: Denitrification and Anaerobic Bacterial Reduction

RSC systems can potentially improve water quality through increased microbial denitrification. Microorganisms are able to transform nitrate (NO_3^-) in the RSCs step pools to N_2O or N_2 gas, removing it from the water and releasing it into the atmosphere (Collins, 2010). The hyporheic zone of an RSC, the region of sediment beneath and alongside a streambed, is a hotspot for microbial activity and is where much nutrient reduction occurs (Groffman et al., 2005). Organic carbon (C) in an RSC can lower surface and groundwater pH as well as dissolved oxygen (DO) (Keller et al., 2008). Sources of organic carbon in an RSC include the woodchips placed in the step pools during construction and leaf litter that is buried in the step pools due to reduced flow velocity (Kochi et al., 2009). The lowered DO in the step pools allows for nitrogen removal through microbial denitrification, a redox process that requires anoxic conditions (Saleh-Lakha et al, 2009; Duan et al., 2014). The retention of nitrogen in an RSC is also dependent on the quantity and quality of carbon (Duan et al., 2019).

In addition to denitrification, low DO also favors anaerobic bacterial reduction of Fe(III) and Mn(III) and release iron (Fe^{2+}) and manganese (Mn^{2+}) in to solution (Williams et al., 2016). High amounts of organic carbon within the RSC step pools should decrease DO levels, increasing reduction of RSEs such as iron and manganese inside of the RSC system. Anaerobic bacterial reduction in a stream system is dependent primarily on factors such pH, temperature, and DO (Lee et al., 2019). Seasonal changes in the environment such as temperature, precipitation, and quantity and quality of leaf litter have a large influence on these factors (Swan et al., 2004). These seasonal changes impact the redox potential for species such as nitrogen, iron, and manganese and limit their abilities to be reduced. Because of this seasonal factors are likely to play a significant role in the concentration variation of RSEs in an RSC system.

1.4: Broader Impacts

Despite the growing popularity of RSC systems as a restoration and stormwater management practice, few studies exist evaluating the impact RSCs have on water quality. More specifically the effect that seasonality has on redox sensitive elements within an RSC system is yet to be understood. Understanding the changes in elemental concentrations can help to better our understanding of and RSC systems ability to improve water quality and will aid is determining the efficacy of an RSC system as a best management practice (BMP).

1.5: Hypotheses

This project will examine the changes in RSE concentrations that occur along the length of an RSC and how they are impacted by seasonality. Because RSC step pools have decreased DO relative to riffle zones, allowing for more favorable conditions for anaerobic microbial reduction, I hypothesize that there will be a change in redox sensitive element concentrations (Fe, Mn) along the length of the RSC, with the null hypothesis that there is not a change in the RSE concentrations along the length of the RSC Additionally, since redox reactions are heavily dependent on seasonal factors, I hypothesize that RSE concentrations will be dependent on temperature, and organic carbon content, with the null hypothesis that RSE concentrations will not be dependent on temperature and organic carbon content.

Chapter 2: Methods

2.1: Sample Sites

Water samples were collected from six step pools spanning the entire length of an RSC system. These samples were collected from an RSC constructed on Campus Creek in College Park, Maryland, an urban stream located on the University of Maryland's campus. The stream begins west of the university's campus and ends where it drains into Paint Branch stream. Five additional sites located downstream of the conveyance system along Campus Creek were also sampled to serve as a comparison. Sampling sites can be seen in figure 2.

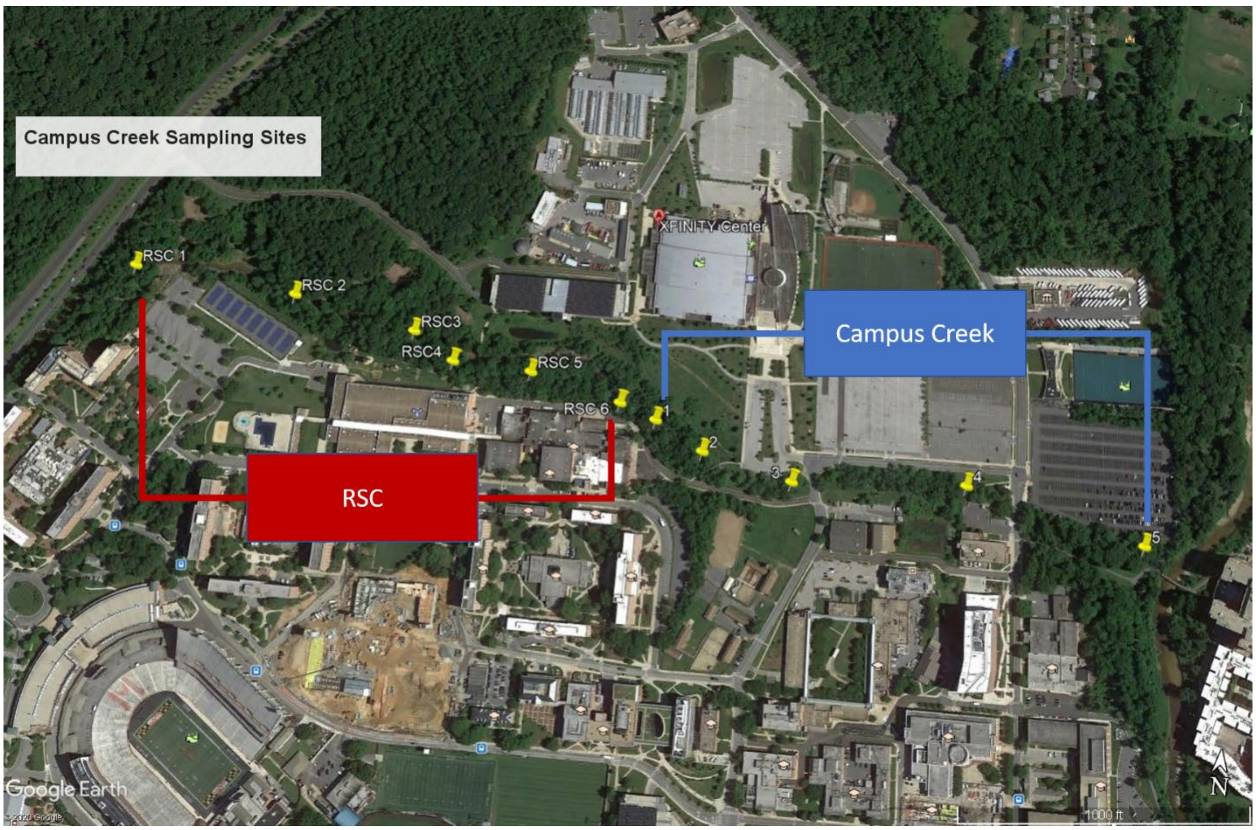

Figure 2: Map of Campus Creek with sampling sites marked. Sites bracketed in red are sampling sites within the RSC system and sites bracketed in blue are part of the unaltered portion of the stream.

2.2: Sample Collection and Processing

Five sample sets were collected in total, during autumn, winter, and spring. Sampling occurred on October 8th, 2020, February 3rd, 12th, and 19th 2021, and April 2nd, 2021. Samples were collected in 125 mL acid washed HDPE Nalgene bottles. In addition to collecting water samples, readings of pH, temperature, conductivity, Total Dissolved Solids (TDS), and salinity will be recorded in the field at each sampling location using an Oakton pH meter. Water velocity, depth, and width measurements were recorded for only the April 2nd sample set using a Hach FH950 Handheld Velocity Meter.

Water samples were then filtered using a 0.7 µm glass fiber filter and refrigerated until analyzed. 60 mL of each sample was acidified in a small acid-washed HDPE Nalgene bottle with 0.3 mL of nitric acid for elemental analysis and was stored at room temperature. The acidified water samples were analyzed using a Shimadzu Inductively Coupled Plasma – Optical Emission Spectrum (ICP-OES) located in the Biogeochemistry Lab at the University of Maryland to measure concentrations of redox sensitive elements (Fe, Mn) and base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}). This technique uses inductively coupled plasma that, when the sample is sent through it, produces excited atoms that emit wavelengths associated to specific elements. Each sample is analyzed three times and a relative standard deviation (RSD) value is taken to serves as the uncertainty for each element concentration. The RSD value can tell how precise the average of the results are. The higher the RSD, the more spread out the results are from the mean of the data. Inversely, the lower the RSD the more precise the measurement of data.

The remaining refrigerated samples were analyzed using a Shimadzu Total Organic Carbon (TOC) analyzer. This instrument is able to determine the amount of inorganic and organic carbon in a sample as well as total nitrogen (N) concentrations. Inorganic carbon is calculated by injecting the sample with an acid to convert inorganic carbon into carbon dioxide, the amount of carbon dioxide produced is equal to the amount of inorganic carbon in the sample. Total organic carbon is calculated from subtracting calculated inorganic carbon from the total carbon concentration. The rest of the sample is then combusted and passed through a non-dispersive infrared detector to calculate total nitrogen concentrations.

