Investigating the Urban Stream Syndrome in the Schenectady-Schoharie Region of Upstate New York

Elizabeth Andonie

Submitted in partial fulfillment of the requirements

for the degree of Bachelor of Science

Environmental Science, Policy and Engineering Program

Union College, Schenectady, New York

April, 2019

ABSTRACT

The urban stream syndrome is defined as the typical effects that cities have on watersheds and has been identified in urban regions worldwide. Symptoms include a higher risk of flooding, increased erosion, reduced biodiversity, and elevated concentrations of nutrients and contaminants. The objective of this study is to determine the extent of the urban stream syndrome in and around the Schenectady area. More specifically, this study focuses on two separate aspects: 1) the influx of road salt, and 2) the influx of organic waste. In addition, data were compared with previous data of the same streams to determine changes over time. A total of 31 urban and 18 rural sites from 11 streams were visited during the summer of 2018. At each site, conductivity, DO%, and pH were measured. When present, different algae were collected, cleaned, dried and analyzed for nitrogen isotopes. Water samples from each site were analyzed for nitrite, nitrate, and chloride ion concentrations. This study found that urban streams had a higher influx of organic waste as well as elevated conductivity and chloride ion concentrations. This confirms the conclusions of a 2016 study on the same streams that the urban stream syndrome exists in the area. However, compared to 2016, the influx of organic waste seems to be higher in 2018 as indicated by the higher $\delta^{15}N$ values of the algae. This study is of significance because it can be used as a baseline to determine the efficiency of upgrades to sewage systems as well as upgrades to storm water systems in the area of study.

ACKNOWLEDGEMENTS

I would like to thank all those who were involved in any part of this research including Max McGeown for assisting in sample collections and helping run water samples on the ion chromatograph with Matt Manon, and Madelyn Miller for helping analyze the samples for stable nitrogen isotopes. Thank you to Union College for funding this project through a student research grant, summer research fellowship and a student conference travel grant and thank you to the NSF for funding the isotope ratio mass spectrometer and peripherals (NSF-MRI #1229258). My gratitude also goes out to the Geology Department for additional funding of this research and funding my participation to the NEGSA conference. Finally, and most importantly I would like to thank Anouk Verheyden-Gillikin for all of her guidance, patience, and all the time she took to make this research possible.

TABLE OF CONTENTS

INTRODUCTION

According to the National Rivers and Streams assessment of 2008-2009, 46% of the United States' river and stream length is in poor biological condition (EPA, 2016). The most affected area is the northeastern United States where 50.1% of river and stream length is in poor condition (EPA, 2016). The quality of streams is of great importance, because they can be host to unique and diverse species, and can contribute to sources of drinking water for communities by providing a continuous flow of water to reservoirs and by helping to recharge underground aquifers. In the continental United States, 357,000 miles of streams contribute to public drinking water, which supplies approximately 117 million people with freshwater (EPA, 2016). Streams also have economic value by providing fishing areas, contributing freshwater to industries and by being a source of irrigation for agriculture (EPA, 2013). The overall health of streams is crucial to the health of the entire surrounding river network; meaning that the condition of streams can have an effect on many bodies of water (EPA, 2013). For this reason, it is imperative that the health of streams be a priority. Land usage surrounding waterways can have a big impact on the health of streams (Zanden et al. 2005). Agricultural lands have a significant effect on stream health causing fertilizer, animal waste and other chemicals to enter waterways. Additionally, urban environments increase the input of pollutants by adding to the amount of impervious surfaces and sources of anthropogenic nitrogen (Barton and Vose, 2005).

Urban Stream Syndrome

In 2016, it was estimated that 54.5% of the global population lives in urban areas, this number is projected to increase to 60% by 2030 (UN, 2016). The magnitude and concentration of human activity in urban areas causes major impacts on the environment, leading to changes in water and air quality through dispersion of pollutants such as trace metals, toxic organic compounds and human waste (Walsh et al. 2012). The typical effects that cities have on watersheds has been referred to as the “urban stream syndrome” (Lyons & Harmon, 2012; Walsh et al. 2005). Impacts of this include, a higher risk of flooding, loss of habitat, increased erosion, reduced biodiversity, and elevated concentrations of nutrients and contaminants (Lyons & Harmon, 2012). Drivers of urban stream syndrome vary but the primary sources include urban storm water runoff, sewer overflows, and discharge from wastewater treatment plants (Walsh et al. 2005).

Cases of urban stream syndrome can be seen all over the world (Booth et al. 2015; Halstead et al. 2014; Ramírez et al. 2009; Driscoll et al. 2003). For example, in order to understand the specifics of urban stream syndrome in the tropics, a study set out to assess streams in Puerto Rico (Ramírez et al. 2009). Thirty-two streams were analyzed and all urban streams exhibited the typical symptoms of urban stream syndrome including increased nutrient concentrations, and elevated conductivity (Ramírez et al. 2009). Studies like this are especially important as the growth of cities in the tropics is outpacing management of wastewater and clean drinking water (Ramírez et al. 2009).

Similar to the study in Puerto Rico, a study conducted in Saratoga County of upstate New York, found that various parameters increased with the amount of urban development, including total nitrogen, total phosphorous, nitrate (NO_3^-), chloride ion concentrations and conductivity (Halstead, 2014). The elevated conductivity and ion concentrations were attributed to the large amounts of road salt used in upstate New York, and the increased nutrient content in surface waters was attributed to the leakage of septic systems, use of fertilizers and the presence of pet waste. The results of this study point out that specific human activities have a broad impact on freshwater streams. To maintain the health of streams and their surrounding ecosystems it is imperative to understand the various kinds of pollution and their sources.

Road Salt

One pollutant of freshwater ways that is typical in the northeastern United States and increases with urban areas is road salt (USGS, 2019). In New York State, in which this study takes place, 840,340 tons of salt and 1,104,830 gallons of salt brine are applied each year to state highways (NYSDOT, 2019). The heavy usage of road salt can have serious impacts on both human health and that of natural ecosystems by contaminating drinking water wells and changing ecosystem conditions (Hinsdale, 2018). In a recent study, it was found that in Duchess County, New York, 48 % of 128 sampled wells had sodium concentrations that exceeded EPA guidelines for drinking water, this was attributed to the use of road salt in the area (Hinsdale, 2018). High chloride concentrations from road salt are toxic to aquatic life and road salt runoff may also cause oxygen depletion, further degrading aquatic ecosystems. The increased concentrations of salt in our freshwater will be an issue for years to come as the road salt in ground water slowly reaches surface waters over decades (Hinsdale, 2018). It is important to monitor impacted waterways especially those in urban areas where the concentrations of road salt have been rapidly increasing over the past several years.

Organic Pollution

Along with elevated conductivity, elevated nutrient concentration is another major symptom of urban stream syndrome that severely degrades the health of streams (Walsh et al. 2012). Nutrients in this case are mainly nitrogen and phosphorous. Both are natural parts of an aquatic ecosystem and support algae and plant growth. However, when found in excess they result in eutrophication, which causes an overgrowth of algae, also known as an algal bloom (Khan & Ansari, 2005). The decay of this organic matter causes a decrease in oxygen and can lead to a dead zone in which no life can survive due to the reduced oxygen levels. Some algal blooms are caused by cyanobacteria, which can release toxins causing sickness if ingested and killing aerobic organisms in the affected body of water (Michalak, 2013). In the United States 28% of streams have high concentrations of nitrogen and 40% have high concentrations of phosphorous (UNEP n.d.), however, eutrophication is observed in all types of water bodies and is the leading threat to water quality around the world (World Resources Institute, n.d.). The presence of nutrient pollution has become more prevalent through human activities such as the production of fertilizers, cultivation of nitrogen fixing plants, accumulation of sewage, and fossil fuel combustion (Driscoll, et al. 2003, Vitousek et al. 1997).

A specific case of disastrous organic pollution is Lake Erie where the severity of eutrophication continues to increase annually (Parshina-Kottas & Patel, 2017). During the fall of 2017 there was an algal bloom of 700 km^2 on the lake (Parshina-Kottas & Patel, 2017). The largest bloom recorded was 5,000 km^2 and occurred in 2011, covering 19% of the entire lake (Michalak, 2013). On average the blooms have become larger since the 2000s and have caused economic and health problems for the region (Parshina-Kottas & Patel, 2017). In the past, drinking water has been shut down because of toxins released by algal blooms, and people have been kept off the lake while the bloom is present. This has had a negative financial impact in the area due to a decline in tourism which accounts for

50 billion dollars of Lake Erie's annual revenue (Parshina-Kottas & Patel, 2017; Watson et al. 2016). The huge algal blooms in Lake Erie are most likely caused by phosphorous loading from agricultural practices around the lake (Kane et al. 2014; Michalak, 2013). Agriculture run off is in many regions the cause of eutrophication and dead zone occurrence (Parshina-Kottas & Patel, 2017; Abell et al. 2010), but this is not the case everywhere. In the northeastern United States, the area on which this study focuses, it was found that the main source of nitrogen loading was wastewater effluent, which accounted for 31% to 81% of nitrogen loading in the northeast (Driscoll et al. 2003).

Cape Cod, located in the northeastern United States, has experienced eutrophication caused by wastewater effluent, attributed to recent urbanization which has led to a decrease in forest cover, as well as an increase in impervious surfaces (Valiela, 2016). These factors contribute to the urban stream syndrome, and lead to increased urban storm water runoff, and sewer overflows (Valiela, 2016). A recent study set out to discern the consequences of changing sources and rates of nitrogen loads in estuaries around Cape Cod (Valiela, 2016). It was found that the wastewater nitrogen loads increased by 80%, likely due to an increase in developed land and leakage from septic tanks, but the atmospheric deposition decreased by 41% since 1990. The study concludes that the rapid local and global changes in costal zones warrants adaptive strategies that can accommodate the changing sources of nitrogen. The identification of the pollution source is a significant step towards fixing the problem, as management plans can be made to target the source of nutrients.

Nitrogen

The present study will focus specifically on nitrogen pollution in and around the Schenectady area. In order to understand eutrophication, it is important to understand how nitrogen flows through ecosystems. The nitrogen cycle is crucial to life on earth but can be severely altered by human activities. Most nitrogen on earth is in crystalline rocks (98%) while 2% is in air and around 0.001% is found in organic matter (Sharp, 2017). During the nitrogen cycle N_2 gas is removed from the atmosphere by nitrogen fixation which makes ammonia (NH_4^+) (Sharp, 2017). Ammonia can then be nitrified by nitrifying bacteria and converted to nitrate (NO_3^-) which creates a large oxygen demand. Further nitrification of NO_3^- results in nitrite (NO_2^-) (Sharp, 2017). Ammonia and NO_3^- can be assimilated into living tissue by organisms and the reverse of assimilation is the decay of organic matter by bacteria which releases ammonia (Sharp, 2017). The final piece of the cycle is denitrification which is the conversion of ammonia, NO_3^- or NO_2^- back to N_2 gas (Sharp, 2017). Some ways in which humans alter the cycle are by adding excess ammonia into systems via synthetic fertilizer and decaying garbage in landfills. Wastewater treatment plants also contribute to excess ammonia and nitrate, since wastewater is high in both nitrogen compounds (Sharp, 2017). It is crucial to understand and track inputs of nitrogen into waterways for it can have disastrous effects on natural ecosystems as previously explained. Stable isotopes are one useful tool in monitoring sources of nitrogen pollution.

