
University of Maryland
GEOL394

Diurnal variations in urban stream chemistry

Author:
Kevin Mei

Advisor:
Dr. Sujay Kaushal

April 26, 2018

1 Abstract

Long-term trends in nitrogen, carbon and pH contribute to water quality issues such as eutrophication, hypoxia, and acidification. However, less is known regarding their dynamics over day and night cycles related to whole stream metabolism. Most of the information on carbon, nitrogen and pH in streams comes from discrete grab samples rather than continuous samples taken throughout full diurnal cycles. Diurnal cycles in urban stream chemistry are driven by metabolic processes such as primary production (photosynthesis) and respiration (organic matter decomposition). Stream metabolism is affected by factors such as nutrient availability, temperature, and physical stream characteristics. Dissolved organic carbon (DOC) is produced from stream metabolism (primary production and photosynthesis) so I hypothesized that DOC and dissolved oxygen (O_2) cycles may coincide over diurnal time scales. Diurnal chemistry was studied at the Northeast Branch Anacostia River. This site is a USGS water data gauging station, which also measures instantaneous dissolved oxygen, specific conductance and pH. DOC, dissolved inorganic carbon (DIC), and total dissolved nitrogen (TDN) concentrations were analyzed on water samples taken every 30 minutes for a full 24 hours during fall and winter seasons. Base cations and other elements were analyzed with an ICP-OES. Results indicated that dissolved oxygen and pH showed diurnal variations of 2.5 mg/L and 1.6 pH amount, and both are significantly influenced by floods. DOC and O_2 showed similar diurnal patterns typically but also had a lag time with DOC lagging 2 hours behind dissolved O_2 . For carbon the diurnal variation can vary as much as 20%. Of the elements studied, manganese and phosphorus appeared to show diurnal variation similar to DOC, TDN, and DIC. Calcium and sodium behaved conservatively as expected because they are not significantly consumed in stream metabolism, and should not have a strong diurnal signal. Overall, diurnal variations in elemental chemistry and physical and biological controls should be considered in studies of urban water quality, geochemistry and biogeochemistry.

Contents

1	Abstract.....	1
2	Introduction	3
	2.1 Carbon.....	3
	2.2 Hypotheses	5
3	Methods	5
	3.1 Site Description.....	5
	3.2 Sample Collection	6
	3.3 Shimadzu TOC-L.....	8
	3.4 Shimadzu ICPE-9820.....	9
4	Diurnal Sampling Campaigns and Analyses	9
5	Results	11
	5.1 Carbon.....	11
	5.2 Manganese and Phosphorus.....	14
	5.3 Other elements	18
6	Discussion.....	18
	6.1 Diurnal Variations in Carbon.....	18
	6.2 Na and Ca.....	19
	6.3 Fe and P.....	19
7	Summary.....	20
8	Bibliography	22
9	Appendix	24
	9.1 Fall Data Set.....	24
	9.2 Winter Data Set.....	29

2 Introduction

Many studies have focused on analyzing long-term trends in carbon in rivers (Worral 2004, Evans 2005, Findlay 1990, Raymond 2007, Kaushal 2014). However, there have not been as many studies on diurnal carbon concentrations in urban streams. There have been some studies that focus on carbon fluxes (Spencer 2007, Smith and Kaushal 2015) and some that focus on diurnal cycles of dissolved oxygen and stream metabolism (Beaulieu 2013, Smith and Kaushal). An analysis of diurnal cycles in carbon is important for understand the role of organic matter as a transport vector of metals and organic contaminants and as a food source for aquatic foodwebs. The purpose of this study is to analyze diurnal variations of carbon quantity and make comparisons to diurnal variations in concentrations of selected elements. I found that carbon quantity and form (organic carbon vs. inorganic carbon) exhibit diurnal variations in an urban stream across seasons, which were related to dissolved oxygen levels (a proxy for stream ecosystem metabolism).

Urban stream chemistry has been studied extensively to compare the effects of urbanization on stream chemistry (Kaushal 2014, Pennino 2014). Urban streams are characterized by hydrologic alterations due to impervious surface cover (Pouyat, 2007). Urban streams exhibit a behavior known as “urban stream syndrome”. Symptoms of urban stream syndrome are flashier discharge responses, elevated concentrations of runoff pollutants, channelization/altered channel morphology, and reduced biodiversity (Walsh, 2005). Urban streams generate a large volume of runoff, which carries surface contaminants and other trace elements (Kaushal et al., 2014). Higher concentrations of pollutants can be attributed to human-accelerated weathering in urbanized watersheds and also urban channel erosion control. With elevated amounts of various elements and the strong potential for growth of algae and microbial activity in urban streams, any diurnal variation should be easier seen than compared to very low trace amounts of these elements in a non-urban watershed.

Concentrations of a broad range of elements have not been extensively studied for a diurnal cycle. Although this study focuses primarily on carbon, an element involved in a variety of metabolic pathways, there are comparisons with other elements. For example, calcium and sodium behave more or less conservatively, which are not active in stream metabolism, and should not have a diurnal signal. Calcium and sodium was used as a baseline for comparison to the other elements for any sort of diurnal variation. Other elements such as Fe and P are more bioreactive and involved in metabolic pathways and may behave more similarly to carbon.

2.1 Carbon

Carbon is classified as either organic or inorganic and categorized based on size and volatility. Carbon is difficult to precisely characterize so it is operationally defined; one such defined component of carbon is dissolved carbon. Dissolved carbon is further divided into dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC).

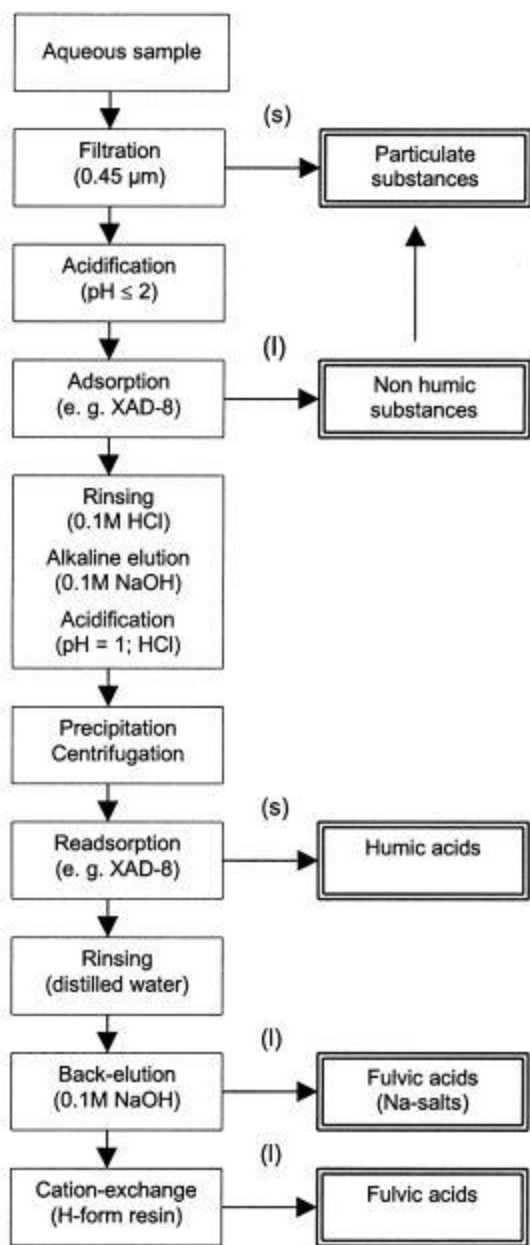


Figure 1. Adapted from Frimmel (2005). This diagram shows how carbon is operationally defined through filtration, rising, acidification, etc. to treat and pull out the respective components. Humic and fulvic acids are both organic carbon molecules that differ by size and physical properties.

Dissolved organic carbon is complex and heterogeneous by nature with each component having its own elemental composition, molecular weight and its own set of chemical and physical properties (Stedmon et al., 2003). DOC can be sourced from terrestrial inputs such as soil and leaf litter. It can also be sourced from bacterial breakdown of labile organic matter. Dissolved organic carbon can be further categorized by humic and fulvic components. Humic acid is alkali-soluble, acid-insoluble fraction of soil organic matter. Humic acids are high molecular weight organic molecules. Fulvic acids have much lower molecular weights and are soluble in water of

any pH (Hudson et al., 2007). Figure 1, shows that humic and fulvic carbon can be separated and defined. DOC is a good indicator of stream metabolism, as higher levels of DOC would mean higher rates of metabolism.

2.2 Hypotheses

Carbon quantity and form (organic carbon vs. inorganic carbon) will show diurnal variations in an urban stream across seasons. The null hypothesis for that hypothesis will be that there are no diurnal variation in carbon in an urban stream across seasons.

3 Methods

The USGS has select water gauge sites that collect water quality data such as salinity, dissolved oxygen and pH.

3.1 Site Description

The Northeast Branch of the Anacostia River is the study site selected for this study due to its urban channelized nature, access to USGS Water Data, and also convenient access. The USGS Water Data for the Northeast Branch of the Anacostia River site also gauges dissolved oxygen, specific conductance and pH. The Northeast Branch of the Anacostia River watershed is situated in a heavily urbanized area where buildings are within 400 feet of the stream, with runoff pipes draining directly into the stream. The Northeast Branch Anacostia River gauge station is fed by a basin with an area of 72.8 square miles. The basin area is a medium sized watershed with data back from 2003 and discharge from 1938. The site is situated close to the University of Maryland College Park campus and is located in an urban area. Runoff from the urban areas directly pipe runoff into the river. Figure 2 shows the location of the gauging station as well as the location for the ISCOs.

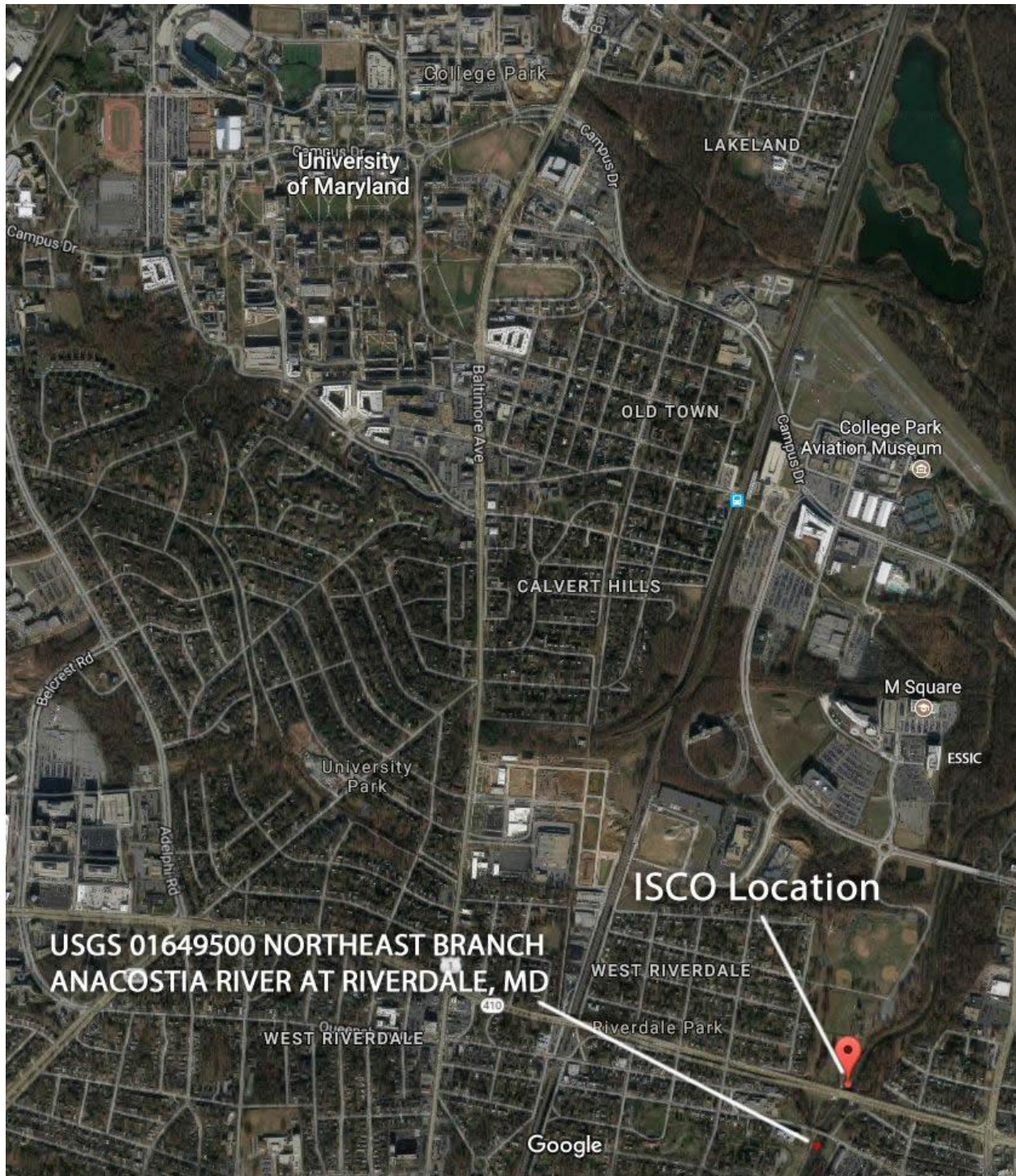


Figure 2. This is a satellite image of the study site selected. The proximity to campus and ease of access were reasons that the site was selected. The ISCO sampler location is about 200 meters (656 feet) upstream from the USGS gauging station at Riverdale, MD.

3.2 Sample Collection

Water samples were collected directly from the Northeast Branch Anacostia River. Carbon shows a diurnal variation in an urban stream across seasons. Nitrogen and DIC was not

compared between seasons due to mechanical issues running the samples for TDN and DIC for the fall sample set. The fall sample set had a 23 hour 30 minute sample window with 30 minute between samples. The winter sample set covered 2 days duration at 1 hour sample intervals over a 47 hour period. Stream chemistry was preserved in the winter data set as the temperatures during sampling were near freezing. The fall sample set was at the end of summer/beginning of leaf fall with the majority of leaves still on trees. The winter sample set was taken when trees were bare. Tree coverage limits sunlight which affects stream metabolism.

Samples were collected on days when the river was at or close to base flow, and with good weather with clear skies. An automated sampler called an ISCO was used to take automated samples and was programmed to take samples with some time interval between samples taken. The fall set had 30 minute interval and the winter sample set used 1 hour intervals. Samples were taken about a foot away from the stream edge using ISCOs with the intake tube as deep and close to thalweg as possible. Each sample drew about 250 mL of water which was sufficient to perform multiple analysis if needed. Figure 3 shows an image of an ISCO set up and ready to collect water. The ISCOs have 24 sample bottles, next to the sample bottles is an ice pack. The ice pack mitigates any changes in the stream water by lowering temperature in order to slow or prevent any reactions or changes to the water chemistry. A 23 hour 30 minute sampling of water with 30 minute intervals will require 48 sample bottles, or two ISCOs. One day of water samples were collected on October 20th 2017 around 5:00 PM. The next morning, half the sample was collected and filtered, with the other ISCO still sampling until 4:30 PM later that day. After all the samples were filtered the samples were to be stored in a large walk in refrigerator to preserve water chemistry. Because the water samples were filtered, the sample lifetime was dramatically extended. Sample chemistry can quickly change so it is imperative to filter samples and refrigerate as soon as possible to prevent any changes. The water chemistry would be representative and accurate of the actual composition if samples were properly refrigerated after being taken. The winter data set was collected starting on March 3rd 2018 and had a 1 hour sample interval. The samples still had 48 samples but was over a 47 hour sample window. This was performed to provide two periods of data instead of one and provide a better view of a diurnal cycle if there is one present.



Figure 3. Automated sampler ISCOs are set up along the bank of the Northeast Branch Anacostia River at Riverdale, MD. Each ISCO can hold up to 24 samples and two are therefore needed to take a 24 hour sampling period at 30 minute intervals. Each water sample had a volume of 250 mL. To minimize tampering, the ISCOs were located away from the nearby path and locked to a tree.

After sampling, the water samples were filtered to mitigate any changes in water chemistry post sampling. Samples were processed through a Shimadzu TOC-L machine where DIC, DOC, and TDN concentrations were measured. Due to downtime, only DOC was measured for the fall sample set.

The water samples were also acidified and processed through the Shimadzu ICPE-9820 and analyzed for: silver, aluminum, arsenic, boron, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, mercury, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, antimony, selenium, silicon, tin, strontium, thallium, vanadium, and zinc.

3.3 Shimadzu TOC-L

The Shimadzu TOC-L measures DOC, DIC and also total dissolved nitrogen (TDN) concentrations. All concentrations are measured by using chemiluminescence methods that first begin with catalytic thermal decomposition. Depending on which concentration is calculated, the Shimadzu TOC-L can acidify, sparge and combust samples. The treatment of the sample then

passed through an infrared gas analyzer (NDIR). Total carbon is first measured by adding air to the sample and combusting. This combusts both DIC and DOC. To get DIC the sample is acidified and then sparged to isolate CO₂. The difference results in the DOC amount since TOC=TC-IC. Water samples are filtered before being analyzed in the TOC-L to only contain dissolved carbon or the TOC-L would become clogged from large particulate carbon. The TOC-L is equipped with a total nitrogen module and an automated sampler device, which can analyze a series of samples automatically. The TOC-L will measure the carbon quantity in the water.

