High Frequency Sampling of the Campus Creek RSC

Walter Boger

Department of Geology
University of Maryland, College Park

Advisor: Sujay Kaushal & Jenna Reimer

April 2021

Abstract

The growing urban landscape has contributed to rising concentrations of nutrients and metals in watersheds due to pollution from urban runoff. These elevated concentrations of nutrients and metals have highlighted the need for effective forms of stream restoration in waterways. Regenerative Stormwater Conveyance (RSC) systems, a type of stormwater control measure (SCM), have the ability to be an effective form of stream restoration. Previous research has shown that RSCs are effective at reducing peak discharges, total nitrogen (TN), and total phosphorus (TP) in the water ways (Cizek et al., 2018). The University of Maryland's (UMD) RSC system, installed on Campus Creek, was studied to help understand its efficacy as a form of stream restoration through measurements of nutrients and metal concentrations.

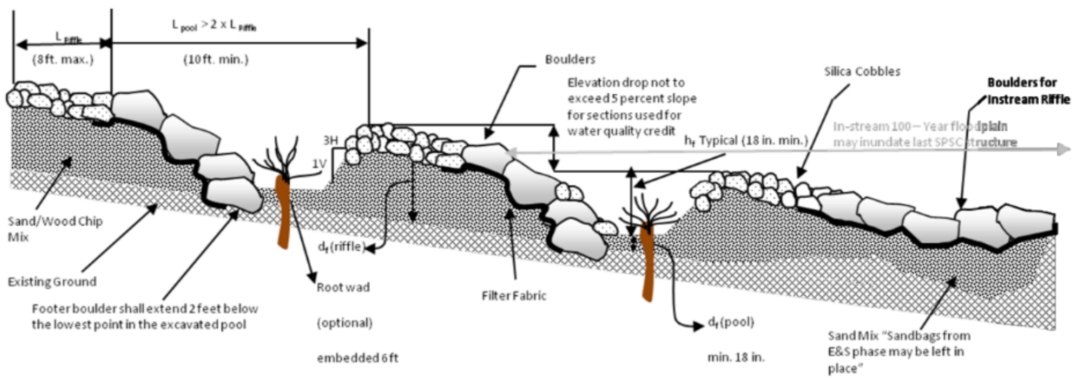
Water samples were collected from Campus Creek during October 2020 and February 2021. These samples were collected from the rapidly flowing water in two riffle weirs as well as from a more stagnant pool (see Fig. 1). Samples were collected both during the day and at night. The October 2020 samples were collected after a rain event; the February 2021 samples were collected on two separate occasions following a snow and rain-on-snow (ROS) event, respectively. Samples were collected following these events to examine how they affect water quality, which could be seen in spectrofluorometric and optical emission analysis of the water samples.

Spectrofluorometric analyses of the October 2020 samples show that the dissolved organic matter was recently introduced into the stream above the upstream riffle weir. However, changes in microbial indices (FI, HIX, BIX, PH) over the sampled 24-hour period indicate some level of microbial activity. The elemental analyses, done via inductively coupled plasma - optical emission spectrometry, are also consistent with some level of microbial activity. No day-night variation in fluorometric indices or in elemental concentrations was observed. This suggests that there is a constant rate of microbial activity independent of temperature and sunlight, which may mean that overall water discharge rate through the weirs and pool does not allow the byproducts of photosynthesis to accumulate. Nonetheless, water quality seems to be acceptable as indicated by only trace amounts of Fe^{2+} and Mn^{2+} ions.

With regards to the analysis of the February 2021 data, samples were collected on two sperate occasions following either a snow or ROS events. Analysis of the samples for salinity, specific conductance (SC), and total dissolved solids (TDS) reveal two peaks in the data separated by two days. These peaks show a rapid increase in specific conductance, TDS, and salinity over the course of approximately one day. This exponential rise is followed by a slower decay over several days without fully returning to pre-event levels. Data from the pools were collected for four days and showed a plateau in TDS and salinity that endured for several days beyond the snow event. The data suggests that it takes minimally three to four days and possibly longer for the RSC to wash out these salts. The presence of salts in the RSC suggests that precipitation events with urban runoff are the driving force that affect water quality in the UMD RSC system.

Introduction

Most urban runoff starts as rainwater that collects in urban landscapes and eventually finds its way into streams through an extensive array of surface and groundwater flow paths (Kaushal and Belt 2012). This surface flow mobilizes contaminants that are scattered across the urban landscape and concentrates them into a waterway, such as a stream or river (Walsh et al., 2005). Urban runoff is associated with elevated concentrations of nutrients, metals, and dissolved organic matter (DOM) (Kaushal et al., 2014). High concentrations of nutrients and organic matter in these waterways can lead to conditions of hypoxia, which can be harmful to organisms such as shellfish. High concentrations of metals can lead to toxic conditions for aquatic life (Walsh et al., 2005). A possible solution to treating urban runoff is to implement RSCs at key points in watersheds (see Fig. 1). However, there may also be unintended water quality consequences that need to be investigated.



Typical Profile – Alternating Pools and Riffles

Figure 1: A depiction of a typical standard RSC system. Pools are separated by riffle weirs constructed of silica cobbles, sand/wood ship mix, and boulders (Flores et al., 2012).

Regenerative stormwater conveyance (RSC) systems were originally designed for storm water management; to reduce peak discharge. However, they have advantages for stream restoration as well. An RSC in Anne Arundel County, Maryland showed a 75% reduction in peak flow during a 25-year storm event. In Brunswick County, North Carolina a watershed fitted with an RSC had reduced peak flow by 90% (Cizek et al., 2017). Previous research has shown that RSCs are effective at reducing peak discharges, total nitrogen (TN), and total phosphorus (TP) in water (Cizek et al., 2018).

In general, RSCs are designed to both oxygenate the water and increase water residence time by flowing the water through a series of pools and riffle weirs. The goal is to immobilize and retain nutrients biologically or in sediments and recharge the local groundwater. However, RSCs may increase concentrations of unwanted biologically influenced elements, such as iron and manganese, and retain elements associated with urban runoff such as salts. The retention and release of these elements is the byproduct of increasing water residence time. Increasing water residence time might be effective at immobilizing nutrients but may also retain or release unwanted elements. Thus, regenerative stormwater Conveyance (RSC) systems can possibly reduce concentrations of limiting nutrients, such as nitrogen (N), phosphorus (P), and potassium (K), metals, and organic matter. However, a byproduct of RSC might be the retention of unwanted compounds and the release of harmful dissolved ions.

The purpose of this study was to study: (1) if the day and night cycle affects concentrations of P, Fe, Mn, and microbial activity; (2) the immobilizing, retention, and release of nutrients, metals, and dissolved organic matter; and (3) how rain and rain-on-snow (ROS events affect water quality. In should be noted that data on the effects of hydrologic events like rain events and snow events are particularly lacking. This is because it is very difficult to continuously sample these urban stormwater systems during such events. This study attempts to fill this gap with high-frequency sampling.

Methods

<u>**Site Description**</u>

<u>Campus Creek Regenerative Stormwater Conveyance System</u>

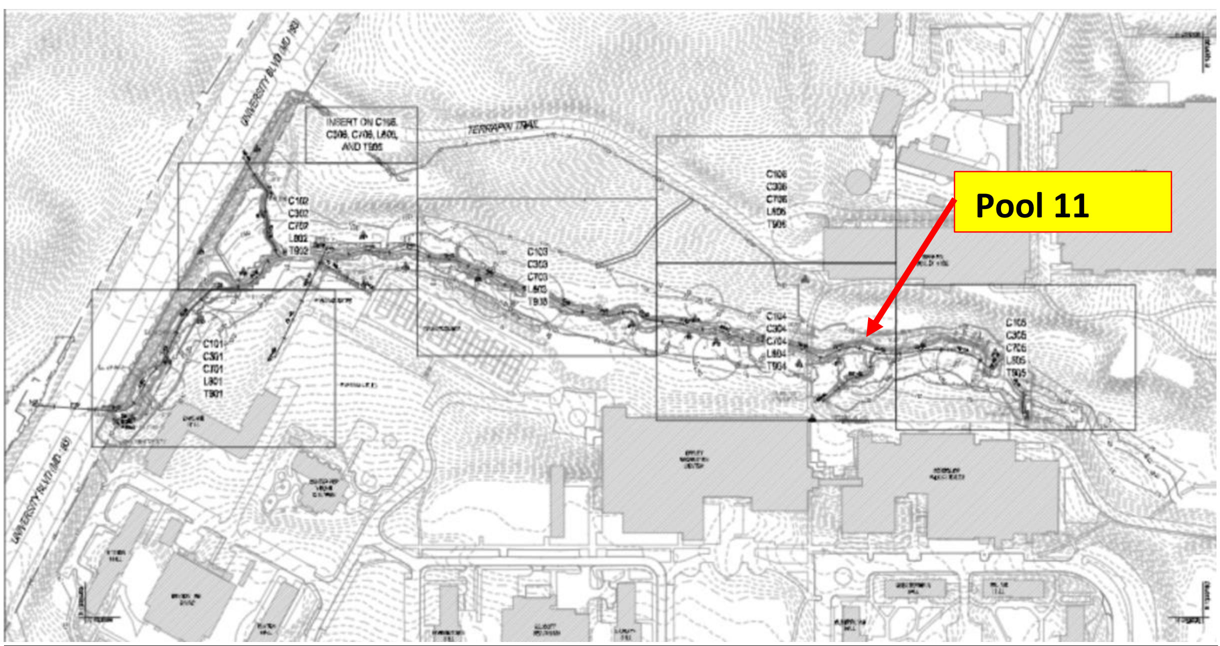


Figure 2: Schematic of the Campus Creek Restoration Design (UMD Campus Creek Stream Restoration Design Build, Proj. No: 14-659-056-00 QC 14484). Samples were taken from pool 11 and its upstream and downstream riffle weirs.

The Campus Creek RSC system was built 2 years ago. This RSC system is roughly 700m in length and has 18 individual pools. The pools are chemically and physically different from each other, varying in shape, size, depth, input, and surrounding material. A preliminary study conducted on September 9, 2020, found that there can be roughly 2 mg/L difference in non-purgeable organic carbon between pools (as measured by the author). The preliminary study sampled all 18 pools for pH, conductivity, TDS, salinity, HIX, BIX, FI, PH, NPOC, TC, and TN (see appendix C). Work is currently being conducted on the Campus Creek RSC system to study methane emissions, removal of vegetation and its effect on water quality, retentions of road salts, etc. Further research is needed on the Campus Creek RSC system to observe the effects rain and snow has on water quality and the difference between pools and riffle weirs. Samples were drawn from the 11th pool and its adjacent upstream and downstream riffle weirs. The location of pool 11 is indicated in Fig. 2.

<u>Sources of runoff into Campus Creek</u>

Runoff in the Campus Creek catchment can be categorized as either both agricultural or urban runoff. Agricultural runoff originates from the University of Maryland (UMD) golf course. The golf course uses fertilizer that has high concentrations of limiting nutrients: nitrogen, phosphorus, and potassium. Urban runoff, on the other hand, is the surface flow from the UMD campus. Urban runoff typically has high concentrations of metals, nutrients, and DOM. Lastly, water coming from the Eppley Recreational Center HVAC system drains directly into the Campus Creek. The runoff from Eppley may have high in concentrations of metals (Dr. Kaufman). As mentioned above, measuring the concentrations of these nutrients, metals, and DOM is one focus of this project.

Data Collection and Analysis

Water samples were collected during October 2020 and February 2021 using a Teledyne ISCO automated sampler. These 150 ml samples were collected from three locations in the Campus Creek RSC: a slow-moving pool and two rapidly flowing riffle weirs, one above and the other below the pool (see Table 1). Samples were collected in October 2020 every hour, both during the day and night. Sample were collected in February 2021 every couple of hours during the day and night. The October samples were collected during an autumn rain event, whereas the February samples were collected during winter, snow, and rain-on-snow (ROS) events. The water samples were analyzed using an Oakton pHtestr Model 50 pH meter, after which the samples were then filtered with a Whatman GF/f 47 mm glass microfiber filter to remove solids for further analysis of dissolved materials. Filtered samples were then acidified with 300 μl of high-purity nitric acid to stabilize samples. An elemental analysis for Mn, Fe, Na, and P was done using an inductively coupled plasma optical emission spectrometer (ICP-OES) made by Shimadzu. Spectrofluorometric indices were obtained with a FluoroMax-4 a Horiba Yvon spectrofluorometric. Table 1 summarizes where and how samples were taken.

Date of Collection	**October 2020**	**February 2021**
Sample Location	Upstream, Downstream riffle weir, RSC pool	Upstream Riffle Weir, RSC pool
Time Between Samples Collection	1 hour	2, 3, and 4 hours

Equipment	Spectrofluorometer & ICP-OES	Oakton pHtestr Model 50 pH meter & Spectrofluorometer

Table 1: Summary of different times, and equipment used for the October 2020 and February 2021 datasets. Oakton pHtestr Model 50 pH meter was not used for October 2020 samples due to a lack of lab time. ICP-OES analysis for February 2021 was not conducted due to complications with the ICP-OES's chiller.