Stable Isotopes

Sources of nitrogen can be monitored through the use of stable isotopes (Heaton, 1986). Isotopes are atoms with the same number of protons and electrons but a different number of neutrons. Therefore, isotopes belong to the same element but have a different mass. Stable isotopes, on which this study focuses, are non-radioactive isotopes that do not decay overtime, and they can be useful in studying multiphase systems because of the mass difference between isotopes of the same element. The difference causes isotopes to behave differently in regards to bond strength and reactivity. Heavier isotopes have stronger atomic bonds that are harder to break, making them move and react slower than lighter isotopes. This results in isotopic fractionation which is the preferential incorporation of either the heavy or light isotope in a system (Sharp, 2017).

The way in which isotopic compositions are reported is the delta (δ) notation. δ values are a ratio of heavy over light isotopes denoting a difference relative to a standard (Fry, 2001). A delta value (δ) can be defined as:

$$\delta^{H}X= [(R_{sample}/R_{standard}-1)]*1000$$

In this equation R is the ratio of heavy over light isotopes. The more light isotopes in a sample relative to the standard, the lower the δ value will be, the more heavier isotopes in the sample, the higher it will be.

Using Nitrogen Stable Isotopes to Monitor Organic Pollution in Streams

The three main sources of nitrogen pollution in aquatic systems are the mineralization of soil nitrogen, synthetic fertilizer, and animal or sewage wastes (Heaton, 1986). Each has a distinct nitrogen isotopic signature allowing them to be identified as the source in aquatic environments. The differences are a result of the process of nitrification being a unidirectional kinetic reaction, meaning nitrifying bacteria take up the lighter isotope of nitrogen (^{14}N) preferentially over the heavier isotope (^{15}N) (Sharp, 2017). Nitrate and ammonium fertilizers have a $\delta^{15}N$ value close to 0‰ while animal and sewage wastes have a high $\delta^{15}N$ value between +10‰ and +20‰ (Heaton, 1986). The reason for the high values is that organic wastes become depleted in ^{14}N during microbial processing (Heaton, 86). High nitrogen isotopic signatures from organic waste is assimilated from the water column by organisms such as algae, this nitrogen is incorporated into the living tissues of the algae making it a viable tracer of organic waste (Sharp, 2017). Algae or other organisms can be collected and analyzed for $\delta^{15}N$ values, this is a particularly useful method in that it can identify the source of nitrogen and average the nitrogen over time rather than reflect only a single point in time like analyzing water samples does. Depending on where the algae derives its nutrients from, its isotopic signature will reflect the source through the $\delta^{15}N$ value. Low $\delta^{15}N$ values close to 0‰ may indicate the presence of ammonia such as that in synthetic fertilizer. Higher $\delta^{15}N$ values in algae are indicative of pollution from organic wastes. According to Cabana and Rasmussen (1996) background levels of nitrogen are between -5‰ and +5‰, values above this range are indicative of pollution from organic waste. This study and many previous studies have employed the use of stable isotopes of nitrogen from aquatic algae to detect the presence and the source of organic pollution (Costanzo et al. 2005; Steffy and Kilham, 2004; Savage and Elmgren, 2004; Cabana and Rasmussen, 1996). In this study, we used filamentous algae which was chosen because it is easy to identify, it persists in waterways giving us a time average of the nitrogen in the streams and it uses nutrients directly from the water column (Salls, 2009; Cambra and Aboal, 1992).

Urban Stream Syndrome in the Schenectady Schoharie Region

Three years of previous studies have investigated the urban stream syndrome in the Schenectady-Schoharie Region, the first of these studies was done by a former Union

College student, Michelle Berube (2015). In her study of the Capital region she monitored water quality and nutrient loading in streams by collecting algae and water samples. The algae were analyzed for $\delta^{13}C$ and $\delta^{15}N$ and the water samples were used to detect ion concentrations. She found that urban streams contained much higher levels of organic pollution than rural ones. The concentrations of fluorine and the ratio of chlorine to sodium ions were indicative of waste water leakage and road salt being used in the urban areas, respectively (Berube, 2015). However, Berube's study was not designed to study the urban stream syndrome, but rather to study water sheds in different geological regions. As a consequence, her sampling locations were not spread equally between rural and urban regions. The preliminary conclusions of Berube's study led to further exploration by Carolyn Connors, another Union College student in 2016. Connors sampled streams in the Schenectady-Schoharie region and specifically targeted rural and urban locations. She concluded her results were consistent with Berube's (2015): the urban streams were more polluted than the rural ones (Connors, 2017). Finally, Cameron Bechtold (2017), a Union College sophomore resampled some of the same streams as Connors (2017), to investigate temporal consistency. More specifically, he was interested in determining whether streams that showed a high input of organic waste pollution in one year, would show the same results in another year. Temporal consistency means that the pollution could be pinpointed to certain locations in the stream and pollution can be reduced by, for example, identifying leaking septic tanks and repairing or removing them. However, if the organic pollution showed inconsistencies with prior years, this would mean the pollution would be more influenced by weather patterns or by disturbances to the stream caused by developments. In this case, reduction in organic waste input should be tackled through a more large-scale regional approach such as limiting development along streams. Bechtold's (2017) study found a very good correlation between the isotopic compositions of Connor's study and his own study (r^2=0.79), indicating that organic waste input is most likely a point-source pollution in those streams.

In this study, algae and water samples were collected from the same rural and urban streams as studied by Connors (2017). Additional sites were chosen to expand the study and one site was visited once a week over four months to track variations in isotope ratios of nitrogen over time. The same method as Bechtold (2017) and Connors (2017) was employed to obtain $\delta^{15}N$ data from algae samples to determine the presence of organic pollution.

This study focuses on the temporal and spatial analysis of organic pollution and input of road salt in urban and rural streams. More specifically, this study sets out to determine which streams in urban and rural Schenectady County show the presence of organic pollution and if this pollution has been present in the past. This was done by collecting filamentous algae samples and analyzing them for isotopes of nitrogen. It is expected that the urban streams will display higher $\delta^{15}N$ values, and higher specific conductivity indicating urban stream syndrome, similar to past studies (Connors, 2017; Bechtold, 2017). However, during this study many streams lacked filamentous algae so different types of algae were sampled at each site to observe differences in their $\delta^{15}N$ values and to compare them as tracers of nutrient pollution. The two types included, filamentous, and algae that was rooted to rock. Filamentous algae is preferred for this type of study because it is free floating so that it can only integrate nitrogen from the water column. Algae attached to rocks may obtain nitrogen from their substrate and cause noise in the isotope signal.

MATERIALS AND METHODS

During the summer of 2018, water and algae samples were collected from 49 sites along 11 different streams (Table 1) in upstate New York in the Schenectady-Schoharie region (Figure 1). The Hans Groot's Kill, one of the sites, was sampled multiple times, once every week from June into October to examine how $\delta^{15}N$ values in algae vary over the growing season. Most sites were chosen because they were sampled in a previous study (Connors, 2017). Additional sites were chosen in the same geographic region to expand the data set. Each site was classified as rural or urban based on the amount of fixed structures and impermeable surfaces within a 0.5 kilometer radius, a classification that Connors (2017) defined in her study. Sites that had 10 or more of these features within the radius were classified as urban (Connors, 2017).

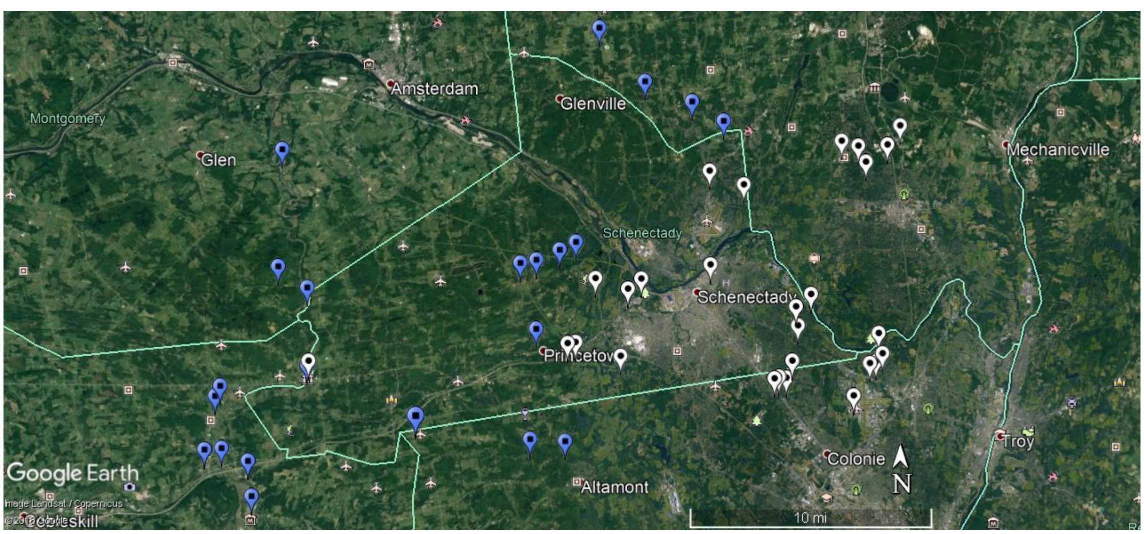

Figure 1: Map of study area marking the sampling sites. The blue makers containing a square represent rural sites and the white markers containing a circle represent urban sites.

Table 1: List of streams sampled in this study with labels used for each and the number of sites along each stream.

Stream Name	Site label	Number of sites
Hans Groot Kill	HGK	1
Alplaus Kill	AK	5
Indian Kill	IK	1
Poentic Kill	POK	3
Normans Kill	NK	4
Schoharie Creek	SC	11
Shakers Creek	SHC	5
Cooley Kill	CK	5
Bozen Kill	BK	3
Lisha Kill	LK	7
Plotter Kill	PK	4

At each site, the temperature, dissolved oxygen content, conductivity, pH, and salinity were recorded using a YSI, multi-parameter water quality meter. Other observations were noted such as weather conditions. Water samples were filtered using a 0.2 micron mini sart high-flow single use syringe filter and stored in 50 ml falcon tubes to later be analyzed on Union College's Dionex ion chromatograph to identify nitrate, nitrite and chloride ion concentrations. In addition, all types of algae present at each site were sampled. The target algae was filamentous *Cladophora*, a genus of the group Chlorophyta or green algae (Salls, 2009). This is a general classification as it is impossible for us to identify on the species level. Since our target algae was often absent from streams we collected other types and classified the two groups we found into our target type, filamentous *Cladophora* (FA), and algae rooted to rocks (RA).