3.4 Shimadzu ICPE-9820

The

Elements Analyzed by the ICPE-9800 Series

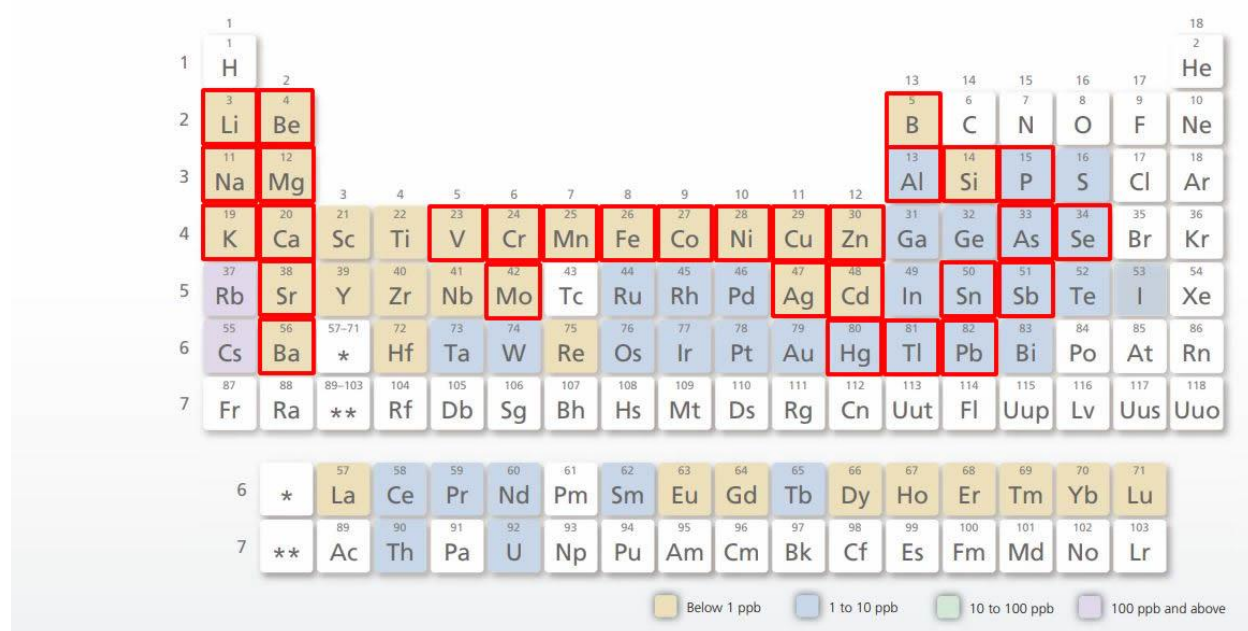


Figure 4. This periodic table shows the 30 elements that were processed by the ICP-OES. Concentration levels for the majority of elements fell close to detection limits. Elements that had concentrations well above the detection limits include Ca, K, Na and Mg.

The Shimadzu ICPE-9820 is an ICP-OES which measures elemental concentrations of various elements. Samples are first acidified and then introduced to plasma which has the resulting photon emission rays measured. The ICP-OES can detect concentrations below 1 ppb. Figure 4 shows the 30 elements that were analyzed. Most of the 30 elements were off by a factor for minimum detection concentrations so concentrations should be representative.

4 Diurnal Sampling Campaigns and Analyses

The sunrise and sunset times give an idea of when to look for low and high concentrations. If stream metabolism affected concentrations then there should be a difference in concentration at noon and midnight. Figure 5 is a plot of USGS Water Data of dissolved oxygen exhibiting a diurnal cycle. The lowest levels of dissolved oxygen is at night and have the highest values

during the day as a result of stream metabolism. Dissolved oxygen is used to compare samples as it exhibits a strong diurnal signal and is driven by stream metabolic processes.

The fall sample set started at 5 PM on October 19th and ended at 4:30 PM on October 20th. The sunset was at 6:21 PM and sunrise was at 7:21 AM and on October 20th the sunset was at 6:20.

The winter sample set was bracketed at March 3rd 2018 at 5:30 PM to March 5th 4:30 PM. The Sunrise-sunset times were at 6:47 AM to 7:31 PM, 6:46 AM to 7:32 PM and 6:44 AM to 7:32 PM, for March 3rd, 4th and 5th respectively.

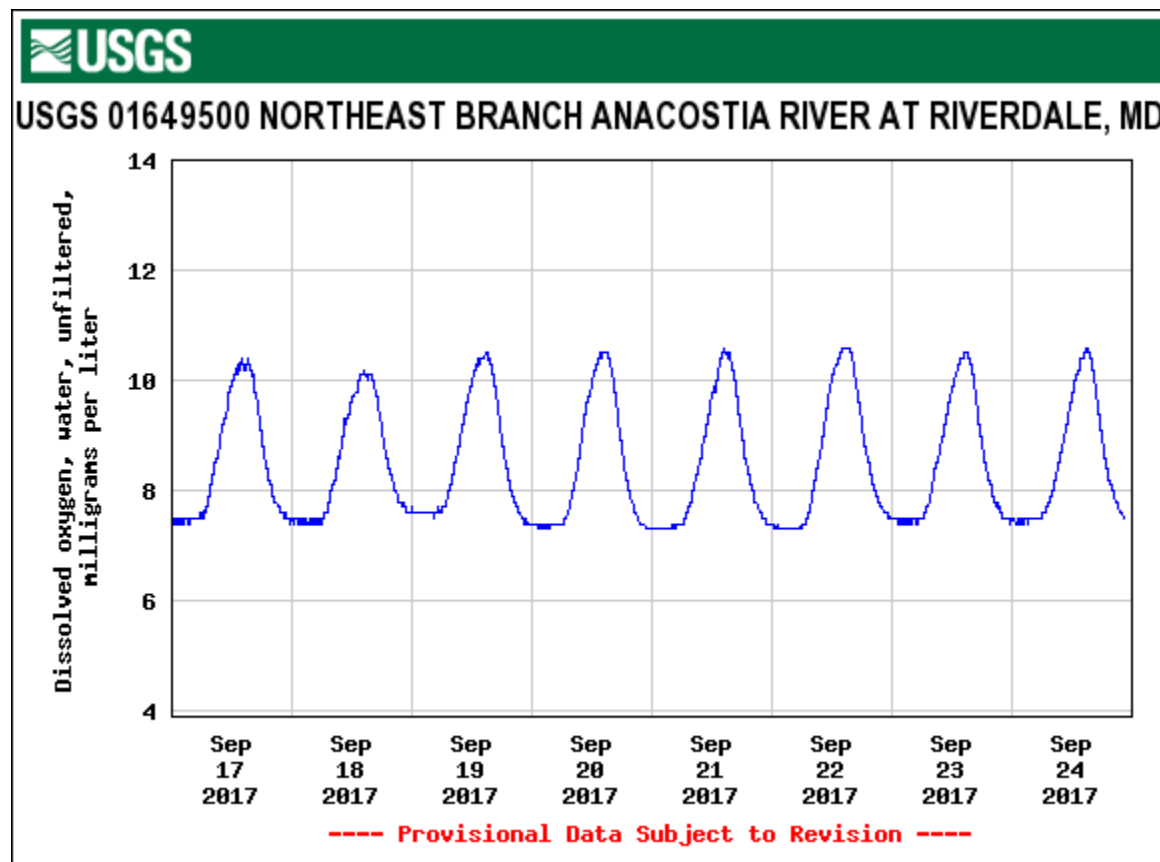


Figure 5. This graph shows dissolved oxygen levels at the Northeast Branch Anacostia River at Riverdale, MD. Diurnal variation of dissolved oxygen is displayed for a typical week during base flow. Variations of dissolved oxygen can vary as much as 50% from lowest levels. Highest levels correspond to daylight hours with the minimum at late night/early morning hours.

The fall 23 hour 30 minute sample set did not provide any discernable diurnal cycle from the elemental analysis (see Section 9.1 Fall Sample Set). The DOC concentrations appeared to have a diurnal cycle but it was difficult to interpret as the data was only across one day. This was refined by collecting two days of samples in the winter data set.

Collected water samples were also analyzed using an ICP-OES for elemental concentrations. The suite of elements examined were: silver, aluminum, arsenic, boron, barium, beryllium, calcium, cadmium, cobalt, chromium, copper, iron, mercury, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, antimony, selenium, silicon, tin, strontium, thallium, vanadium, and zinc. Of these elements, manganese and phosphorus appeared to be the

only elements that exhibited some sort of diurnal variation. The fall sample set data did not discern any usable information as most elements had some sort of inconsistent curve showing huge jumps in concentrations between 30 minute samples. The fall sample set is included in appendix 9.1 and the winter sample set is included in 9.2.

5 Results

5.1 Carbon

Dissolved organic carbon concentrations as a function of time showed a similar shape to dissolved oxygen (Figure 7). There appears to be a slight lag time between concentrations of DOC and DO_2 with a lag time of about 2 hours of DOC behind DO_2 (Figure 5). Dissolved inorganic carbon and specific conductance should show a relationship but does not appear to show any relationship (Figure 8). However, the DIC and specific conductance does show a similar shape when looking at the last 24 hours (Figure 9). DIC and specific conductance should show a relationship as specific conductance is linked to DIC and has been use to predict DIC concentrations. DIC does show a diurnal signal

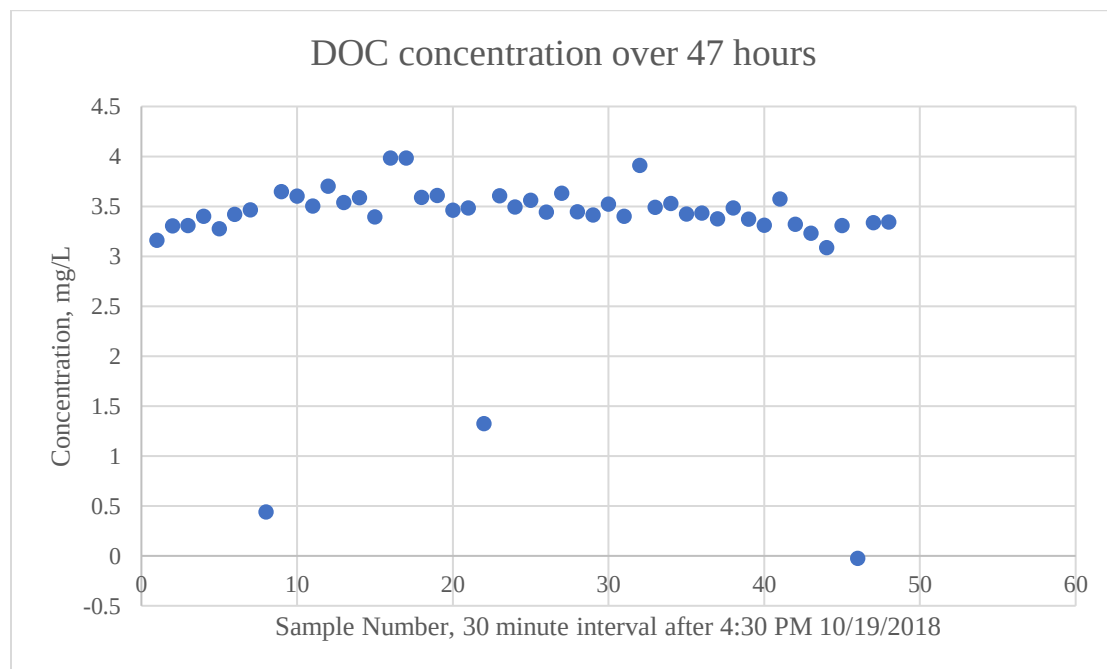


Figure 6. This graph shows DOC concentrations vs time for the fall sample set. The x-axis is sample number which are 30 minute intervals after 4:30 PM on 10/19/2018. This set represents a 23 hour 30 minute sample window with 30 minute intervals in the fall.

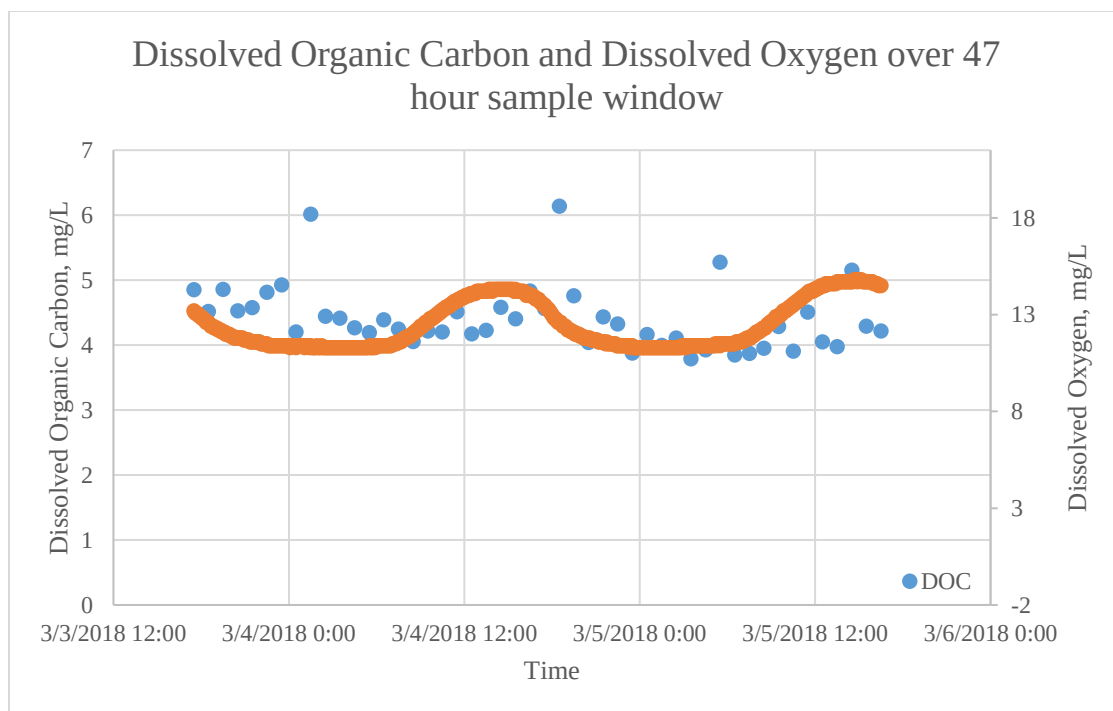


Figure 7. This graph shows dissolved organic carbon concentrations and dissolved oxygen concentrations vs time. Dissolved oxygen is in orange and dissolved organic carbon is in blue. Both exhibit a similar shape, with dissolved organic carbon lagging behind dissolved oxygen levels two hours.

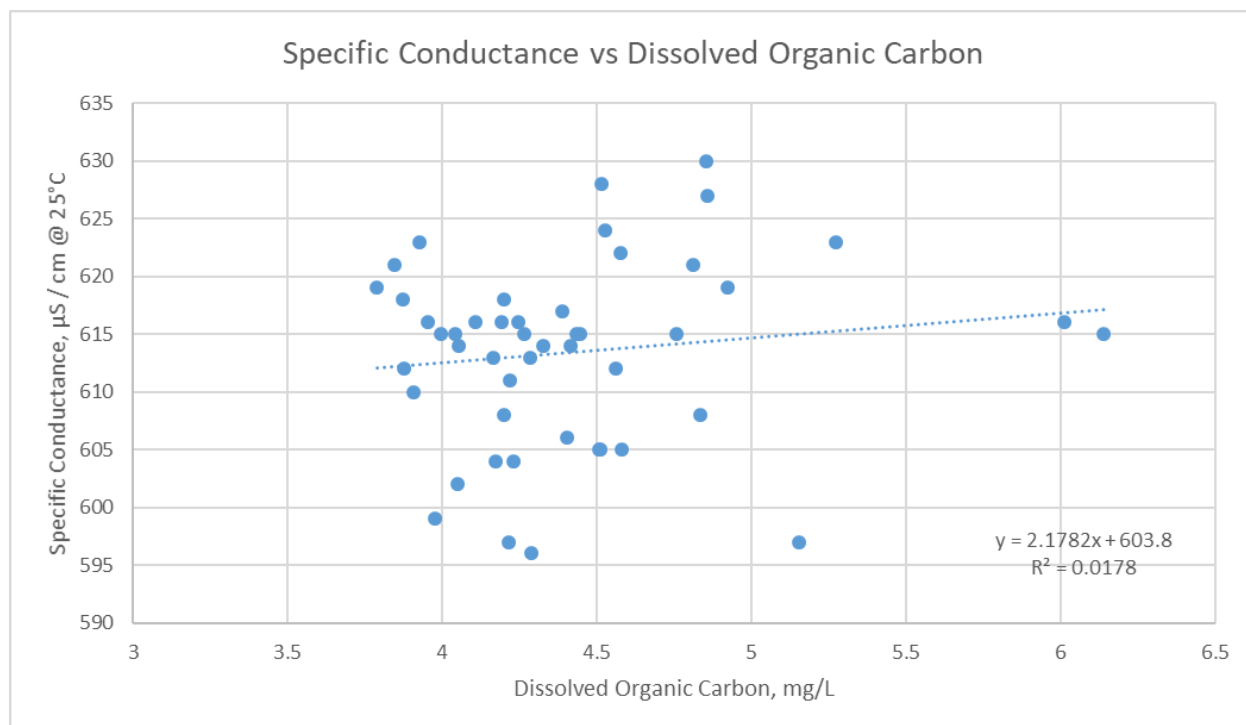


Figure 8. Specific conductance vs dissolved inorganic carbon. There should be a relationship between specific conductance and dissolved inorganic carbon but no discernable relationship appears when plotting the two against each other. The data in this figure is part of the winter data set. The R-squared value is 0.0178 showing no correlation between the two.

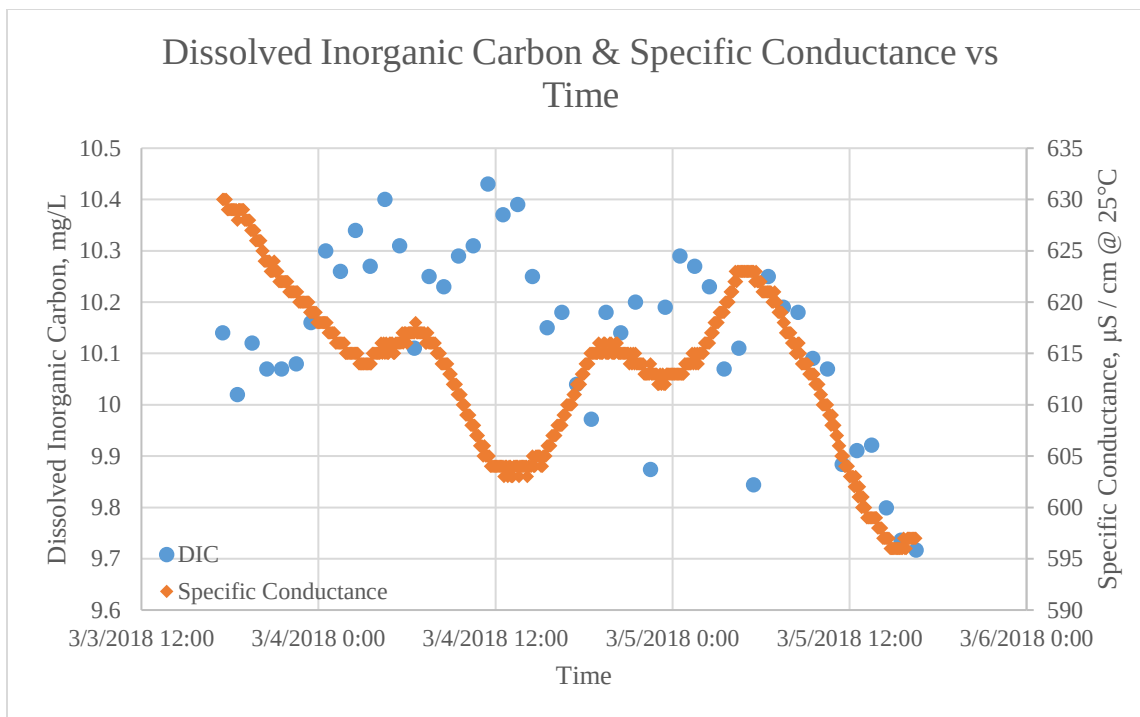


Figure 9. Plot of dissolved inorganic carbon (DIC) and specific conductance. Although DIC and specific conductance show no exact correlation when plotted against each other, their plots are similar on the last half of the data set.