A. Analysis of Dissolved Organic Matter Quality by Fluorescence Spectroscopy

The fluorescence data was obtained for each water sample with a FluoroMax-4 a Horiba Jobin Yvon Spectrofluorometer, which uses excitation wavelengths ranging from 240 to 450 in 5 nm increments to induce fluorescence with wavelengths ranging from 300 to 600 nm with 2 nm increments. The data was blank subtracted and normalized by Raman scattering. The single point emission spectra were used to calculate several indices: Fluorescence index (FI), Humification index (HIX), Biological index (BIX), and a ratio of protein-like and humic-like matter (PH). The analytical uncertainty associated with each individual sample was less than 2% (Jiang and Kaushal, 2013). Each of these indices reveals something about the composition of the sample and its source:

- FI is a measure of whether organic matter is terrestrial (~1.4) or microbial (~1.9) in origin. FI is measured at an excitation wavelength of 370 nm and emission at 448 nm (Spreadsheet provided by Dr. Duan).
- HIX provides information about the humification of DOM (Personal Discussion with Dr. Kaushal). High humic content means either the DOM is hard to break down by microbial activity or has already been broken down and this is what is left. Clean water has a HIX of about 0.3. A HIX higher than 2 suggests sewage impacted rivers and streams (Ghervase et al., 2010). HIX was calculated as the ratio of peak area under the emission spectra at 432-478 nm to peak area at 300-346 nm obtained at excitation wavelength of 255 nm (Spreadsheet provided by Dr. Duan).
- BIX indicates how biologically fresh the dissolved organic matter is and therefore what it is associated with. Terrestrial (<0.7), algal (0.8-1.0), or aquatic bacterial (>1.0). BIX is the ratio of the intensities of emissions spectra at 378 nm and 428 nm obtained at an excitation wavelength 310 nm (Spreadsheet Provided by Dr. Duan).
- PH index is the ratio of protein-like to humic-like dissolved organic matter. A higher PH means that the DOM is more protein-like and therefore a larger microbial food source (Personal discussion with Dr. Kaushal). The PH is the measured intensity at excitation and emission wavelengths of 275 nm and 340 nm respectively divided by the intensities at 350 nm and 480 nm (Spreadsheet provided by Dr. Duan).

B. Analysis of pH, total dissolved solids, and salinity in water

Hand-held readings of pH, specific conductance (SC), total dissolved solids (TDS), and salinity were measured using an Oakton pHtestr Model 50 pH meter. pH is a measurement of how acidic (<7) or basic (>7) the water sample is. The pH of water determines the solubility and biological availability of nutrients and heavy metals. For example, metals tend to be present in higher concentrations at lower pH because they are more soluble in an acidic environment. An acidic environment is generally not indicative of a healthy stream (Heshthagen 2011).

Specific conductance is a measurement of the water's ability to pass an electric current due to the presence of ions. Specific conductance measurements of water are used to establish a baseline for water quality. If a stream's SC changes, this indicates that the chemistry of the water has also changed, usually as the result of runoff. TDS and salinity are similar to SC. Total dissolved solids and salinity measurements are also used as indicators for water quality. Baseline measurements for conductivity, TDS, and salinity are represented in Table 2.

Campus Creek		
Cond. (mμS)	TDS (ppt)	Salinity (ppt)
350	248	0.18

Table 2: Specific conductance, TDS, and salinity measurements for Campus Creek on 7/13/2020. Measurements were taken by Interns in Dr.Kaushal's Biogeochemistry Lab.

C. Analysis of elemental concentrations by Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES)

Composition and concentration of elements in the water samples were measured using an ICP-OES. The ICP-OES uses an argon plasma to generate light incident on a water sample to cause it to emit light in the optical region. The water sample is turned into an aerosol and then injected into an argon plasma. In the ICP-OES the plasma is generated at the end of a quartz torch by a cooled induction coil, through which a high frequency alternating current flows. The alternating current creates an oscillating magnetic field which accelerates electrons into a circular trajectory. Collisions between argon atoms and electrons leads to ionization. Due to the energy taken up by the electrons, they reach a higher "excited" state. When the electrons drop back to lower or ground levels, energy is emitted as light (photons) with discrete values. Each element has its own emission spectrum that is measured by the spectrometer. Each measurement is calibrated using known concentrations of elements with standardized samples. The ICP-OES looks at wavelength ranging from 100 Å–1 mm.

For purposes of this study, concentrations of such biologically reactive ions as Fe^{2+}, Mn^{2+}, P^{3-}, and Na^{+} were measured. These elements exist naturally in our waterways through the weathering of rocks that contain these elements. Additional sources of these elements can come from urban runoff, for example, metallic Fe^{3+} and Mn^{4+} used in building construction can enter a waterway through runoff. Phosphorus can find its way to streams through the use of fertilizers, and sodium from road salts.

Each of these elements may have harmful effects on the health of a stream. Too much sodium, although not affected by microbes, can, for example, kill plant life, erode metals, and mobilize other elements (Corsi et al., 2010; Kaushal et al., 2018; Kaushal et al., 2019; Mohod and Dhote, 2013). Dissolved iron and manganese can be poisonous if in high enough concentrations. And phosphorus promotes growth of algae. If the algae deplete the phosphorus, it then dies and decomposes through the microbial activity that leads to conditions of hypoxia. In general, trace amounts of Fe^{2+} and Mn^{2+} ions (< 1.0 mg/L) indicate a healthy stream (Gailardet et al., 2003). Higher concentrations of P^{3-} and Na^{+} ions can be tolerated but need to be watched.

Anoxic conditions may lead to soluble Fe^{2+} and Mn^{2+} (see Fig. 3). These can remain mobile and, as noted above, if in high concentrations become toxic. On the other hand, under non-anoxic conditions, Fe^{3+} is formed which quickly precipitate outs as solid $Fe(OH)_3$ which precipitates out. Microbial activity can promote this reaction. This renders the Fe^{3+} immobile and lowers the concentrations of this ion in the stream. Similar chemistry occurs for Mn^{2+}. Mn^{2+} and Fe^{2+} in their dissolved forms should not exceed concentrations of 1 mg/L (Gailardet et al., 2003). Solid Mn^{4+} and Fe^{3+} exists as MnO_2 and $Fe(OH)_3$ and can be seen on Campus Creek as black residue and red clouds respectively.

Anoxic

- $MnO_2 + 2e^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O$
- $Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$

Oxic

- $4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$
- $Mn^{2+} + 1/2O_2 + 3/2H_2O \rightarrow MnO_2$

Figure 3: The anoxic and oxic equations associated with Fe^{2+}, Fe^{3+}, Mn^{2+} and Mn^{4+}. The oxic equations result in a precipitant. The anoxic equations result in dissolved ions (Schelsinger et al., 2013).

Analysis of High-Frequency Water Chemistry during Hydrologic Events

The October 2020 dataset consists of three simultaneous 24-hour studies on upstream and downstream riffle weirs relative to the 11th RSC pool in between. The February 2021 dataset is comprised of a 4-day study and a 7-day study. The 4-day study started on February 11, 2021 and ended February 15, 2021. The 7-day study started on February 18, 2021 and ended February 25, 2021. The dataset consisted of DOM indices (FI, BIX, HIX, and PH), elemental composition of (Fe^{2+}, Mn^{2+}, and P^{3-}), and water quality (pH, TDS, specific conductance, and Salinity). The data are presented in Appendices A and B.

<u>Linear Regression Analysis of October 2020 dataset</u>

The OES and spectrofluorometric data were inputted into Excel, where a linear regression was fitted to the data, and a corresponding R^2 value were calculated. The Linear regression followed the standard y-intercept format. Linear regressions do not work with date data, so the dates were converted into numerical points. The first date datum was denoted as one, the second as two, and so on. A line of best fit was calculated with the numerical data. The slope on the linear fit was recorded and the y-intercept was discarded. The slope provides information about the rate of change observed in the data. The y-intercept is arbitrary and thus not important.

R^2 is a statistical measure of how correlated the data and the fitted linear regression line are to each other. R^2 values can range from 0 to 1. An R^2 value of 0, for example, indicates a poor correlation whereas an R^2 of 1 indicates that the fitted linear regression matches the data exactly. In general, a higher R^2 means a stronger correlation between data and the linear regression. However, R^2 values are highly dependent on the type of study. With regards to the water samples taken for this study, an R^2 of 0.3 or greater is considered to be indicative of a strong correlation given the many variables involved in a complicated system such as an RSC (Personal Discussion with Dr.Kaushal). Some of these variables are leaf litter, tree shade, human inputs, and groundwater influence.

Influence of Rain on October 2020 dataset

The October 2020 data set was taken after a rain event. The hydrological conditions of the UMD RSC were impacted by the rain and thus the water chemistry was possibly altered. The rain event could have diluted concentration of trace elements and deposit terrestrial sourced DOM. Furthermore, the rain event could have overshadowed any diurnal cycle present in the RSC system.

October 2020 Dataset (After Rain Events)

A. Spectrofluorometric data

Plots of the Fluorescent Index (FI) for the upstream and downstream riffle weirs and the pool are shown in Fig. 4 a-c. Sampling started on 10/27/2020 2:00 pm and ended 10/28/2020 2:00 pm. The data points are separated by an hour. The y-axis is the calculated index for each water sample. The RSC pool, downstream, and upstream riffle weirs are plotted next to each other. Nighttime is denoted as a grey background, and day is denoted as a clear background. A line of best fit and an R^2 value is displayed within the plot. This format is used to plot all the spectrofluorometric data for the October 2020 data set.

FI values ranged from 1.47 to 1.56 for all RSC localities. We note that the average values for the three positions are 1.53 (pool), 1.49 (upper weir) and 1.50 (lower weir). These values suggest a predominantly terrestrial source for the organic matter. In the RSC pool, FI increased linearly over a 24-hour period with a slope of 0.045, and a R^2 value of 0.56. In the downstream riffle weir, FI increased linear over the 24-hour period. The linear slope was 0.0150, with an R^2 valued of 0.18. In the upstream riffle weir, a decreasing linear trend was observed. A calculated slope of -0.0133, with an R^2 value of 0.21.

As noted above, the FI provides information on the source of organic matter found in the stream. The observed average values clustered about 1.5 suggest a terrestrial origin as the predominant source of the organic matter, that is, it has recently entered the stream from urban runoff and not being generated in the stream itself. However, the steeper slope observed in the pool suggests an increase in microbial

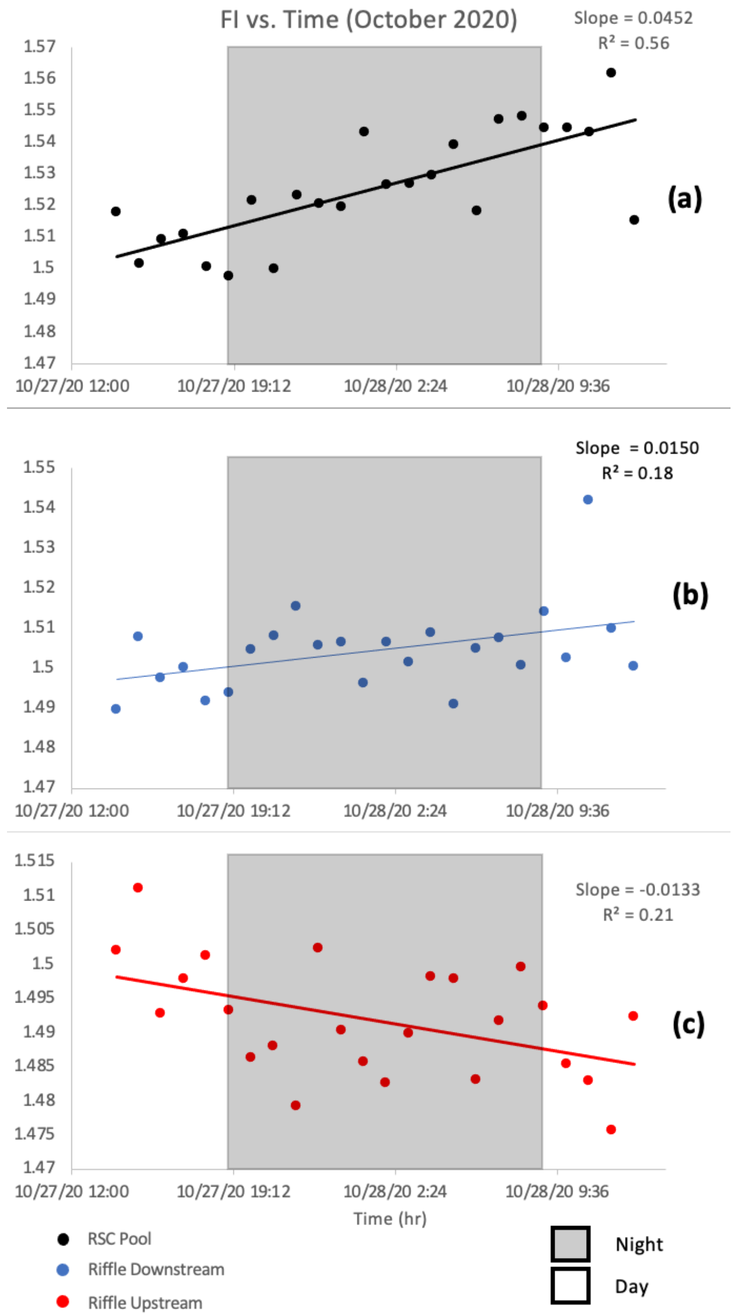


Figure 4 a-c: FI for each sample is plotted against time. A Linear Least Square fit is plotted on the graphs. Error bars not plotted as analytical uncertainty is less than 2% (Jiang and Kaushal, 2013).

activity in the pool when compared with the slopes of the two riffle weirs. In the downstream and upstream riffle weir, there was different observation. The downstream riffle weir saw an increase in microbial sourced DOM. However, in the upstream riffle weir, an increase in terrestrial sourced DOM was observed, the downward slope over time. One possibility for this observation is that the upstream riffle weir was closer to the source of the urban runoff leading to a decrease in FI. There was no observed difference between day and night from the FI data.