Algae were cleaned in the lab to remove any dirt or small critters from the sample, then placed in a drying oven at 50 °C and removed when they were completely dry. The dried algae were then crushed into a powder using liquid nitrogen and a mortar and pestle. A subsample of between 0.48 and 0.52 mg was packed into tin cups to be later combusted at 980 °C using a Costech Elemental Analyzer. The gas released during combustion enters a Thermo Delta Advantage mass spectrometer via a ConFlo IV, to determine isotopes of nitrogen and carbon. Reference standards used were sorghum flour, acetanilide, ammonium sulfate [IAEA-N-2] and caffeine [IAEA-600]. Corrections were done using a regression method. The analytical uncertainty for $\delta^{15}N$ (Air) is ± 0.03‰, based on 4 acetanilide standards over 1 analytical session.

Finally, for the statistical analysis, data from urban and rural sites were compared using an unpaired t-test and data from 2018 were compared with data from 2016 using a paired t-test. The results of both were reported through the p-value. These statistical tests were performed using JMP statistical software. Regressions were compared using R^2 values generated by Microsoft excel.

RESULTS

Specific Conductivity

The average specific conductivity (SPC) for urban sites (1014.0 ±305.5 μS/cm, n=26) was significantly higher (p= < 0.00001) than the average recorded in the rural sites (530.2 ± 156.1 μS/cm, n=18, Figure 2).

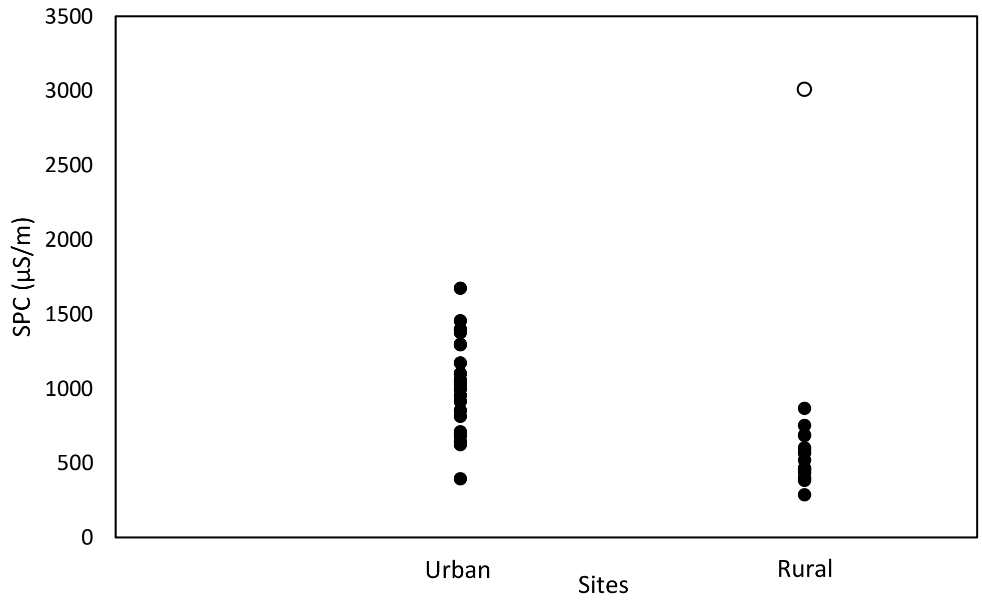

Figure 2: Comparison of specific conductivity (SPC) at urban and rural sites measured in µS/cm. The average SPC of the urban sites (1014.0 ±305.5 µS/cm, n=26) was almost double that observed at the rural ones (530.2 ± 156.1 µS/cm, n=18). Although there is some overlap in the values the difference was significant (p=< 0.00001).

In 2018, sampled streams had an average SPC of 818.1 ± 360.1 µS/cm (n=44), compared to 2016 which had an average of 823.3± 417.6 µS/cm (n=44, Figure 3). However, the two data sets were not significantly different but rather they were fairly similar (p=0.89). Three outliers were removed from the statistical analysis, due to their unusually low or high values (Figure 3, see open circles, see discussion).

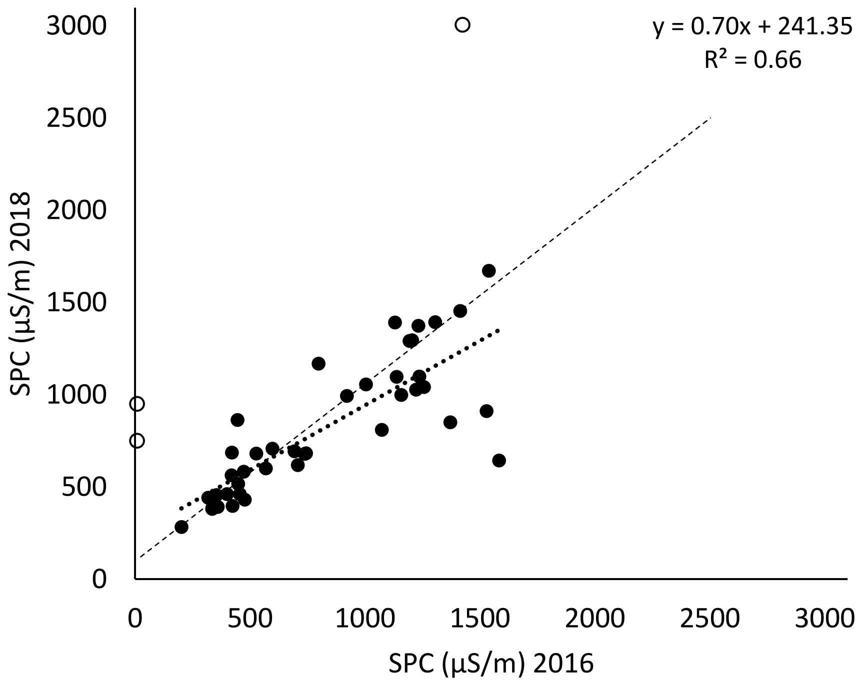

Figure 3: Comparison of specific conductivity (SPC) of sites in 2016 and 2018 (n=44) measured in µS/cm. The open points represent outliers that were not included in the statistical analysis (see discussion). The dashed line represents the 1:1 line. A decent correlation exists between the two data sets (R^2=0.66). The difference that exists between the two years was not significant (p=0.89).

Chloride Ion Concentration

Chloride ion concentration at urban sites was significantly higher than in rural sites (n=22, p= 0.03, Figure 4) However, in the comparison of chloride ion concentrations from 2016 and 2018 the difference was not significant (p=0.32, Figure 5).

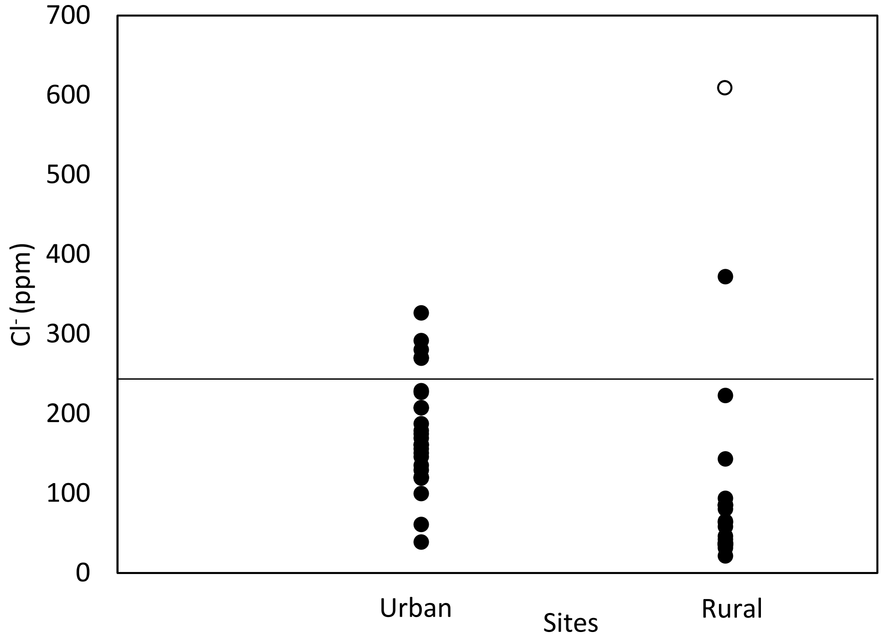

Figure 4: Comparison of chloride ions in urban (n=26) and rural sites (n=22) measured in ppm. The urban sites have significantly higher concentrations of chloride ions compared to the rural sites (p=0.03). The line at 230 ppm represents the threshold line for the EPA limit for chronic effects from chloride ions (EPA, 2019). The open point represents an outlier that was much higher than any other values and was not included in the statistical analysis (see discussion).

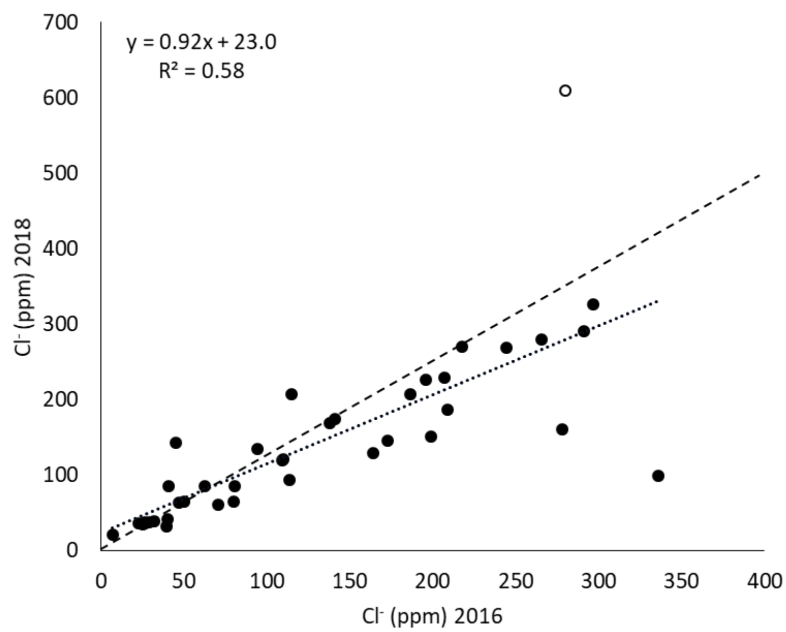

Figure 5: Comparison of chloride ion concentration in 2016 and 2018 (n=39). The 1:1 line is represented by the dashed line. The difference between the two sets of data was not significant (p=0.32). The very high chloride value represented by the open circle was an outlier that was not included in the statistical analysis or the regression calculation.

Dissolved Oxygen

The average percent of dissolved oxygen in the rural sites was 99.5% ±17.1% (n=18), while the average in the urban sites was 92.2% ± 12.5% (n=26). The difference between the two site types was not significant (p=0.11, Figure 6). One outlier was found in the rural sites with an unusually low DO% (29.9%, see discussion). All outliers were not used in the calculation of the p-value or the averages.