5.2 Nitrogen

Similar to DOC, total dissolved nitrogen (TDN) is also affected by stream metabolism, thus showing a diurnal cycle. This diurnal cycle does include the two hour lag similar to DOC in figure 9.

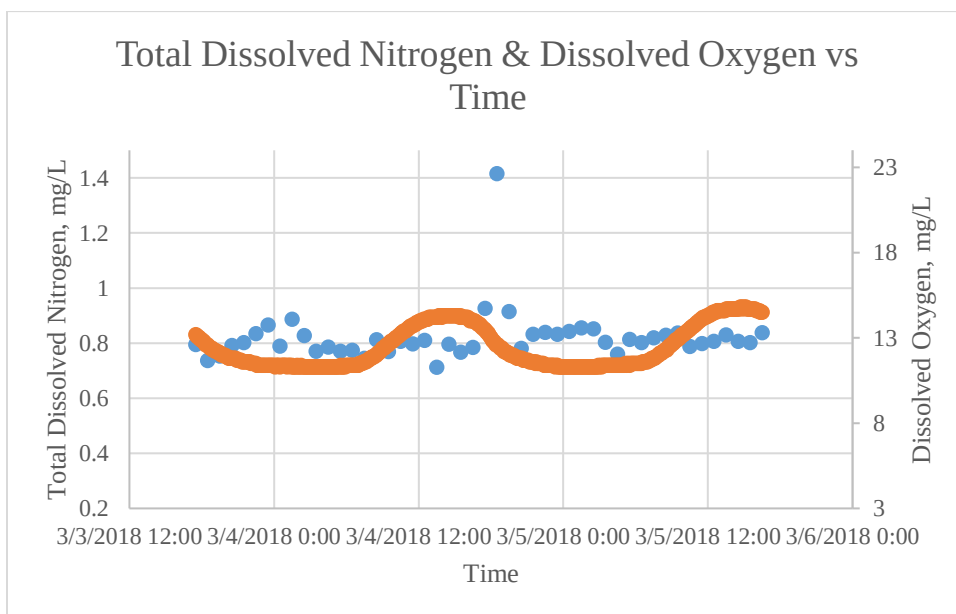


Figure 10. Plot of total dissolved nitrogen plotted with dissolved oxygen. These should exhibit a similar shape and appear to have a similar shape with the same similar two hour lag time as with dissolved organic carbon and dissolved organic carbon.

5.2 Manganese and Phosphorus

Of the elements sampled, manganese and phosphorus show a diurnal variation. Figure 11 shows the plots of both Mn and P. These two plots have been plotted with dissolved oxygen which shows that both of these two elements exhibit a diurnal signal. The other elements were mostly similar to calcium, an inert baseline comparison element.

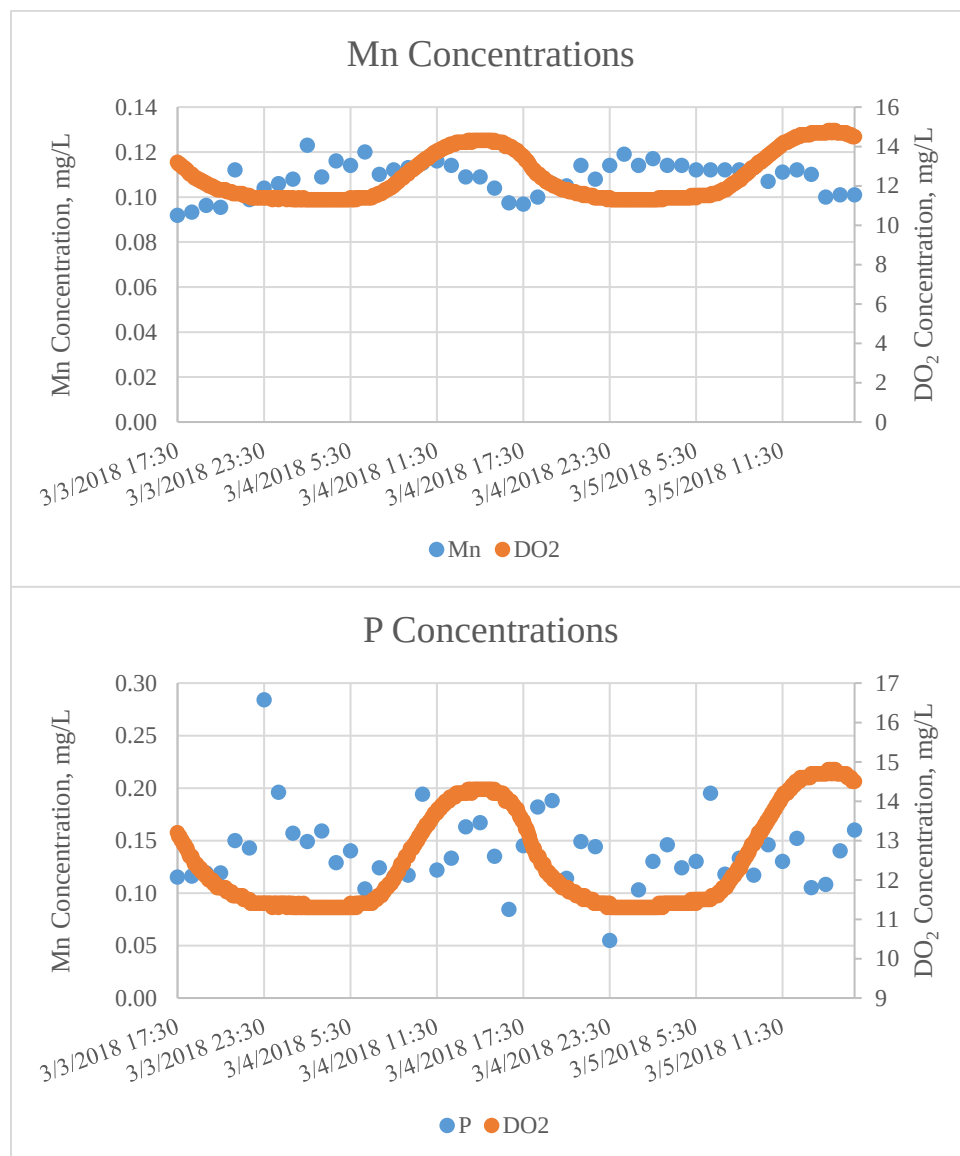


Figure 11. Plots of manganese (top) and phosphorus (above) concentrations vs time. These two elements both show diurnal variation but are offset from one another. Dissolved oxygen was plotted on top of the plots as a reference which show that both elements do not exhibit inert behavior such as calcium.

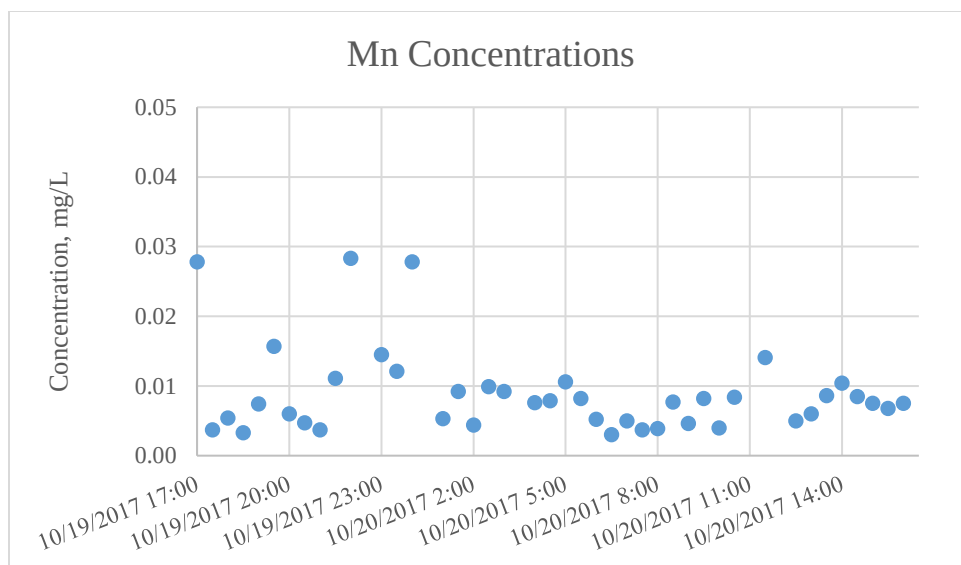


Figure 12. Plot showing manganese concentrations for the fall sample set. Manganese appears to increase in concentration toward the daylight hours and lower during the nighttime hours similar to the winter sample set.

5.3 Normalized Data

In order to better compare data sets, the data was normalized. Data was handled by subtracting out the average and then dividing by the standard deviation. This allowed for the data to fall around zero and relative changes be compared. Of the normalized data there were pairs of data that revealed similar shapes. These pairs include: Si and DIC, K and Na, and Ca and Mg. In Figure 12 the Si and DIC normalized concentrations are plotted. From the plot, both elements exhibit a very similar shape. K and Na also exhibit a very similar shape when normalized. Figure 13 shows that an earlier winter storm may still have been carrying elevated levels of road salt. At first glance calcium did not appear to exhibit any similar behavior to any other element but when normalized and compared with magnesium then a similar shape can be seen in Figure 14. Iron should exhibit a diurnal pattern and does appear to show a pattern when normalized. Figure 15 shows the Fe normalized and shows a tiny dip in the center of the sample period.

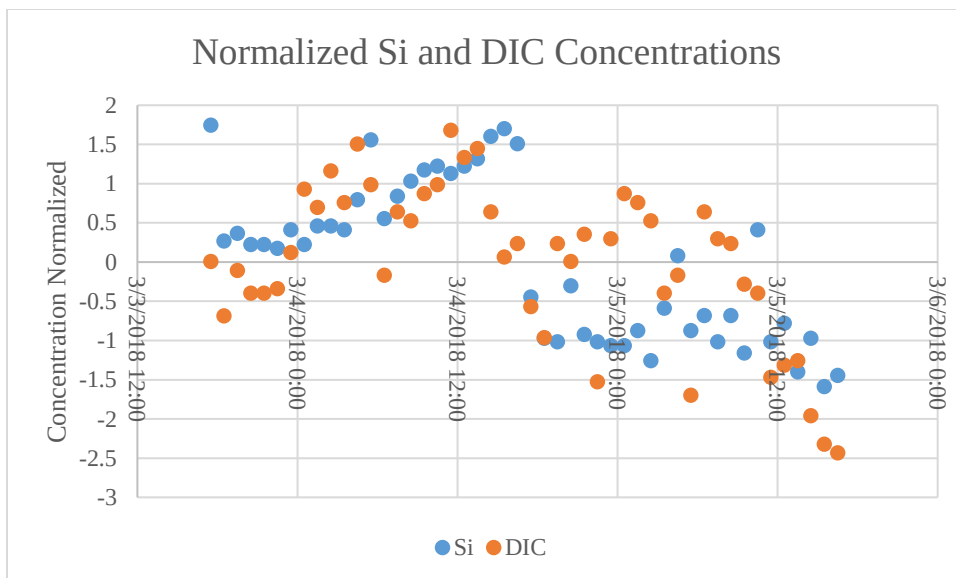


Figure 13. Plot of normalized Si and DIC concentrations. Both concentrations when normalized show similar concentrations. This could indicate the same source or control.

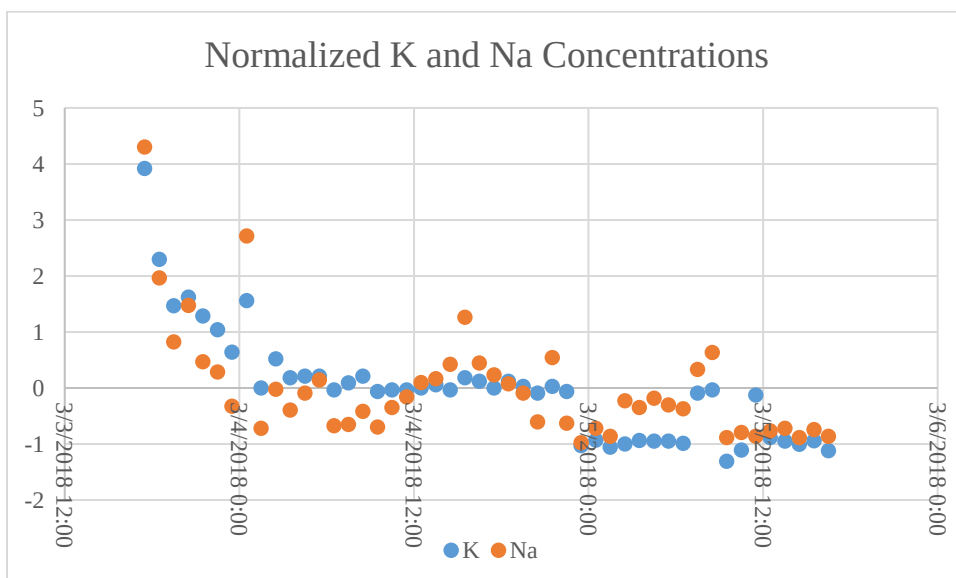


Figure 14. Plot of normalized K and Ca concentrations. Both concentrations have been normalized and both show a similar shape in concentrations. Both are used in road salt so their shape could be indicative of leftover road salt runoff.

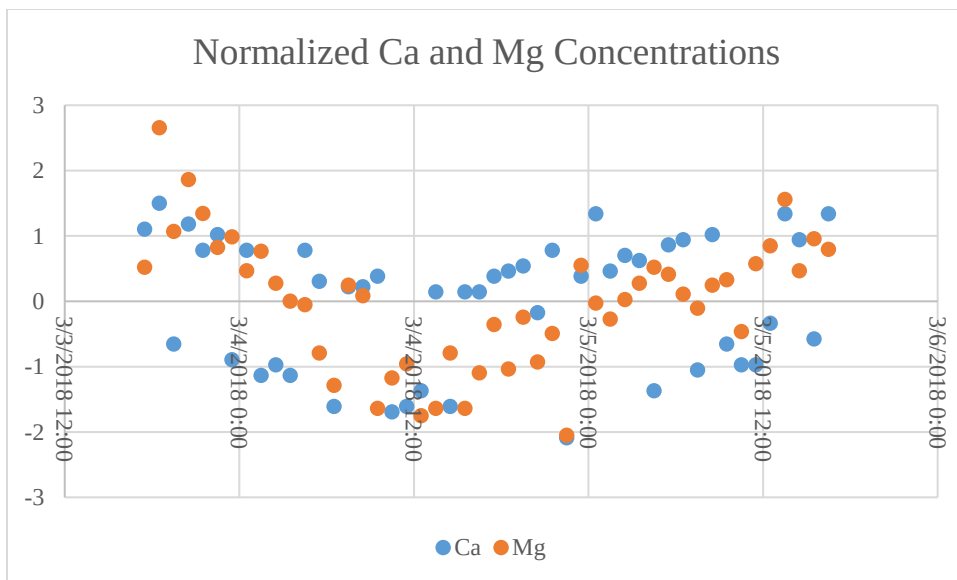


Figure 15. Normalized calcium and magnesium concentrations. This plot shows calcium and magnesium exhibiting similar concentrations. Ca and Mg main sources are from weathering of buildings, mainly concrete.

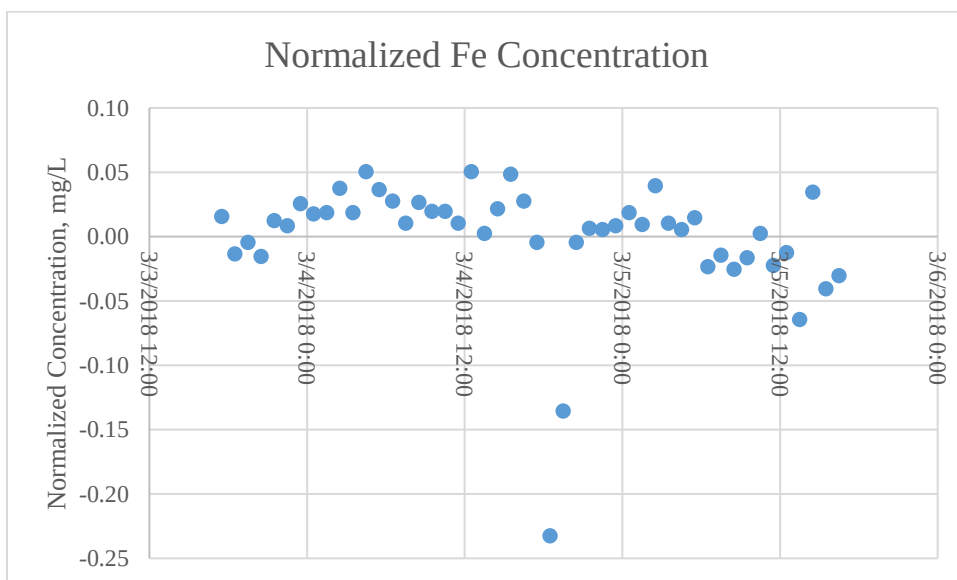


Figure 16. Normalized iron concentration. Iron should demonstrate a diurnal cycle but does not have a strong clear signal. Iron was normalized in order to better see a diurnal signal. The center of the data between 3/4/2018 12:00 to 3/5/2018 0:00 does show a dip relative to the few hours before and after.