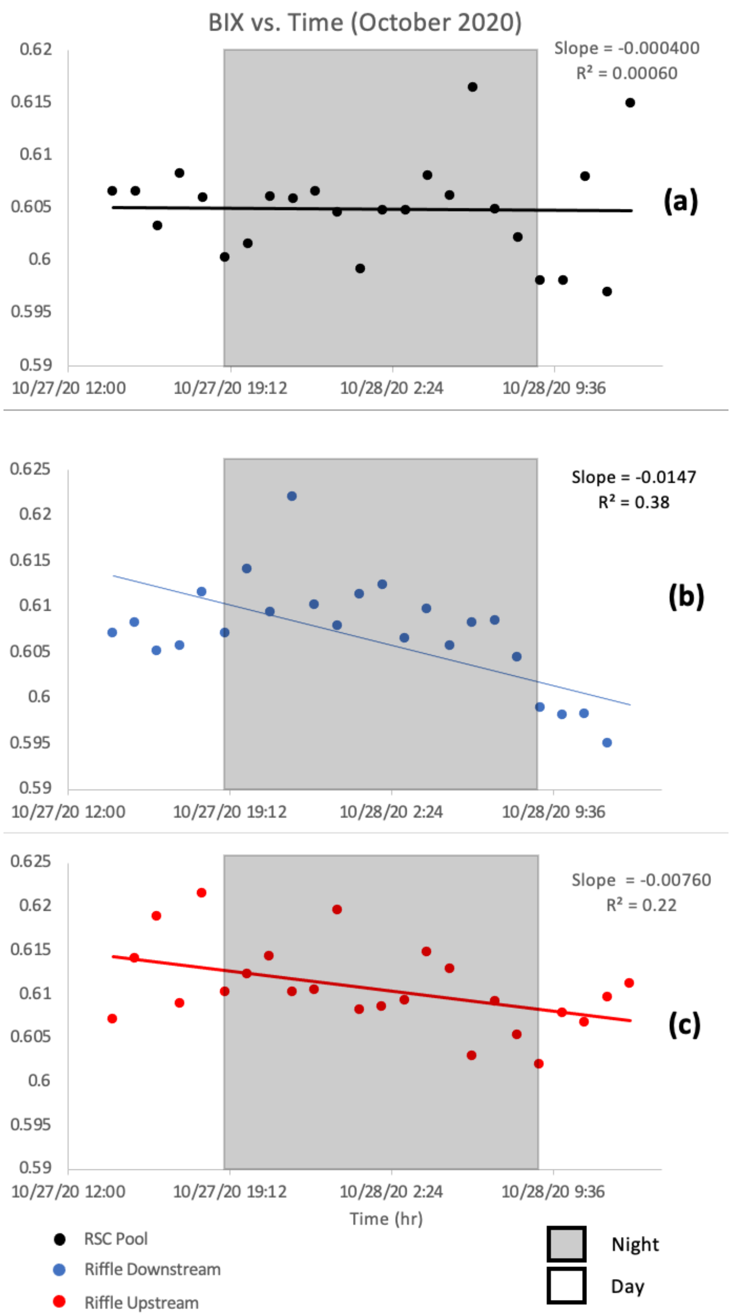


Figure 5 a-c: BIX for each sample is plotted against time. A Linear Least Square fits are plotted on the graphs. Error bars not plotted as analytical uncertainty is less than 2% (Jiang and Kaushal, 2013).

Plots of the Biological index (BIX) for the upstream and downstream riffle weirs and the pool are shown in Fig. 5 a-c. BIX values ranged from 0.60 to 0.65 for all three localities. We note that the average values for the three positions are 0.60 (pool), 0.61 (upper weir) and 0.61 (lower weir). These values suggest a predominantly terrestrial source for the organic matter. This is consistent with the FI data discussed above.

Linear least square fits to the data have been made for all three positions. Although there is considerable scatter in the data, all three slopes are negative. These are indicated in Fig. 5 a-c for each plot. This suggests there might be a recent introduction of some terrestrial sourced organic matter into the Campus Creek system. Otherwise, one might expect the BIX values to be constant over time. We note that the negative slope in the FI data for the upstream weir may indicate a recent influx of terrestrial organic matter and if so, this may be borne out by the consistent negative slopes in the BIX data. Further work would be needed to confirm this. There was no observed difference between day and night in the BIX data.

Plots of the Humification Index (HIX) for the upstream and downstream riffle weirs and the pool are shown in Fig. 6 a-c. HIX values ranged from 8.4 to 11.6 for all RSC localities. We note that the average values for the three positions are 10.4 (pool), 10.7 (upper weir) and 10.7 (lower weir). These values suggest a predominantly terrestrial source for the organic matter. This is again consistent with the FI and BX results.

Linear least squares fits are shown for each location in Fig. 6 a-c. The slopes for the three sites are -1.39 (pool), -0.88 (lower weir), and -0.12 (upper weir). The HIX data agree with the BIX and FI data and indicate the introduction of fresh DOM that is either hard to break down through microbial activity or there hasn't been sufficient time for it to be broken down. With regard to the latter, we note that the negative slope in the pool is steeper than both weirs. This may indicate more intensive microbial activity in the pool where the water is less mobile, thereby driving down the HIX values faster than in the weirs. In all three cases, however, the slopes are negative suggesting the presence of microbial activity. There was no observed difference between day and night for HIX.

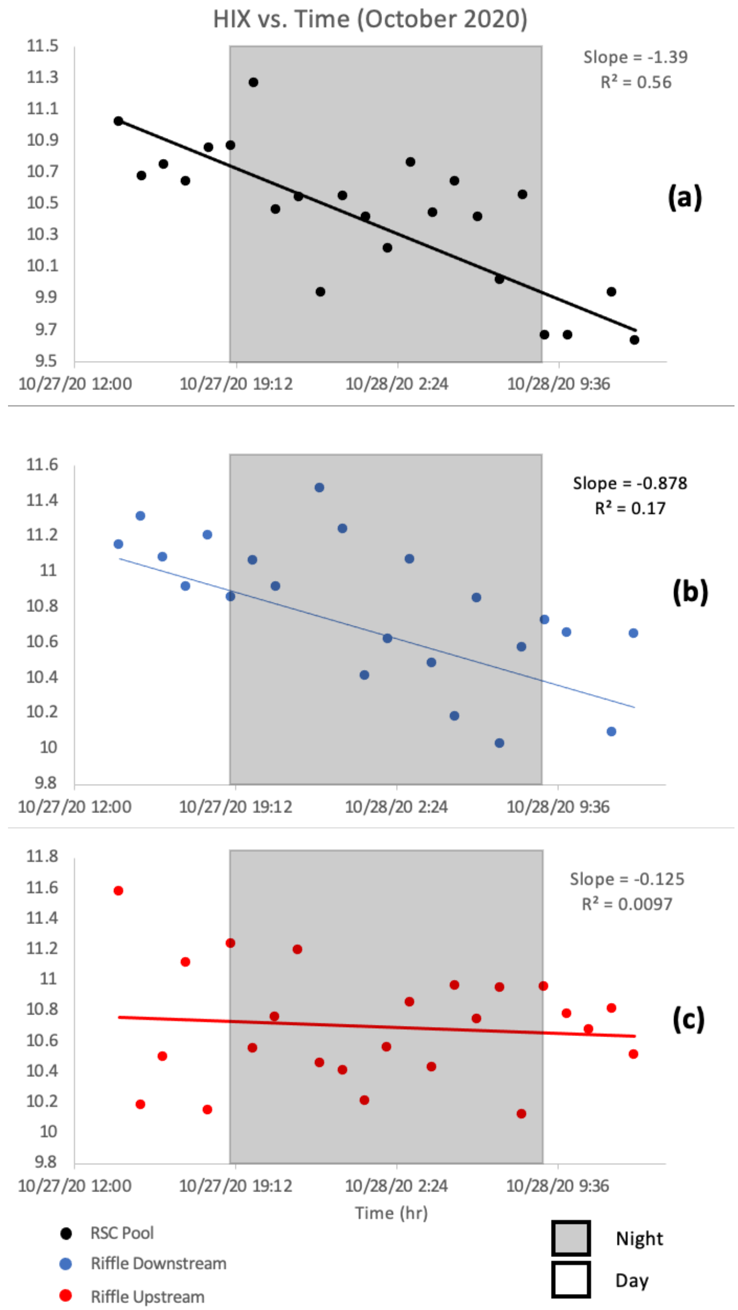


Figure 6 a-c: HIX for each sample is plotted against time. A Linear Least Square fits are plotted on the graphs. Error bars not plotted as analytical uncertainty is less than 2% (Jiang and Kaushal, 2013).

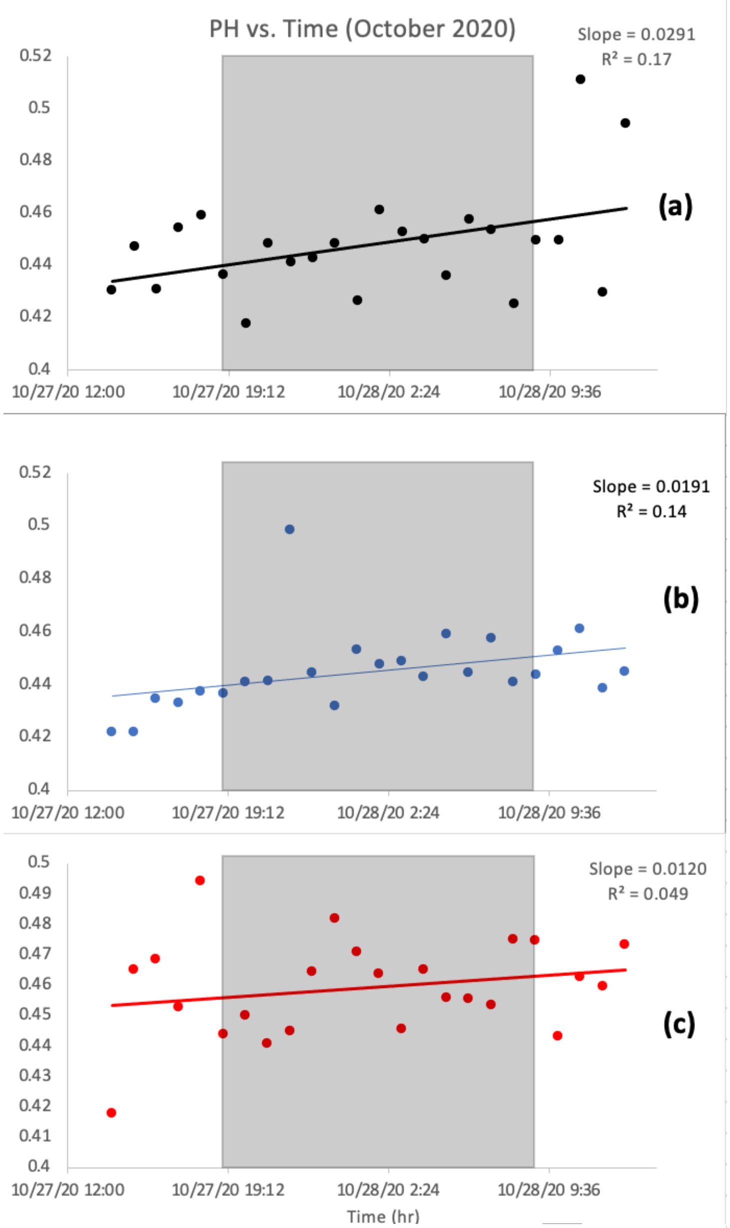


Figure 7 a-c: PH for each sample is plotted against time. A Linear Least Square fits are plotted on the graphs. Error bars not plotted as analytical uncertainty is less than 2% (Jiang and Kaushal, 2013).

Plots of the protein-like to humic-like organic matter (PH) for the upstream and downstream riffle weirs and the pool are shown in Fig. 7 a-c.PH values ranged from 0.41 to 0.51 for all RSC localities. We note that the average values for the three positions are 0.45 (pool), 0.46 (upper weir) and 0.44 (lower weir). These values suggest a predominantly terrestrial source for the organic matter, consistent with the FI, BIX, and HIX data.

The upstream riffle weir had higher values of PH than the RSC pool and downstream riffle weir. The RSC pool saw the highest change with a slope of 0.0291, with a R^2 value of 0.17. The downstream riffle weir saw the second highest change with a slope of 0.0191, with a R^2 value of 0.137. The upstream riffle weir saw the smallest degree of change, with a slope of 0.012, with a R^2 value of 0.049. There was no difference between day and night in relation to PH index.

A. OES data (elemental analysis)

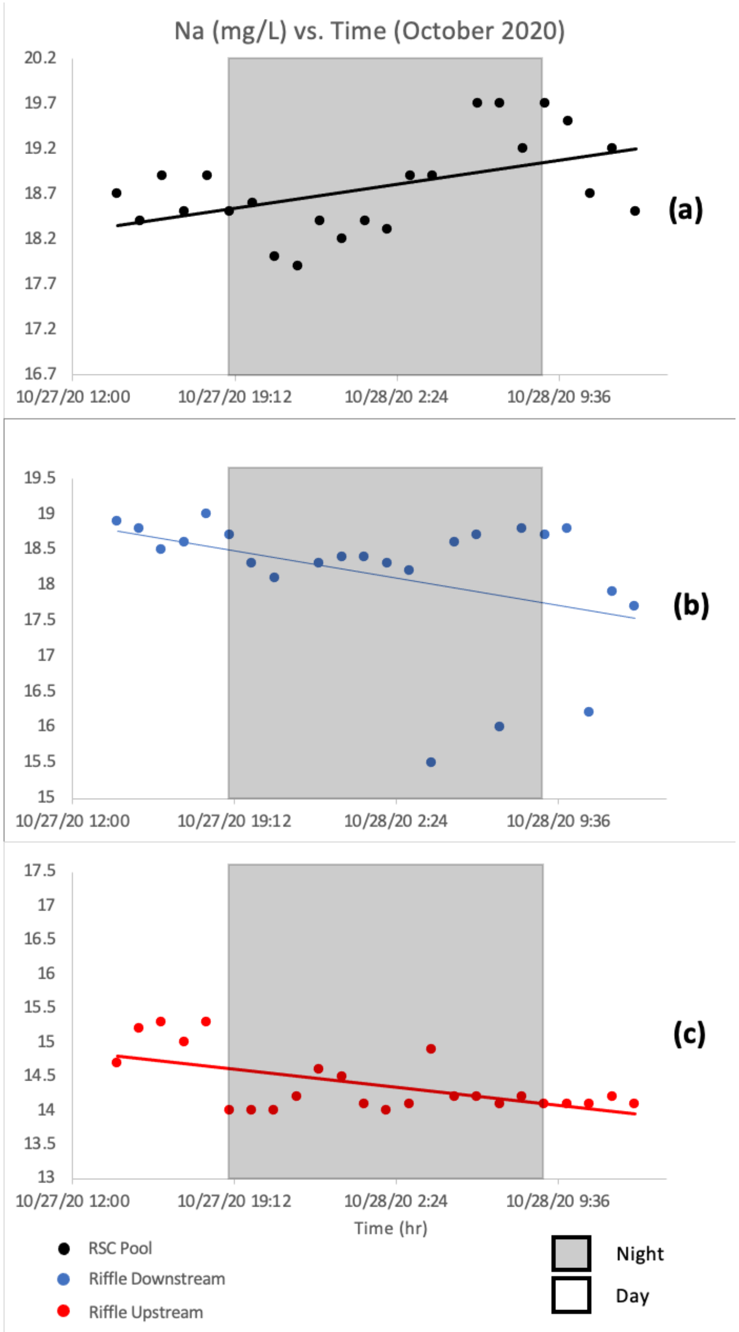


Figure 8 a-c: Sodium concentrations for each sample is plotted against time. A Linear Least Square fits are plotted on the graphs.