2.3: Longitudinal Comparisons

RSE and base cation concentrations were then plotted against distance downstream for the conveyance system and remaining stream reach. This allows for longitudinal trends in concentrations to be visualized, linear regressions of each data set allow for statistical evaluation of linear trends seen in the data. An R^2 value was used to evaluate if linear relationships in data were statistically significant, the higher the R^2 value that the regression has the more significant the relationship, $R^2 > 0.2$ was used as a threshold for significance

Discharge (Q) was calculated using velocity (v), depth (d), and width (w) measurements of a cross-sectional area of each sampling site for the April 2nd sample collection using the equation:

$$Q = V * A$$

where A is the cross-sectional area of the stream. The total load of nitrogen (L) was calculated from discharge and concentration values of nitrogen at each sampling site using the equation:

$$L = C * Q * F$$

where C is the concentration of nitrogen in mg/L, Q is discharge in cubic feet per second (cfs), and F is a conversion factor of 5.39 to convert the value to lbs/day. The total load can then be divided by basin area (BA) of the watershed at each sampling site to obtain the unit area load of nitrogen along the lengths of Campus Creek. Drainage for each site was determined using USGS StreamStat data (Fig. 3).

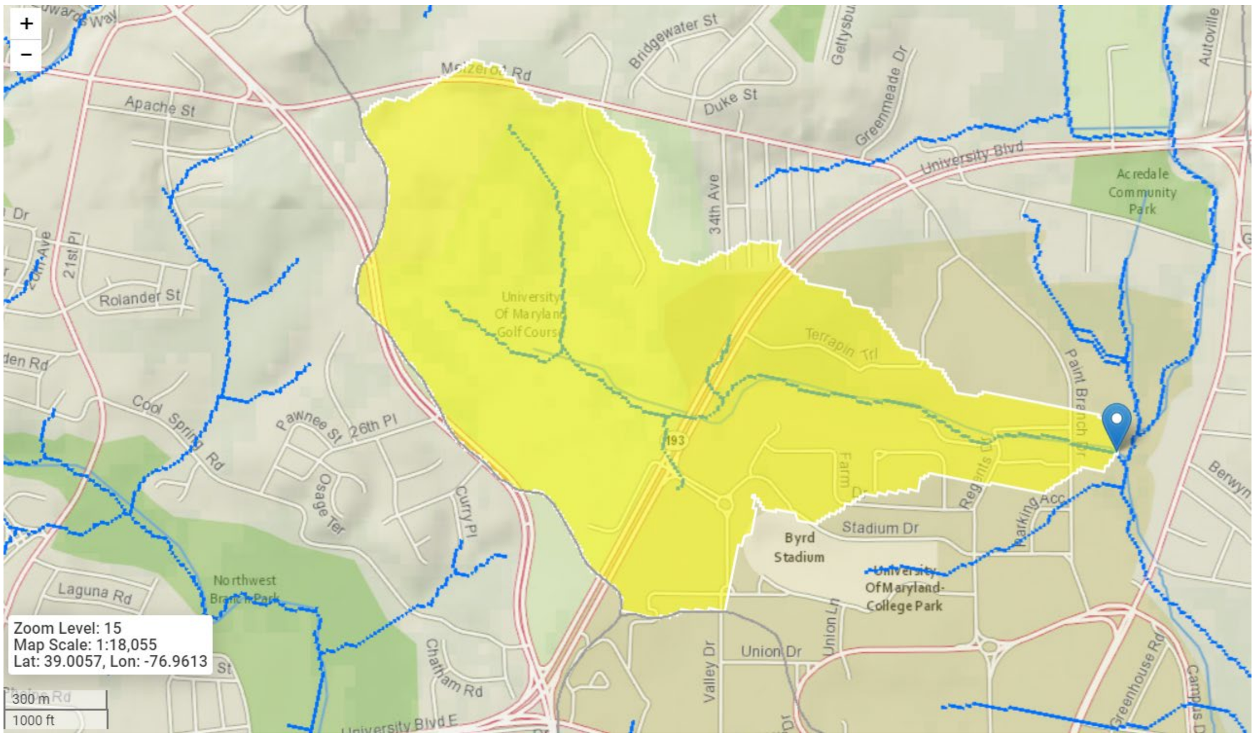

Figure 3: Basin area of Campus Creek from USGS StreamStat data. Total basin area is marked in yellow on map

Chapter 3: Results and Discussion

3.1: Results

Longitudinal Patterns

Longitudinal patterns were analyzed to understand how RSE, and base cation concentrations vary along the length of an RSC system and further downstream. Base cation and RSE concentrations were first plotted against distance downstream (Fig. 4).

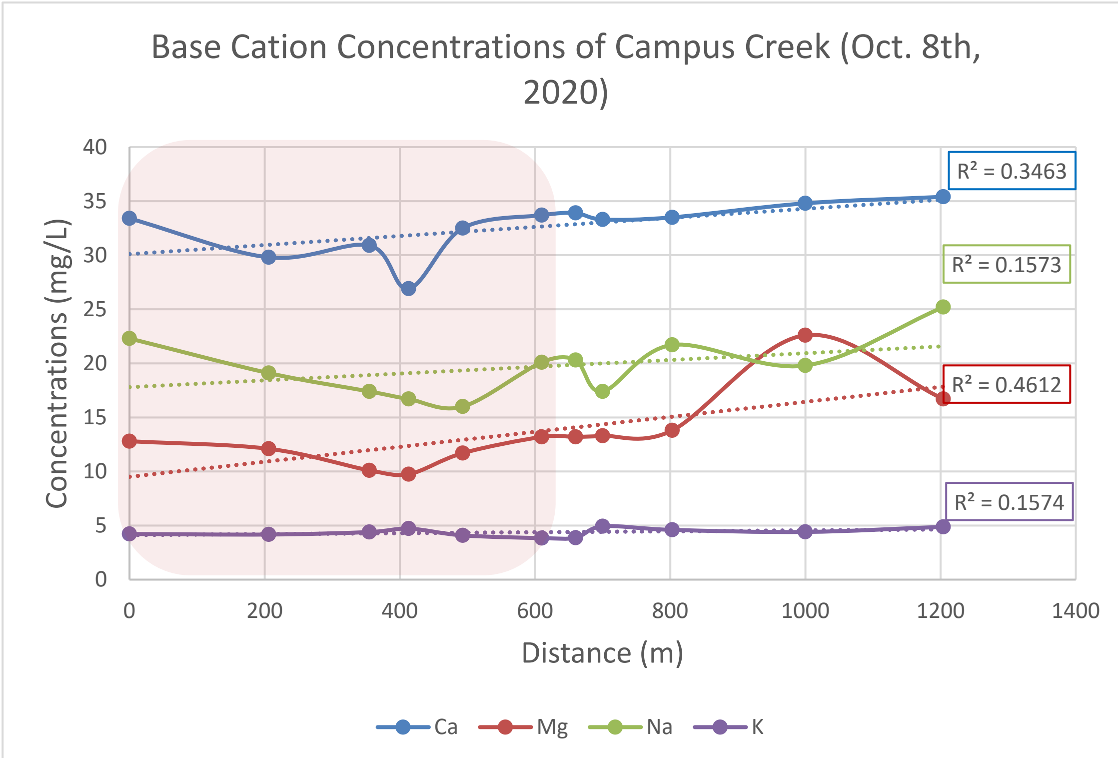

Figure 4: Base cation concentrations versus distance along Campus Creek from the 1st sample locality The red portion of the graph represents the length of the RSC sites; control sites downstream are outside of the colored portion.

Base cations concentrations display significant overall increasing trends throughout the length of the RSC and the reach downstream. When the RSC system is considered alone, a decreasing trend in Ca, Mg, and Na concentrations can be observed. Once downstream of the conveyance system, base cation concentrations begin to increase. The decrease in base cation concentrations in the RSC could be attributed to dilution of the ions from retention of water in the step pools. The step pools hold a larger volume of water than in the unaltered portion of Campus Creek, lowering the concentration of these elements. K concentrations remain consistent with little variation between sampling sites and is lower in concentration that Ca, Mg, and Na. K may exist at lower concentrations, compared to Ca, Mg, and Na, due to plant uptake in the stream's watershed. K is a limiting nutrient to vegetation and is readily taken up by plants, lowering its concentration in the stream compared to other base cations.

Base cation concentrations can be contrasted with RSE concentrations (Fe, Mn, and N) in which different longitudinal patterns can be observed along the stream for the October 8th, 2020 collection (Fig. 5).