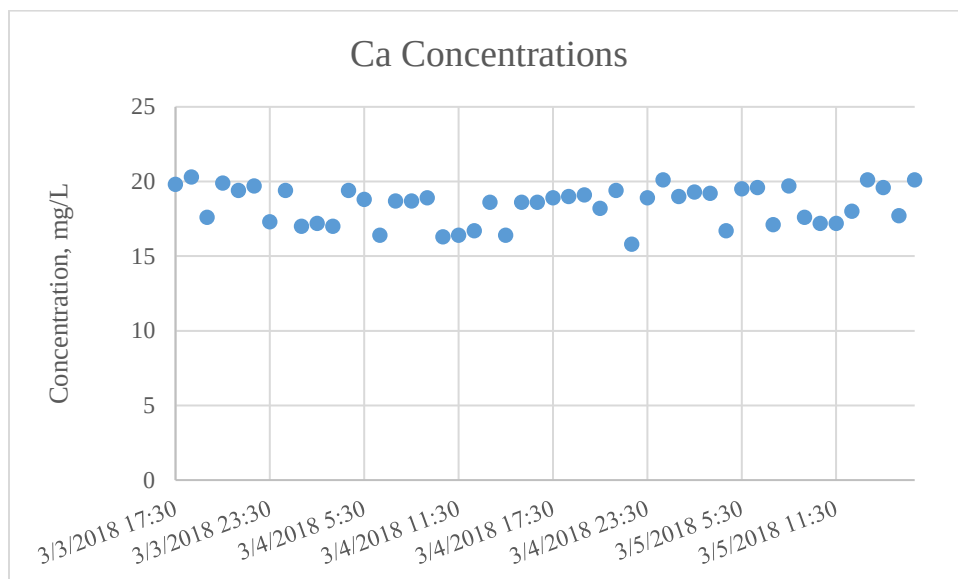


Figure 17. Calcium vs time plot shows no diurnal cycle. Calcium and sodium are two elements that behave conservatively and should not be affected by stream metabolism.

5.4 Other elements

The other elements sampled all showed a relatively flat line with no diurnal variation and just sample and instrumental variation. For many elements, the concentrations are very low that discerning any diurnal variation is difficult. Element sample levels typically fell below detection limits or had relative standard deviations (RSD) levels higher than recorded concentrations. Sections 9.1 and 9.2 show all thirty elements processed for each sample set.

6 Discussion

6.1 Diurnal Variations in Carbon

I found diurnal variations of carbon is 20% between low and high concentrations. The low and high concentrations are just within a few hours. By looking at dissolved oxygen concentrations, the peak dissolved organic carbon levels can be estimated. Most stream studies use discrete grab samples that may vary on time sampled. It is important to collect grab samples with similar times as diurnal variation of DOC can be about 20%. The first fall sample set was taken over 30 minute intervals for 23 hours and 30 minutes with clear skies and no recent large storm. This allowed for the stream to readjust to a base flow with typical stream chemistry. The winter sample set was more difficult to collect as the winter season has more storm events. Consistent with the conclusion from Smith and Kaushal (2015), this study found that DIC was the prominent component and was higher than DOC concentrations. DOC was concentrations average 4.4 mg/L and DIC concentrations averaged 10.14 mg/L in the winter set. DOC concentrations in the fall averaged to 3.3 mg/L which fits the conceptual model from Smith and

Kaushal. DOC levels were higher in the winter when there were no leaves and lower when there were peak day lengths and leaves on trees.

6.2 Na and Ca

Calcium, magnesium, potassium and sodium exhibited changes in concentrations but did not show any diurnal pattern. These elements were not expected to have any diurnal pattern as these are inert elements in stream chemistry (Kaushal, 2017). These elements are not part of the stream metabolism and have concentrations influenced by anthropogenic forces. Despite being inert the elements did exhibit some sort of change during the time period. Potassium and sodium are introduced into urban areas during the winter season as rock salt. As rock salt is used to salt roads concentrations accumulate during the winter season. Potassium and sodium exhibited similar behaviors when concentrations were normalized.

Sodium, calcium, potassium and magnesium all exhibited similar behaviors which would suggest that the same processes are affecting those elements.

Calcium is controlled by weathering of carbonates and in urban areas, the main source of calcium is from concrete weathering. Magnesium is a main element in rocks and is present in aggregate used in concrete. These two elements exhibit a similar behavior as shown in Figure 15. Ca and Mg is driven by weathering and both exhibit a similar behavior so the same mechanism is most likely controlling their concentrations. Sodium, potassium, calcium and magnesium all do not show a diurnal pattern.

6.3 Fe and P

In this study there are diurnal variations in Fe similar to other diurnal studies (McKnight, 1988). Fe had a diurnal cycle in this study similar to the Fe diurnal cycle study which could've been driven by photoreduction. Similar to the McKnight study, both exhibited a concentration maximum to minimum ratio of 1.2. P may be related to Fe as a response to photoreduction of Fe (McKnight, 1988). Redox conditions may also be influencing diurnal P concentrations (Kim, 2003). Both P and Fe diurnal variations are limited but both do exhibit some diurnal behavior

6.4 Other Observations

There does not appear to be any seasonal differences in diurnal DOC concentrations. In a seasonal study of diurnal variations in carbon chemistry of two acidic peatland streams in Scotland, it was found that highest diurnal ratios occurred in spring and summer (Dawson, 2008). Diurnal ratios are calculated to be the difference in maximum and minimum concentrations. However, for the Northeast Branch of the Anacostia River the difference in diurnal ratios are negligible. The DOC maximum to minimum ratio in the winter period was 1.29 and the ratio in the fall was 1.3. The ratios are similar to one another and do not exhibit the same findings in Dawson, 2008 but in fact demonstrate the reverse. This could potentially be attributed to the urban nature of the stream. Dawson et al. also found that DIC fluxes were high with 2.4 times higher during the night than day at a similar discharge. This was not the case for the Northeast Branch of the Anacostia River which only showed about a difference of about 1.07 times.

Elemental diurnal variations have not been extensively researched. The winter data shown was properly processed in a reasonable time window. Although the fall sample set was quickly

Sb Concentrations

Concentration, mg/L

Date/Time	Concentration (mg/L)
10/19/2017 17:00	1.52
10/19/2017 18:00	0.05
10/19/2017 19:00	0.06
10/19/2017 20:00	0.07
10/19/2017 21:00	0.07
10/19/2017 22:00	0.05
10/19/2017 23:00	0.05
10/20/2017 00:00	1.57
10/20/2017 01:00	1.54
10/20/2017 02:00	1.60
10/20/2017 03:00	1.53
10/20/2017 04:00	1.50
10/20/2017 05:00	1.50
10/20/2017 06:00	0.05
10/20/2017 07:00	1.25
10/20/2017 08:00	0.03
10/20/2017 09:00	0.06
10/20/2017 10:00	0.04
10/20/2017 11:00	0.05
10/20/2017 12:00	0.03
10/20/2017 13:00	0.02
10/20/2017 14:00	0.10
10/20/2017 15:00	0.03
10/20/2017 16:00	0.08
10/20/2017 17:00	0.03
10/20/2017 18:00	0.02
10/20/2017 19:00	0.02
10/20/2017 20:00	0.02
10/20/2017 21:00	0.02
10/20/2017 22:00	0.02
10/20/2017 23:00	0.02
10/21/2017 00:00	0.02
10/21/2017 01:00	0.02
10/21/2017 02:00	0.02
10/21/2017 03:00	0.02
10/21/2017 04:00	0.02
10/21/2017 05:00	0.02
10/21/2017 06:00	0.02
10/21/2017 07:00	0.02
10/21/2017 08:00	0.02
10/21/2017 09:00	0.02
10/21/2017 10:00	0.02
10/21/2017 11:00	0.02
10/21/2017 12:00	0.02
10/21/2017 13:00	0.02
10/21/2017 14:00	0.02
10/21/2017 15:00	0.02
10/21/2017 16:00	0.02
10/21/2017 17:00	0.02
10/21/2017 18:00	0.02
10/21/2017 19:00	0.02
10/21/2017 20:00	0.02
10/21/2017 21:00	0.02
10/21/2017 22:00	0.02
10/21/2017 23:00	0.02
10/22/2017 00:00	0.02
10/22/2017 01:00	0.02
10/22/2017 02:00	0.02
10/22/2017 03:00	0.02
10/22/2017 04:00	0.02
10/22/2017 05:00	0.02
10/22/2017 06:00	0.02
10/22/2017 07:00	0.02
10/22/2017 08:00	0.02
10/22/2017 09:00	0.02
10/22/2017 10:00	0.02
10/22/2017 11:00	0.02
10/22/2017 12:00	0.02
10/22/2017 13:00	0.02
10/22/2017 14:00	0.02
10/22/2017 15:00	0.02
10/22/2017 16:00	0.02
10/22/2017 17:00	0.02
10/22/2017 18:00	0.02
10/22/2017 19:00	0.02
10/22/2017 20:00	0.02
10/22/2017 21:00	0.02
10/22/2017 22:00	0.02
10/22/2017 23:00	0.02
10/23/2017 00:00	0.02
10/23/2017 01:00	0.02
10/23/2017 02:00	0.02
10/23/2017 03:00	0.02
10/23/2017 04:00	0.02
10/23/2017 05:00	0.02
10/23/2017 06:00	0.02
10/23/2017 07:00	0.02
10/23/2017 08:00	0.02
10/23/2017 09:00	0.02
10/23/2017 10:00	0.02
10/23/2017 11:00	0.02
10/23/2017 12:00	0.02
10/23/2017 13:00	0.02
10/23/2017 14:00	0.02
10/23/2017 15:00	0.02
10/23/2017 16:00	0.02
10/23/2017 17:00	0.02
10/23/2017 18:00	0.02
10/23/2017 19:00	0.02
10/23/2017 20:00	0.02
10/23/2017 21:00	0.02
10/23/2017 22:00	0.02
10/23/2017 23:00	0.02
10/24/2017 00:00	0.02
10/24/2017 01:00	0.02
10/24/2017 02:00	0.02
10/24/2017 03:00	0.02
10/24/2017 04:00	0.02
10/24/2017 05:00	0.02
10/24/2017 06:00	0.02
10/24/2017 07:00	0.02
10/24/2017 08:00	0.02

Section 9.1 shows the complete sample set plots with most elements exhibiting no diurnal behavior. Note that potassium and sodium exhibit similar behavior but have no diurnal pattern. The DOC data for the fall showed concentration differences in time and was processed a month and a half after collection, which should still be representative.

Dissolved oxygen can be compared to dissolved organic carbon. The concentrations have similar shapes with a lag time of two hours. Diurnal variations of organic carbon can vary as much as 20%. Dissolved inorganic carbon is also similar and exhibits a diurnal cycle. There are not many elements that exhibit a diurnal cycle. Manganese and phosphorus exhibited a diurnal cycle whereas Na and Ca did not.

20

affected by some other factor such as weathering. This study showed that DIC and Si, K and Na, Ca and Mg each are linked and show similar patterns between each pair.

Acknowledgements

I would like to thank Dr. Sujay Kaushal for providing me guidance and direction to the research. I would also like to thank Shahan Haq and Kelsey Wood for showing me lab procedures and for showing how to operate lab equipment. Thanks to Tom Doody in providing assistance on running the TOC-L and ICP-OES. I would like to thank Dr. Michael Evans for assistance in answering my questions and for direction in manipulating the USGS gauge data. Also thanks to Dr. Philip Piccoli and to the University of Maryland Geology Department for constructive feedback.

8 Bibliography

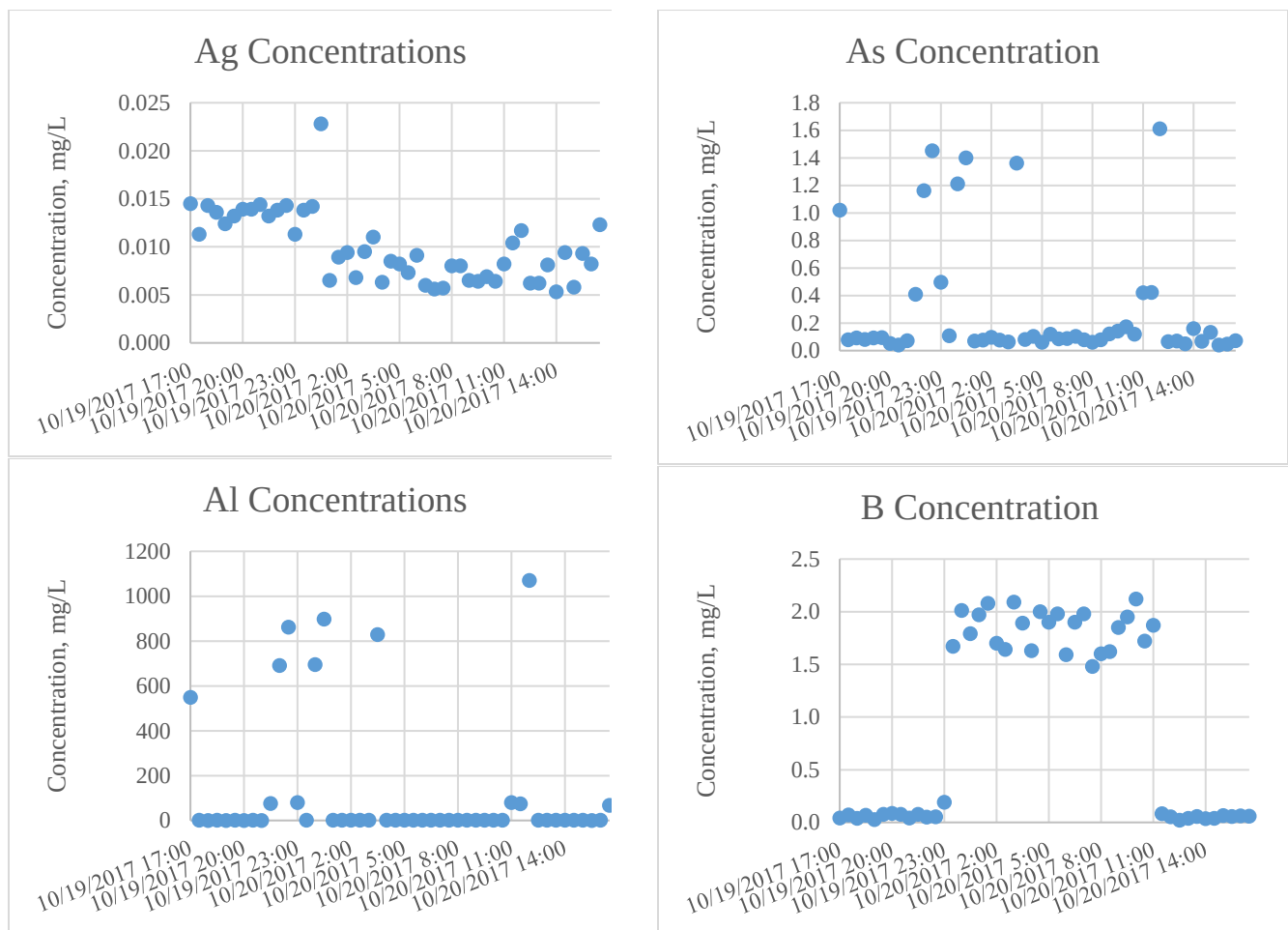
- Beaulieu, J. J., Arango, C. P., Balz, D. A., & Shuster, W. D. (2013). Continuous monitoring reveals multiple controls on ecosystem metabolism in a suburban stream. *Freshwater Biology*, 58(5), 918-937.
- Evans, C.D., Monteith, D.T., and Cooper, D.M. (2005). Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environmental Pollution*. Vol 137, Issue 1, 55-71. Doi: 10.1016/j.envpol.2004.12.031
- Findlay, S., Pace, M., and Lints, D. (1990). Variability and transport of suspended sediment, particulate and dissolved organic carbon in the tidal freshwater Hudson River. *Biogeochemistry*. 12: 149-169. <https://doi.org/10.1007/BF00002605>
- Frimmel, F. H. (2005). Aquatic Humic Substances. *Biopolymers Online*. 1.
- Hudson, N., Baker, A. and Reynolds, D. (2007), Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. *River Research and Applications*, 23: 631–649. doi:10.1002/rra.1005
- Hutyra, L. R., Duren, R., Gurney, K. R., Grimm, N., Kort, E. A., Larson, E. and Shrestha, G. (2014), Urbanization and the carbon cycle: Current capabilities and research outlook from the natural sciences perspective. *Earth's Future*, 2: 473–495. doi:10.1002/2014EF000255
- Kaushal, S.S. and Belt, K.T. (2012), The urban watershed continuum: evolving spatial and temporal dimensions. *Urban Ecosystem* 15: 409. <https://doi.org/10.1007/s11252-012-0226-7>
- Kaushal, S. S., Delaney-Newcomb, K., Findlay, S. E., Newcomer, T. A., Duan, S., Pennino, M. J., Sviridchi, G.M., Sides-Raley, A.M., Walbridge, M.R., and Belt, K. T. (2014). Longitudinal patterns in carbon and nitrogen fluxes and stream metabolism along an urban watershed continuum. *Biogeochemistry*, 121(1), 23-44.
- Kaushal, S.S., McDowell, W.H. and Wollheim, W.M. (2014), Tracking evolution of urban biogeochemical cycles: past, present, and future. *Biogeochemistry*. 121: 1. <https://doi.org/10.1007/s10533-014-0014-y>
- McKnight, D., and Bencala, K.E., (1988), Diel Variations in Iron Chemistry in an Acidic Stream in the Colorado Rocky Mountains, U.S.A. *Arctic and Alpine Research*. Vol. 20, No. 4 (Nov., 1988), pp. 492-500. DOI: 10.2307/1551347
- Mulholland P.J, Houser J, and Maloney K. (2005), Stream diurnal dissolved oxygen profiles as indicators of in-stream metabolism and disturbance effects: Fort Benning as a case study. *Ecological Indicators*, 5: 243–252. Doi: 10.1016/j.ecolind.2005.03.004