In Fig. 8, sodium concentrations (mg/L) are plotted against time for a 24-hour period in October 2020. The sampling started on 10/27/2020 13:00 and ended 10/28/2020 13:00. The x-axis is date and time. The individual data points are separated by an hour. On the y-axis is concentration is mg/L. The grey area coincides with night, and the white area coincides with day.

In the RSC pool concentrations of sodium appear to oscillate with a period of about 16 hours. The highest sodium concentration occurs around 7:00 am. The lowest sodium concentration appears to happen shortly after sunset around 20:00. The seconded peak is higher than the first peak.

In the downstream riffle weir, an oscillating pattern for sodium concentration was also observed. The peaks for sodium concentrations appear to occur before sunset and shortly after sunrise. The lowest sodium concentrations occur after sunset around 20:00. The oscillating pattern of sodium concentrations between the downstream riffle weir and RSC pool are similar.

In the upstream riffle weir, there was no observed oscillating pattern in sodium concentration. Instead, we see a decrease over the 24-hour period. Sodium is a major dissolved ion in water and the concentration of which is dependent on the surrounding lithology and human input. In the campus creek RSC system, a 24-hour sampling run in October 2020 saw an oscillating pattern for the RSC pool and downstream weir. Peaks coincide with the hour before sunset and after sunrise. Lows were observed shortly after sunset. In the upstream riffle weir, a decreasing trend was observed.

Plots of Fe^{2+} concentrations against time are shown in Fig. 9 a-c. The upper plot is for the pool, the middle is the downstream weir, and the bottom plot the upstream weir. Average iron concentrations are 0.27 mg/L (pool), 0.27 mg/L (lower weir), and 0.25 mg/L (upper weir). Overall, these trace amounts (<1 mg/L) suggest that the Campus Creek is well oxygenated by the riffle weirs otherwise larger values might be expected.

Ferrous iron (Fe^{2+}) is a biologically reactive element. Under well-oxygenated conditions, microbial activity oxidizes Fe^{2+} to Fe^{3+} which quickly precipitates as the oxide $Fe(OH)_3$. This immobilizes the iron. The trace amounts of Fe^{2+} suggest the Campus Creek RSC system is working. Conversely, under anoxic conditions, microbial activity reduces the iron to Fe^{2+} and we might expect Fe^{2+} concentrations to increase.

The positive slopes observed in the weirs and the pool indicate the production of Fe^{2+} possibly under anoxic conditions although overall concentrations are low. The steepest slope is seen in the RSC pool with a slope of 0.1544. Presumably the more stagnant waters of the pool create an anoxic environment and lead to the highest growth rate of Fe^{2+}.The concentrations of dissolved Fe^{2+} in the RSC system were not affected by the day and night cycle.

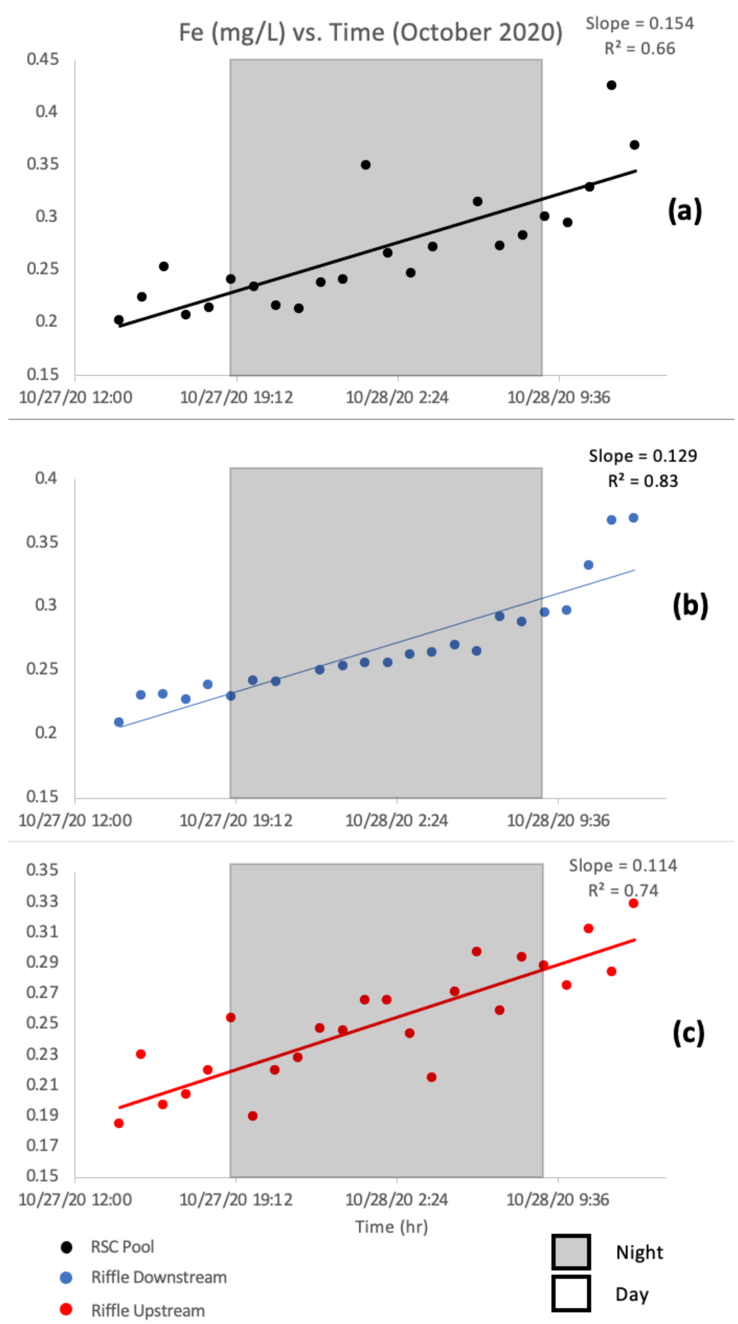


Figure 9 a-c: Iron concentrations for each sample is plotted against time. A Linear Least Square fits are plotted on the graphs.

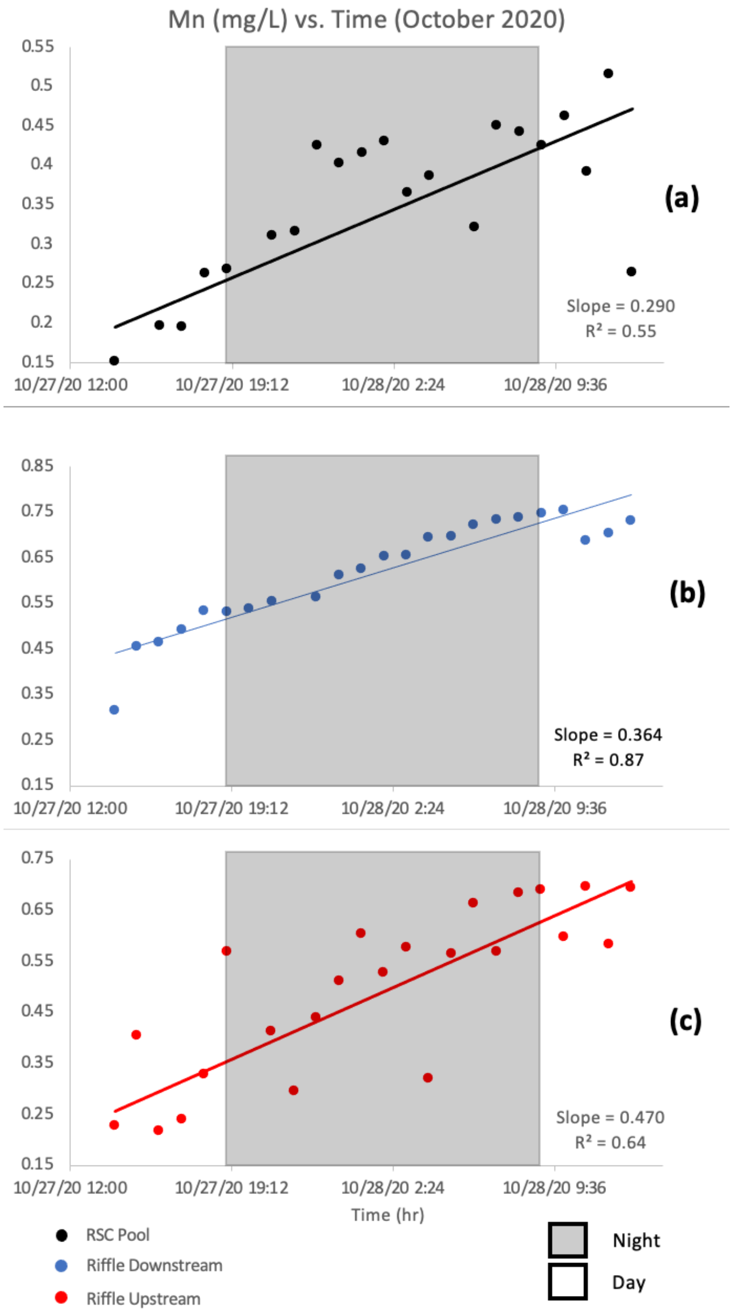


Figure 10 a-c: Manganese concentrations for each sample is plotted against time. A Linear Least Square fits are plotted on the graphs.

Like iron, manganese is a biologically reactive metal. Dissolved Mn^{2+} is the product of anoxic redox reactions. In Fig. 10 the concentration of dissolved Mn^{2+} is plotted against time. Average concentrations are: 0.33 mg/L (pool), 0.62 mg/L (lower weir), and 0.48 mg/L (upper weir). Concentrations of Mn^{2+} were higher than concentrations of Fe^{2+}.

In the upstream riffle weir, the largest change was observed. The upstream riffle weir has a calculated slope of 0.470 and a R^2 value of 0.64. The downstream riffle weir saw second largest observable change in the 24-hour period. The downstream riffle weir had a calculated slope 0.364 and a R^2 value of 0.87. The RSC pool had the smallest observable change in concertation. The RSC pool has a calculated slope of 0.290 and a R^2 value of 0.55.

Although concentrations are low in all three positions, suggesting as was the case with the Fe, that the Campus Creek is well oxygenated, the positive slopes do indicate some anoxic activity on the part of microbes present in the stream. No day-night effect was observed.

Plots of the phosphorus concentrations for the upstream and downstream riffle weirs and the pool are shown in Fig. 11 a-c. Phosphorus concentrations ranged from 0.01 to 0.11 mg/L for all RSC localities. We note that the average values for the three positions are 0.07 mg/L (pool), 0.06 mg/L (upper weir), and 0.09 mg/L (lower Weir).

In the RSC pool phosphorus concentrations decreased linearly over a 24-hour period with a slope of -0.02 with a R^2 value of 0.13. In the downstream riffle weir, P decreased linearly over time with a slope of -0.06, with a R^2 value of 0.23. In the upstream riffle weir, P decreased linear with a slope of -0.007 with a R^2 value of 0.01. There was no observed difference between day and night for P concentrations.

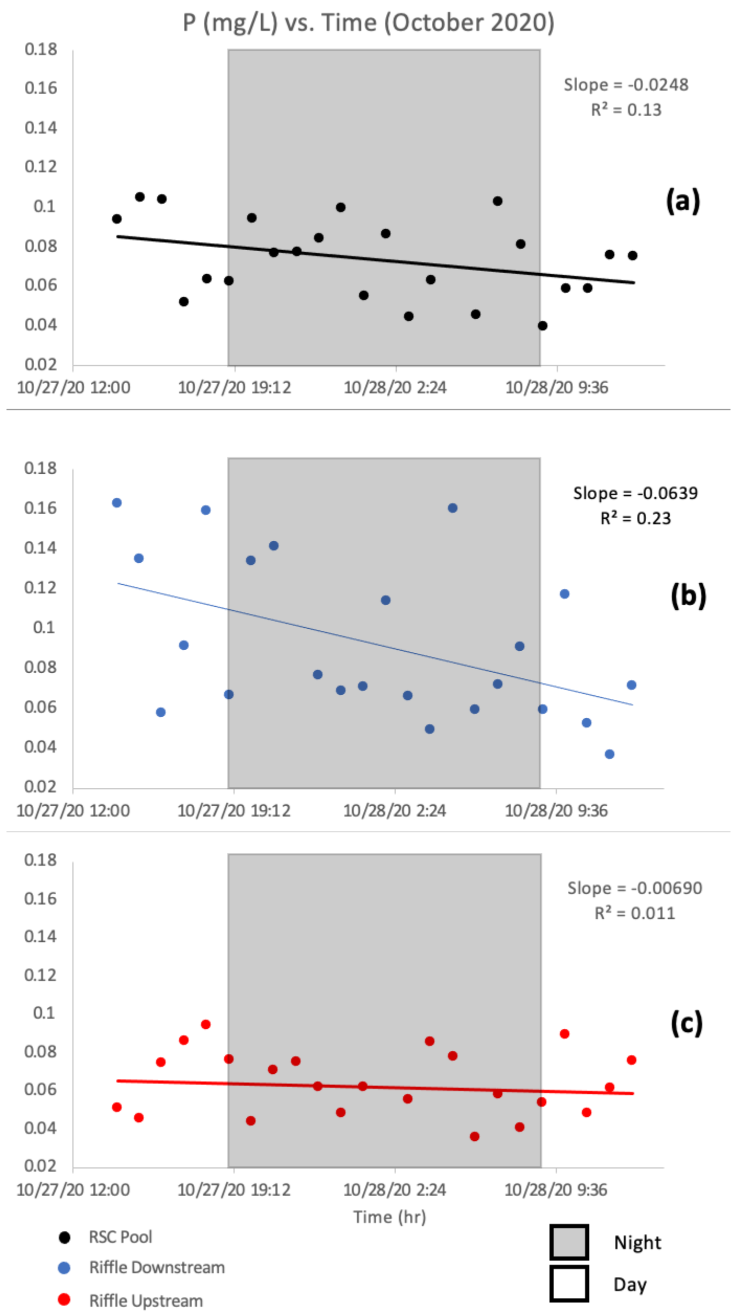


Figure 11 a-c: Phosphorus concentrations for each sample is plotted against time. A Linear Least Square fits are plotted on the graphs.