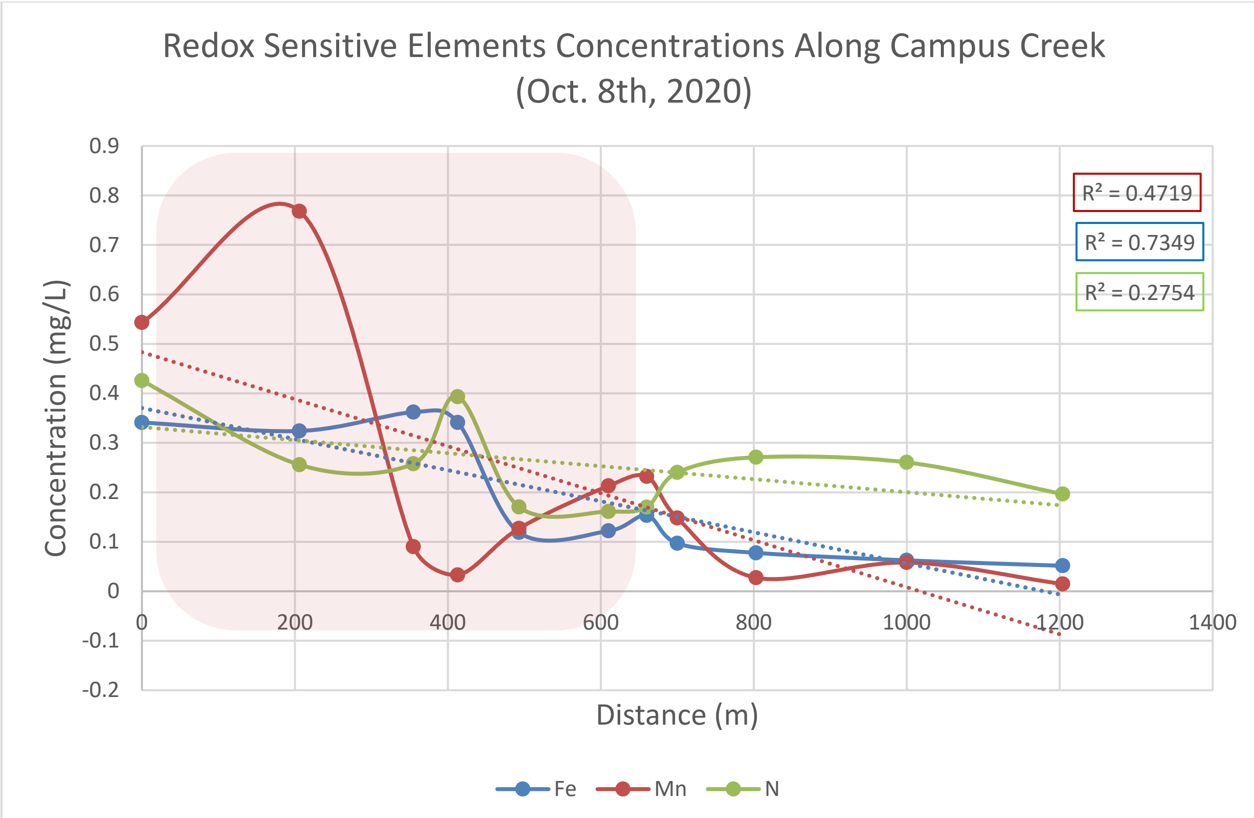

Figure 5: Redox sensitive element (RSE) concentrations versus distance along Campus Creek from 1st sample locality. The red portion of the graph represents regions within the RSC, and control sites downstream are outside of the colored portion.

RSE concentrations display overall significant decreasing trends along the entire length of the stream, an inverse of the increasing trends that were observed in base cation concentrations. Elevated concentrations of Fe and Mn can be seen in the RSC sites compared to the reach downstream, the highest concentration values for these elements are found in the RSC sites. Interestingly, nitrogen concentrations are lower in the RSC compared to downstream sites. The elevated concentrations of Fe and Mn, and lowered concentrations of N in the RSC are an indicator that there is elevated microbial activity in the step pools as more Fe and Mn is being reduced at released into solution and N is removed from the stream through denitrification.

To compare seasonal variations in RSE concentrations along the RSC and Campus Creek, nitrogen concentrations for all five sample sets were plotted against distance from the first sampling locality (Fig. 6).

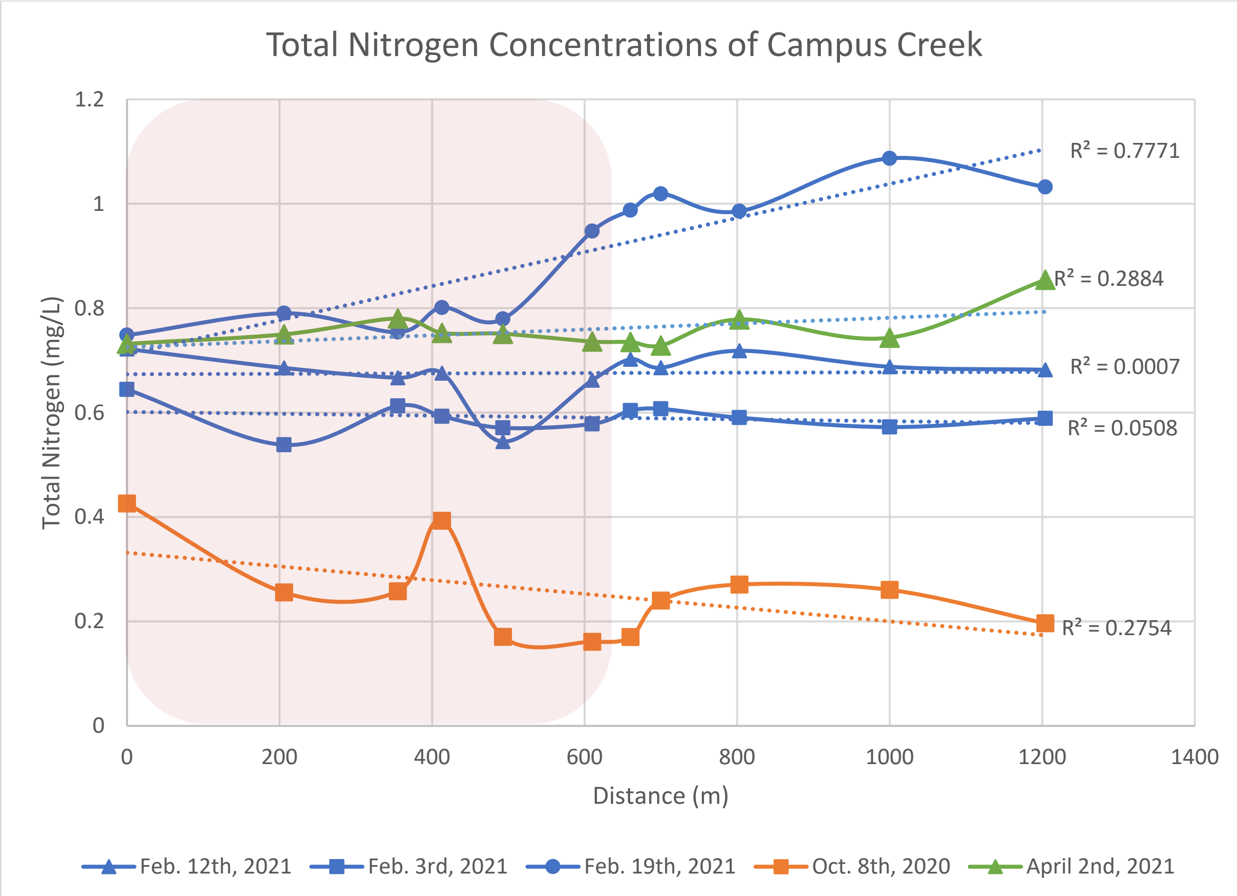

Figure 6: Total nitrogen concentrations along Campus Creek from 1st sample locality. Red portion of graph represents locations with the RSC system.

Seasonal variations in nitrogen concentrations were observed in the conveyance system. Nitrogen concentrations for the Oct. 8th sample collection are lower both within the RSC system and downstream compared to all other sample sets. The Feb. 19th and April 2nd sample sets exhibit increasing nitrogen concentrations with distance downstream and the Feb. 3rd and 12th see little variation in N concentrations through the length of the stream. The lowered N concentrations seen in the October sample set in the RSC could be attributed to increased denitrification and increased removal of N through plant uptake compared to data from other seasons.

Nitrogen Retention

To further assess longitudinal patterns of RSEs in an RSC system, hydrologic conditions were considered. Discharge was calculated from depth, width, and velocity measurements of a cross-section were taken at each sampling site for the April 2nd, 2021 sample collection. Using the calculated total load value and the known basin area for the Campus Creek watershed at each sampling site, the unit area load of nitrogen could be plotted against distance (Fig. 5) to understand how nitrogen is retained in the ecosystem of the RSC.