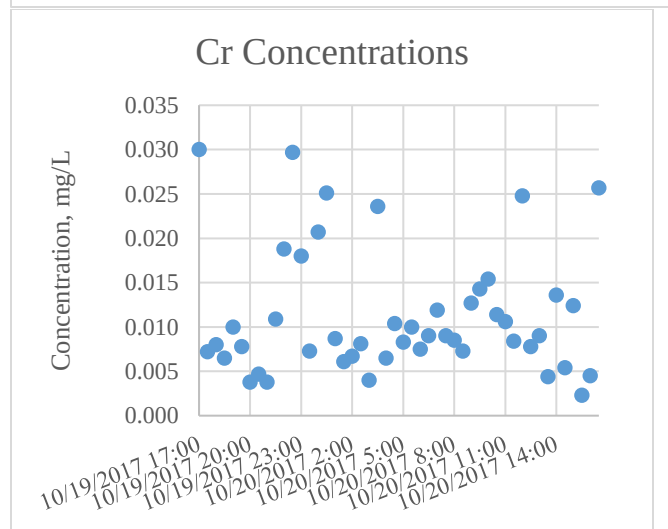
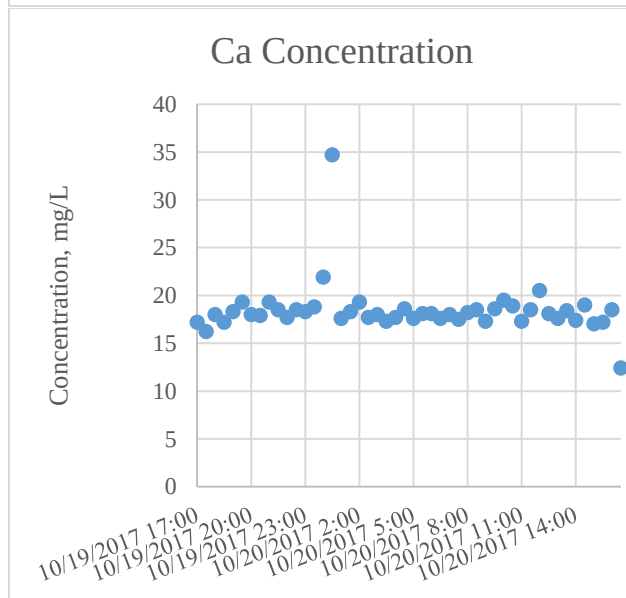
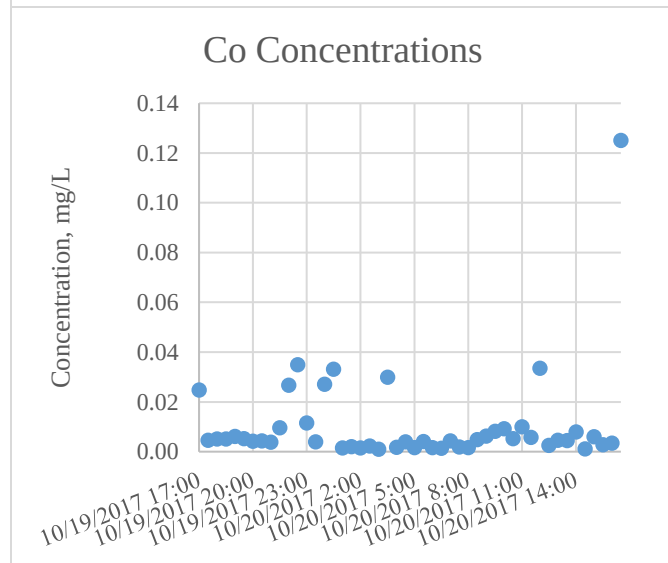
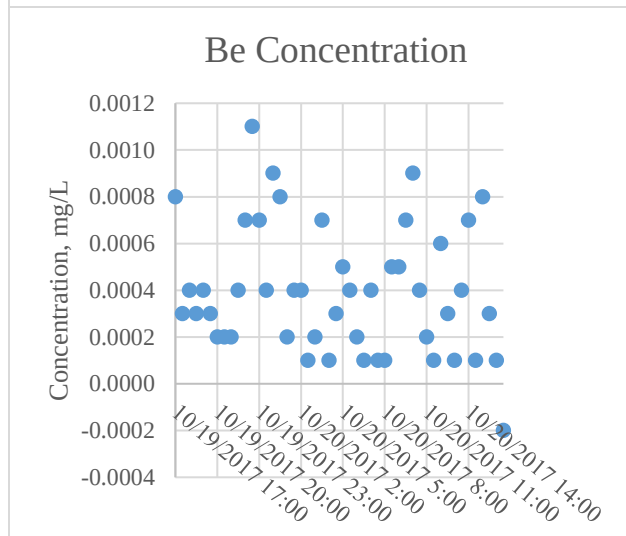
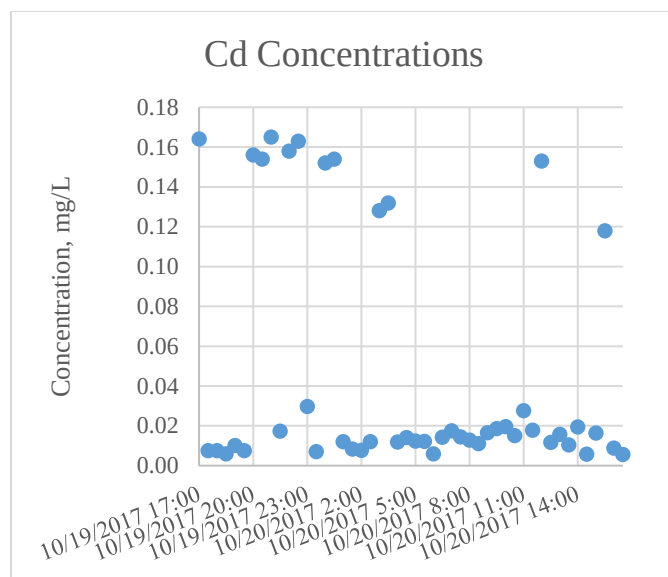
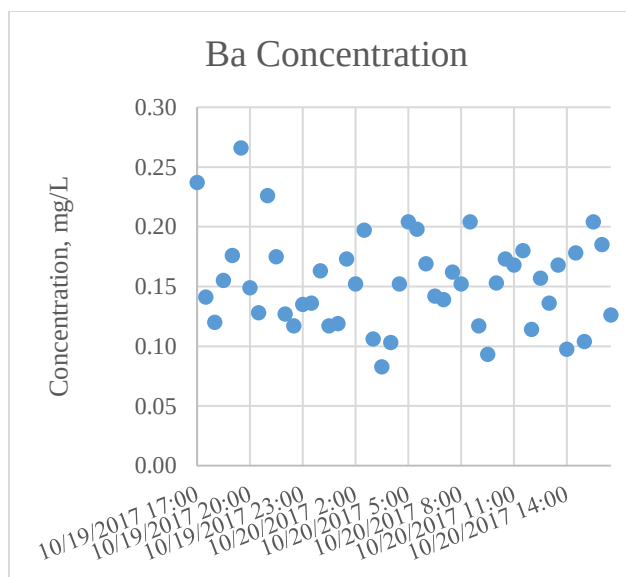
- Mulholland, P. J., Thomas, S. A., Valett, H. M., Webster, J. R., and Beaulieu, J. (2006). Effects of light on NO₃⁻ uptake in small forested streams: diurnal and day-to-day variations. *Journal of the North American Benthological Society*, 25(3), 583-595. DOI: 10.1899/0887-3593(2006)25[583:EOLONU]2.0.CO;2
- Pennino, M.J., Kaushal, S.S., Beaulieu, J.J., Mayer, P. M., and Arango, (2014), C.P. Effects of urban stream burial on nitrogen uptake and ecosystem metabolism: implications for watershed nitrogen and carbon fluxes *Biogeochemistry*. 121: 247. <https://doi.org/10.1007/s10533-014-9958-1>
- Pouyat, R.V., Pataki, D.E., Belt, K.T., Groffman, P.M., Hom, J., and Band, L. E. (2007), Effects of urban land-use change on biogeochemical cycles. In: Canadell, J.G., Pataki, D.E., Pitelka, L.F., eds. *Terrestrial ecosystems in a changing world*. Berlin. Springer-Verlag: 45-58.
- Raymond, P.A., McClelland, J.W., Holmes, R.M., Zhulidov, A.V., Mull, K., Peterson, B.J., Striegl, R.G., Aiken, G.R., and Gurtovaya, T.Y. (2007). Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. *Global Biogeochemical Cycles*, 21(4). <https://doi.org/10.1029/2007GB002934>
- Sivirichi, G., Kaushal, S.S., Mayer, P., Welty, C., Belt, K., Newcomer, T., Newcomb, K., and Grese, M. (2011), Longitudinal Variability in Streamwater Chemistry and Carbon and Nitrogen Fluxes in Restored and Degraded Urban Stream Networks. *Journal of environmental monitoring : JEM*. 13. 288-303. 10.1039/c0em00055h.
- Smith, R.M. and Kaushal, S.S. (2015), Carbon cycle of an urban watershed: exports, sources, and metabolism. *Biogeochemistry* November 2015, Volume 126, Issue 1–2, pp 173–195. <https://doi-org.proxy-um.researchport.umd.edu/10.1007/s10533-015-0151-y>
- Spencer, R. G. M., Pellerin, B. A., Bergamaschi, B. A., Downing, B. D., Kraus, T. E. C., Smart, D. R., Dahlgren, R. A. and Hernes, P. J. (2007), Diurnal variability in riverine dissolved organic matter composition determined by in situ optical measurement in the San Joaquin River (California, USA). *Hydrological Processes*, 21: 3181–3189. doi:10.1002/hyp.6887
- Stedmon, CA., Markager, S., Bro, R. (2003), Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry* 82:239–254
- Worrall, F., and Burt, T., (2004). Time series analysis of long-term river dissolved organic carbon records. *Hydrological Processes*. Vol 18, Issue 5, 893-911. Doi: 10.1002/hyp.1321

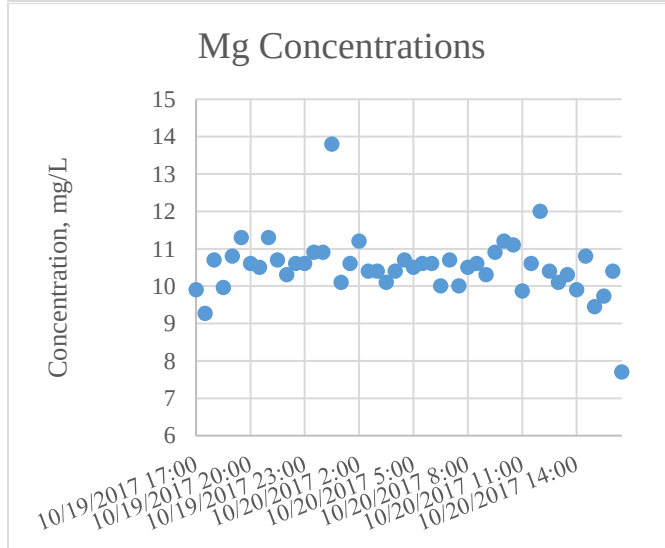
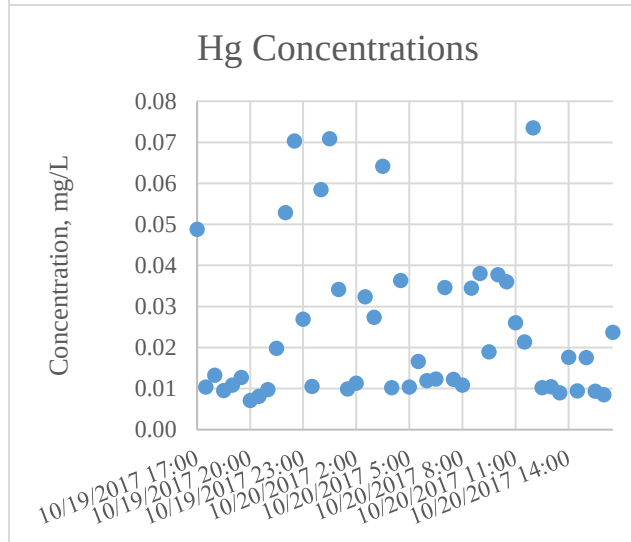
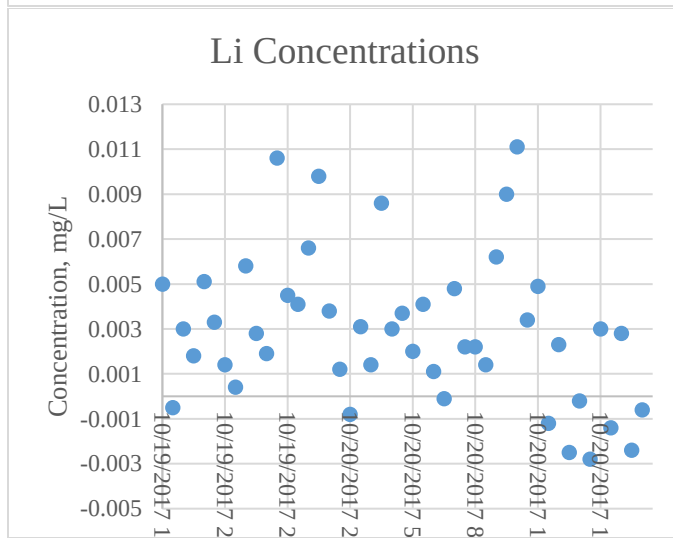
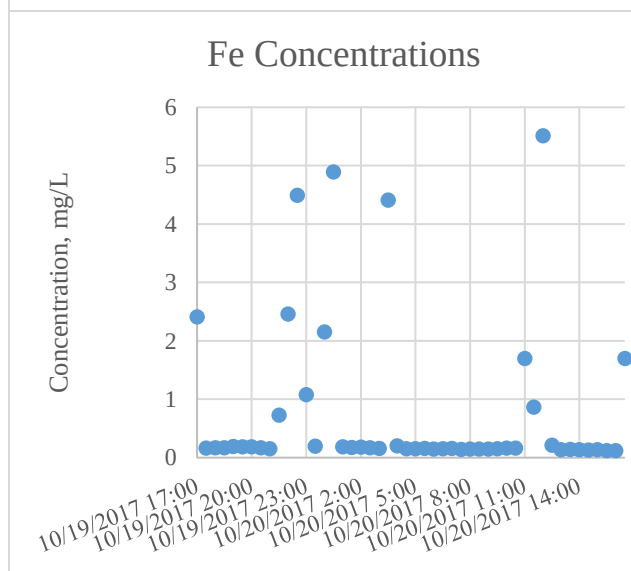
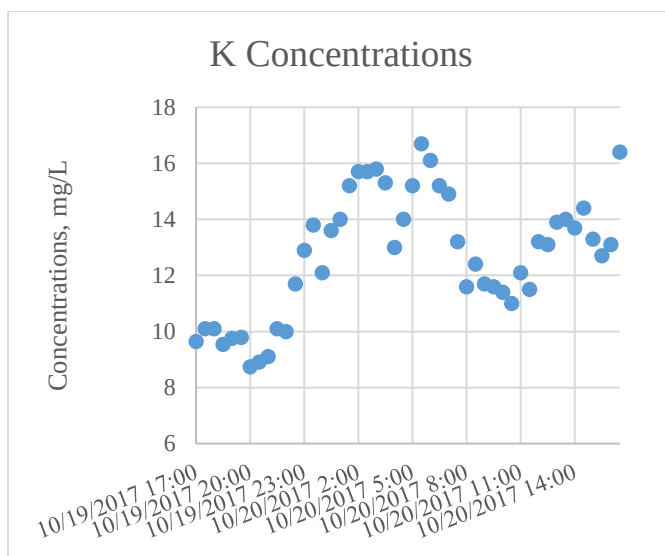
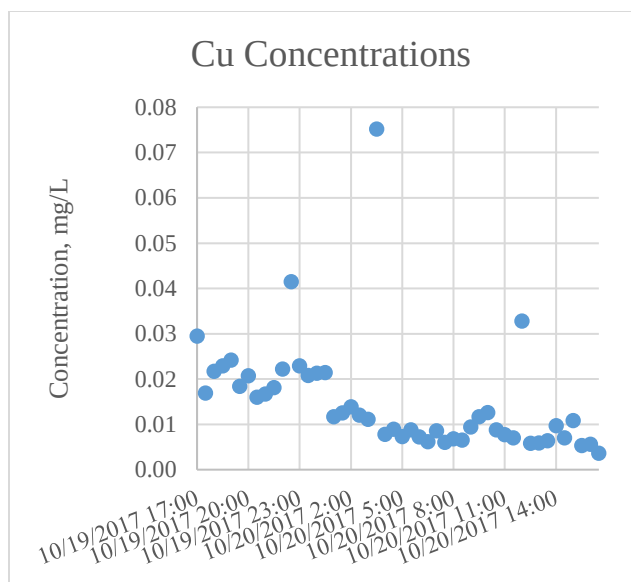
9 Appendix