Summary of October 2020 data (After Rain Event)

The October 2020 OES and spectrofluorometric data suggest that similar relationships were occurring in the riffle weirs and RSC pool. The FI, BIX, HIX, and PH suggest that DOM was terrestrial sourced, fresh, and had a large amount of humic material. This suggests that DOM was recently added into Campus Creek by urban runoff. However, an observed increasing trend in FI and PH suggests that DOM was becoming more suitable for microbes. The OES data suggests that conditions were becoming more anoxic because the concentrations of Fe^{2+} and Mn^{2+} were increasing (see Fig. 9 & 10), although overall were well below 1 mg/L, which means the riffle weirs are doing their job to oxygenate the stream. The increasing concentrations could be attributed to microbial redox reactions. Furthermore, Fe^{2+} and Na^+ were observed at higher concentration in the RSC pool when compared to the riffle weirs. This suggests that Fe^{2+} and Na^+ are being deposited and stored in the stagnant pools. Lastly, phosphorus concentrations were decreasing, which can be attributed to the presence of algae. The October 2020 dataset suggests that microbial activity is increasing over the 24-hour period, as indicated by the observed trends in Fe^{2+}, Mn^{2+}, FI, and PH.

February 2021 Dataset (Before, During, and After Snow Events)

The February datasets consists of two sampling runs. The first dataset is composed of sample taken from February 11, 2021 to February 15, 2021 for the RSC pool. Samples were taken every 2 hours over the 4-day timespan. The second dataset was taken from February 18, 2021 to February 25, 2021. Samples were taken every 3 hours for the first three days and then samples were taken every 4 hours for the next 4 days. The February samples were taken in conjunction with snow and rain on snow (ROS) events. All samples were analyzed with an Oakton pH Testr for pH, total dissolved solids (TDS), salinity, and conductivity. The samples were also analyzed with a spectrofluorometer for FI, BIX, HIX, and PH values as was done for the October dataset. No elemental analysis was performed.[1]

Oakton pH Testr Model 50 data

<u>pH of RSC pool 18</u>

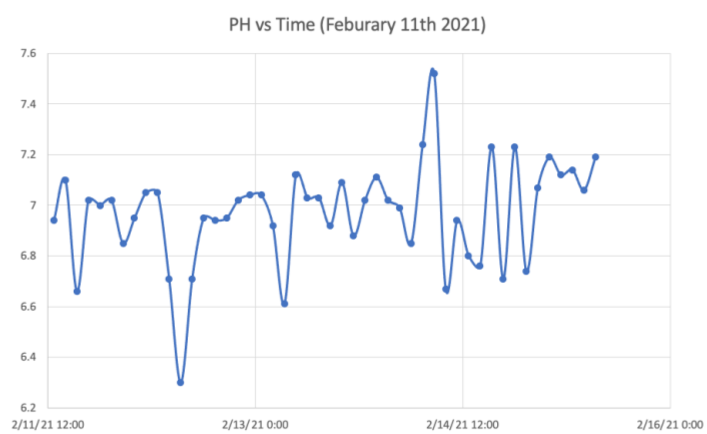


Figure 12: pH for each sample plotted against time.

In Fig. 12, pH is plotted against time for a 4-day period in February. The sampling started on February 11, 2021 and ended February 15, 2021. The x-axis is date and time. The individual points are separated by two hours. pH ranged from 6.28 to 7.52 on 2/12/21 11:00 and 2/14/21 19:00 respectively. There is variation in the data, but the average pH (6.97) is nearly neutral.

[1]The OES was not available. There was a problem with the OES chiller. Samples are stored and will be analyzed when the OES is operational.

pH of the Upstream Riffle Weir

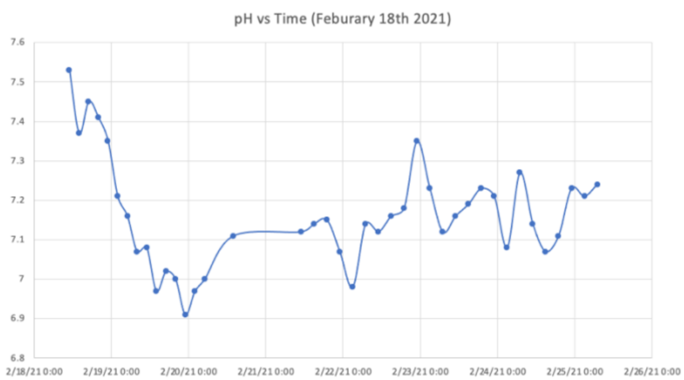


Figure 13: pH for each sample plotted against time.

In Fig.13, pH is plotted against time for the 7-day period sampling event: The sampling started on February 18, 2021 11:00 and ended February 25, 2021 7:00. The x-axis is date and time. The individual points are separated by three hours in the first three days. In the last four days, points are separated by four hours. pH ranged from 6.91 to 7.53 on 2/19/21 23:00 and 2/18/21 11:00 respectively. The average pH (7.16) is slightly alkaline. The pH initially drops from the maximum to the minimum at the start of sampling. This decreasing trend is defined as episodic acidification. Episodic acidification can be the result of salt dissolutions. As salts dissolve, the anion attaches itself to hydrogen atoms to form strong and weak acids. The creation of these acids can quickly decrease the pH of water over a short time span. After that the, pH rebounds and hovers around neutral pH. The cation from the salt is dissolved in the water column where it is transported to the soil or the coast.

The February 11 pH data shows many fluctuations; however, the high and low values oscillate above and below a neutral pH of 7 when averaged over time. A neutral pH is consistent with the October 2020 elemental data in which only trace amounts of Fe^{2+} and Mn^{2+} were measured as one might expect their solubility to increase with a lower pH. The Feb 18 pH data, on the other hand, exhibits a different behavior. Initially the samples are basic, but over the course of a day the pool becomes increasingly acidic until it reaches a pH of 6.91, after which the pH rebounds to about 7.12 then oscillates about this value in a fashion similar to the February 11 data. This episodic acidification followed a rain on snow event after which it is believed road salts entered the stream around February 18.

Conductivity, Salinity, and Total Dissolved Solids

The February 11 samples were also analyzed for conductivity, total dissolved solids, and salinity. Results are shown in Fig. 14 a-c. One can observe a marked change in these three parameters starting about Feb 13. Prior to that, a baseline for the variables was calculated as the average of data before the sudden spike. The baseline for conductivity, TDS, and salinity are calculated to be 749 muS, 538 ppm, and 0.376 ppt, respectively. These are indicated by the orange lines in the plots.

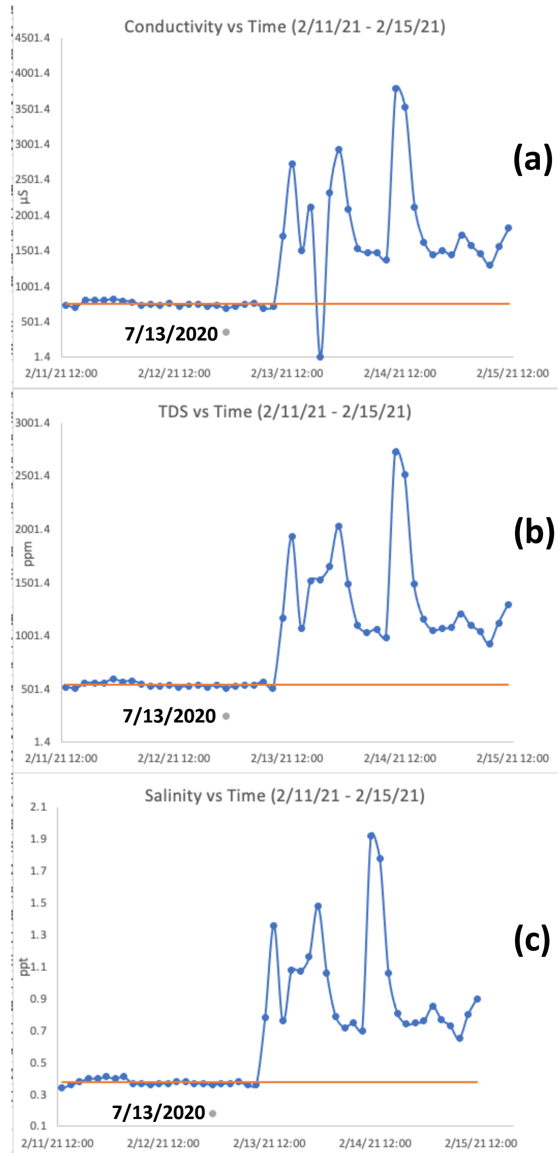


Figure 14 a-c: Specific Conductance (mµS), TDS (ppm), and salinity (ppt) for the upstream riffle weir. All figures have the same x-axis. A baseline is plotted in orange and represents stable conditions prior to the increase in these parameters. The gray dot made indicates values measured on 7/13/20.

An explanation for the rapid increase in these three parameters, all occurring at the same time, can be attributed to the addition of road salts to Campus Creek by urban runoff and snow melt. The Campus Creek has been measured weekly for conductivity, TDS, and salinity since the summer of 2018. As a point of reference, the July 15 data are indicated by the gray data point in each of the plots. The data point, taken during the summer, was chosen as a reference point to indicate what these parameters would be if there were a no-snow event and consequently no road salt runoff.

Nonetheless, all the Feb 11 data show elevated values for conductivity, TDS, and salinity when compared to the summer data as indicated by the July 13 data point. This suggests these values remain elevated during the winter months and that road salts are continually added to the creek and not completely flushed out.

The February 18 conductivity, TDS, and salinity data are shown in Fig. 15 a-c. We note each plot has a double peak, the first peak being larger than the second peak. The first peak is at 3110 muS (conductivity), 2210 ppm (TDS), and 1.58 ppt (salinity). The second peak is 2130 muS (conductivity), 1560 ppm (TDS), and 1.09 ppt (salinity). Both peaks are followed by a rapid decline, but like the February 11 data do not fully return to the levels seen at the outset of the measurements.

These double peaks can be attributed to two snow events separated by about 1.5 day that occurred on Feb 19, 2021 23:00 and Feb 22, 2021 15:00 respectively. That the two peaks are clearly separated suggests that most of the road salts are flushed by the creek in roughly a day.

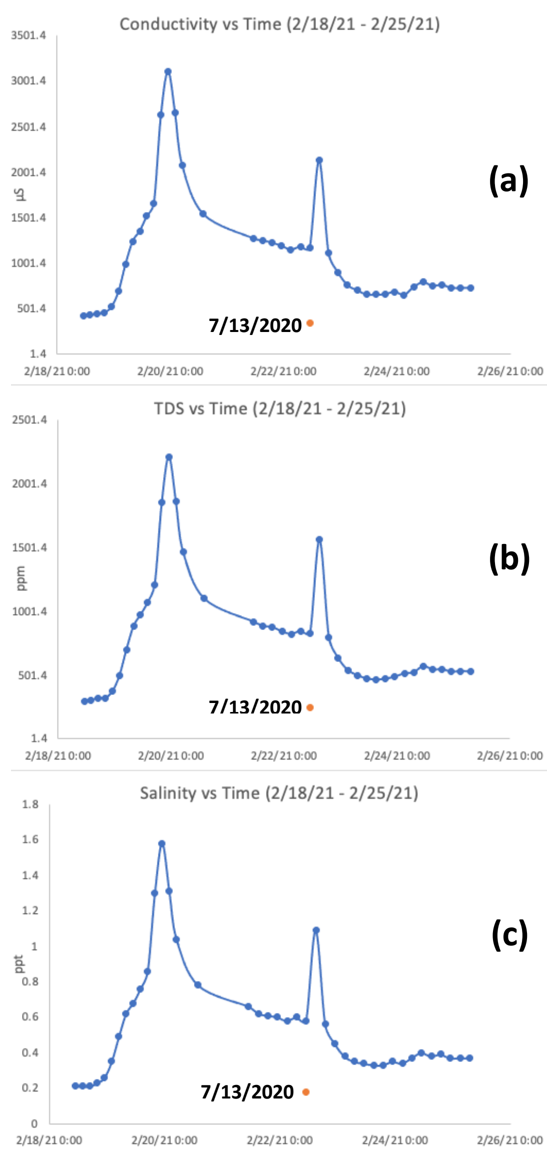


Figure 15 a-c: Specific Conductance (mµS), TDS (ppm), and salinity (ppt) for the RSC pool. All figures a-c have the same x-axis. The red dot seen a-c are measurements made on 7/13/20.

Spectrofluorometer data

The dissolved organic matter indices are Fluorescence Index (FI), Biological Index (BIX), Humification Index (HIX), and Protein-like to humic-like ratio (PH). Plots of FI, BIX, HIX, and PH for the RSC pool are shown in Fig. 16 a-d. On the x-axis is time. On the y-axis is the FI, BIX, HIX, and PH are plotted for each sample. The FI ranges between 1.4 to 1.5, which represents terrestrial sourced DOM. The BIX is below 0.67 for a majority of the data. The HIX ranges between 7 and 12 for the majority of the data. The PH ratio stays below 0.3 to 0.7 for a majority of the data. These values are similar to those observed for the October 2020 data suggested again that the DOM is terrestrial, fresh, and hard to break down.