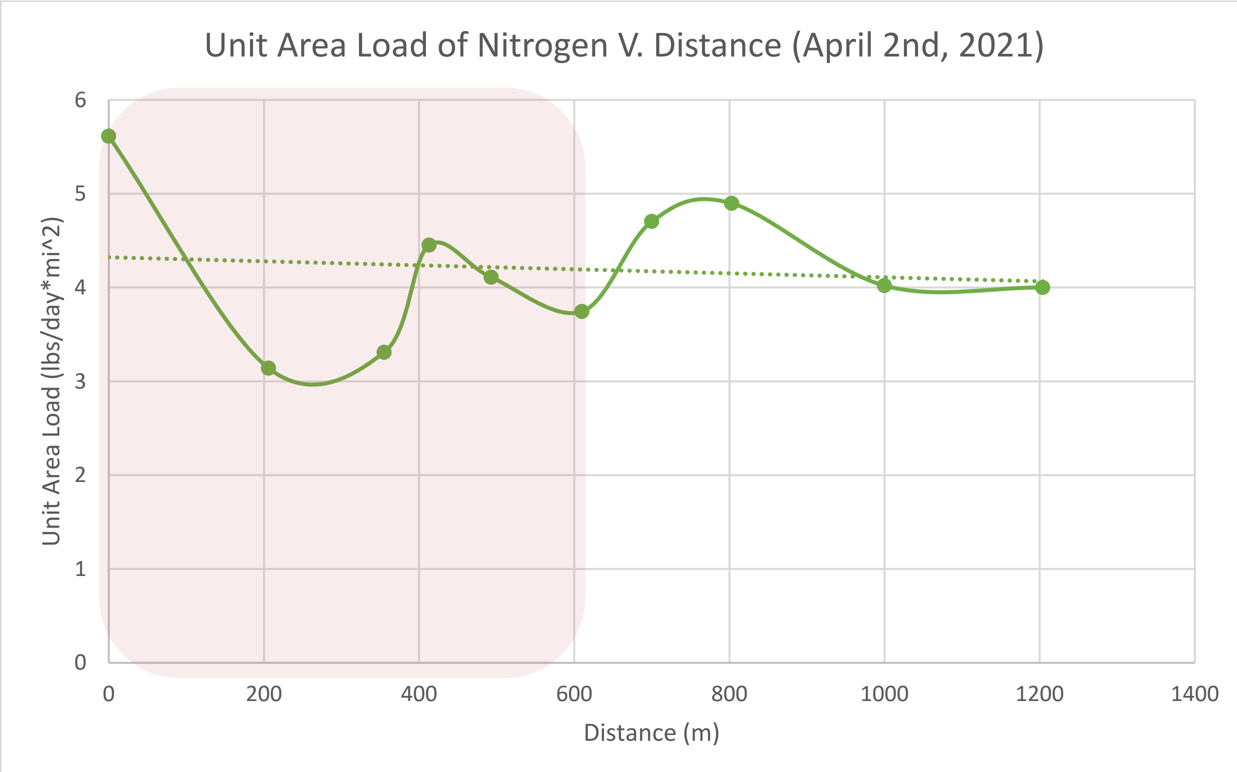

Figure 5: Unit area load versus distance from 1st sample locality for the April 2nd, 2021 sample set, red portion of graph represents locations within the RSC system.

A slightly decreasing trend in the unit area load of nitrogen can be seen in Campus Creek. This decrease indicates that over distance, the total amount of nitrogen that is being exported from the watershed is decreasing and is being retained in Campus Creeks watershed. Additionally, the lowest calculated loads are within the RSC system, indicating that the step pools are retaining more nitrogen per watershed area than the portions downstream which have large unit area loads.

Seasonal Impacts

In order to assess the impact seasonal factors, such as temperature and organic carbon content, have on RSEs, nitrogen concentrations for each sampling site for all five sample sets was plotted against water temperature recorded at each site (fig. 6).

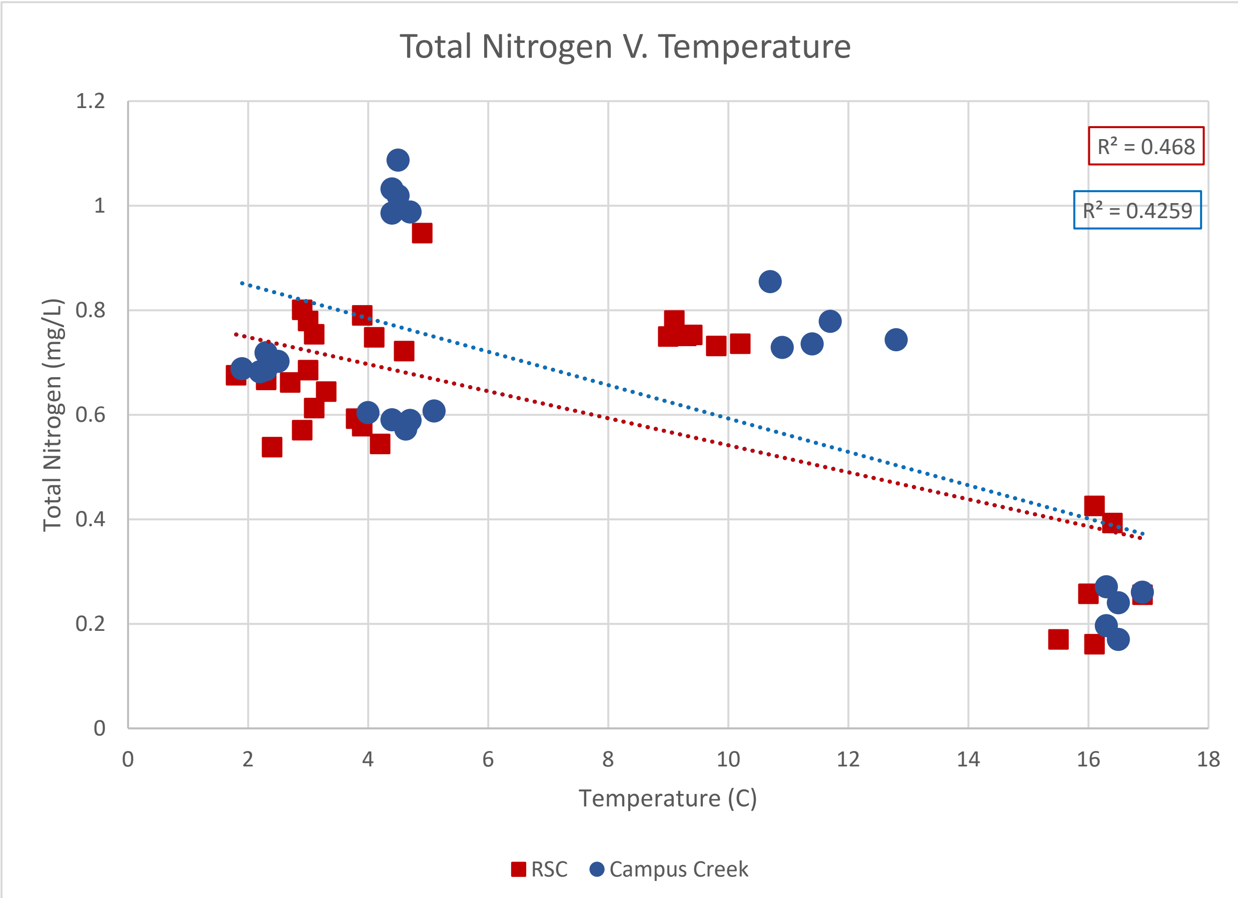

Figure 6: Total nitrogen concentrations from all five sample sets versus temperature, values are separated between samples collected in the RSC system (red) and further downstream in the unaltered reach of Campus Creek (blue)

This graph shows a linearly decreasing relationship between total nitrogen concentration and temperature for both RSC sites and Campus Creek sites. Linear regressions conducted for each data set provide R^2 values of 0.47 for the RSC values and 0.43 for the Campus Creek values. These high R^2 values indicate a statistically significant relationship between total nitrogen and temperature values.

To further assess seasonal impacts on nitrogen, nitrogen concentrations were plotted against non-purgeable organic carbon (NPOC) concentrations for all sample sets (fig. 7). Sample sets were grouped seasonally and relationships in N concentrations were evaluated.