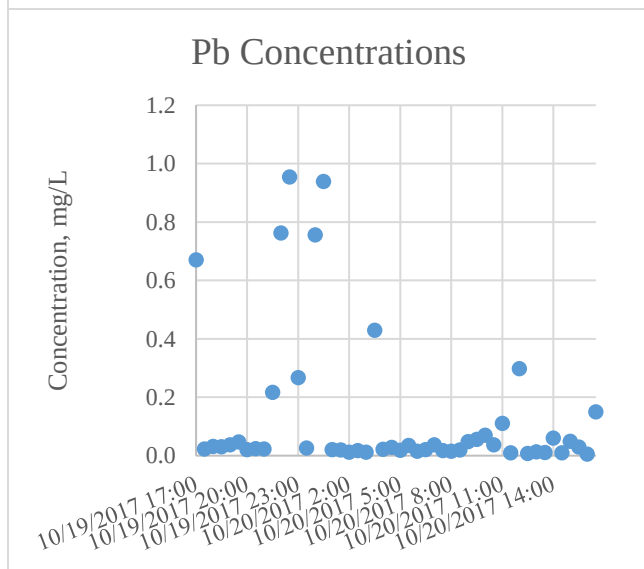
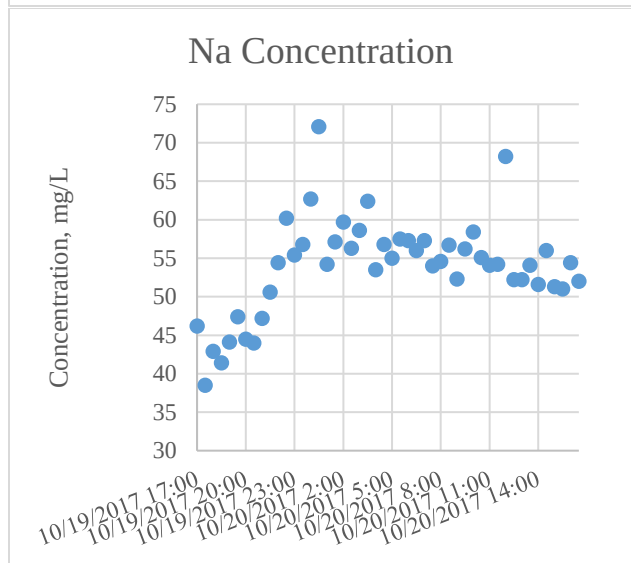
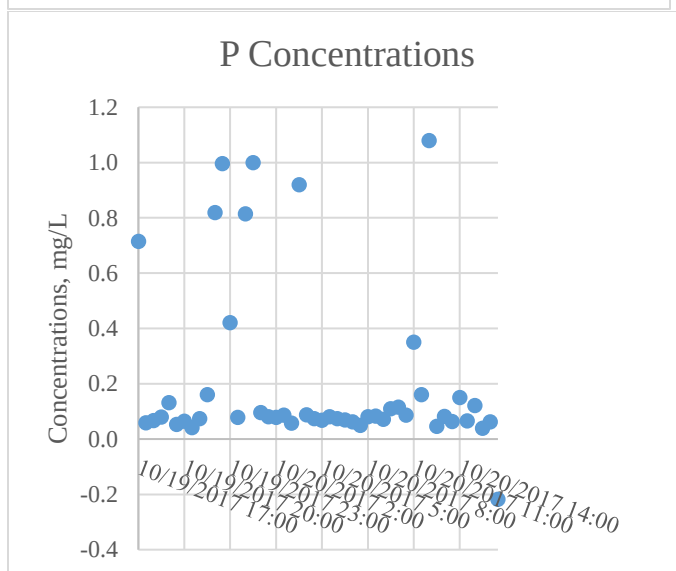
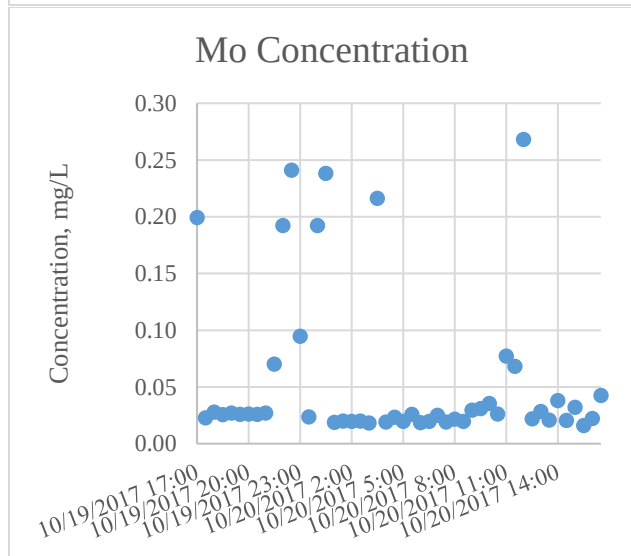
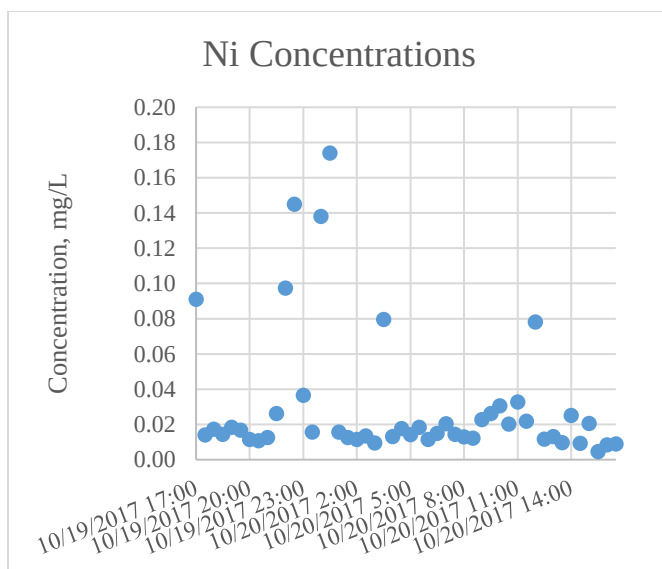
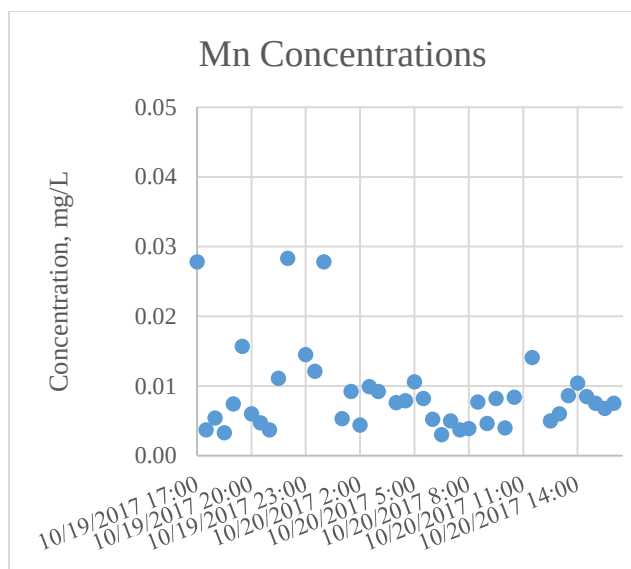
9.1 Fall Data Set

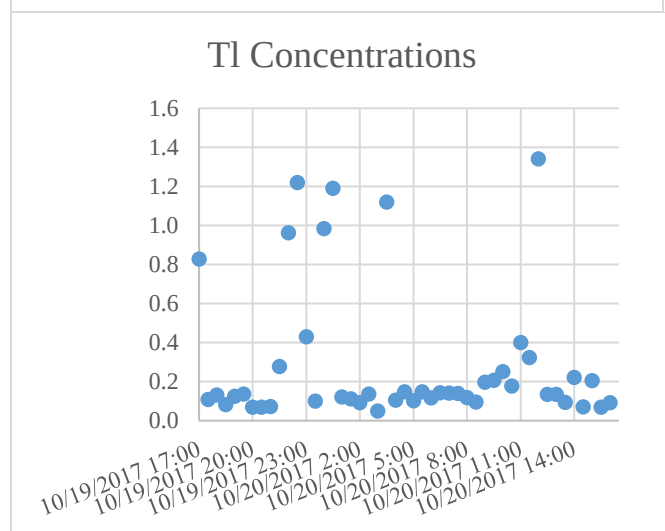
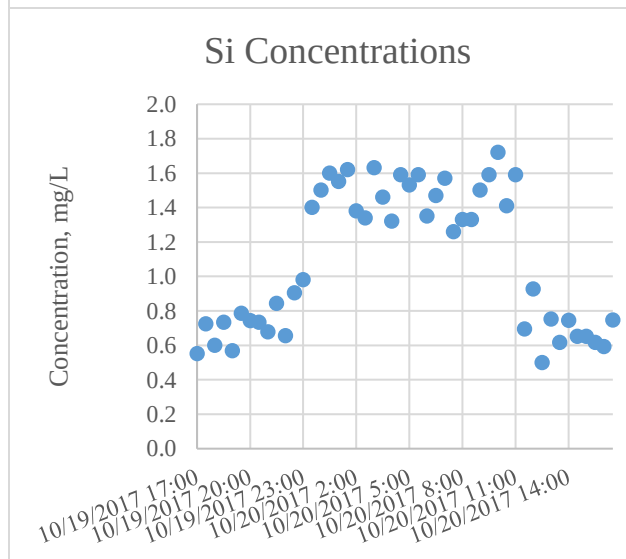
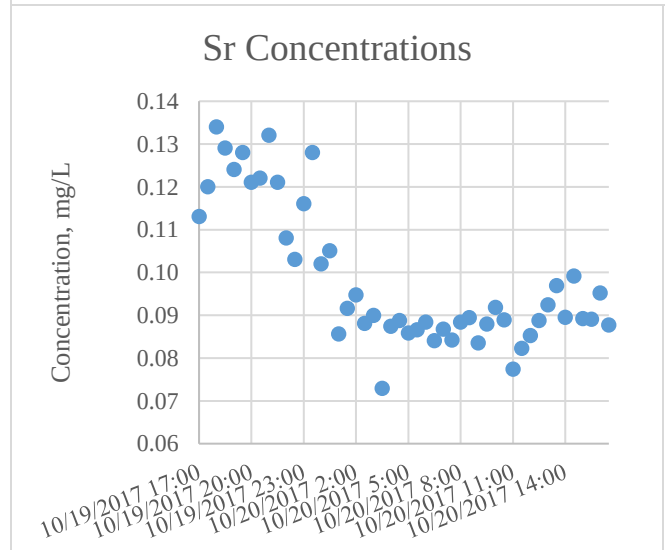
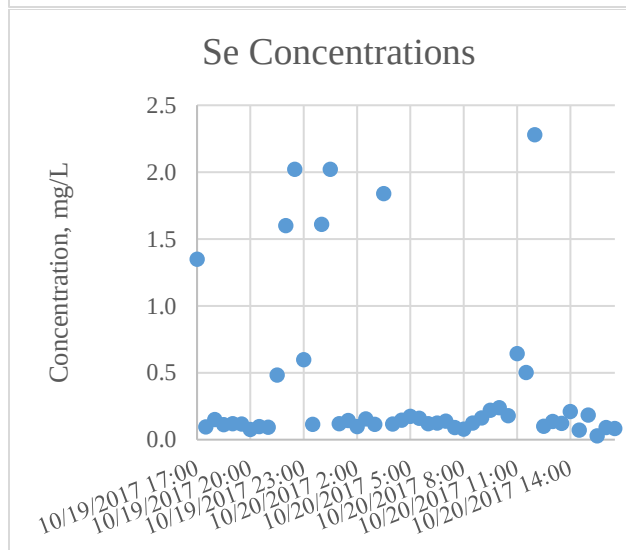
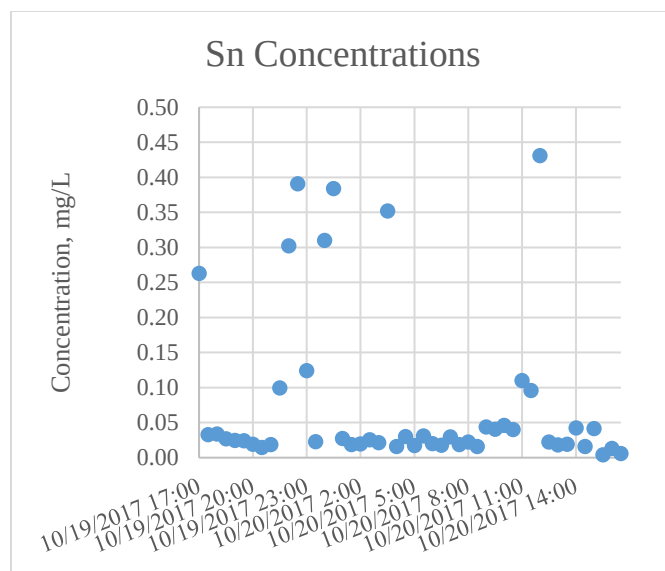
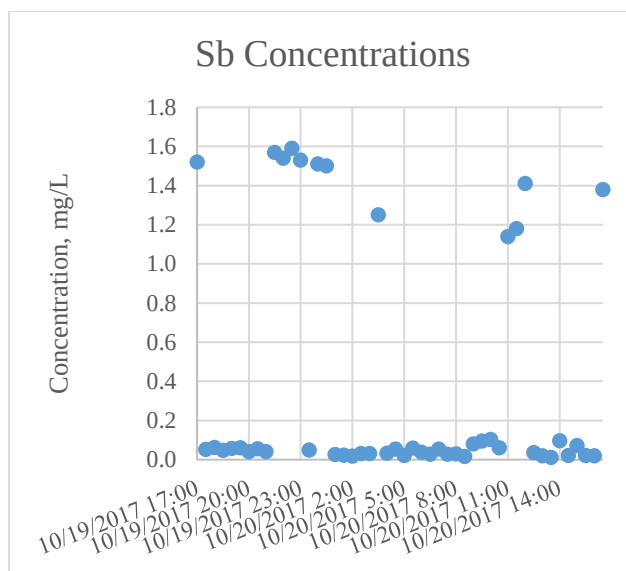
Below are plots of the thirty elements processed. Graphs are provided for each element that was processed. It should be noted that the samples were processed on 3/13/2018 which is almost five months after collection (10/19/2017-10/20/2017). The samples were filtered and acidified during a proper time frame but the long time sitting idle in the lab could have affected the samples. The majority of the data shows that for the majority of elements, there are no diurnal patterns. The fall data set only includes one sampling day.

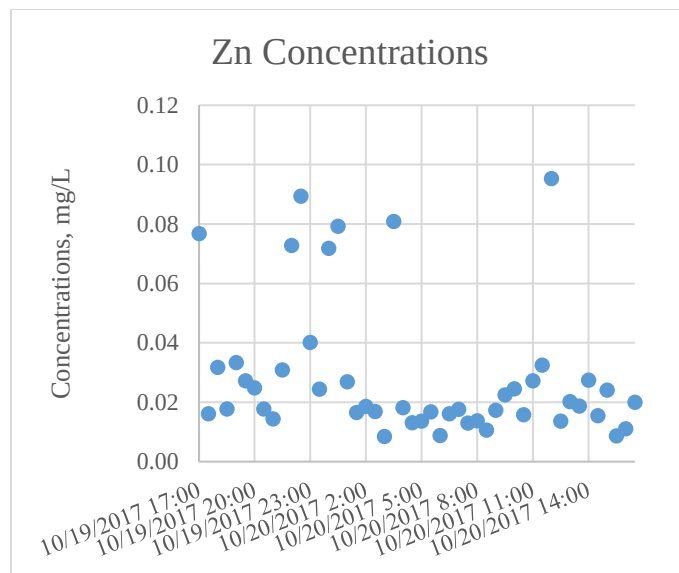
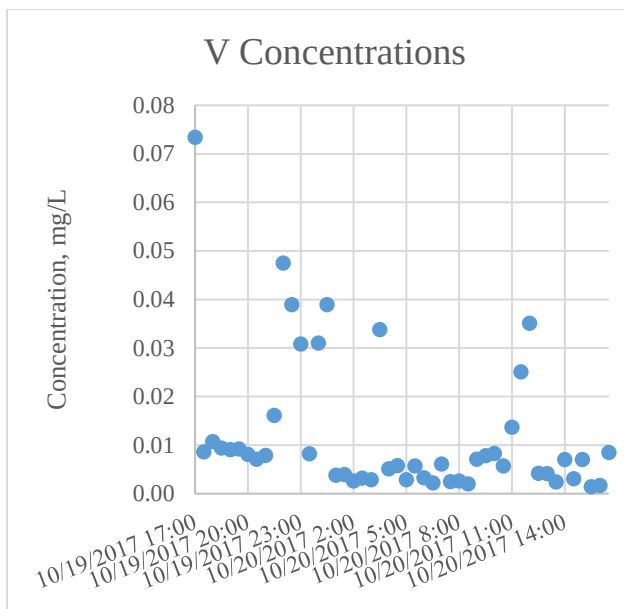






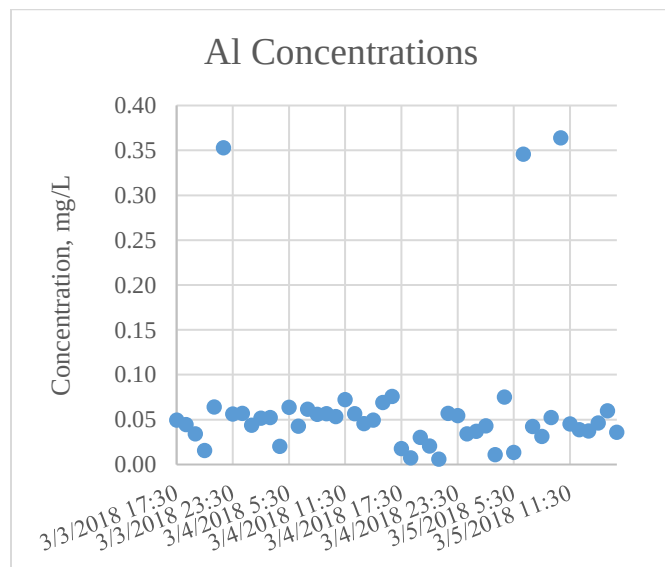
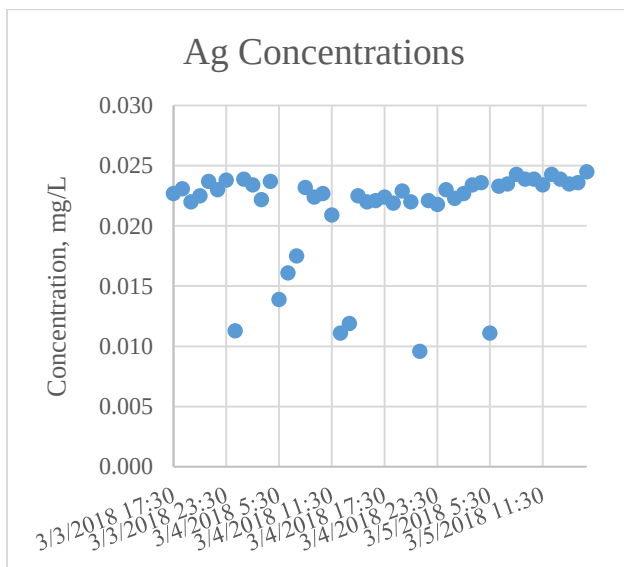