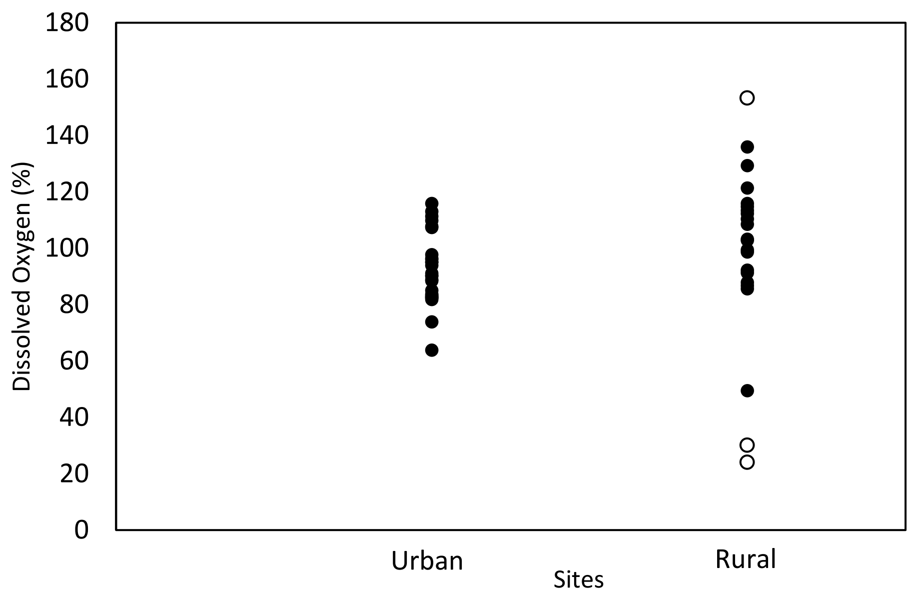

Figure 6: Percent dissolved oxygen (DO%) in urban (n=26) and rural sites (n=18) in 2018. Open points represent outliers that were unusually high or low and were not included in statistical analysis (see discussion). The DO% between the two classifications of sites was very similar. Any difference was not significant (p=0.11).

The average dissolved oxygen values of 2018 (96.0 ± 14.1%, n=44) were higher than in 2016 (91.0 ± 16.3%, n=44, Figure 7). The difference is mildly significant (p=0.02). Three outliers exist within the data that were unusually low (see discussion) but these were not used in the calculation of the R^2 value, the averages or in the paired t-test.

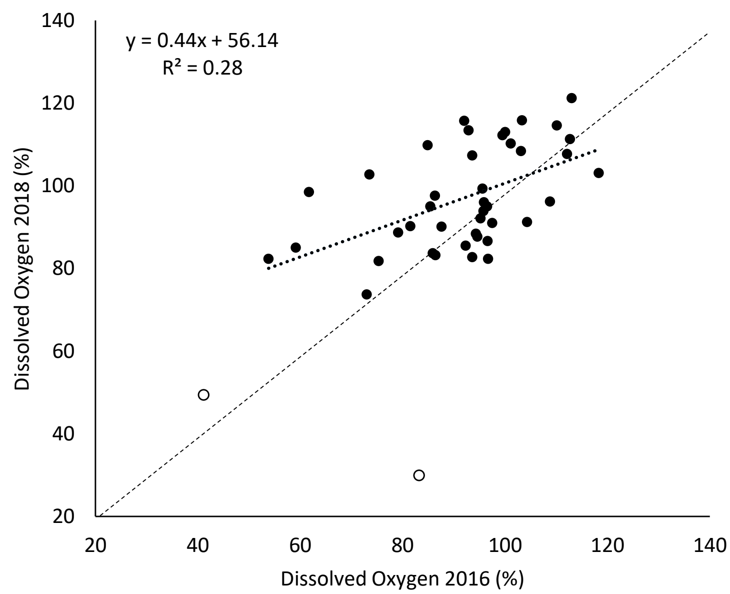

Figure 7: Comparison of DO% values in 2016 and 2018 (n=44). Open points represent outliers (see discussion). There is little correlation between the two data sets (R^2=0.28). 2018 yielded slightly higher values than 2016 (p=0.02) as represented by the dashed 1:1 line.

pH

On average the pH for the rural sites (7.9± 0.3, n=18) is slightly higher than that of the urban sites (7.7 ± 0.3, n=26, Figure 8). The difference is significant at the 95% confidence level (p=0.04).

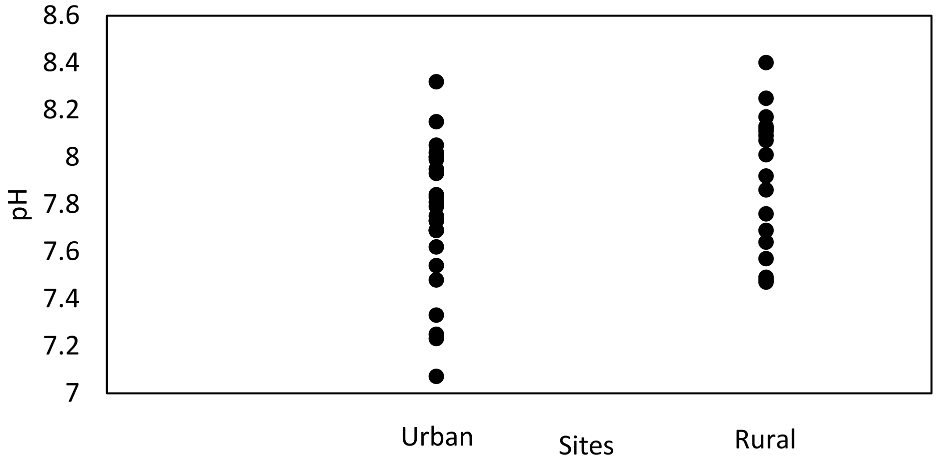

Figure 8: pH of urban (n= 26) and rural sites (n=18) measured in 2018. The rural sites on average have a significantly higher pH. (p=0.04).

The average pH in 2018 (7.8± 0.3, n=44) was lower than the average of 2016 (8.0±0.2, n=44, Figure 9). The difference between the two data sets was significant (p=0.0003).

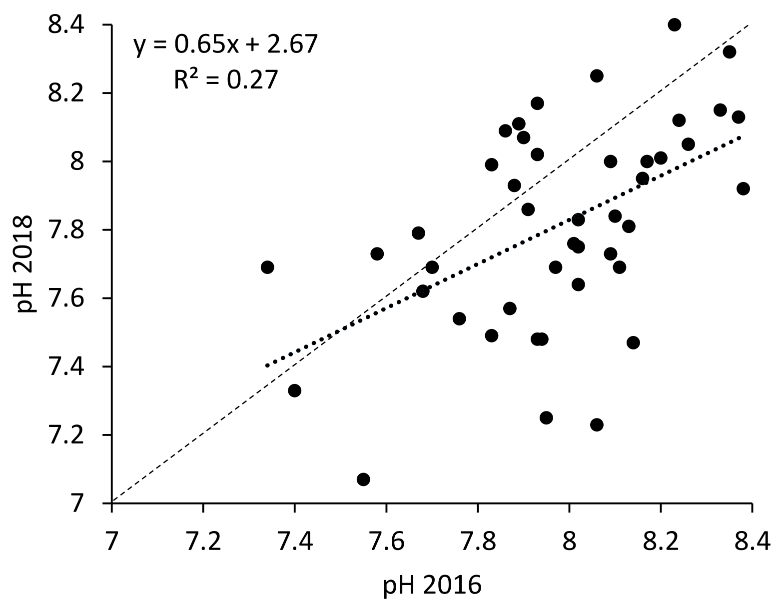

Figure 9: Comparison of pH measured in 2018 and in 2016. There is little correlation between the two years (R^2= 0.27). 2018 values are significantly lower than 2016 (p=0.0003). The dashed 1:1 line shows that most site values in 2018 are lower than in 2016.

Suitability of Other Types of Algae in the Detection of Nitrogen Pollution Sources

There seems to be no discernable correlation between the $\delta^{15}N$ values of filamentous algae (FA) and algae attached to the rocks (RA) (Figure 10). Samples of each type of algae collected from the same site varied in their relationship to one another, at some sites the FA had a higher $\delta^{15}N$ value, while sometimes this relationship was reversed. As a result of the variability of RA only data obtained from FA was used for further analyses.

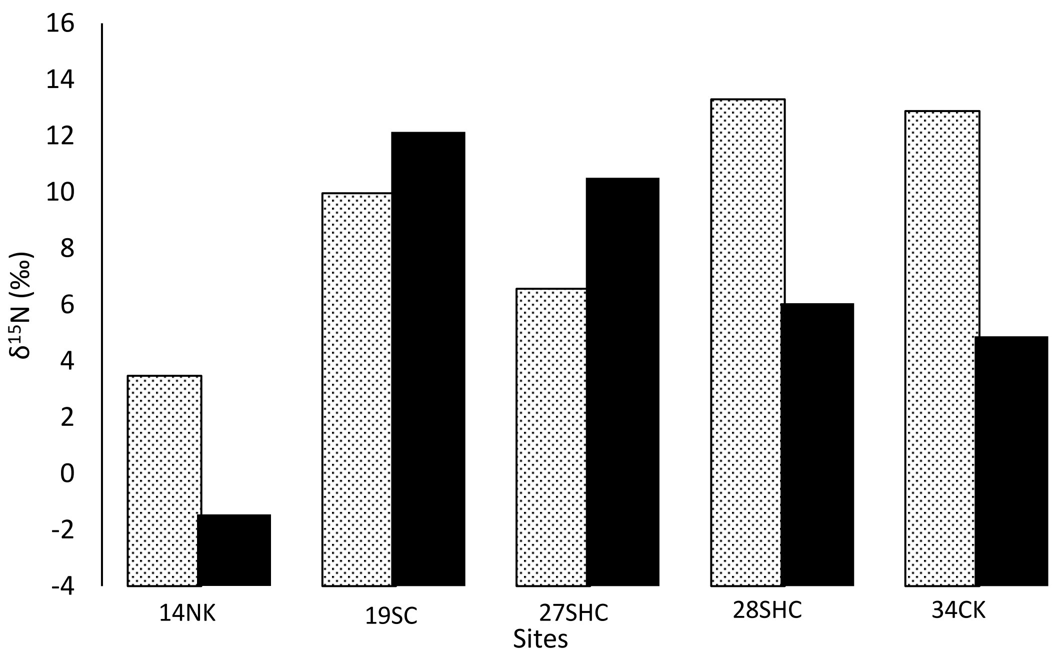

Figure 10: Comparison of $\delta^{15}N$ values of both FA (dotted bars) and RA (solid bars) from the same sites. The labels beneath the bars are the sites at which both samples were collected, refer to table 1 for stream names. There is no discernable pattern in $\delta^{15}N$ between the two types of algae.

$\delta^{15}N$ of Filamentous Algae

The average $\delta^{15}N$ value of FA found at urban sites (+9.3 ± 4.5 ‰, n=10) was significantly higher than the average at the rural sites. (+5.26 ± 3.0 ‰, n=10, p=0.03). The urban sites ranged from +16.9‰ to +1.8‰, while the rural sites ranged from +9.97‰ to +0.27‰. When using the +5‰ threshold (Cabana and Rasmussen, 1996; see discussion) 90% of urban streams in this study are indicative of organic pollution and only 40% of rural streams are (Figure 11).