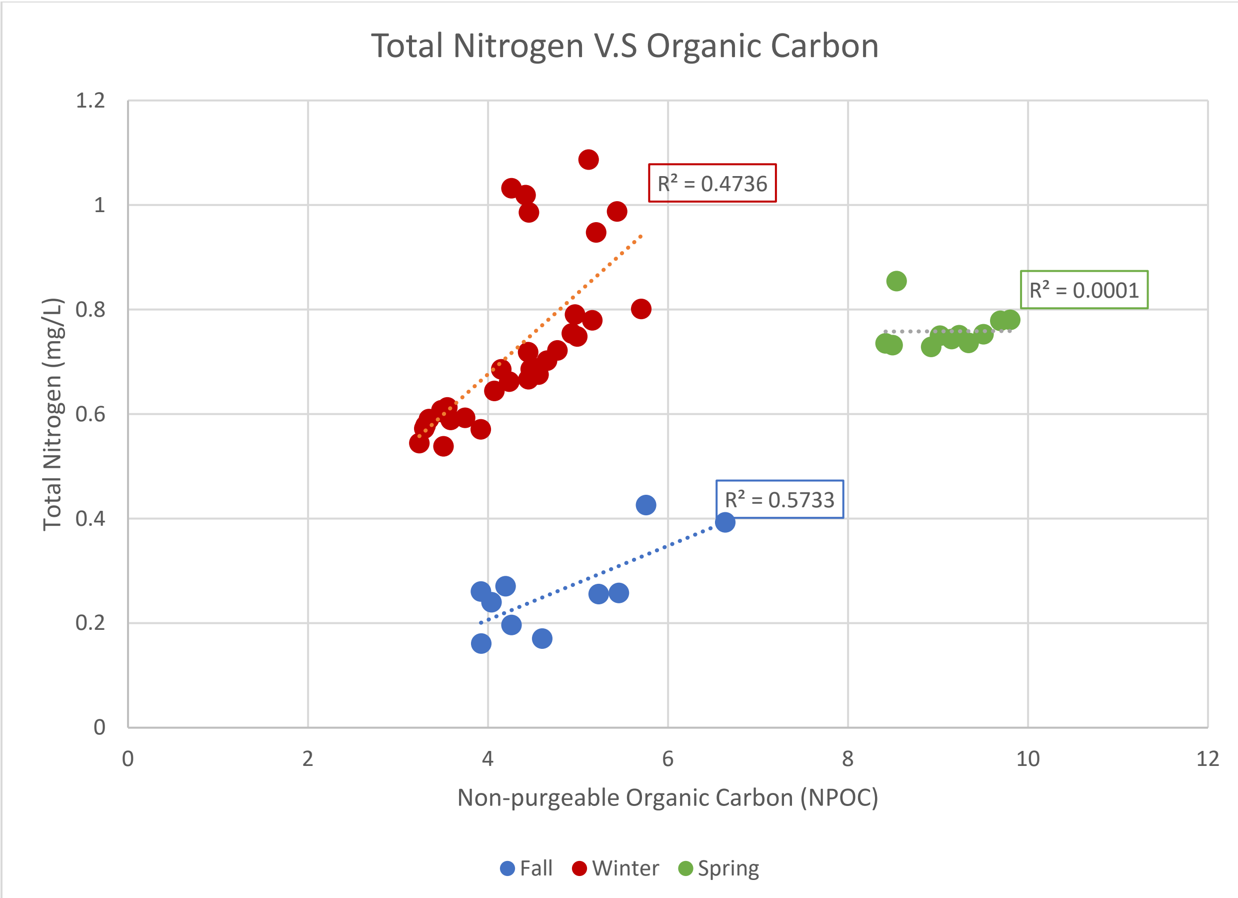

Figure 7: Total nitrogen concentrations plotted against non-purgeable organic carbon (NPOC) concentrations for all sample sets. Data is grouped seasonally, fall (blue), winter (red), and spring (green) samples.

Nitrogen concentrations show a significant linearly increasing relationship with NPOC for the fall (R=0.57) and winter (R=0.47) sample sets. The low R^2 value of the spring sample could be due to scattering as there is still a significant relationship ($P = 0.009$) between N and NPOC. Winter nitrogen concentrations are higher than fall concentrations that have similar NPOC concentrations, this can be attributed to limited removal of N through plant uptake during the winter. Plants more readily take up nitrogen in warmer temperatures, decreasing nitrogen concentrations in the stream compared to data with similar NPOC concentrations at colder temperatures.

3.2: Discussion

It can be seen that an RSC system has an impact on the concentrations of RSE elements within the step pools. Concentrations of Fe and Mn were highest in the conveyance system and N was lowest within the conveyance system. The elevated concentrations of Fe and Mn and decreased concentration of N found in the step pools could be an indicator of increased microbial activity. Microbial reduction of Fe and Mn would release these ions into solution in the step pools, causing them to be in higher concentration than downstream. The lowered concentration of nitrogen seen in the step pools could also be an indicator of increased microbial activity through denitrification. Nitrogen is removed from the RSC ecosystem and is found in lower concentrations as well as lower total loads per watershed area. An RSCs ability to remove nitrogen from the stream ecosystem could benefit aquatic ecosystems by lowering nutrient pollution and decreasing eutrophication of ecosystems such as the Chesapeake Bay, which Campus Creek ultimately connects to. However the increase in trace metals like Fe and Mn that are released into solution can have unintended negative effects on the health of the ecosystem the RSC is constructed into. It is also worth noting that the variations in these elemental concentrations do not appear to drastically impact the stream outside of the conveyance system, concentrations appear to return to a baseline shortly after leaving the step pools. This could suggest that the impact an RSC has on water quality is localized to the area the RSC is constructed in and will not affect that larger area downstream.

Additionally, RSE concentrations are dependent on temperature and organic carbon concentrations. N concentrations in Campus Creek decrease with increasing temperature, and increase with increasing organic carbon, this relationship indicates that RSCs may be less effective at removing nitrogen from streams during colder months where there is less microbial activity. The relationship seen between organic carbon and N at Campus Creek contrasts with other RSC sites that show inverse relationships between N concentrations and organic carbon. This increase of nitrogen seen in Campus Creek with increase in organic carbon concentration could be attributed to the decomposition of organic matter into amino acids. Amino acids contain nitrogen, as organic matter is broken down in the stream more nitrogen in released into solution. This could explain the linearly increasing relationship that is seen in Campus Creek.

Furthermore, data from Campus Creek pre-restoration can be compared to post-restoration data. Nitrogen concentration data of winter samples for this project were compared with a previous senior thesis project that examined longitudinal patterns in campus creek before the conveyance system was constructed (Fig. 8).

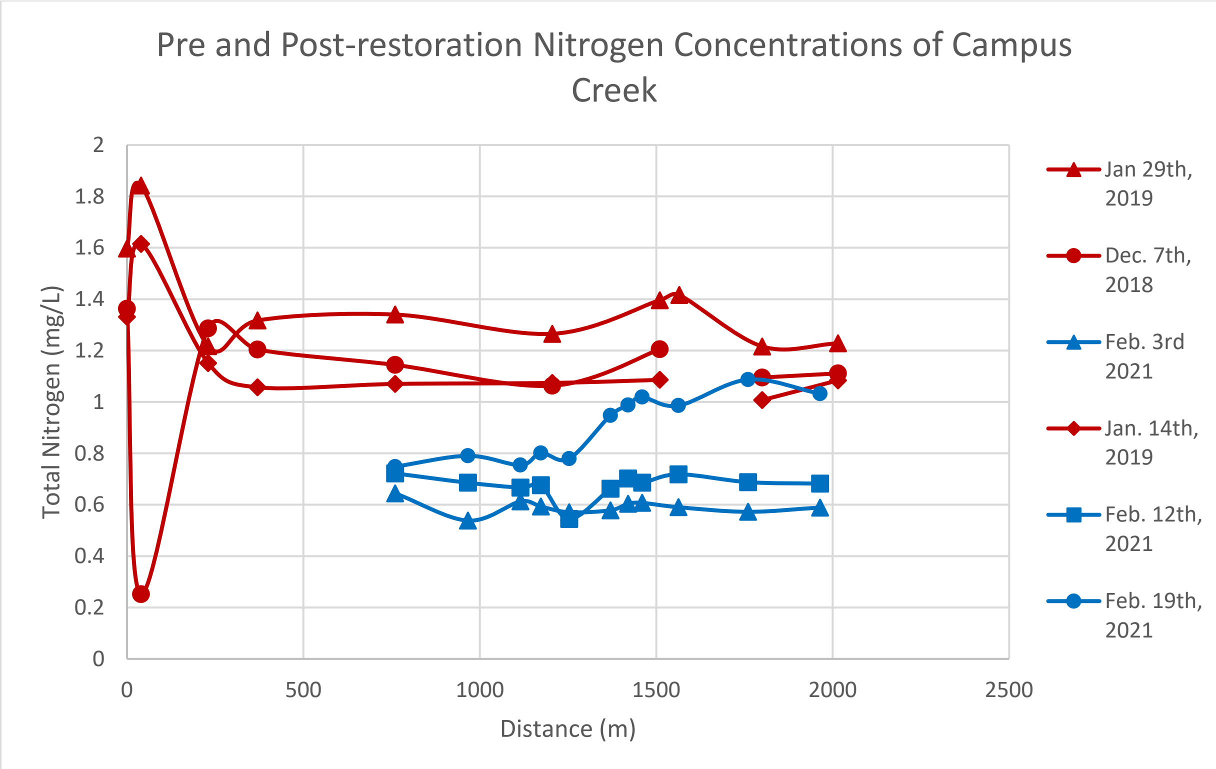

Figure 8: Pre-restoration (red) and post-restoration (blue) N concentrations of Campus Creek against distance from first sampling locality. Pre-restoration data was taken in a similar fashion to post- restoration data (Silverstein, 2019).