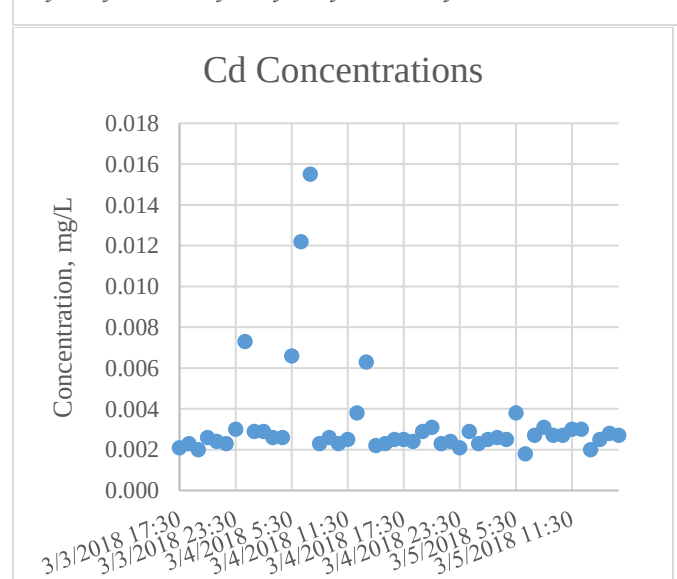
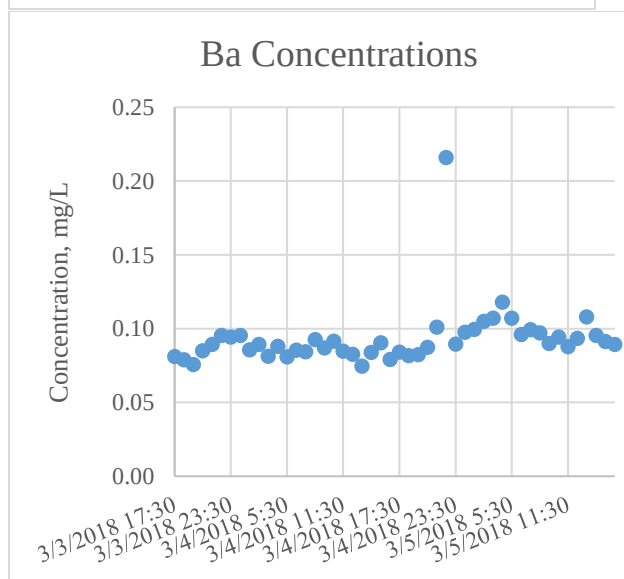
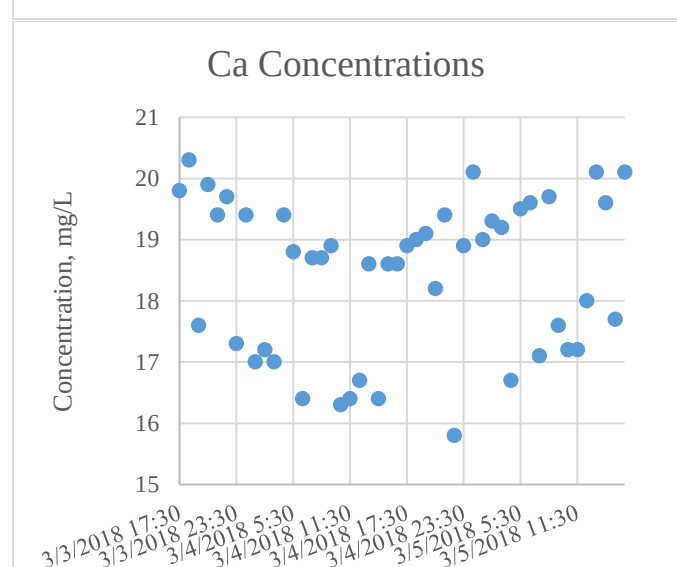
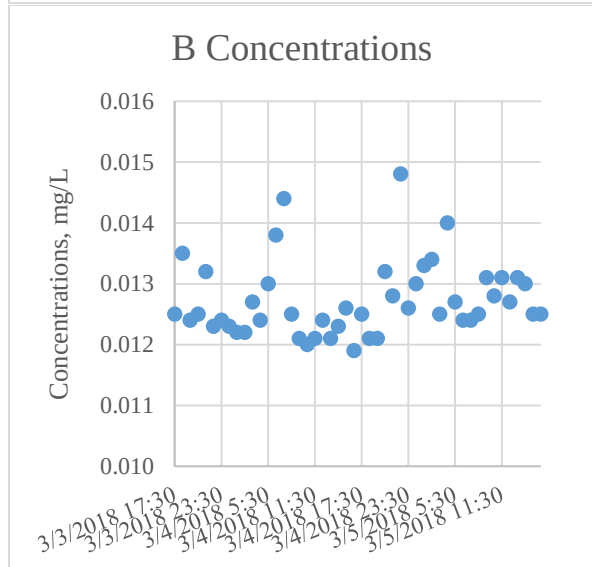
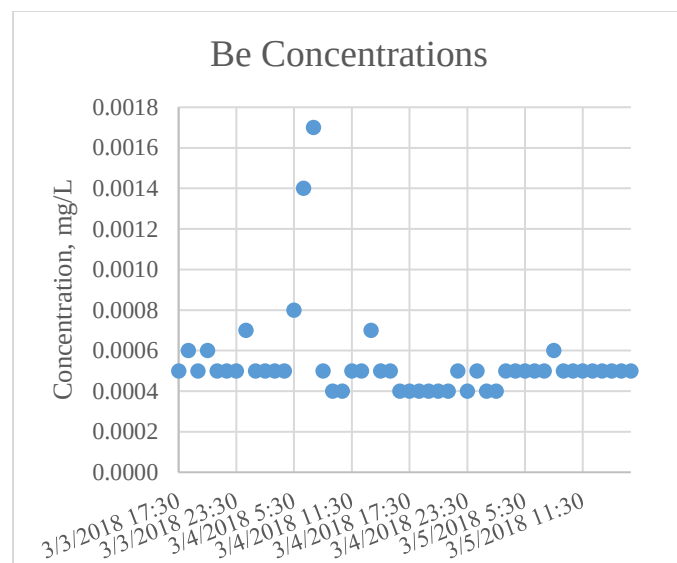
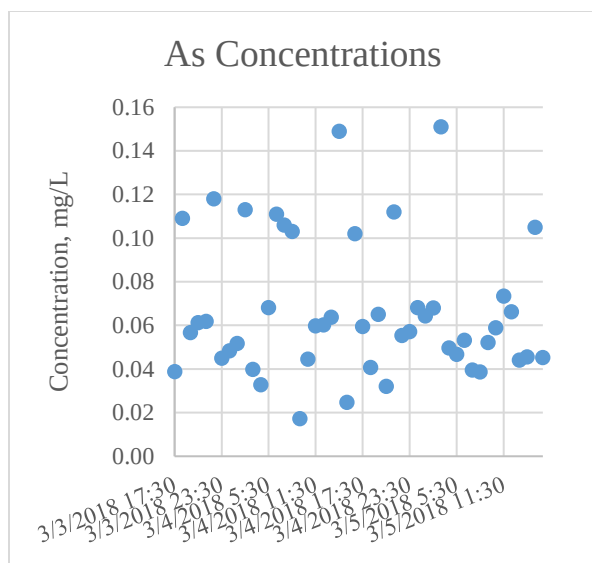


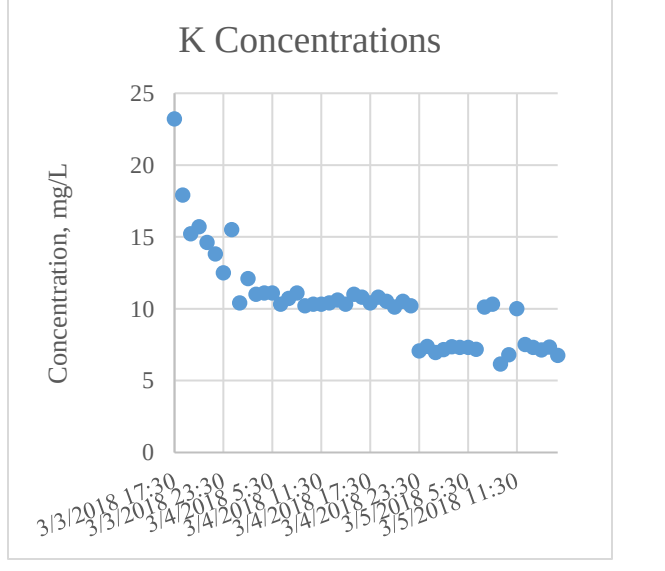
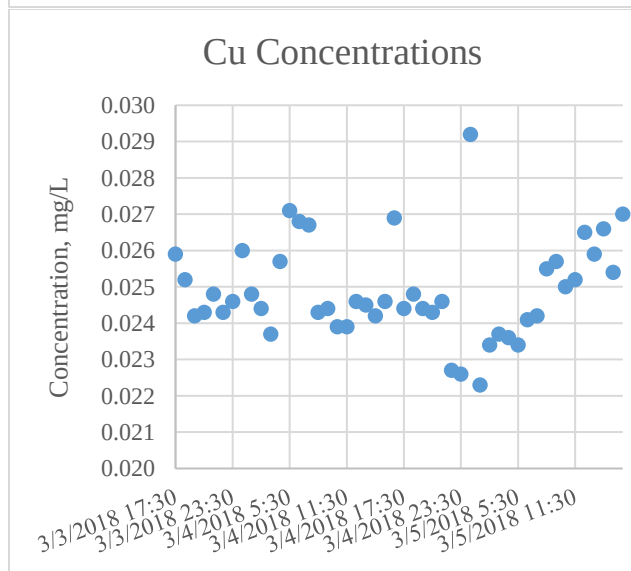
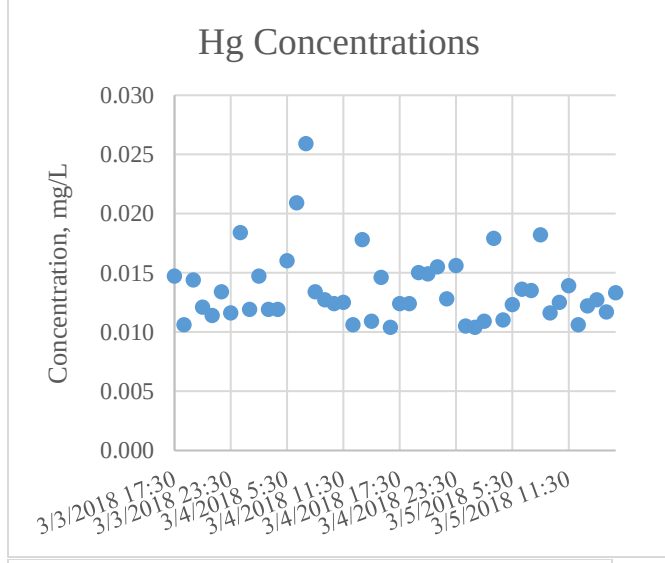
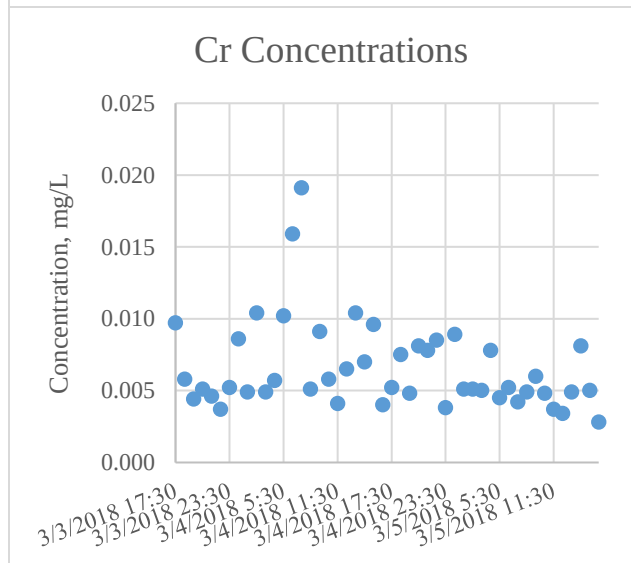
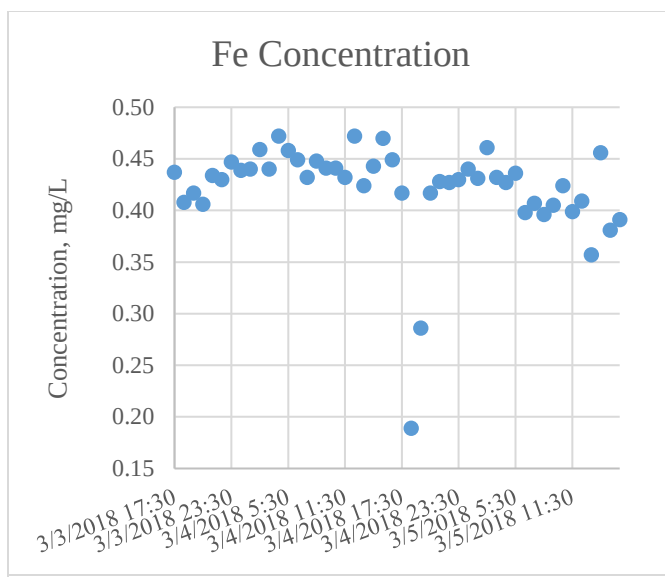
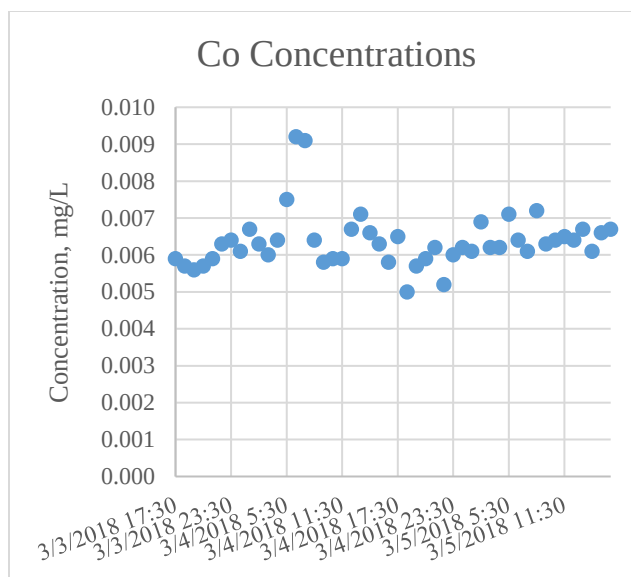


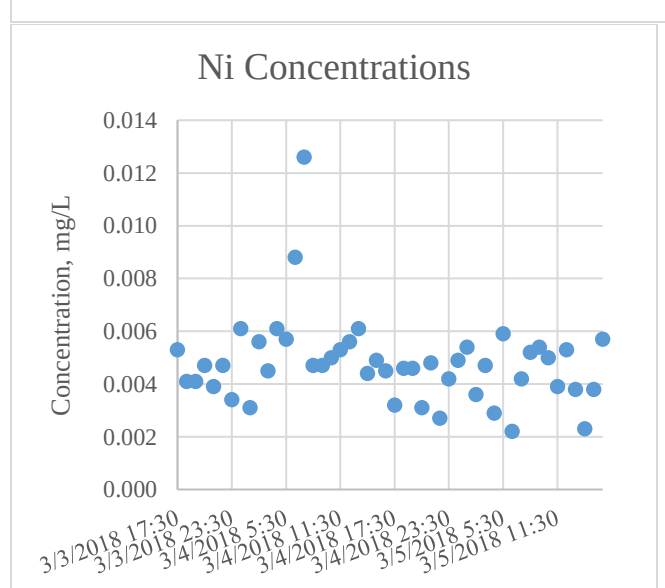
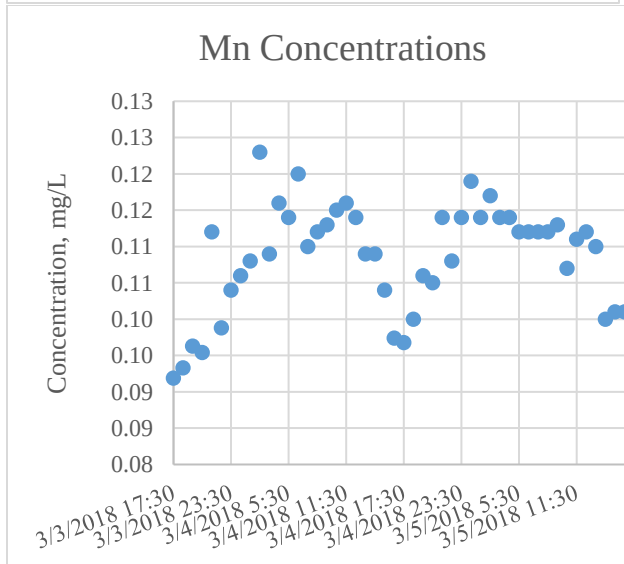
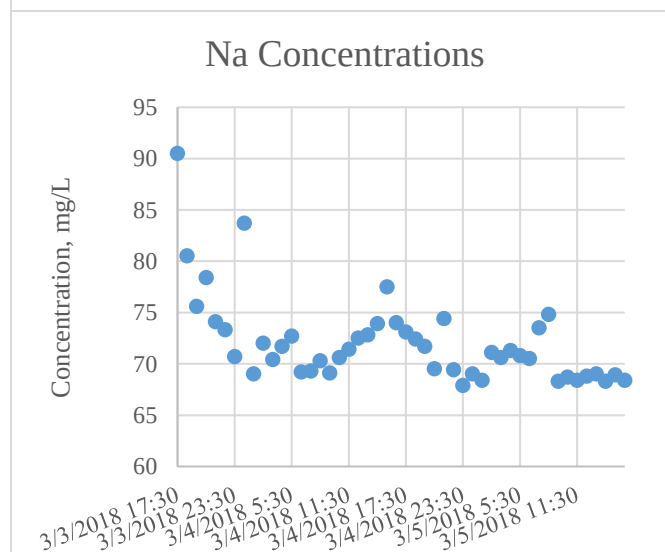
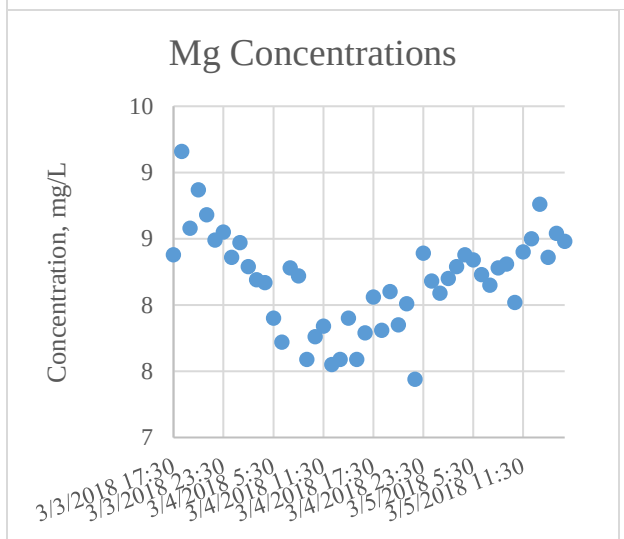
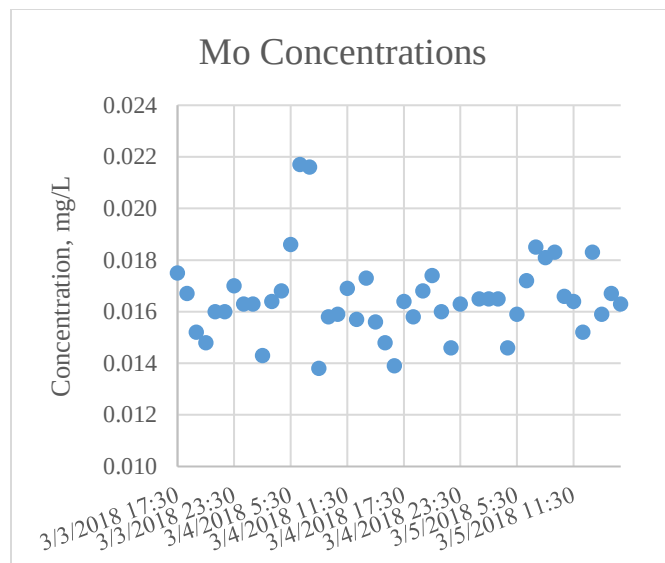
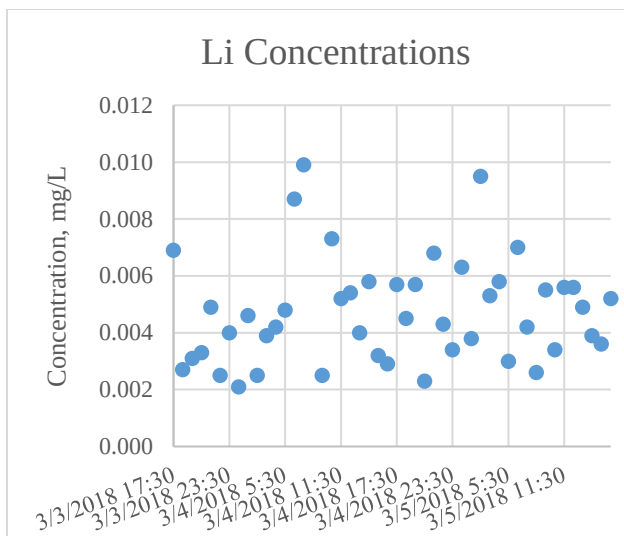
9.2 Winter Data Set