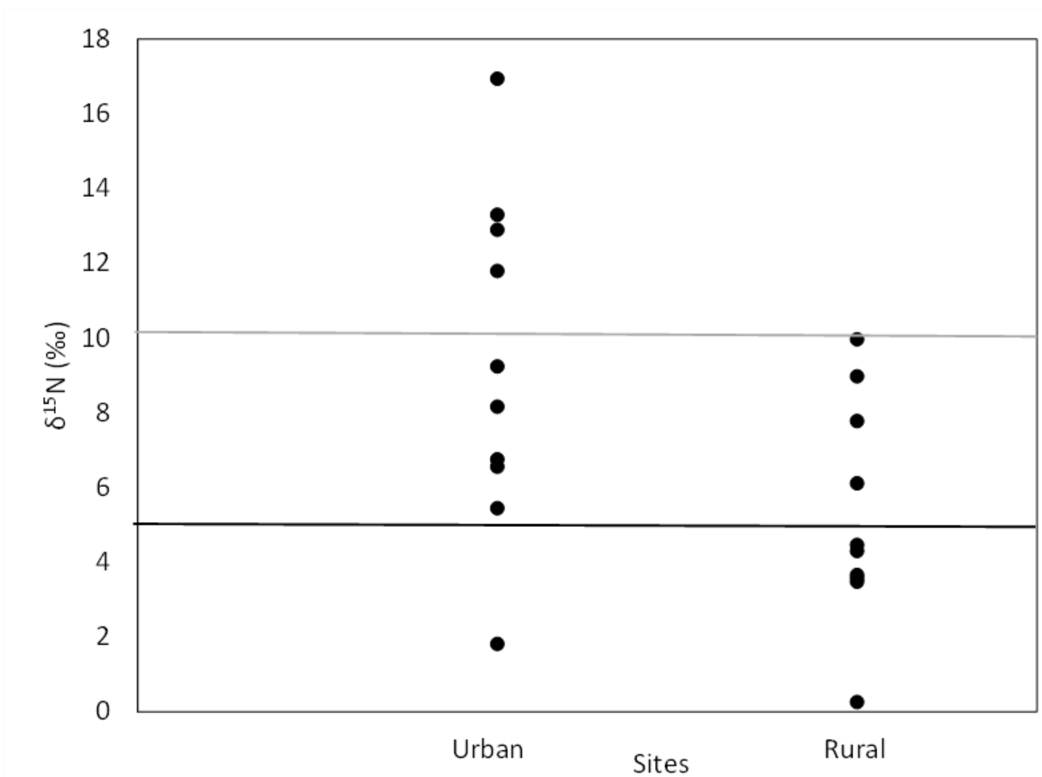

Figure 11: Comparison of $\delta^{15}N$ values in urban and rural sites in 2018. The solid line represents the 5‰ threshold for nutrient pollution caused by organic waste (Cabana and Rasmussen, 1996). The other lighter colored line at 10‰ represents the threshold above which nitrogen is most definitely derived from organic waste (Heaton, 1986). Values above this line indicate sites at which organic pollution is present. The urban sites (+9.3 ± 4.5‰, n=10) generally had higher $\delta^{15}N$ values than the rural ones (+5.26 ± 3.0 ‰, n=10). In addition, the rural sites had the lowest $\delta^{15}N$ value (0.27‰) and the urban sites had the highest $\delta^{15}N$ value (16.94‰). The difference between urban and rural was significant (p=0.03).

Sites at which FA were found and were sampled in both 2016 and 2018 were compared. The average $\delta^{15}N$ value for both rural sites and urban sites was significantly lower in 2016 (+0.74 ± 2.71‰, +4.94 ±0.70‰) than in 2018 (+4.19 ± 3.53‰, +8.30 ± 5.11‰, p=0.005, Figure 12). Only one site located on the Cooley Kill stream had a higher $\delta^{15}N$ value in 2016 than in 2018.

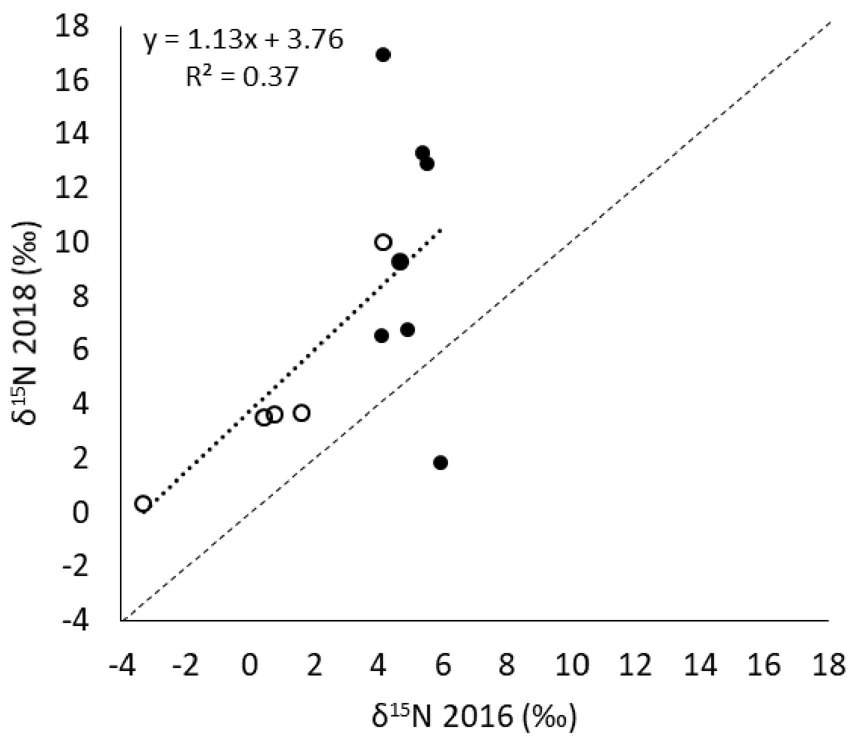

Figure 12: Comparison of $\delta^{15}N$ values in 2016 and 2018 (n=12). The open circles represent rural sites while black dots represent urban sites. The dashed line is the 1:1 line. FA were present in both sampling years in only 12 sites. $\delta^{15}N$ values are significantly higher in 2018 than in 2016 in both urban and rural sites (p=0.005).

Repeated Measurements of Algal $\delta^{15}N$ Values in the Hans Groot's Kill

Throughout the study, no FA were detected in the Hans Groot's Kill, despite FA having been collected from this stream in the past. Therefore, the data shown below are from RA. The $\delta^{15}N$ values of algae samples from the Hans Groot's Kill from early June to late October varied over time. The $\delta^{15}N$ values ranged from +3.6‰ to +13.3‰. A large drop in the $\delta^{15}N$ value occurred on October 12th with 3 significant peaks on July 7th, September 7th and October 26th. When compared to the precipitation of the day before and the day of sample collection, there seemed to be no correlation (Figure 13). Two dates, 8/30/18 and 10/12/18 were days of high precipitation that correlated with low $\delta^{15}N$ values but this trend was not consistent.

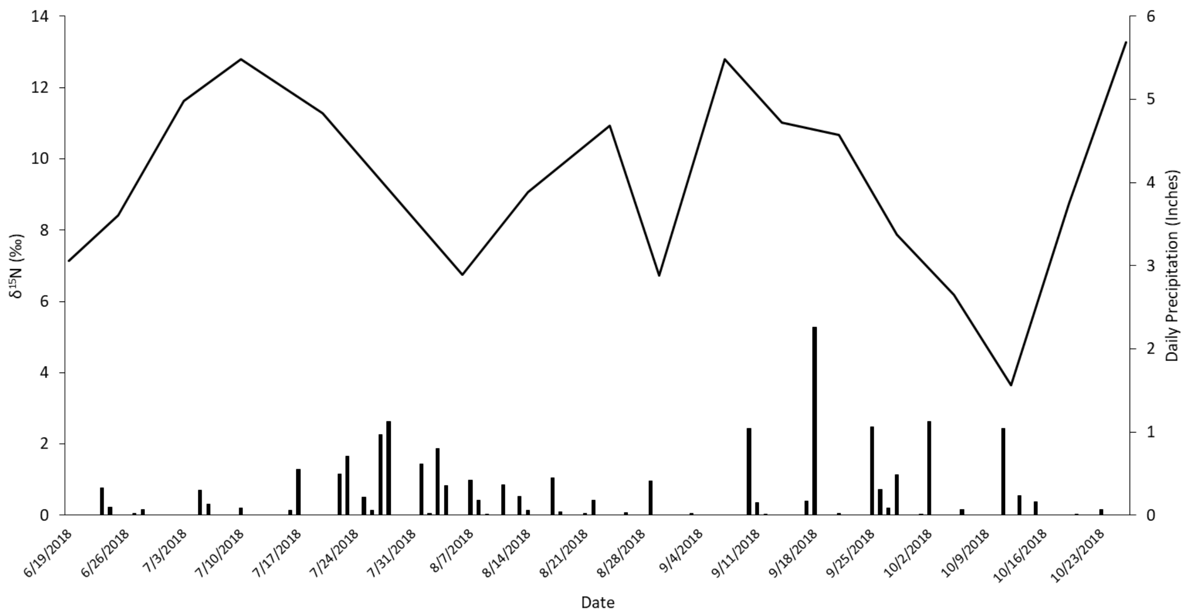

Figure 13: Daily precipitiaion (bars) measured in inches and $\delta^{15}N$ values of the Hans Groot Kill between early June and late October (line). There doesn't seem to be a constant trend between the precipitation and the $\delta^{15}N$ values. On 8/30/18 and 10/12/18 higher precipitation correlates with lower $\delta^{15}N$ values. However, other dates with low $\delta^{15}N$ values do not match up with high precipitation.

Nitrite and Nitrate Ions

The $\delta^{15}N$ values of the FA generally increase with the concentration of nitrite but the correlation is very weak, the relationship only accounts for 42% of variance (R^2=0.42, Figure 14). However, the relationship between the $\delta^{15}N$ values and nitrate ions shows even less correlation as the model below can only explain 27% of variance (R^2=0.27, Figure 15). Overall nitrate and nitrite ion concentrations were low.

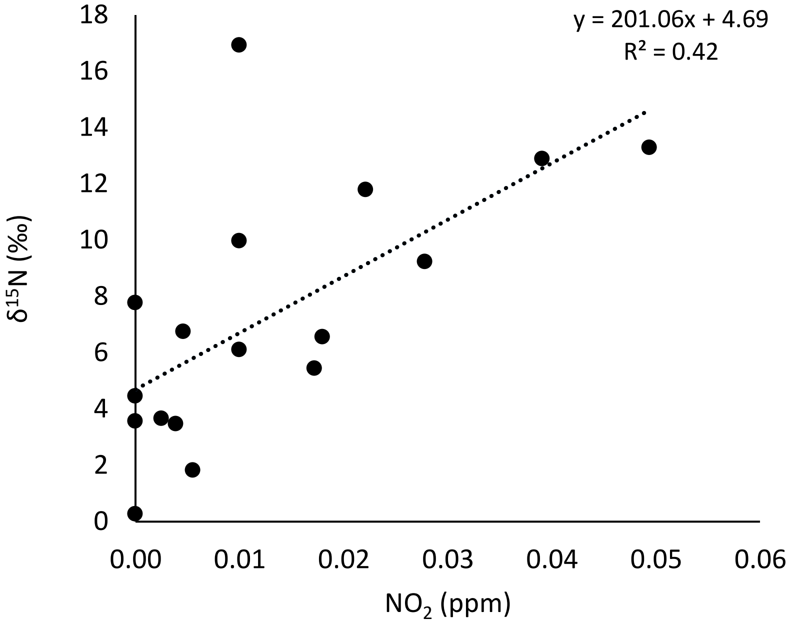

Figure 14: Comparison of nitrite ion (NO_2) concentration and $\delta^{15}N$ values of all FA samples. There is a weak correlation between the two sets of data (R^2=0.42).