Nitrogen concentrations in campus creek from winter samples before and after the construction of the conveyance system show distinct differences in values. Nitrogen concentrations after the RSC's construction are lowered compared to pre-restoration values throughout the entire stream; in some cases, concentrations for similar locations along the stream can be near 1 mg/L lower than pre-restoration values. This indicates that the restoration could be effective at lowering nitrogen, and potentially other elements, in the stream over time in addition to the localized decrease seen in the conveyance system.

Chapter 4

Conclusions

RSE elements, Fe and Mn, display a statistically significant linearly decreasing relationship with distance, indicating that the highest concentrations of these ions are found in the RSC step pools and they decrease downstream of the conveyance system. While N displays a statistically significant increasing relationship with distance, indicating that nitrogen concentrations are lowered in the RSC step pools and increase downstream of the conveyance system. This rejects the first null hypothesis that concentrations do not change over distance. For the second hypothesis, the null is rejected as nitrogen has a statistically significant linear relationship with both temperature and organic carbon concentrations, this indicates that nitrogen, and by extension other RSE concentrations, are dependent on temperature and organic carbon. By examining longitudinal patterns of redox sensitive elements and base cations along Campus Creek, we can see that the impacts on water quality that an RSC has on a stream appear to be localized to the area the conveyance system occupies; patterns in element concentrations observed within the conveyance system were not observed downstream. The RSC also appears to have lowered the overall nitrogen concentrations of the entire length of Campus Creek compared to pre-restoration values.

In the future, research could be expanded to include examining the effect that precipitation events have on the concentration of these elements. Analysis of ground water in the flood plain of the RSC could be used to examine the impact RSC systems have on groundwater chemistry. Finally, further data can be compared with historical data from the stream to examine how water chemistry in the RSC changes over a longer period of time.

References

Booth, D.B., Aumen, N., Gurtz, M., 2005. Challenges and prospects for restoring urban streams: a perspective from the Pacific Northwest of North America. *North America Benthol Society.* 24 (3), 724–737

Brown, T., Berg, J., & Underwood, K. (2010). Regenerative stormwater conveyance: an innovative approach to meet a range of stormwater management and ecological goals. In *World Environmental and Water Resources Congress 2010: Challenges of Change* (pp. 3399-3413).

Burton, G. A., & Pitt, R. (2001). Manual for evaluating stormwater runoff effects in receiving waters. Lewis.

Cizek, A. R., Hunt, W. F., Winston, R. J., Waickowski, S. E., Narayanaswamy, K., & Lauffer, M. S. (2018). Water quality and hydrologic performance of a regenerative stormwater conveyance in the Piedmont of North Carolina. *Journal of Environmental Engineering*, *144*(8), 04018062.

Collins, K. A., Lawrence, T. J., Stander, E. K., Jontos, R. J., Kaushal, S. S., Newcomer, T. A., ... & Ekberg, M. L. C. (2010). Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis. *Ecological Engineering*, *36*(11), 1507-1519.

Duan, S., Delaney-Newcomb, K., Kaushal, S. S., Findlay, S. E., & Belt, K. T. (2014). Potential effects of leaf litter on water quality in urban watersheds. *Biogeochemistry*, *121*(1), 61-80.

Duan, S., Mayer, P. M., Kaushal, S. S., Wessel, B. M., & Johnson, T. (2019). Regenerative stormwater conveyance (RSC) for reducing nutrients in urban stormwater runoff depends upon carbon quantity and quality. *Science of The Total Environment*, *652*, 134-146.

Groffman, P.M., Dorsey, A.M., Mayer, P.M. (2005). N processing within geomorphicstructures in urban streams. J. N. Am. Benthol. Soc. 24 (3), 613–625

Kaushal, S. S., Duan, S., Doody, T. R., Haq, S., Smith, R. M., Johnson, T. A. N., ... & Wood, K. L. (2017). Human-accelerated weathering increases salinization, major ions, and alkalinization in fresh water across land use. *Applied Geochemistry*, 83, 121-135.

Kaushal, S. S., Wood, K. L., Galella, J. G., Gion, A. M., Haq, S., Goodling, P. J., ... & Nguyen, W. (2020). Making 'chemical cocktails'–Evolution of urban geochemical processes across the Periodic Table of elements. *Applied Geochemistry*, 104632.

Keller, W., Paterson, A. M., Somers, K. M., Dillon, P. J., Heneberry, J., & Ford, A. (2008). Relationships between dissolved organic carbon concentrations, weather, and acidification in small Boreal Shield lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 65(5), 786-795.

Koryto, K. M., Hunt, W. F., & Page, J. L. (2017). Hydrologic and water quality performance of regenerative stormwater conveyance installed to stabilize an eroded outfall. *Ecological Engineering*, *108*, 263-276.

Kochi, K., Asaeda, T., Chibana, T., & Fujino, T. (2009). Physical factors affecting the distribution of leaf litter patches in streams: comparison of green and senescent leaves in a step-pool streambed. *Hydrobiologia*, 628(1), 191-201.

Lee, S., Roh, Y., & Koh, D. C. (2019). Oxidation and reduction of redox-sensitive elements in the presence of humic substances in subsurface environments: A review. *Chemosphere*, *220*, 86-97.

Saleh-Lakha, S., Shannon, K. E., Henderson, S. L., Goyer, C., Trevors, J. T., Zebarth, B. J., & Burton, D. L. (2009). Effect of pH and temperature on denitrification gene expression and activity in Pseudomonas mandelii. *Applied and environmental microbiology*, 75(12), 3903-3911.

Silberstein, D. (2019). A Synoptic Survey of Campus Creek. University of Maryland Geology Senior Thesis

Smith, V. H. (2003). Eutrophication of freshwater and coastal marine ecosystems a global problem. Environmental Science and Pollution Research, 10(2), 126-139.

Swan, C. M., & Palmer, M. A. (2004). Leaf diversity alters litter breakdown in a Piedmont stream. Journal of the North American Benthological Society, 23(1), 15-28.

Thompson, J., Pelc, C. E., Brogan III, W. R., & Jordan, T. E. (2018). The multiscale effects of stream restoration on water quality. *Ecological Engineering*, *124*, 7-18.

Weibel, S., Anderson, R., & Woodward, R. (1964). Urban Land Runoff as a Factor in Stream Pollution. *Journal (Water Pollution Control Federation), 36*(7), 914-924.

Williams, M. R., Wessel, B. M., & Filoso, S. (2016). Sources of iron (Fe) and factors regulating the development of flocculate from Fe-oxidizing bacteria in regenerative streamwater conveyance structures. *Ecological Engineering*, 95, 723-737.

Williams, M. R., Bhatt, G., Filoso, S., & Yactayo, G. (2017). Stream restoration performance and its contribution to the Chesapeake Bay TMDL: Challenges posed by climate change in urban areas. Estuaries and Coasts, 40(5), 1227-1246.