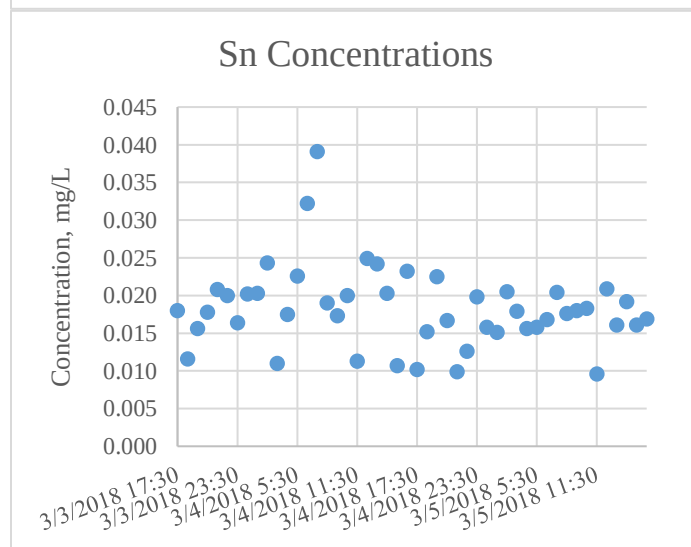
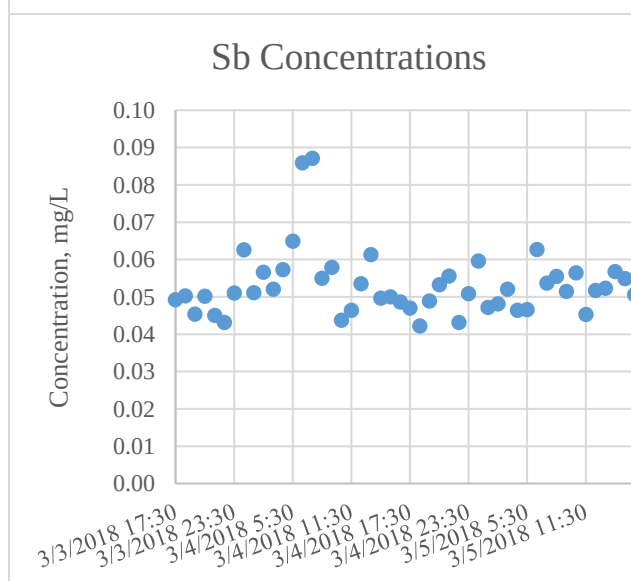
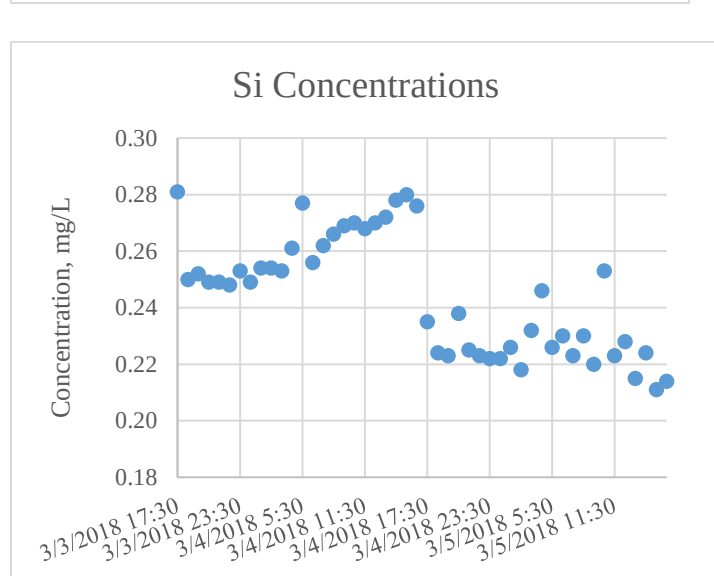
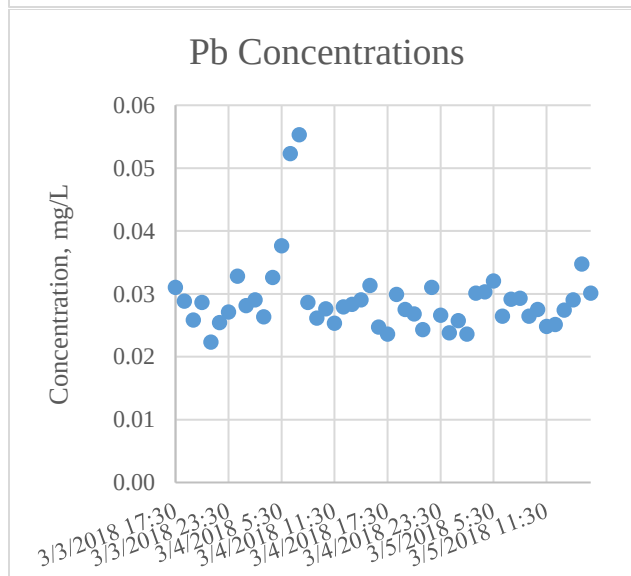
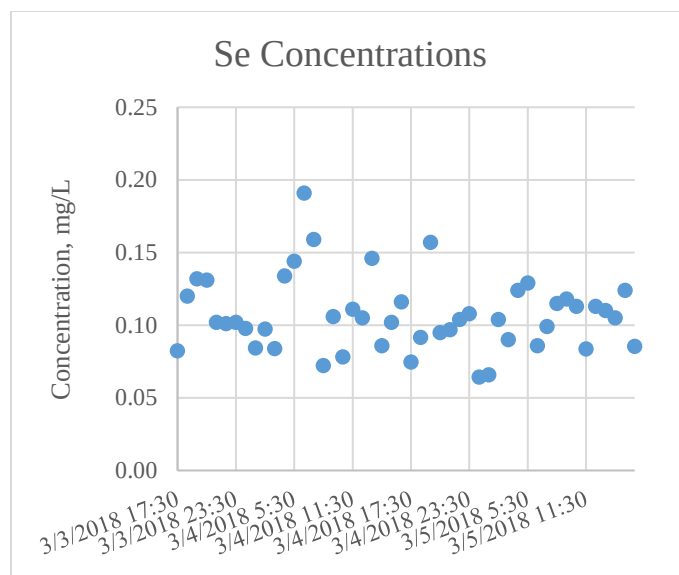
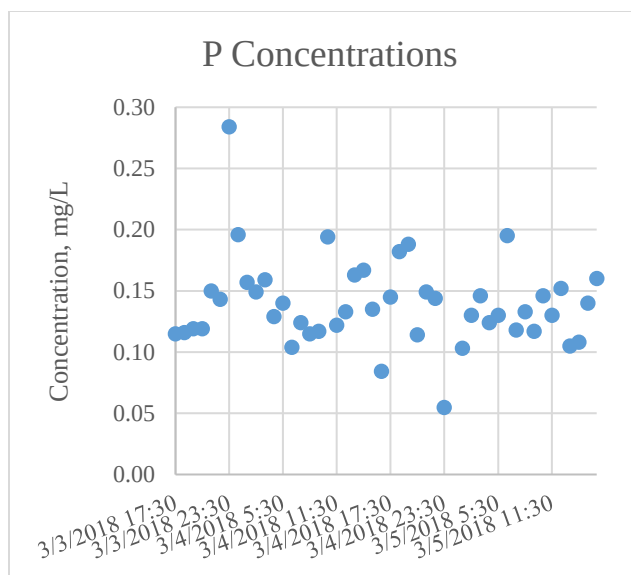
The data included in this section is from the second data collection set which was started on March 3rd 2018 and completed on March 6th 2018. The data from this dataset is across two sampling days in comparison to the fall sample set of one day.

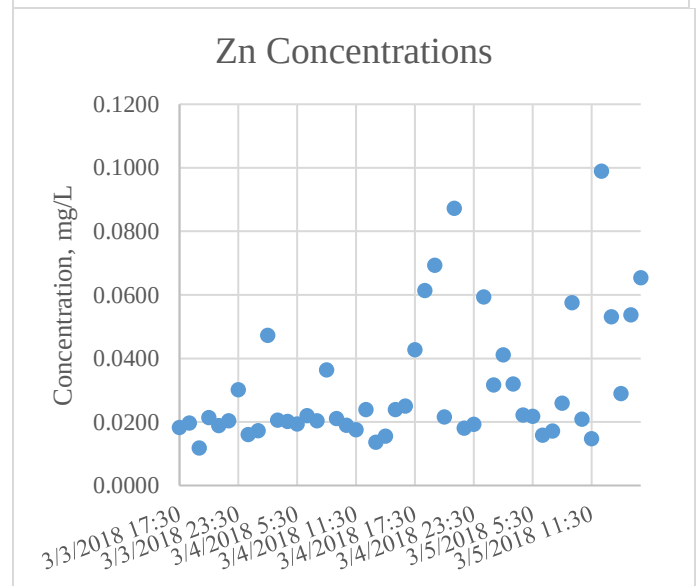
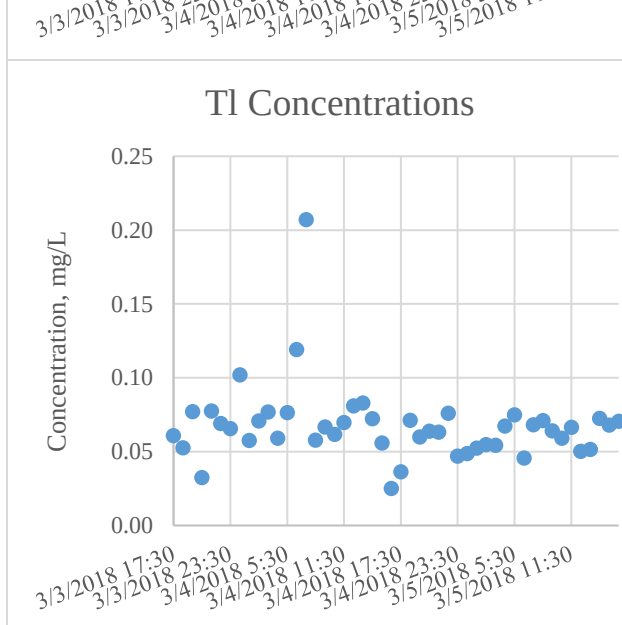
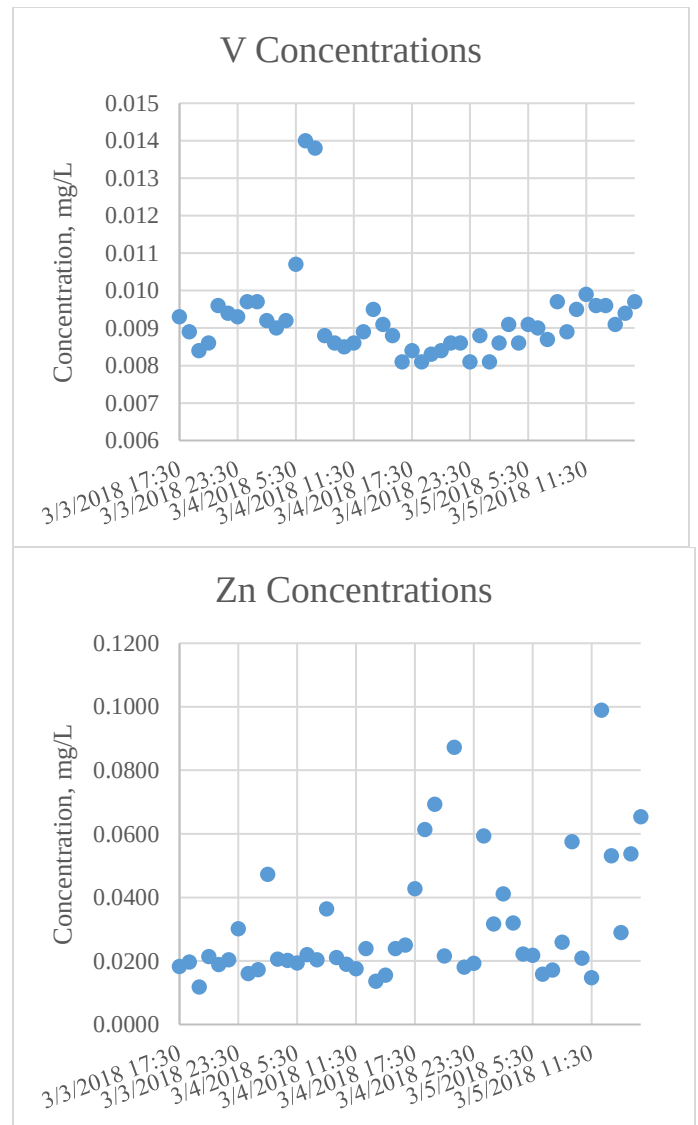
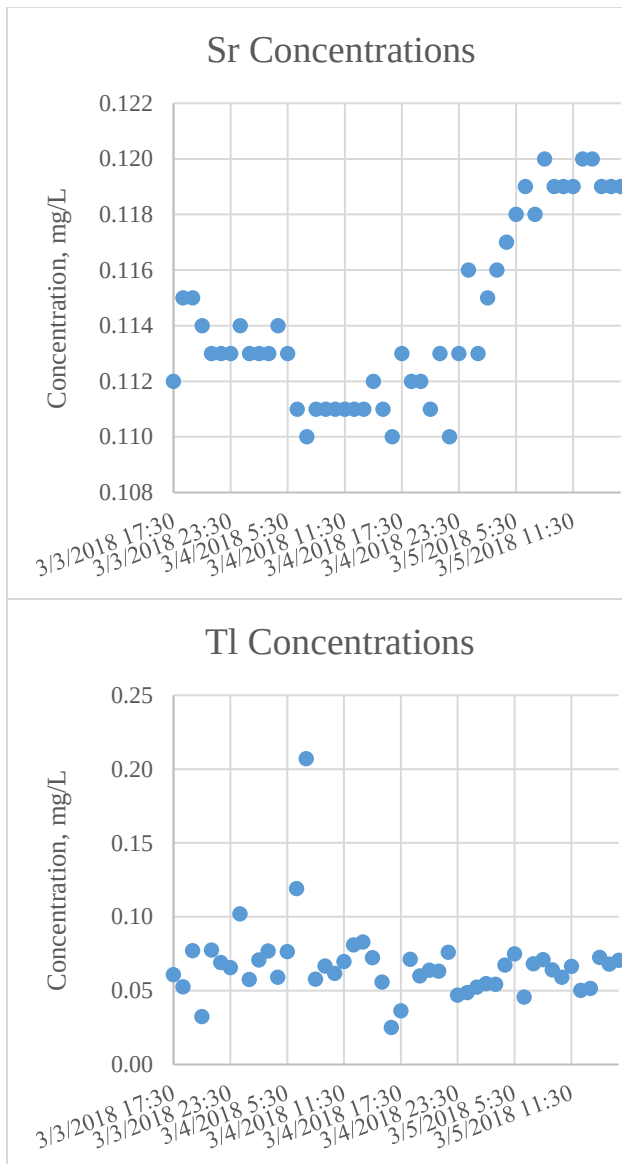












Honor Pledge

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

Kevin Mei