The one outlier that occurs on 2/14/21 at 9:00 am for all indices. That outlier point has values of 1.67 (FI), 0.88 (BIX), 1.6 (HIX), and 5.8 (PH) and may result from the sudden influx of DOM that has enhanced microbial activity. The width of this peak is about 4 to 6 hours, suggesting that the Campus Creek has flushed this organic matter out thereby lowering the microbial activity.

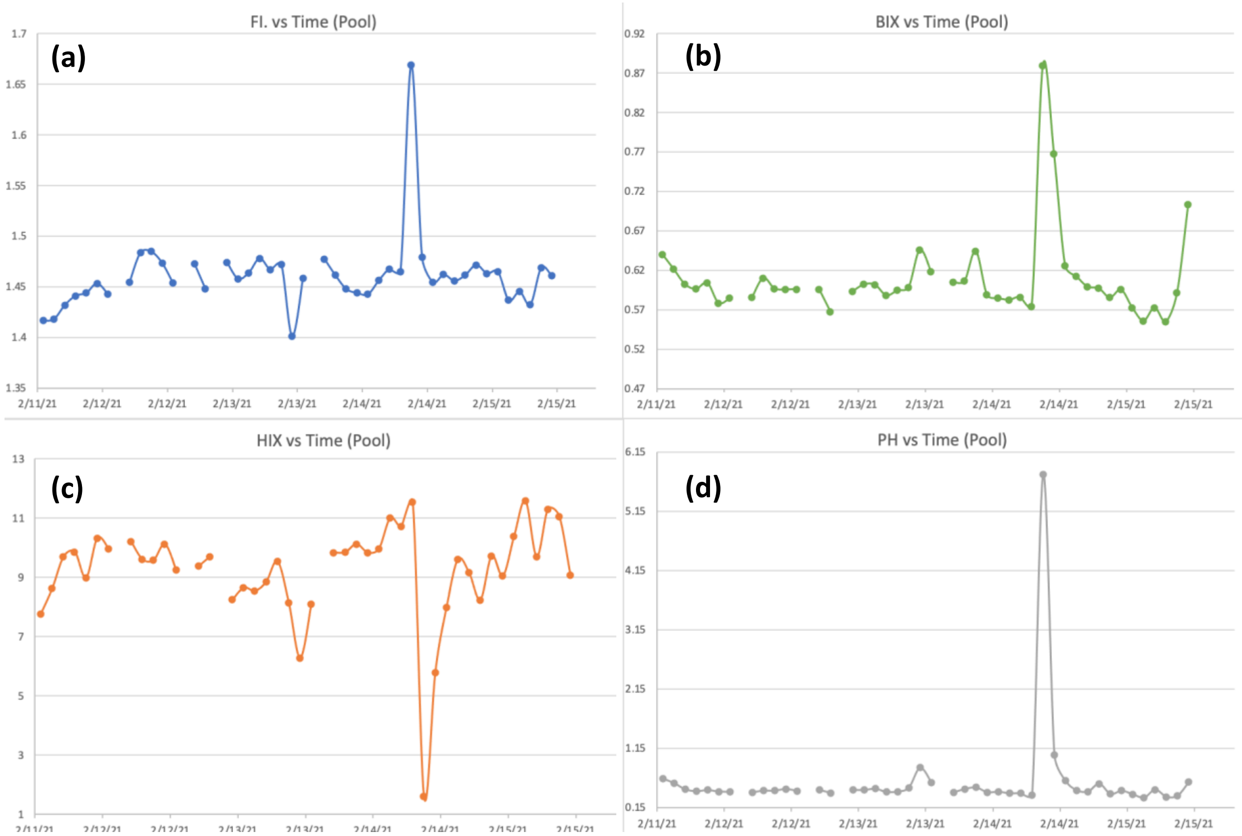


Figure 16 a-d: FI, BIX, HIX, and PH are plotted against time for the upstream riffle weir. The x-axis is the same for each plot. Error bars not plotted as analytical uncertainty is less than 2% (Jiang and Kaushal, 2013).

Plots of FI, BIX, HIX, and PH for the upstream riffle weir are shown in Fig. 17 a-d. On the x-axis is time. On the y-axis is the FI, BIX, HIX, and PH values measured for each sample. The FI ranges between 1.36 to 1.46, which indicates terrestrial sourced DOM. The BIX is below 0.61. The HIX stays between 7 and 12. The PH ratio stays below 0.2 to 0.45 for a majority of the data. The FI, BIX, HIX, and PH suggests that the DOM is terrestrial, fresh, and hard to break down. HIX and PH have a great deal of variation throughout the sample set. The microbial indices agree with each other. The trends seen in FI and BIX are similar to trends in conductivity, TDS, and salinity. FI and BIX increase from 2/18/21 11:00 to 2/19/21 23:00. The FI and BIX stay elevated around 1.44 and 0.56 respectively until 2/21/21 19:00. Then the FI and BIX decreased to 1.37 and 0.50 respectively by 2/22/21 23:00.

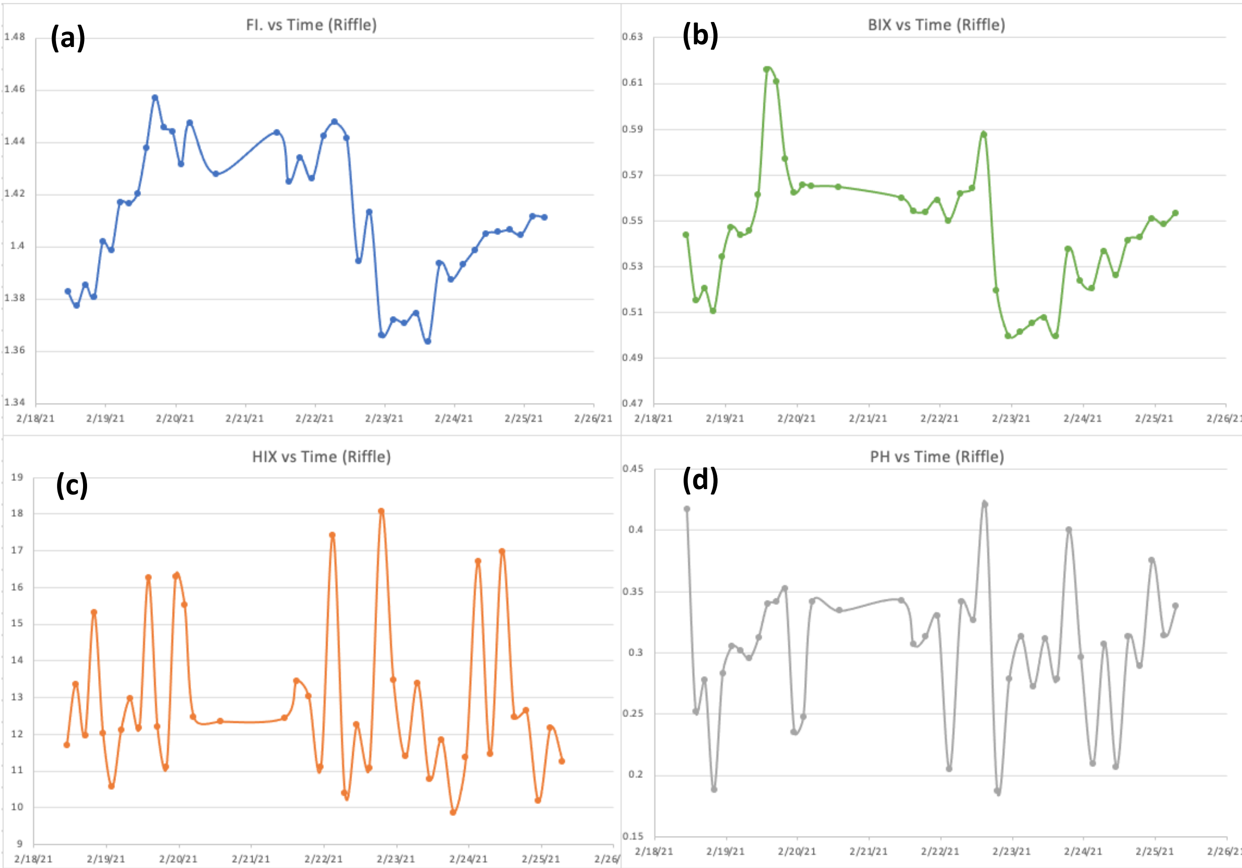


Figure 17 a-d: FI, BIX, HIX, and PH are plotted against time for the RSC pool. The x-axis is the same for each plot. Error bars not plotted as analytical uncertainty is less than 2% (Jiang and Kaushal, 2013).

Summary of February 2021 Data (Before, During, and After Snow Events)

The February 2021 Oakton pHtestr Model 50 pH meter and spectrofluorometer data suggested that salts and DOM entered the RSC pool as urban runoff. SC, TDS, and salinity rapidly increased to form peaks, that in the span of 4 to 6 hours decreased. However, the decrease never returned back to base levels. This suggests that the majority of salts are flushed out of the system in 4 to 6 hours, but some salts are retained in the upstream riffle weir and pool for longer than the data was taken (>4 days). FI and BIX are each 1.4 and 0.6 respectively. This suggests that DOM is terrestrial and fresh. However, peaks were observed with base widths of 4 to 6 hours. This agrees with the Oakton pHtestr Model 50 pH meter data that it takes 4 to 6 hours for the RSC pool to be flushed out. The peaks in the spectrofluorometric data could be the result of a first runoff following the rapid melting of snow. First runoffs usually have significantly higher concentrations of contaminants (Mangani et al., 2005).

Discussion

RSCs are a growing form of stormwater management. This work showed that there could be large changes in water chemistry in response to hydrologic events. Several aspects of water chemistry were affected: concentration of major trace elements, concentration of DOM, and concentration of nutrients. The change in water chemistry could have impacts on aquatic life and out drinking water supply. High concentrations of salts were observed in winter months, which could impact aquatic life and our drinking water supplies. More work is necessary to evaluate the influence RSC's have on water quality under a range of hydrologic conditions.

<u>Potential Sources of chemical pollution as runoff into Campus Creek</u>

Runoff in the Campus Creek catchment can be categorized by both agricultural and urban runoff. In the October 2020 data set, a slight decrease in phosphorus concentrations is observed over a 24-hour period. This suggests that phosphorus is being taken up by algae at the same rate as it enters Campus Creek. In other words, there is a nearly steady state influx of P. A possible source of P is the UMD golf course. The golf course uses fertilizers that have high concentrations of limiting nutrients: nitrogen, phosphorus, and potassium. Urban runoff is the surface flow from the UMD campus that often follows a rain or snow event. Urban runoff can also include high concentrations of metals.

In addition to the golf course, the UMD campus has many buildings and is scattered with metal pipes. The pipes can release metal ions when in contact with acidic water and salt corrosion (Wen et al., 2019) and find their way into the ground water and Campus Creek. This is a possible source of Fe^{2+} and Mn^{2+} in Campus Creek. One can observe multiple red clouds and black residue the Campus Creek RSC system. The red clouds are formed by precipitating $Fe(OH)_3$ from creek water. Likewise, the black residue is formed by precipitating Mn^{4+} from the creek water. The creek has effectively immobilized these elements. The concentrations of both Fe^{2+} and Mn^{2+} are overall low in the creek (< 1 mg/L) but have a tendency to increase over the 24 hours the measurements were made. This suggests that some microbial activity is taking place to drive this observation. This is supported by the spectrofluorometric data.

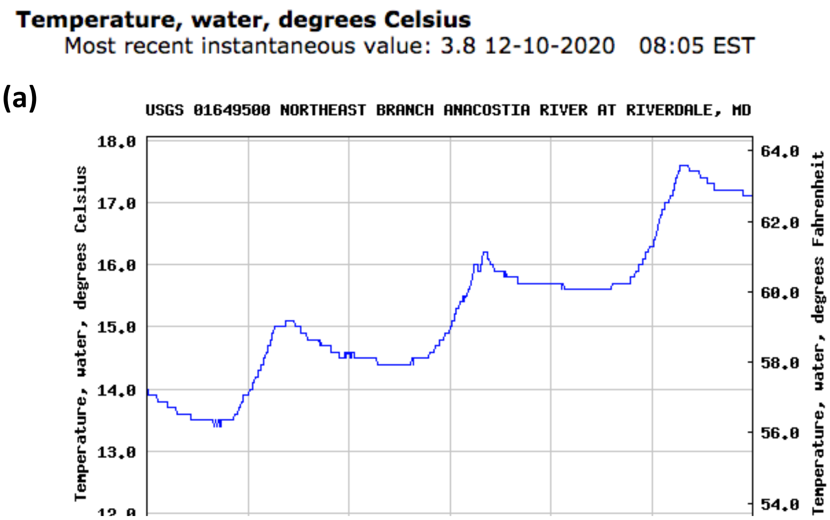
Urban runoff of salts often mobilizes trace metals ions. In MD-Washington streams during winter months experienced increased of Mn^{2+} (Kaushal et al., 2018). The increase of trace metal ions was the result of snow melt and road salt applications. Concentrations of Mn^{2+} decayed slowly back to prior conditions. In the Campus Creek RSC system, a similar trend is observed in February snow events for SC, TDS, and salinity.

<u>The Role of Rain Events on Diurnal Water Chemistry in RSCs</u>

Turning to the question of diurnal cycle, the October dataset had no observable day and night trend seen above. There could be more than one reason for this. One possibility is that no day and night cycle exist for the Campus Creek. A second possibility is that recent rain event reset the conditions of the Campus Creek system and indications of microbial activity had to grow back in. Since the Campus Creek watershed is too small to monitor on a regular basis, the Northeast Anacostia River was used as a reference.

Data was taken from the USGS waterwatch in 15 min intervals of discharge and temperature as seen in Fig. 18 a-b. The increasing temperature and decreasing discharge suggest two things. The discharge could have flushed out the Campus Creek system of Fe^{2+} and Mn^{2+}. There also was an observed increased in temperature over the same time period, which could have increased microbial activity during both day and night. This is why we may not see a diurnal cycle in the spectrofluorometric and OES analyses.