Appendix

Sample Name	Sample	Ca Quant [1] mg/L	Ca Quant [2] mg/L	Ca Quant [3] mg/L	**Ca Quant Average mg/L**	Ca RSD	Ca Wavelength (nm)
RSC 1	1	33.3	33.5	33.3	**33.4**	0.44	396.847
RSC 2	2	30	29.9	29.5	**29.8**	0.95	393.366
RSC 3	3	30.8	30.8	31.2	**30.9**	0.64	396.847
RSC 4	4	26.7	26.9	26.9	**26.9**	0.45	393.366
RSC 5	5	32.4	32.6	32.4	**32.5**	0.3	393.366
RSC 6	6	33.9	33.6	33.8	**33.7**	0.48	393.366
CC 1	7	33.8	34	34	**33.9**	0.43	393.366
CC 2	8	33.2	33.5	33.2	**33.3**	0.49	393.366
CC 3	9	33.6	33.6	33.3	**33.5**	0.42	393.366
CC 4	10	35	34.8	34.8	**34.8**	0.41	393.366
CC 5	11	35.4	35.4	35.3	**35.4**	0.25	393.366

Table 1: Concentration of Ca and RSD values for Oct. 8th, 2020 collection of Campus Creek

Sample Name	Sample	K Quant [1] mg/L	K Quant [2] mg/L	K Quant [3] mg/L	**K Quant Average mg/L**	K RSD	K Wavelength (nm)
RSC 1	1	4.08	4.19	4.37	**4.22**	3.46	766.490
RSC 2	2	4.12	4.33	4.07	**4.17**	3.34	766.490
RSC 3	3	4.27	4.37	4.55	**4.4**	3.28	766.490
RSC 4	4	4.82	4.56	4.77	**4.72**	2.98	769.896
RSC 5	5	4.24	4.01	4.01	**4.09**	3.23	769.896
RSC 6	6	3.8	3.81	3.91	**3.84**	1.63	766.490
CC 1	7	3.58	4.05	3.99	**3.87**	6.52	766.490
CC 2	8	5.05	4.86	4.87	**4.93**	2.18	769.896
CC 3	9	4.77	4.56	4.47	**4.6**	3.38	766.490
CC 4	10	4.59	4.52	4.11	**4.41**	5.98	766.490
CC 5	11	4.95	4.89	4.79	**4.88**	1.59	769.896

Table 2: Concentration of K and RSD values for Oct. 8th, 2020 collection of Campus Creek

Sample Name	Sample	Mn Quant [1] mg/L	Mn Quant [2] mg/L	Mn Quant [3] mg/L	**Mn Quant Average mg/L**	Mn RSD	Mn Wavelength
RSC 1	1	0.541	0.542	0.545	**0.543**	0.34	257.610
RSC 2	2	0.768	0.768	0.769	**0.768**	0.05	257.610
RSC 3	3	0.0893	0.0899	0.0906	**0.09**	0.73	257.610
RSC 4	4	0.0327	0.0329	0.0329	**0.0328**	0.38	257.610
RSC 5	5	0.127	0.127	0.127	**0.127**	0.33	257.610
RSC 6	6	0.213	0.213	0.213	**0.213**	0.06	257.610
CC 1	7	0.232	0.231	0.233	**0.232**	0.34	259.373
CC 2	8	0.147	0.149	0.148	**0.148**	0.47	257.610
CC 3	9	0.0281	0.0277	0.0264	**0.0274**	3.23	257.610
CC 4	10	0.0577	0.0587	0.0579	**0.0581**	0.98	257.610
CC 5	11	0.0147	0.0141	0.0149	**0.0146**	2.92	257.610

Table 3: Concentration of Mn and RSD values for Oct. 8th, 2020 sample collection of Campus Creek

Sample Name	Fe Quant [1] mg/L	Fe Quant [2] mg/L	Fe Quant [3] mg/L	**Fe Quant Average mg/L**	Fe RSD	Fe Wavelength
RSC 1	0.339	0.341	0.344	**0.341**	0.72	238.204
RSC 2	0.326	0.322	0.323	**0.324**	0.61	238.204
RSC 3	0.363	0.361	0.363	**0.362**	0.23	238.204
RSC 4	0.342	0.341	0.341	**0.341**	0.23	238.204
RSC 5	0.121	0.117	0.12	**0.119**	1.93	238.204
RSC 6	0.12	0.125	0.122	**0.122**	2.31	238.204
CC 1	0.151	0.156	0.152	**0.153**	1.9	238.204
CC 2	0.0948	0.0985	0.0977	**0.097**	2	238.204
CC 3	0.0778	0.0759	0.0791	**0.0776**	2.04	238.204
CC 4	0.0636	0.0615	0.0624	**0.0625**	1.64	238.204
CC 5	0.0546	0.0491	0.051	**0.0515**	5.45	238.204

Table 4: Concentration of Fe and RSD values for the Oct. 8th, 2020 sample collection of Campus Creek

Sample Name	Mg Quant [1] mg/L	Mg Quant [2] mg/L	Mg Quant [3] mg/L	**Mg Quant Average mg/L**	Mg RSD	Mg Wavelength
RSC 1	12.8	12.7	12.9	**12.8**	0.56	280.270
RSC 2	12.1	12.1	12	**12.1**	0.46	280.270
RSC 3	10.1	10	10	**10.1**	0.36	280.270
RSC 4	9.7	9.79	9.75	**9.75**	0.49	280.270
RSC 5	11.7	11.7	11.7	**11.7**	0.28	280.270
RSC 6	13.2	13.2	13.2	**13.2**	0.3	280.270
CC 1	13.2	13.2	13.2	**13.2**	0.28	280.270
CC 2	13.3	13.3	13.3	**13.3**	0.1	280.270
CC 3	13.8	13.8	13.8	**13.8**	0.03	280.270
CC 4	22.6	22.7	22.6	**22.6**	0.2	279.553
CC 5	16.7	16.7	16.6	**16.7**	0.38	280.270

Table 5: Concentration of Mg and RSD values for the Oct. 8^{th}, 2020 sample collection of Campus Creek

Sample Name	Na Quant [1] mg/L	Na Quant [2] mg/L	Na Quant [3] mg/L	**Na Quant Average mg/L**	Na RSD	Na Wavelength
RSC 1	22.3	22.2	22.3	**22.3**	0.1	588.995
RSC 2	19.1	19.1	19.2	**19.1**	0.2	589.592
RSC 3	17.5	17.4	17.5	**17.4**	0.18	588.995
RSC 4	16.6	16.8	16.7	**16.7**	0.59	588.995
RSC 5	16.1	16	15.9	**16**	0.54	588.995
RSC 6	20.1	20.2	20.1	**20.1**	0.27	588.995
CC 1	20.3	20.4	20.3	**20.3**	0.06	588.995
CC 2	17.3	17.4	17.4	**17.4**	0.4	589.592
CC 3	21.7	21.8	21.7	**21.7**	0.3	588.995
CC 4	19.8	19.8	19.9	**19.8**	0.31	589.592
CC 5	25.2	25.3	25.1	**25.2**	0.26	588.995

Table 6: Concentration of Na and RSD values for the Oct. 8^{th}, 2020 sample collection of Campus Creek

Distance (m)	Sample	IC (mg/L)	NPOC (mg/L)	TN (mg/L)	Temp (ºC)
0	CC21221RSC1	9.364	4.771	0.7219	4.6
206	CC21221RSC4	10.43	4.148	0.6856	3.0
355	CC21221RSC7	8.891	4.449	0.6668	2.3
413	CC21221RSC8	8.962	4.562	0.6757	1.8
493	CC21221RSC11	11.09	3.237	0.5444	4.2
610	CC211221RSC15	9.413	4.236	0.662	2.7
660	CC21221DS1	9.328	4.656	0.7021	2.5
700	CC21221DS2	9.175	4.474	0.686	2.3
803	CC21221DS3	9.642	4.445	0.7185	2.3
1000	CC21221DS4	9.891	4.528	0.6878	1.9
1204	CC21221DS5	10.52	4.52	0.6821	2.2

Table 7: Inorganic Carbon, Organic Carbon, Total Nitrogen Concentrations, and Temperature values for Feb. 12th, 2021 sample

Distance (m)	Sample	IC (mg/L)	NPOC (mg/L)	TN (mg/L)	Temp (ºC)
0	CC RSC 1 2_19_21	11.27	4.992	0.7483	4.1
206	CC RSC 4 2_19_21	11.98	4.966	0.7903	3.9
355	CC RSC 7 2_19_21	9.935	4.932	0.7542	3.1
413	CC RSC 8 2_19_21	10.19	5.702	0.801	2.9
493	CC RSC 11 2_19_21	10.08	5.158	0.7795	3
610	CC RSC 15 2_19_21	10.61	5.201	0.9475	4.9
660	CC DS 1 2_19_21	10.61	5.434	0.9877	4.7
700	CC DS 2 2_19_21	10.63	4.417	1.019	4.5
803	CC DS 3 2_19_21	10.87	4.455	0.9857	4.4
1000	CC DS 4 2_19_21	11.14	5.117	1.087	4.5
1204	CC DS 5 2_19_21	12.47	4.261	1.032	4.4

Table 8: inorganic carbon, organic carbon, total nitrogen concentrations for Feb. 19th, 2021 samples

Distance	Sample	IC (mg/L)	NPOC (mg/L)	TN (mg/L)	Temp (ºC)
0	CC020321RSC1	7.672	4.07	0.6444	3.3
206	CC020321RSC4	8.779	3.506	0.5382	2.4
355	CC020321RSC7	9.175	3.548	0.6129	3.1