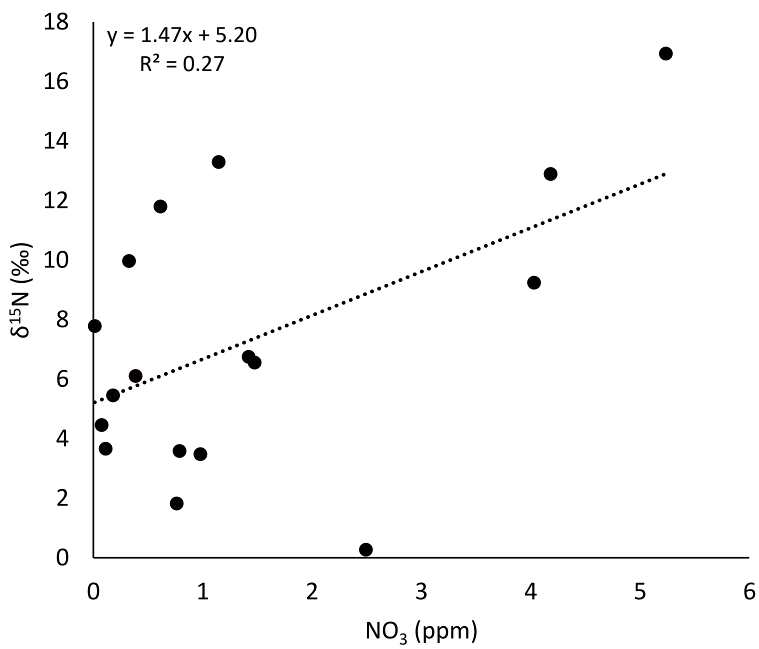

Figure 15: Comparison of Nitrate ion (NO_3) concentration and $\delta^{15}N$ values of FA. Overall, the $\delta^{15}N$ value increased with NO_3 concentration however the relationship is not significant (R^2=0.27).

DISCUSSION

Road Salt in Streams

Both SPC and chloride ion concentrations at urban sites were almost double what they were in rural ones, which is most likely due to the presence of more road salt in urban streams (Figures 2 and 4). Road salt was found to be the cause of elevated conductivity in a previous study of the same streams by looking at the ratios of sodium and chloride ions (Connors, 2017). In addition, road salt is widely used in the northeastern United States due to the amount of snow fall each year. In general, road salt runoff is an increasing problem in places that receive a significant amount of snowfall in North America and will continue to be a problem for decades to come as salt persists in groundwater and makes its way to surface waters over years (Hinsdale, 2018; Tiwari and Rachlin, 2018). In our study, we found that most of our streams were at healthy levels of SPC and chloride ion concentrations. The U.S. Environmental Protection Agency (EPA) has established water quality standards for chloride to protect aquatic freshwater ecosystems. The water quality standard for chronic exposures of chlorine ion concentrations is 230 ppm, this is not to be exceeded more than once every 3 years (EPA, 2019). The water quality standard for acute exposures is 860 ppm which is also not supposed to be exceeded more than once every 3 years (EPA, 2019). Fortunately, none of the streams in this study are at acute exposure levels but 6 sites do exceed the chronic exposure threshold, two of which were rural including the one outlier that was much higher than any other site (Figure 4). Most of these sites stayed around the same chloride ion concentrations and were also categorized as chronic exposure in 2016, however, one site on the Shakers Creek went from normal levels to chronic exposure. In general, sites only increased between 0.1 and 52 ppm except for the one outliner in our data which was a rural site located on the Schoharie Creek with the highest SPC and chloride ion concentration of 3007 μS/cm and 608.9 ppm respectively. This site increased significantly in 2018 from 2016, increasing by 329 ppm. After further investigation it was found that this site is less than half a mile away from a major highway. The end of the stream in question lies right next to the road which could explain the high SPC and chloride ion concentrations as road salt could easily fall into or runoff into the stream. This would have the greatest effect in the spring or winter when the road salt is actually being used, but since salt persist in ground water and makes its way back into streams over time the close proximity to the highway could have an impact all year round (Hinsdale, 2018; Tiwari and Rachlin, 2018).

The level of chloride ions in streams is of concern since samples were collected in the summer which is not when road salt concentrations would be at their highest. During the winter or spring when runoff from melting snow increases the input of road salt, the chloride ion concentrations could be higher, showing more sites with chronic or acute levels of pollution. The effects that road salt can have on streams includes, groundwater salinization, changes in soil structure, changes in the composition of fish or aquatic invertebrate assemblages and it also poses threats to birds, mammals, and roadside vegetation (Tiwari and Rachlin 2018). Mitigation is imperative to avoid these negative impacts from road salt and this study can be useful as SPC has been cited as the most consistent indicator of water quality in urban areas (Brown et al. 2009) and our data may be used as a baseline for stream health in the Schenectady area. In addition, the locations of sites with higher chloride ion concentrations that identified as chronic exposures should be monitored more closely and actions to mitigate these areas should take place, like working to improve storm water systems, planting vegetation cover around streams and finding ways to reduce the usage of road salt.

Algae as Tracers for Nitrogen Pollution

The $\delta^{15}N$ value of filamentous *Cladophora* algae (FA) were sought out in this study and have been used as a tracer for nitrogen pollution in a previous study (Salls, 2009). FA are easy to identify and the lack of a rooting system results in the water column being their only source of nitrogen, making them ideal to record nitrogen pollution. However, FA were only present in 19 out of the 49 sites sampled during this study, limiting their use as a tracer. For this reason, the use of other algae as tracers of nitrogen pollution was investigated by comparing the $\delta^{15}N$ values of FA with those obtained from algae rooted to rocks (RA).

It was found that the $\delta^{15}N$ values of FA differed inconsistently from the values of RA that were found at the same site. Some sites exhibited higher $\delta^{15}N$ values for FA, while other sites exhibited higher values for RA (Figure 10). An explanation for the differences in $\delta^{15}N$ values between FA and RA could be that different primary producers have different preferences for NH_4^+ versus NO_3^- (Peterson et al. 1997). Alternatively, an explanation could be that RA may have a quick turnover rate and its $\delta^{15}N$ values may not reflect the nitrogen content over a longer period of time like FA (Cambra and Aboal, 1992, see introduction). Evidence for this was seen in the Hans Groot Kill where only RA was obtained each week over four months. It was observed that the RA was found in different places along the stream each week and the density would change with each collection time, indicating a fast turnover rate. Precipitation was explored in the Hans

Groot Kill to see if the $\delta^{15}N$ values reflected the inputs of nitrogen which we assumed would change with precipitation, however, no correlation was found (Figure 13). According to Cabana and Rasmussen (1996) measurement of $\delta^{15}N$ values at the base of a food chain can be problematic because small freshwater organisms tend to show temporal variability in their $\delta^{15}N$ signature due to a number of factors including, variation in nitrogen source, and temporal variation in nitrogen concentration which affects the fractionation of nitrogen uptake. This is applicable to RA since it may have a fast turnover rate which would decrease the period of time averaging compared to FA (see introduction). A study that specifically looks at the turnover rate of RA would need to be conducted to confirm the growth habits of the algae. Additionally, higher resolution (daily) sampling of FA and other types of algae from the same site would help to gain insight on how and when $\delta^{15}N$ values change in primary producers. Overall, this study could have benefitted from more specific classifications of algae for RA as well as more types of algae sampled from each site to have additional data to study the differences between the $\delta^{15}N$ values of primary producers.

Due to the uncertainty in the relationship between $\delta^{15}N$ values of FA and RA, only the $\delta^{15}N$ values of FA were used to assess organic pollution in streams since it has been used before in previous studies (Salls, 2009, Connors, 2017). There have been other studies in which different primary producers have been used as tracers of organic pollution in waterways, however the threshold values applied to determine the presence of organic pollution change with the different kinds of algae and different aquatic environments. In Costanzo et al. (2005), $\delta^{15}N$ values of red macroalga (*Catenella nipae)* were used in a marine environment to map sewage nitrogen. A value of 3‰ was said to indicate sewage-derived nitrogen in red macroalga, while in another marine study (Savage & Elmgren, 2004), brown macroalgae (*Fucus vesiculosus)* were used as a tracer and a value of 8-9‰ was indicative of sewage. In Steffy and Kilham (2004), different freshwater organisms were shown to exhibit higher δ^{15}N values in areas that used septic tanks that were leaking human sewage. A value of 11‰ in primary consumers indicated an input of anthropogenic nitrogen and accounting for trophic enrichment (3.4‰, Steffy and Kilham, 2004) the threshold value for primary producers would be around 7.6‰ in that particular study. In each of these studies the threshold values were determined through mixing models created based on the locations of each study. They compared pristine systems or areas away from sewage outfalls to areas of known waste input. The varying threshold values that indicate pollution from organic waste may be a result of the different species being used or the different environments at which each study took place. In order to have a true threshold value one must fully understand the mechanisms of incorporating nitrogen for that particular organism in a particular ecosystem. However, according to Heaton (1986) analysis of nitrate that originates from organic waste will most definitely show values above 10‰. This is a safe value because samples of primary producers with δ^{15}N values above this threshold are certain to have an input of organic waste and it indicates that all nitrogen in that sample is from waste. Since δ^{15}N values are a mix of various sources of nitrogen which each have specific δ^{15}N values, we cannot know every source from a single δ^{15}N value (Figure 16). However, values above 10‰ do indicate a high input of organic waste (Heaton, 1986). Since there is this discrepancy in the threshold value and we were not able to create a mixing model for this study we can have a general range of inputs based on our knowledge of nitrogen sources. Above 10‰

is a high input, between 5‰ and 9‰ is a medium input and low to none is below 5‰. This is an arbitrary categorization mainly based on the different sources of nitrogen and the threshold values created in previous studies (Costanzo et al. 2005, Savage & Elmgren, 2004, Steffy and Kilham, 2004, Figure 16).