(a)



(b)

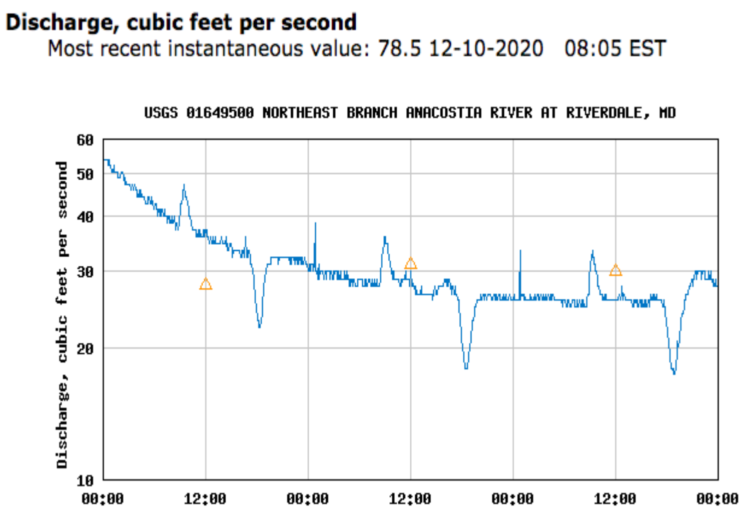


Figure 18 a-b: Temperature and discharge against time for the North East Anacostia. The dates line up with the October 2020 dataset. The data is from USGS waterwatch and the data points are separate by 15 mins.

The February 11 pH data indicates that the creek was nearly neutral with some fluctuation. Over the 4-day period, the average pH was 6.97. However, the February 18 pH data shows a different behavior, one of episodic acidification. This can be attributed to the introduction of salts into the stream which shifts the water equilibrium to more acidic values.

Impacts of Snow Events on Water Chemistry in RSCs

The introduction of salts is indicated by the rapid increase in SC, TDS, and salinity. The peak is followed by a rapid decay; however, measurements never return to base levels over the observed timespan. The peaks had widths of about 6 to 9 hours. This suggests that it takes 6 to 9 hours for Campus Creek to flush out most of the salts. In the riffle weir this is seen as a double peak created by two separate snow and rain on snow event. In the RSC pool this is two separate peaks separated by about 1.5 days.

The spectrofluorometric data for February match the data from October. In both months the DOM was terrestrial, fresh, and hard to break down. However, in the February conductivity, TDS, and salinity measurements spectra there are peaks that have widths of 4 to 6 hours. The peaks could be the result of first runoff. Before snow melts it retains much urban runoff. After it melts, runoff rapidly enters a stream. This can create conditions favorable for microbial activity. This could explain the peaks observed in the February 11 data set on February 14.

Conclusions

The Campus Creek RSC system was used for this study. Water samples were taken once in October and twice in February. The October dataset followed an autumn rain event. The spectrofluorometric analyses are consistent with a terrestrial DOM is terrestrial in origin. The Fe^{2+} and Mn^{2+} are in acceptable limits for trace metals (< 1 mg/L) but do suggest some microbial activity (Gaillardet et al., 2003). No diurnal effect was observed in either the OES data or the spectrofluorometric data. If such an effect does exist it may have been masked by a warming trend over the time the data was collected as seen in the Anacostia River where measurements are made daily.

Data were collected twice in February: (1) during a snow event, and (2) during a snow and rain on snow event. In both cases SC, TDS, and salinity increased with the application of road salts and snow melt. SC, TDS, and salinity rapidly decreased, however never returning to baseline levels. The spectrofluorometric analysis suggests that the DOM is terrestrial in origin. However, peaks were seen in microbial indices associated with first runoff. The peaks were 4 to 6 hours in width. This suggests that the Campus Creek flushes out the majority of the salts in that time. This is supported by the February 18 conductivity, salinity, and TDS datasets in which two clearly defined peaks are observed separated by 1.5 days.

The Author would like to acknowledge the kind assistance of Sujay Kaushal and Jenna Reimer for their help and many valuable discussions.

References

Cizek, A.R., Hunt, F.W., Winston, J.R., Lauffer, M.S. (2017). “Hydrologic performance of regenerative stormwater conveyance (RSC) in the North Carolina coastal plain.” *Journal of Environmental Engineering.* 143 (9): 05017003.

Cizek, R. A., Hunt, F. W., Winston, J. R., Waickowski, E. S. (2018). “Water Quality and Hydrologic Performance of a Regenerative Stormwater Conveyance in the Piedmont of North Carolina.” *Journal of Environmental Engineering*. 144 (8): 04018062.

Corsi, S.R., Graczyk, D.J., Geis, S.W., Booth, N.L., and Richards, K.D. (2010). “A Fresh Look at Road Salt: Aquatic Toxicity and Water-Quality Impacts on Local, Regional, and National Scales.” *Environmental Science & Technology.* 44 (19): 7376–7382.

Flores, H., Mcmonigle, D., & Underwood, K. (2012). Regenerative step pool storm conveyance (SPSC)- Design guidelines. Anne Arundel County, MD: Dept. of Public Works.

Gaillardet, J., Viers, J., Dupré, B. (2003). “Trace Elements in River Water.” *Treatise on Geochemistry.* Editors(s): Heinrich D. Holland, Karl K. Turekian. 5: 225-272.

Ghervase, L., Carstea, E. M., Pavelescu, G., Savastru, D. (2010). “Laser Induced Fluorescence Efficiency In Water Quality Assessment.” *Romanian Reports in Physics.* 62 (3): 652-659.

Hayes, K. (2016) “Regenerative Stormwater Conveyance: Design Implications of an Urban Case Demonstration in Baltimore, Maryland.” *Digital Repository at the University of Maryland.*

Hesthagen, T. (2011). “Episodic Fish Kills in an Acidified Salmon River in Southwestern Norway.” *Fisheries*. 14 (3): 10-17.

Jiang, G., Kaushal, S.S. (2013). “Characterizing carbon sources and quality in four Baltimore streams with fluorescence spectroscopy.” *University of Maryland.* GEOL 394H.

Kaushal, S. S., Groffman, P. M., Likens, G. E., Belt, K. T., Stack, W. P., Kelly, V. R., Band, L. E., and Fisher, G. T. (2005). “Increased salinization of fresh water in the northeastern united states.” *Proceedings of the National Academy of Sciences*. 102 (38): 13517–13520.

Kaushal, S.S., Belt, K.T. (2012). “The urban watershed continuum: evolving spatial and temporal dimensions.” *Urban Ecosystems.* 15: *409-435*.

Kaushal, S.S., Mayer, P.M., Vidon, P.G., Smith, R.M., Penino, M.J., Newcomer, T.A., Duan, S., Welty, C., Belt, K.T. (2014). “Land use and Climate Variability Amplify Carbon, Nutrient, and Contaminant Pulses: A Review with Management Implications.” *Journal of the American Water Resources Association.* 50 (3): 585-614.

Kaushal, S. S., Likens, G. E., Pace, M. L., Utz, R. M., Haq, S., Gorman, J., and Grese, M. (2018). "Freshwater salinization syndrome on a continental scale." *Proceedings of the National Academy of Sciences*. 115 (4): E574–E583.

Kaushal, S. S., Likens, G.E., Pace, M.L., Haq, S., Wood, K.L., Galella, J.G., Morel, C., Doody, T.R., Wessel, B., Kortelainen, P., Räik, A., Skinner, V., Utz, R., Jaworski, N. (2019). "Novel 'chemical cocktails' in inland waters are a consequence of the freshwater salinization syndrome." Phil. Trans. R. Soc. B 374: 20180017.

Koryto, M. K., Hunt, F. W., Arellano, C., Page, L. J. (2018). "Performance of Regenerative Stormwater Conveyance on the Removal of Dissolved Pollutants: Field Scale Simulation Study." *Journal of environmental Engineering*. 144 (6): 263-276.

Mangani, G., Berloni, A., Bellucci, F., Tatàno, F., Maione, M. (2005). "Evolation of the Pollutant Content in Road Runoff First Flush Waters." *Water, Air, and Soil Pollution.* 160: 213-228.

Mohod, V. C., Dhote, J. (2013). "Review of Heavy Metals in Drinking Water and their on Human Health." *International Journal of Innovative Research in Science, Engineering, and Technology.* 2 (7): 2319-8753.

Schelsinger, W. H., Bernhardt, E. S. Chapter 6 – The Biosphere: Biogeochemical Cycling on Land, Editor(s): William H. Schlesinger, Emily S. Bernhardt, Biogeochemistry (Third Edition), Academic Press, 2013, Pages 173 – 231, ISBN 9780123858740.

University of Maryland Campus Creek Stream Restoration Design Build. Project No. 14-659-056-00 QC 14484. April 25th , 2018.

Walsh, C.J., Fletcher, T.D., Ladson, A.R. (2005). "Stream restoration in urban catchment through redesigning stormwater systems: looking to the catchment to save the stream." *Journal of the North American Benthological Society.* 23 (3): 690-705.

Wen, X., Lu, L., Wu, J., Lin, Y., Luo, Y. (2019). "Influence of coastal groundwater salinization on the distribution and risks of heavy metals." *Science of The Total Environment*. 652: 267-277.

Appendix A February 2021 Dataset

Missing data is the result of machine or human failure.

Sample Date	pH	Cond (us)	TDS (ppm)	Sal (ppt)	FI	BIX	HIX	PH
2/11/21 13:00	6.94	737	521	0.34	1.42	0.64	7.77	0.64
2/11/21 15:00	7.1	705	503	0.36	1.42	0.62	8.62	0.57
2/11/21 17:00	6.66	798	552	0.38	1.43	0.60	9.69	0.46
2/11/21 19:00	7.02	805	558	0.40	1.44	0.60	9.86	0.43
2/11/21 21:00	7	800	558	0.4	1.44	0.60	8.98	0.45
2/11/21 23:00	7.02	823	591	0.41	1.45	0.58	10.32	0.42
2/12/21 1:00	6.85	797	566	0.4	1.44	0.58	9.96	0.42
2/12/21 3:00	6.95	783	577	0.41				
2/12/21 5:00	7.05	739	545	0.37	1.45	0.59	10.21	0.41
2/12/21 7:00	7.05	740	526	0.37	1.48	0.61	9.61	0.44
2/12/21 9:00	6.71	737	527	0.36	1.48	0.60	9.58	0.43
2/12/21 11:00	6.28	756	538	0.37	1.47	0.60	10.12	0.46
2/12/21 13:00	6.71	724	517	0.37	1.45	0.60	9.24	0.43
2/12/21 15:00	6.95	746	530	0.38				
2/12/21 17:00	6.94	752	535	0.38	1.47	0.60	9.38	0.45
2/12/21 19:00	6.95	723	520	0.37	1.45	0.57	9.70	0.40
2/12/21 21:00	7.02	727	532	0.37				
2/12/21 23:00	7.04	692	505	0.36	1.47	0.59	8.24	0.45
2/13/21 1:00	7.04	723	529	0.37	1.46	0.60	8.65	0.45
2/13/21 3:00	6.92	747	532	0.37	1.46	0.60	8.54	0.47
2/13/21 5:00	6.61	761	538	0.38	1.48	0.59	8.85	0.42
2/13/21 7:00	7.12	692	564	0.36	1.47	0.59	9.54	0.42
2/13/21 9:00	7.03	724	509	0.36	1.47	0.60	8.14	0.49

2/13/21 11:00	7.03	1703	1170	0.78	1.40	0.65	6.28	0.82
2/13/21 13:00	6.92	2730	1930	1.36	1.46	0.62	8.10	0.58
2/13/21 15:00	7.09	1507	1070	0.76				
2/13/21 17:00	6.88	2110	1520	1.08	1.48	0.61	9.84	0.41
2/13/21 19:00	7.02	2.13	1530	1.07	1.46	0.61	9.84	0.46
2/13/21 21:00	7.11	2320	1650	1.16	1.45	0.64	10.13	0.49
2/13/21 23:00	7.02	2920	2030	1.48	1.44	0.59	9.84	0.41
2/14/21 1:00	6.99	2080	1490	1.06	1.44	0.58	9.96	0.42
2/14/21 3:00	6.85	1534	1100	0.79	1.46	0.58	11.00	0.39
2/14/21 5:00	7.24	1473	1030	0.72	1.47	0.59	10.72	0.39
2/14/21 7:00	7.52	1475	1060	0.75	1.46	0.57	11.54	0.36
2/14/21 9:00	6.67	1370	982	0.7	1.67	0.88	1.60	5.77
2/14/21 11:00	6.94	3780	2730	1.92	1.48	0.77	5.79	1.03
2/14/21 13:00	6.8	3520	2520	1.78	1.45	0.63	7.99	0.60
2/14/21 15:00	6.76	2120	1490	1.06	1.46	0.61	9.60	0.44
2/14/21 17:00	7.23	1624	1160	0.81	1.46	0.60	9.16	0.42
2/14/21 19:00	6.71	1448	1050	0.74	1.46	0.60	8.24	0.55
2/14/21 21:00	7.23	1505	1070	0.75	1.47	0.59	9.73	0.38
2/14/21 23:00	6.74	1442	1080	0.76	1.46	0.60	9.05	0.43
2/15/21 1:00	7.07	1726	1210	0.85	1.46	0.57	10.39	0.38
2/15/21 3:00	7.19	1572	1100	0.77	1.44	0.56	11.58	0.32
2/15/21 5:00	7.12	1452	1040	0.73	1.45	0.57	9.69	0.45
2/15/21 7:00	7.14	1301	926	0.65	1.43	0.55	11.31	0.33
2/15/21 9:00	7.06	1568	1120	0.8	1.47	0.59	11.06	0.35
2/15/21 11:00	7.19	1817	1290	0.9	1.46	0.70	9.08	0.58
2/18/21 11:00	7.53	420	298	0.21	1.38	0.54	11.70	0.42
2/18/21 14:00	7.37	433	305	0.21	1.38	0.52	13.37	0.25
2/18/21 17:00	7.45	446	319	0.21	1.39	0.52	11.96	0.28