413	CC020321RSC8	9.577	3.746	0.5928	3.8
493	CC020321RSC11	9.26	3.92	0.5707	2.9
610	CC020321RSC15	9.212	3.306	0.5782	3.9
660	CC020321DS1	9.436	3.484	0.6039	4.0
700	CC020321DS2	9.517	3.483	0.6072	5.1
803	CC020321DS3	8.823	3.343	0.5903	4.4
1000	CC020321DS4	10.04	3.292	0.5723	4.63
1204	CC020321DS5	10.54	3.586	0.589	4.70

Table 9: Inorganic Carbon, Organic Carbon, Total Nitrogen Concentrations for Feb. 3rd, 2021 sample

Distance (m)	Sample	IC (mg/L)	NPOC (mg/L)	TN (mg/L)	Temp (°C)
0	CC100820RSC1	13.36	5.756	0.4258	16.1
206	CC100820RSC4	13.81	5.229	0.2557	16.9
355	CC100820RSC7	13.22	5.454	0.2577	16
413	CC100820RSC8	13.23	6.636	0.393	16.4
493	CC100820RSC11	15.2	4.602	0.1704	15.5
610	CC100820RSC15	15.08	3.925	0.1611	16.1
660	CC100820DS1	14.93	No data	0.1701	16.5
700	CC100820DS2	14.93	4.038	0.2401	16.5
803	CC100820DS3	15.08	4.196	0.2708	16.3
1000	CC100820DS4	16.3	3.922	0.2605	16.9
1204	CC100820DS5	16.74	4.261	0.1964	16.3

Table 10: Inorganic Carbon, Organic Carbon, Total Nitrogen Concentrations for Oct. 8th, 2021 sample

Distance (m)	Sample	IC (mg/L)	NPOC (mg/L)	TN (mg/L)	Temp (°C)
0	CC RSC 1 4_2_21	11.87	8.495	0.7318	9.8
206	CC RSC 4 4_2_21	12.06	9.022	0.7499	9.0
355	CC RSC 7 4_2_21	10.81	9.803	0.7803	9.1
413	CC RSC 8 4_2_21	11.04	9.505	0.7527	9.4
493	CC RSC 11 4_2_21	11.23	9.236	0.751	9.3

610	CC RSC 15 4_2_21	11.32	9.341	0.7361	10.2
660	CC DS 1 4_2_21	11.22	8.417	0.7354	11.4
700	CC DS 2 4_2_21	11.26	8.925	0.7286	10.9
803	CC DS 3 4_2_21	11.46	9.692	0.7785	11.7
1000	CC DS 4 4_2_21	12.26	9.151	0.7435	12.8
1204	CC DS 5 4_2_21	11.76	8.54	0.8544	10.7

Table 11: Inorganic Carbon, Organic Carbon, Total Nitrogen Concentrations for April 2nd, 2021 sample set

Site	Distance	Discharge (cfs)	TN	Total Load (lbs/day)	Basin Area (mi^2)	Unit Area Load (lbs/day*mi2)
RSC 1	0	0.64	0.73	2.53	0.45	5.61
RSC 4	206	0.43	0.75	1.73	0.55	3.14
RSC 7	355	0.46	0.78	1.95	0.59	3.31
RSC 8	413	0.66	0.75	2.67	0.6	4.45
RSC 11	493	0.64	0.75	2.59	0.63	4.11
RSC 15	610	0.60	0.74	2.39	0.64	3.74
DS 2	700	0.78	0.73	3.06	0.65	4.70
DS 3	803	0.77	0.78	3.23	0.66	4.89
DS 4	1000	0.68	0.74	2.73	0.68	4.02
DS 5	1204	0.60	0.85	2.76	0.69	3.99

Table 12: Discharge, total nitrogen, total load, basin area, and unit area load for each sampling site for the April 2nd, 2021 sample set

Date	Distance (m)	Site	pH	Temp (Cel)	Cond (uS)	TDS (ppm)	Salinity (ppt)
Oct. 8th, 2020	0	1	6.56	16.1	384	273	0.19
Oct. 8th, 2020	206	2	6.74	16.9	397	283	0.2
Oct. 8th, 2020	355	3	7.04	16	305	224	0.16
Oct. 8th, 2020	413	4	7.25	16.4	341	247	0.17

Oct. 8th, 2020	493	5	7.35	15.5	322	228	0.16
Oct. 8th, 2020	610	6	7.35	16.1	410	284	0.19
Oct. 8th, 2020	660	7	7.4	16.5	406	287	0.2
Oct. 8th, 2020	700	8	7.48	16.5	402	286	0.2
Oct. 8th, 2020	803	9	7.55	16.3	408	288	0.2
Oct. 8th, 2020	1000	10	7.67	16.9	432	307	0.21
Oct. 8th, 2020	1204	11	7.75	16.3	441	314	0.22
Feb. 3rd, 2021	0	1	7.35	3.3	1.726	1.23	0.86
Feb. 3rd, 2021	206	2	7.27	2.4	1.358	1.10	0.70
Feb. 3rd, 2021	355	3	7.19	3.1	2.29	1.63	1.15
Feb. 3rd, 2021	413	4	6.66	3.8	2.44	1.75	1.23
Feb. 3rd, 2021	493	5	7.20	2.9	2.46	1.75	1.15
Feb. 3rd, 2021	610	6	7.24	3.9	2.42	1.71	1.23
Feb. 3rd, 2021	660	7	7.24	4.0	2.26	1.6	1.20
Feb. 3rd, 2021	700	8	7.21	5.1	2.38	1.7	1.12
Feb. 3rd, 2021	803	9	7.18	4.4	2.31	1.66	1.20
Feb. 3rd, 2021	1000	10	7.18	4.63	2.44	1.74	1.17
Feb. 3rd, 2021	1204	11	7.20	4.70	2.48	1.77	1.22
Feb. 12th, 2021	0	1	7.46	4.6	0.785	0.563	0.40
Feb. 12th, 2021	206	2	7.74	3.0	0.759	0.554	0.39
Feb. 12th, 2021	355	3	7.60	2.3	0.790	0.559	0.40
Feb. 12th, 2021	413	4	7.59	1.8	0.770	0.56	0.39
Feb. 12th, 2021	493	5	7.42	4.2	0.888	0.626	0.43
Feb. 12th, 2021	610	6	7.51	2.7	0.891	0.632	0.44
Feb. 12th, 2021	660	7	7.43	2.5	0.895	0.631	0.44
Feb. 12th, 2021	700	8	7.43	2.3	0.887	0.627	0.44
Feb. 12th, 2021	803	9	7.40	2.3	0.896	0.631	0.44
Feb. 12th, 2021	1000	10	7.40	1.9	0.931	0.659	0.46

Feb. 12th, 2021	1204	11	7.37	2.2	0.983	0.69	0.48
Feb. 19th, 2021	0	1	7.75	4.1	3.71	2.66	1.86
Feb. 19th, 2021	206	2	7.69	3.9	0.949	0.812	0.57
Feb. 19th, 2021	355	3	7.34	3.1	1.642	1.16	0.82
Feb. 19th, 2021	413	4	7.34	2.9	1.549	1.12	0.74
Feb. 19th, 2021	493	5	7.19	3	1.553	1.12	0.79
Feb. 19th, 2021	610	6	7.49	4.9	2.73	2.11	0.98
Feb. 19th, 2021	660	7	7.39	4.7	3.00	2.13	1.50
Feb. 19th, 2021	700	8	7.36	4.5	3.40	2.34	1.65
Feb. 19th, 2021	803	9	7.36	4.4	3.67	2.60	1.82
Feb. 19th, 2021	1000	10	7.34	4.5	4.06	2.87	2.02
Feb. 19th, 2021	1204	11	7.29	4.4	4.61	3.25	2.30
April 2nd, 2021	0	1	7.39	9.8	255	188	0.13
April 2nd, 2021	206	2	7.75	9.0	278	198	0.14
April 2nd, 2021	355	3	7.15	9.1	239	170	0.12
April 2nd, 2021	413	4	7.70	9.4	238	170	0.12
April 2nd, 2021	493	5	7.65	9.3	244	171	0.12
April 2nd, 2021	610	6	7.42	10.2	278	197	0.14
April 2nd, 2021	660	7	7.72	11.4	274	195	0.14
April 2nd, 2021	700	8	7.68	10.9	280	198	0.14
April 2nd, 2021	803	9	7.7	11.7	285	203	0.14
April 2nd, 2021	1000	10	7.67	12.8	296	210	0.15
April 2nd, 2021	1204	11	7.67	10.7	340	242	0.17

Table 13: pH, Tempurtature, Conductivity, TDS, and Salinty values for all sample sets

Pledge

I pledge on my honor that I have not given or received any unauthorized assistance on this assignment/ examination.

Alexis Yaculak

4/27/2020