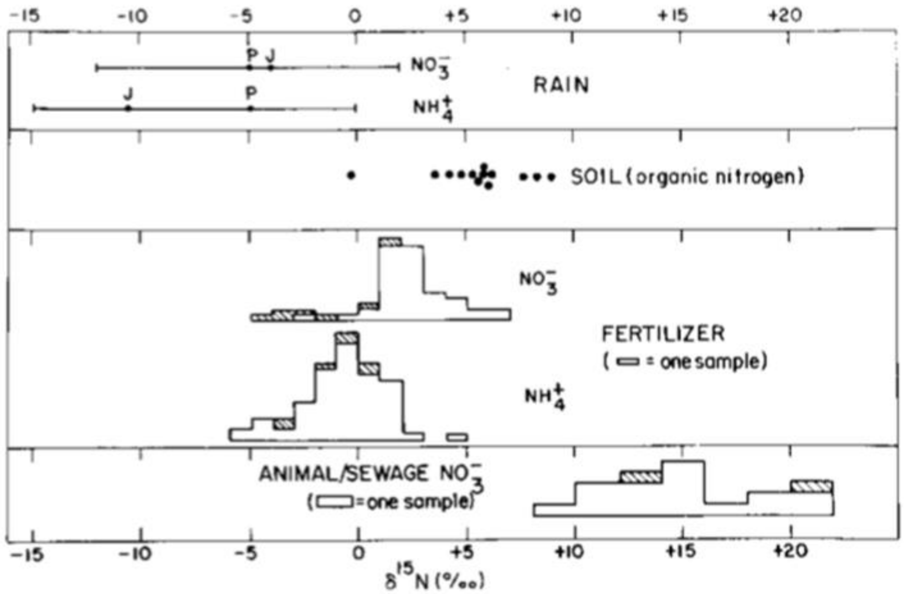

Figure 16: Range of $\delta^{15}N$ values for sources of nitrogen in surface water (Heaton 1986).

Spatial Analysis of Urban and Rural Streams in and around Schenectady, NY.

Looking at the difference between urban and rural sites in this study, we observed that the $\delta^{15}N$ values of urban streams were significantly higher than rural streams, confirming the existence of urban stream syndrome in the Schenectady area (Figure 11). Four of 20 $\delta^{15}N$ values from FA were above 10‰, indicating a high contribution of organic waste to the nitrogen in the stream, all were from urban sites. Nine sites were classified as having a medium contribution of organic waste (<10‰ and ≥ 5‰) 4 were rural and 5 were urban. Finally, 7 sites had $\delta^{15}N$ values classified as having low to no contribution of organic waste, 6 were rural and 1 was urban. Overall, we see that more urban sites had high contributions of organic waste to the stream nitrogen and more rural sites had low to no occurrence of organic waste. According to Driscoll et al. (2003), the main source of nitrogen loading in the northeastern United States is from wastewater effluent. Therefore, elevated $\delta^{15}N$ values in this study are most likely from leakage of septic systems, sewage pipes or sewage treatment plants. However, some $\delta^{15}N$ values are derived from various sources since not all values are above the definitive threshold for organic waste (10‰). For example, lower $\delta^{15}N$ values below 5‰ may derive nitrogen from fertilizers or ammonia and nitrate in precipitation (Figure 16), so low values may still indicate pollution but from different sources.

When we looked at which streams were indicative of high inputs of organic waste we saw that they were not along the same streams. In streams for which we had multiple sites with FA (3 sites at most) we saw that $\delta^{15}N$ values changed along the stream. For example, in the Schoharie Creek, the $\delta^{15}N$ values decrease as you go downstream indicating that there is some dilution effect decreasing the contribution of organic waste (Figure 17). Another case is the Poentic Kill where the $\delta^{15}N$ values increased as you went downstream closer toward the urban center of Schenectady (Figure 17). Using this kind of information we can estimate where the point sources of organic waste input are since the high $\delta^{15}N$ values are only seen at certain points along these streams. It is most likely leakage from sewage pipes that is causing this input of waste especially since none of these locations are in close proximity to wastewater treatment plants which are mainly along the Mohawk River where these streams flow into.

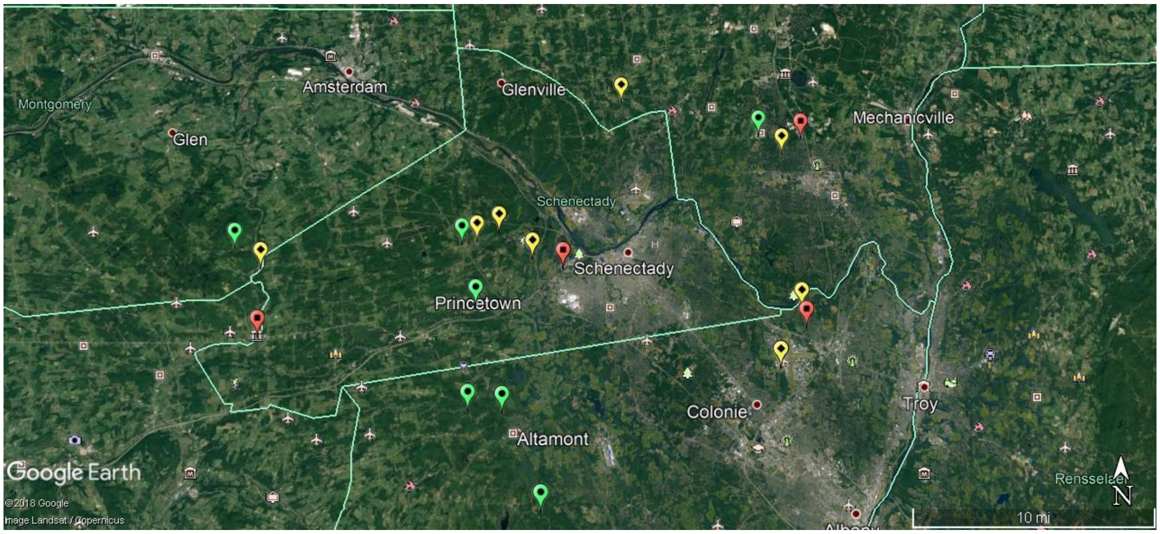

Figure 17: Map of sites at which filamentous algae was collected. The green markers represent sites at which the $\delta^{15}N$ values of algae indicated a low to none input of organic waste (<5‰), yellow makers with a diamond indicate medium input of organic waste (<10‰ and ≥ 5‰) and finally the red markers with squares represent sites at which $\delta^{15}N$ values of algae indicated high inputs of organic waste (>10‰).

Although we did see that over half of our sites indicated medium to high contributions of organic waste, we did not see high concentrations of nitrate or nitrite in the water samples (Figure 14 and Figure 15). This is a good thing indicating that there is little nitrogen pollution in these streams and it may also explain why there was a lack of FA at many sites, since this type of algae thrives in high nutrient environments (Whitton, 1970). In addition, both nitrate and nitrite ion concentrations on average were higher in urban areas (2.08 ± 2.0 ppm and 0.03 ± 0.03 ppm) than in rural ones (1.31 ± 1.58 ppm and 0.01 ± 0.01 ppm), indicating a greater amount of nitrogen input in urban streams. However, it is important to note that water samples are only one point in time, pollution might be higher during rain events, when waste can be pushed out of the soil into surface waters and when runoff increases (Sinha et al. 2017), which could increase effluent entering the stream. In addition, even though pollution is low in theses individual streams, accumulation of that pollution might result in eutrophication downstream or in the Mohawk River where most of these streams run to. For this reason it is still important to track the sources and concentrations of nitrogen into streams.

Although the streams we studied did not show evidence of high nitrogen pollution we also looked at dissolved oxygen levels to detect any anoxic events from possible eutrophic conditions. We found that most streams were at normal dissolved oxygen levels (Figure 6). According to the EPA a dissolved oxygen value under 3 mg/l (36%) is an area of concern and waters with levels below 1 mg/l are considered a dead zone (EPA, 2019). Only one site in our data set yielded a value lower than 3 mg/l on the Alplaus Kill with a value of 2.7mg/l (29%) (Figure 6). This site was not a flowing stream, due to extremely low water levels, and samples were collected from a pool of still water, this explains the low dissolved oxygen levels. One other outlier in our data had a value of 4.45 mg/l (49%) this site was also unusually low in 2016 making it seem like this site is prone to some amount of eutrophication. However, it was observed that this site is downhill from a small pond. It is possible that eutrophication in the pond is causing the lower oxygen levels observed downstream. The processes of photosynthesis and respiration are a main source of variation in DO levels is surface waters (Correa-González et al. 2014). Highly productive systems with high rates of photosynthesis can boost the DO levels to 150% to 200% while respiration continuously depletes DO (Correa-González et al. 2014). Lower DO values could indicate that respiration in the stream is exceeding the photosynthesis rate. It is a possibility that this is happening at sites with low DO levels in this study and higher rates of photosynthesis could be occurring in sites at which the DO is high.

In addition, this study found significantly higher pH values in rural sites compared to urban ones (Figure 8). In previous studies it has been found that pH increases in surface waters with the amount of concrete because it weathers into streams (Ramirez et al. 2014). For this reason we would expect pH to be higher in urban environments, in our study the opposite is the case (Figure 8). One possible explanation for this could be that urban streams could have higher rates of respiration leading to more CO_2 and more carbonic acid in streams lowering the pH. With higher rates of respiration we would expect lower DO levels in urban streams which we do observe but not significantly. Further studies could be done to measure the CO_2 in the streams to verify the rates of respiration and photosynthesis occurring in these streams. This way one could better explain the differences in pH and dissolved oxygen in urban and rural sites.

Temporal Analysis: Comparison of Data from 2018 and 2016

Between 2016 and 2018, δ^{15}N values of FA algae generally increased in both rural and urban streams that were sampled (Figure 12). The significant increase in δ^{15}N values is of concern as it indicates an increase in the contribution of organic waste to the total nitrogen in the streams. One possible explanation for this could be that there was more precipitation during the summer months in 2018 (17.79 inches) than in 2016 (14.83 inches) (Weather Underground, 2019). The increase in precipitation would lead to more waste from groundwater and soil to be pushed out into surface waters and increase runoff of effluent into streams (Sinha, 2017). Either way the increase in δ^{15}N values show that there is more input of organic waste from somewhere. Further studies should be conducted to identify the specific reason for this increase. Locations of sewage systems at the time of each study could be determined and assessed for any leakages that could be repaired and sites at which δ^{15}N values indicated high input of waste should be examined closer for the input source.

The average pH was significantly lower in 2018 (7.8) than in 2016 (8.0, Figure 9). Similar to what may have occurred in urban and rural streams, the respiration rates may be higher in 2018 than in 2016. Higher temperatures in 2018 would support this hypothesis as respiration increases with temperature (Bond-Lamberty and Thomson, 2010). However, higher rates of respiration would lead to lower DO in 2018, but in this study the opposite was found (Figure 7). The shallow nature of the streams sampled could be an explanation for this in that oxygen can easily reach all depths of the stream resulting in little effect of respiration on the oxygen levels. The significantly lower pH values found in the study are not of ecological concern as they were still within the range expected for freshwater streams. According to the EPA the healthy pH limits for freshwater is between 6.5 and 9.0, none of the values in this study violated this range. Nonetheless, the difference indicates that stream biogeochemistry in 2018 is slightly different from those same streams in 2016.