2/18/21 20:00	7.41	462	323	0.23	1.38	0.51	15.32	0.19
2/18/21 23:00	7.35	524	372	0.26	1.40	0.53	12.03	0.28
2/19/21 2:00	7.21	693	496	0.35	1.40	0.55	10.58	0.30
2/19/21 5:00	7.16	994	701	0.49	1.42	0.54	12.12	0.30
2/19/21 8:00	7.07	1244	884	0.62	1.42	0.55	12.96	0.30
2/19/21 11:00	7.08	1358	973	0.68	1.42	0.56	12.17	0.31
2/19/21 14:00	6.97	1520	1070	0.76	1.44	0.62	16.25	0.34
2/19/21 17:00	7.02	1660	1210	0.86	1.46	0.61	12.19	0.34
2/19/21 20:00	7	2630	1850	1.3	1.45	0.58	11.11	0.35
2/19/21 23:00	6.91	3110	2210	1.58	1.44	0.56	16.30	0.24
2/20/21 2:00	6.97	2650	1860	1.31	1.43	0.57	15.51	0.25
2/20/21 5:00	7	2080	1470	1.04	1.45	0.56	12.47	0.34
2/20/21 14:00	7.11	1541	1100	0.78	1.43	0.56	12.34	0.33
2/21/21 11:00	7.12	1278	918	0.66	1.44	0.56	12.45	0.34
2/21/21 15:00	7.14	1253	885	0.62	1.42	0.55	13.45	0.31
2/21/21 19:00	7.15	1230	877	0.61	1.43	0.55	13.04	0.31
2/21/21 23:00	7.07	1196	842	0.6	1.43	0.56	11.09	0.33
2/22/21 3:00	6.98	1152	823	0.58	1.44	0.55	17.42	0.20
2/22/21 7:00	7.14	1186	847	0.6	1.45	0.56	10.38	0.34
2/22/21 11:00	7.12	1169	832	0.58	1.44	0.56	12.26	0.33
2/22/21 15:00	7.16	2130	1560	1.09	1.39	0.59	11.09	0.42
2/22/21 19:00	7.18	1119	797	0.56	1.41	0.52	18.06	0.19
2/22/21 23:00	7.35	903	634	0.45	1.37	0.50	13.47	0.28
2/23/21 3:00	7.23	764	540	0.38	1.37	0.50	11.39	0.31
2/23/21 7:00	7.12	707	501	0.35	1.37	0.51	13.40	0.27
2/23/21 11:00	7.16	661	474	0.34	1.37	0.51	10.78	0.31
2/23/21 15:00	7.19	657	466	0.33	1.36	0.50	11.86	0.28
2/23/21 19:00	7.23	663	471	0.33	1.39	0.54	9.87	0.40

2/23/21 23:00	7.21	690	487	0.35	1.39	0.52	11.36	0.30
2/24/21 3:00	7.08	656	514	0.34	1.39	0.52	16.69	0.21
2/24/21 7:00	7.27	739	522	0.37	1.40	0.54	11.46	0.31
2/24/21 11:00	7.14	796	571	0.4	1.40	0.53	16.98	0.21
2/24/21 15:00	7.07	754	545	0.38	1.41	0.54	12.47	0.31
2/24/21 19:00	7.11	766	546	0.39	1.41	0.54	12.64	0.29
2/24/21 23:00	7.23	733	528	0.37	1.40	0.55	10.18	0.38
2/25/21 3:00	7.21	732	532	0.37	1.41	0.55	12.18	0.31
2/25/21 7:00	7.24	734	528	0.37	1.41	0.55	11.26	0.34

Appendix B October 2020 Dataset

Missing data is the result of machine or human failure.

Riffle Upstream	**FI**	**BIX**	**HIX**	**PH**	**Fe^{2+}(mg/L)**	**Mn^{2+} (mg/L)**	**Na^{+} (mg/L)**	**P^{3-}(mg/L)**
10/27/20 14:00	1.50	0.61	11.58	0.42	0.185	0.227	14.7	0.0511
10/27/20 15:00	1.51	0.61	10.18	0.46	0.23	0.404	15.2	0.0459
10/27/20 16:00	1.49	0.62	10.49	0.47	0.197	0.217	15.3	0.0745
10/27/20 17:00	1.50	0.61	11.11	0.45	0.204	0.24	15	0.0865
10/27/20 18:00	1.50	0.62	10.15	0.49	0.22	0.328	15.3	0.0946
10/27/20 19:00	1.49	0.61	11.24	0.44	0.254	0.569	14	0.0763
10/27/20 20:00	1.49	0.61	10.55	0.45	0.19	0.139	14	0.0439
10/27/20 21:00	1.49	0.61	10.76	0.44	0.22	0.413	14	0.071
10/27/20 22:00	1.48	0.61	11.20	0.44	0.228	0.296	14.2	0.0753
10/27/20 23:00	1.50	0.61	10.46	0.46	0.247	0.439	14.6	0.0622
10/28/20 0:00	1.49	0.62	10.41	0.48	0.246	0.511	14.5	0.0482
10/28/20 1:00	1.49	0.61	10.21	0.47	0.266	0.605	14.1	0.0624
10/28/20 2:00	1.48	0.61	10.56	0.46	0.266	0.527	14	0.0145
10/28/20 3:00	1.49	0.61	10.85	0.45	0.244	0.578	14.1	0.0557
10/28/20 4:00	1.50	0.61	10.43	0.46	0.215	0.321	14.9	0.0859
10/28/20 5:00	1.50	0.61	10.97	0.46	0.271	0.564	14.2	0.078
10/28/20 6:00	1.48	0.60	10.75	0.46	0.297	0.663	14.2	0.0361
10/28/20 7:00	1.49	0.61	10.95	0.45	0.259	0.57	14.1	0.0582
10/28/20 8:00	1.50	0.61	10.12	0.47	0.294	0.685	14.2	0.041
10/28/20 9:00	1.49	0.60	10.95	0.47	0.288	0.691	14.1	0.0539
10/28/20 10:00	1.49	0.61	10.78	0.44	0.275	0.598	14.1	0.0895
10/28/20 11:00	1.48	0.61	10.68	0.46	0.312	0.696	14.1	0.0483

10/28/20 12:00	1.48	0.61	10.81	0.46	0.284	0.583	14.2	0.0617
10/28/20 13:00	1.49	0.61	10.51	0.47	0.329	0.695	14.1	0.0759
Riffle Downstream	**FI**	**BIX**	**HIX**	**PH**	**Fe^{2+} (mg/L)**	**Mn^{2+} (mg/L)**	**Na^{+} (mg/L)**	**P^{3-} (mg/L)**
10/27/20 14:00	1.49	0.61	11.15	0.42	0.209	0.314	18.9	0.163
10/27/20 15:00	1.51	0.61	11.31	0.42	0.23	0.454	18.8	0.135
10/27/20 16:00	1.50	0.61	11.08	0.43	0.231	0.464	18.5	0.0578
10/27/20 17:00	1.50	0.61	10.91	0.43	0.227	0.491	18.6	0.0912
10/27/20 18:00	1.49	0.61	11.20	0.44	0.238	0.534	19	0.159
10/27/20 19:00	1.49	0.61	10.86	0.44	0.229	0.53	18.7	0.0665
10/27/20 20:00	1.50	0.61	11.06	0.44	0.242	0.538	18.3	0.134
10/27/20 21:00	1.51	0.61	10.92	0.44	0.241	0.555	18.1	0.141
10/27/20 22:00	1.52	0.62	8.51	0.50				
10/27/20 23:00	1.51	0.61	11.47	0.44	0.25	0.563	18.3	0.0765
10/28/20 0:00	1.51	0.61	11.24	0.43	0.253	0.612	18.4	0.0686
10/28/20 1:00	1.50	0.61	10.42	0.45	0.256	0.626	18.4	0.0709
10/28/20 2:00	1.51	0.61	10.62	0.45	0.256	0.652	18.3	0.114
10/28/20 3:00	1.50	0.61	11.07	0.45	0.262	0.656	18.2	0.0659
10/28/20 4:00	1.51	0.61	10.48	0.44	0.264	0.695	15.5	0.0493
10/28/20 5:00	1.49	0.61	10.18	0.46	0.27	0.697	18.6	0.16
10/28/20 6:00	1.50	0.61	10.85	0.44	0.265	0.722	18.7	0.0594
10/28/20 7:00	1.51	0.61	10.03	0.46	0.292	0.733	16	0.0717
10/28/20 8:00	1.50	0.60	10.57	0.44	0.288	0.739	18.8	0.0908
10/28/20 9:00	1.51	0.60	10.73	0.44	0.295	0.747	18.7	0.0594
10/28/20 10:00	1.50	0.60	10.65	0.45	0.297	0.755	18.8	0.117
10/28/20 11:00	1.54	0.60	9.70	0.46	0.332	0.687	16.2	0.0526
10/28/20 12:00	1.51	0.60	10.09	0.44	0.367	0.704	17.9	0.0367

10/28/20 13:00	1.50	0.59	10.65	0.44	0.369	0.731	17.7	0.0714
Pool	**FI**	**BIX**	**HIX**	**PH**	**Fe^{2+} (mg/L)**	**Mn^{2+} (mg/L)**	**Na^{+} (mg/L)**	**P^{3-} (mg/L)**
10/27/20 14:00	1.52	0.61	11.02	0.43	0.202	0.152	18.7	0.0937
10/27/20 15:00	1.50	0.61	10.68	0.45	0.224	0.127	18.4	0.105
10/27/20 16:00	1.51	0.60	10.75	0.43	0.253	0.197	18.9	0.104
10/27/20 17:00	1.51	0.61	10.64	0.45	0.207	0.195	18.5	0.0521
10/27/20 18:00	1.50	0.61	10.86	0.46	0.214	0.263	18.9	0.0635
10/27/20 19:00	1.50	0.60	10.87	0.44	0.241	0.269	18.5	0.0625
10/27/20 20:00	1.52	0.60	11.27	0.42	0.234	0.0992	18.6	0.0946
10/27/20 21:00	1.50	0.61	10.46	0.45	0.216	0.311	18	0.0769
10/27/20 22:00	1.52	0.61	10.54	0.44	0.213	0.316	17.9	0.0772
10/27/20 23:00	1.52	0.61	9.94	0.44	0.238	0.425	18.4	0.0844
10/28/20 0:00	1.52	0.60	10.55	0.45	0.241	0.403	18.2	0.0998
10/28/20 1:00	1.54	0.60	10.42	0.43	0.349	0.416	18.4	0.055
10/28/20 2:00	1.53	0.60	10.22	0.46	0.266	0.431	18.3	0.0865
10/28/20 3:00	1.53	0.60	10.77	0.45	0.247	0.365	18.9	0.0447
10/28/20 4:00	1.53	0.61	10.44	0.45	0.272	0.387	18.9	0.0629
10/28/20 5:00	1.54	0.61	10.65	0.44				
10/28/20 6:00	1.52	0.62	10.42	0.46	0.315	0.322	19.7	0.0455
10/28/20 7:00	1.55	0.60	10.02	0.45	0.273	0.45	19.7	0.103
10/28/20 8:00	1.55	0.60	10.56	0.43	0.283	0.443	19.2	0.0812
10/28/20 9:00	1.54	0.60	9.67	0.45	0.301	0.425	19.7	0.0397
10/28/20 10:00	1.54	0.60	9.67	0.45	0.295	0.462	19.5	0.0586
10/28/20 11:00	1.54	0.61	8.81	0.51	0.328	0.392	18.7	0.0589
10/28/20 12:00	1.56	0.60	9.94	0.43	0.425	0.515	19.2	0.0758
10/28/20 13:00	1.52	0.61	9.63	0.49	0.368	0.264	18.5	0.0753

Appendix C Preliminary Dataset (9/3/2020)
Missing data is the result of machine or human failure.

Site	NPOC (mg/L)	TN (mg/L)	IC (mg/L)	FI	BIX	HIX	PH	pH	Cond (us)	TDS (ppm)	Sal (ppt)	Temp (C°)
RSC 1	5.81	0.55	11.05					7.03	231	172	0.13	25.3
RSC 2	5.75	0.51	11.52	1.45	0.57	12.71	0.33	7.03	241	172	0.12	25.1
RSC 3	5.75	0.52	11.56	1.45	0.57	12.31	0.33	7.05	244	167	0.12	24.8
RSC 4	5.97	0.65	11.99	1.46	0.59	12.71	0.36	7.08	255	182	0.13	24.5
RSC 5	5.69	0.49	12.16	1.46	0.59	11.66	0.36	6.82	213	180	0.13	24.5
RSC 6	5.57	0.48	12.12	1.46	0.59	13.14	0.32	6.84	252	181	0.13	24.5
RSC 7	5.74	0.52	12.23	1.47	0.58	15.36	0.25	6.87	253	173	0.13	24.5
RSC 8	5.35	0.50	11.87	1.47	0.59	11.21	0.38	6.94	248	176	0.12	24.6
RSC 9	6.00	1.78	10.98	1.46	0.59	11.94	0.37	6.97	250	179	0.13	24.7
RSC 10	5.27	0.47	12.34	1.49	0.59	11.81	0.35	7.03	252	179	0.13	24.6
RSC 11	5.50	0.75	14.84	1.46	0.61	11.46	0.37	7.18	260	185	0.13	24.7
RSC 12	4.26	0.49	12.70	1.46	0.59	14.76	0.25	7.02	275	197	0.14	24.6
RSC 13	5.41	0.48	12.44	1.47	0.61	11.43	0.37	6.92	279	198	0.14	24.6
RSC 14	5.35	0.53	12.72	1.47	0.59	14.64	0.26	7.03	281	198	0.14	24.6
RSC 15	5.39	0.52	12.71	1.47	0.61	11.49	0.37	7.03	281	199	0.14	24.7
RSC 16	5.50	0.50	12.96					7.05	198	155	0.07	24.7