Overall the input of organic waste in streams in the Schenectady area is of concern as it has seemed to increase since 2016. Also it is reported that nitrogen loading will increase with climate change in the northeastern United States in years to come due to increases in precipitation (Sinha et al. 2017). It is imperative that inputs of anthropogenic nitrogen be monitored and actions be taken to mitigate nitrogen pollution. The results of this study could be useful in the process as a baseline for the input of anthropogenic nitrogen to detect changes in the future and to assess the effectiveness of sewage system upgrades as well as policies put into place to reduce nitrogen loading in streams.

CONCLUSION

This study found that urban streams in and around the Schenectady area are more polluted than the rural streams, confirming the presence of an urban stream syndrome in the Schenectady area. Urban sites had significantly higher SPC and chloride ion concentrations caused by usage of road salt. Urban sites also yielded higher $\delta^{15}N$ values and higher concentrations of nitrite and nitrate ions. However, measured concentrations of nitrates and nitrites were low in streams overall indicating that, at least during the summer months, nitrogen loading in the streams is low. Although nitrogen ion concentrations were low, the $\delta^{15}N$ values show that the contribution of organic waste to total nitrogen in the streams is higher in urban streams, possibly caused by leaking sewage pipes. In addition, all $\delta^{15}N$ values were significantly higher than values found in the previous study conducted in 2016, for both urban and rural sites. This shows that the urban stream syndrome persists in the area and the input of nitrogen derived from organic waste seems to have increased since 2016. This study is of significance because it can be used as a baseline to determine the efficiency of upgrades to sewage systems and storm water systems in the area of study to monitor future changes in organic waste and road salt input into streams.

REFERENCES

Abell, J.M., Özkundakci, D., Hamilton, D.P. (2010). Nitrogen and Phosphorus Limitation of Phytoplankton Growth in New Zealand Lakes: Implications for Eutrophication Control. Ecosystems, 13(7): 966-977.

U.S. Environmental Protection Agency. (1988) Ambient Water Quality Criteria for Chloride. http://www.epa.gov/waterscience/ criteria/library/ambientwqc/chloride1988.pdf (accessed March 01, 2019).

Bechtold, C. (2017). Investigating the Urban Stream Syndrome in the Mohawk Watershed around Schenectady, NY. Schenectady NY: Union College.

Berube, M. (2015). Tracking Pollution in New York Streams Using Stable Carbon and Nitrogen Isotopes. Schenectady, NY: Union College.

Bond-Lamberty B., Thomson, A. (2010) Temperature-associated increases in the global soil respiration record. Nature, 464: 579-583.

Booth, D.B., Roy, A.H., Smith, B., Capps, K.A. (2015). Global Perspectives on the urban stream syndrome. Freshwater Science, 35(1):412-420.

Brown, L.R., Cuffney, T.F., Coles, J.F., Fitzpatrick, F., McMahon, G., Steuer, J., Bell, A.H., May, J.T. (2009). Urban streams across the USA: lessons learned from studies in 9 metropolitan areas. Journal of the North American Benthological Society, 28(4), 1051–1069.

Cabana, G. & Rasmussen, J.B. (1996). Comparison of aquatic food chains using nitrogen isotopes. Proceedings of the National Academy of Sciences of the United States of America, 93(20): 10844-10847.

Clinton, B.D. & Vose, J.M. (2005). Variation in Stream Water Quality in an Urban Headwater Stream in the Southern Appalachians. Water, Air, and Soil Pollution, 169:331-353.

Connors, C. (2017). Impacts of Urbanization on Stream Water Biogeochemistry in Schenectady County and Surrounding Areas in Upstate NY. Schenectady NY: Union College.

Correa-González, J.C., Chávez-Parga, M.C., Cortés, J.A., Pérez-Munguía, R.M. (2014). Photosynthesis, respiration and reaeration in a stream with complex dissolved oxygen pattern and temperature dependence. Ecological Modeling, 273: 220-227.

Costanzo, S.D., Udy, J., Longstaff, B., Jones, A. (2005). Using nitrogen stable isotope rations (δ15N) of macroalgae to determine the effectiveness of sewage upgrades: Changes in the extent of sewage plumes over four years in Moreton Bay, Australia. Marine Pollution Bulletin, 51:212-217.

Driscoll, C.T., Whitall, D., Aber, J., Boyer, E., Castro, M. Cronan, C., Goodale, C.L. Groffman, P., Hopkinson, C., Lambert, K., Lawrence, G. and Ollinger, S. (2003). Nitrogen Pollution in the Northeastern United States: Sources, Effects, and Management Options. BioScience, 53(4): 357-574.

Hale, R.L., Scoggins, M., Smucker, N.J., Suchy, A. (2015). Effects of climate on the expression of the urban stream syndrome. Freshwater Science. 35(1):421–428.

Heaton, T.H.E, Isotopic Studies of Nitrogen Pollution in the Hydrosphere and Atmosphere: A Review. Chemical Geology (Isotope Geoscience Section). 59: 87-102.

Halstead, J.A., Kliman, S., White Berheide, C., Chaucer, A., Cock-Esteb, A. (2014). Urban stream syndrome in a small, lightly developed watershed: a statistical analysis of water chemistry parameters, land use patterns, and natural sources. Environmental Monitoring and Assessment. 186(6): 3391-3414.

Khan, F.A. & Ansari, A.A. (2005). Eutrophication: an Ecological Vision. Botanical Review, 71(4): 449-482.

Lyons, W.B. & Harmon R.S. (2012). Why Urban Geochemistry?. Elements, 8(6), 417- 422. Smith, V.H., Joye, S.B. and Howarth, R.W. (2006). Eutrophication of Freshwater and Marine Ecosystems. American Society of Limnology and Oceanography, 51(1): 351-355.

McCutchan, J.H., Lewis, W.M. (2000). Seasonal variation in stable isotope ratios of stream algae. Verh. Internat. Verein. Limnol. 27: 3304-3307.

Michalak, A. M., Anderson, E. J., Beletsky, D., Boland, S., Bosch, N. S., Bridgeman, T. B.,… Zagorski, M. A. (2013). Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. Proceedings of the National Academy of Sciences of the United States of America, 110(16): 6448–6452.

Peterson, B.J., Bahr, M., Kling, G.W. (1997). A tracer investigation of nitrogen cycling in a pristine tundra river. Canadian Journal of Fisheries and Aquatic Sciences, 54: 2361-2367.

Ramírez, A., De Jesús-Crespo, R., Martinó-Cardona, D.M., Martínex-Rivera, N., Burgos-Caraballo, S. (2009). Urban streams in Puerto Rico: what can we learn from the tropics?. J.N. Am. Benthol. Soc. 28(4):1070-1079.

Ramírez, A., Rosas, K.G., Lugo, A.E., Ramos-González, O.M. (2014) Spatio-temporal variation in stream water chemistry in a tropical urban watershed. Ecology and Society. 19(2):45.

Savage, C. and Elmgren, R. (2004) Macroalgal (*Fucus vesiculosus*) $\delta^{15}N$ Values Trace Decrease in Sewage Influence. Ecological Applications, 14(2): 517-526.

Sharp, Z. (2017) Principles of Stable Isotope Geochemistry, 2nd Edition. Prentice Hall.

Sinha, E., Michalak, A.M., Balaji, V. (2017) Eutrophication will increase during the 21st century as a result of precipitation changes. Science, 357:405-408.

Smith, V.H., Wood, S.A., McBride, C.G., Atalah, J., Hamilton D.P., Abell, J. (2016) Phosphorus and nitrogen loading restraints are essential for successful eutrophication control of Lake Rotorua, New Zealand, Inland Waters, 6(2): 273-283.

Steffy, L.Y. and Kilham, S.S. (2004). Elevated $\delta^{15}N$ in stream biota areas with Septic Tank Systems in an Urban Watershed. Ecological Applications, 14(3): 637-641.

Tiwari, A. and Rachlin, J.W. (2018) A Review of Road Salt Ecological Impacts. Northeastern Naturalist, 25(1):123-142.

Trowbridge, P.R., Kahl, J.S., Sassan, D.A., Heath, D.L., Walsh, E.M. (2010). Relating road salt to exceedances of the water duality standard for chloride in New Hampshire streams. Environmental Science & Technology, 44(13), 4903– 4909.

Environmental Protection Agency (EPA). (2019, February 28). National Recommended Water Quality Criteria - Aquatic Life Criteria Table | US EPA. Washington DC.

https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table (accessed March 01, 2019)

U.S. Environmental Protection Agency (EPA). (2016). National Rivers and Streams Assessment 2008-2009: A Collaborative Survey Office of Water and Office of Research and Development. Washington, DC. http://www.epa.gov/national-aquatic-resource-surveys/nrsa (accessed February 04, 2018).

U.S. Environmental Protection Agency (EPA). (2013). Streams. Washington D.C. https://archive.epa.gov/water/archive/web/html/streams.html#importance. (accessed February 04, 2019).

U.S. Geological Survey (USGS). (2017, January 20). Dissolved oxygen, from the USGS Water Science School: All about water. https://water.usgs.gov/edu/dissolvedoxygen.html (accessed March 01, 2019).

United Nations, Department of Economic and Social Affairs, Population Division (2016). The World's Cities in 2016 – Data. Booklet (ST/ESA/ SER.A/392).

United Nations Environment Programme. (n.d.). How Bad Is Eutrophication At Present? http://www.unep.or.jp/ietc/publications/short_series/lakereservoirs-3/2.asp (accessed February 04, 2019).

Valiela, I., Owens, C., Elmstrom, E., Lloret, J. (2016). Eutrophication of Cape Cod estuaries: Effect of decadal changes in global-driven atmospheric and local-scale wastewater nutrient loads. Marine Pollution Bulletin, 110: 309-315.

Vitousek P.M, Aber J.D, Howarth R.W, Likens GE, Matson P.A, Schindler D.W, Schlesinger W.H, Tilman D.G. (1997). Human alteration of the global nitrogen cycle: Sources and consequences. Ecological Applications, 7(3): 737–750.

Weather Underground. (2019, January). Schenectady, NY History. Retrieved from https://www.wunderground.com/history/daily/us/ny/schenectady/KSCH/date/2018-6-19

Walsh, C.J., Roy, A.H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., Morgan II, R.P. (2005). The urban stream syndrome: current knowledge and the search for a cure. The North American Benthological Society, 24(3): 706-723.

Watson, S.B., Miller, C., Arhonditsis, G., Boyer, G.L., Carmichael, W., Charlton, M.N., Confesor, R., Depew, D.C., Hook, T.O. , Ludsin, S.A., Matisoffj, G., McElmurry, S.P., Murray, M.W., Richards, R.P., Rao, U.R., Steffen, M.M., Wilhelm, S.W. (2016). The re-eutrophication of Lake Erie: Harmful algal blooms and hypoxia. Harmful Algae 56:44–66.

Whitton, B.A. (1970) Biology of *Cladophora* in Freshwaters. Water Research Pergamon Press 4:457-476.

World Resources Institute. (n.d.). Impacts | World Resources Institute. https://www.wri.org/our-work/project/eutrophication-and-hypoxia/impacts (accessed February 04, 2019).