# Spatial and Temporal Trends in Salinization in the Northeast Branch of the Anacostia River

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## ABSRACT

Freshwater salinization is a growing environmental problem globally but with local impacts. However, the spatial extent of salinization in watersheds and its impacts are not always known in urban river networks across finer spatial scales. I hypothesized that there are increasing spatial gradients of salinity within stream networks (specifically the Northeast Anacostia system) that traverses through urbanized environments. This means that anthropogenic activity increases salinity in freshwater and salts accumulate in watersheds. Salinity, the concentration of all salts in the water, can be studied from major base cations in streams, calcium ($Ca^{2+}$), sodium ($Na^{+}$), potassium ($K^{+}$), and magnesium ($Mg^{2+}$), as well as organic carbon, inorganic carbon, and nitrogen concentrations, which can be used as secondary indicators for salinity sources through sewage inputs. In this research, the spatial distribution of salinity in a stream is evaluated as a function of season. The hypothesis of spatial connection to salinity along the length of the stream was studied within the context of its hydrologic flowpath into increasingly urbanized areas further downstream, i.e. increasing impervious surface cover and decreased forest cover. It is also shown that seasonally there will be a cyclical shifts in overall salinity as well as the in concentrations of individual salt ions. These increasing salt concentrations show that salts don't always dilute downstream, even with increasing flow. A syndrome of freshwater salinization propagates through stream systems downstream.

## INTRODUCTION

Freshwater salinization is increasing on a continental scale (Kaushal et al., 2018). Salinization can have pronounced effects on urbanized streams and rivers due anthropogenic inputs of major ions (Kaushal et al. 2017). Because they are inherently more connected (pipes, ditches, etc.), chemical fluxes can travel more quickly, so much so that Kaushal (2012) proposed this warrants a 4-dimensional approach to the urban watershed continuum across spatial and temporal dimensions. Major base cations as well as dissolved inorganic carbon (DIC) can have elevated concentrations in freshwater systems, draining urbanized watersheds compared with forested watersheds (Baker, 2008; Barnes and Raymond, 2009; Kaushal, 2013). Inorganic carbon and calcium concentrations in streams across the eastern U.S. have shown increasing trends over time (Kaushal, 2013). Freshwater salinization can impact corrosion of pipes, complicate drinking water treatment and safety, increase water hardness and toxicity of metals, and harm aquatic life (Kaushal 2017, Kaushal et al. 2018). Anthropogenic processes are the primary cause of this rise in salinity. Use of road salts (primarily sodium chloride) and agricultural lime (bears high calcium), drainage of wastewater from mines and fracking brines, and dissolution of urban karst (calcium is a primary component in concrete) are all major salinity increasers (Kaushal, 2017). For example, Scott (1976) reported a 50-fold sodium concentration increase in urban streams after road salt application. Ruth (2003) reported a 30-fold increase in sodium in urban streams in Helsinki, Finland, when spring flooding washed out road salts. Demers and Sage (1990) observed chloride concentrations 31 times higher downstream as compared to upstream from a major road whose salted runoff affects Adirondack streams in New York. Road salts disrupt the proportional contributions of nitrate and ammonium nitrogen to the mineral portion causing it to leach into nearby waterways (Green et al., 2008). Green et al. (2009) also looked at this leaching regarding dissolved organic carbon (DOC) and found that initially salinity increases yield higher organic carbon, but on a longer time scale, downstream organic carbon will decrease and only vary seasonally due to most of it being flushed away already. Kaushal (2014) examined organic carbon and nitrogen as well, finding that they can show erratic patterns. He proposed that

the urbanized waterway can act as a reactor modifying and disposing of carbon and nitrogen as well, depending on in stream processes and the degree of urbanization. Significant amounts of nitrogen can be removed by assimilation and denitrification in urbanized areas as well. Urban karst dissolution as a result of construction (bridges, buildings, drainage infrastructure, and pavement on road and parking lots) can also influence base cations such as calcium and magnesium and inorganic carbon (Davies et al., 2010; Kaushal, 2014). Carbonates present within urban impervious surfaces such as concrete may be directly dissolved by acid rain and enter streams.

## METHODOLOGY

The areas of interest are the Northeast branch of the Anacostia River and Indian Creek, one of its tributaries. Nineteen grab samples (250 ml each) were collected over a 9.5 km stretch from the Capital Beltway (upstream) to where the northeast branch converges with the northwest branch into the Anacostia River proper (downstream). The stretch varies from more wooded reaches in the north to more urbanized in the south. A baseflow synoptic sample set was collected in fall on October 20th, winter on February 20th, and spring on April 18th, to compare seasonality effects (unfortunately due to utility and instrument difficulties which extended outside the time constraints of this paper, this final synoptic set of cation data doesn't appear in this paper). The data was normalized for differences in discharge with the data reported from the USGS gauge at Riverdale, right at sample site six as shown below. This gauge records discharge, gauge height, pH, specific conductance, etc.

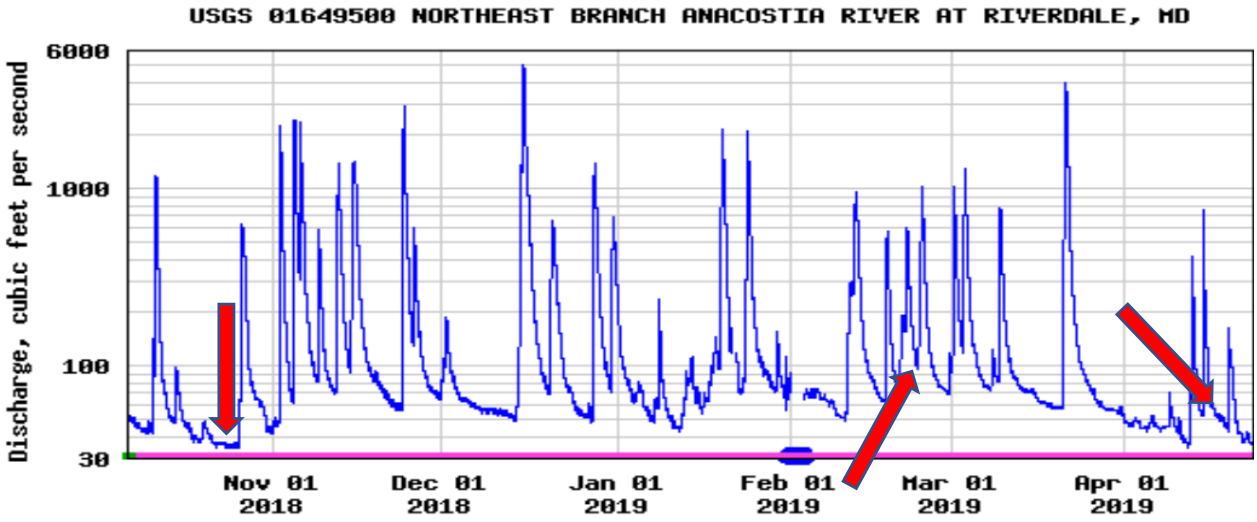


Figure 1. Discharge of the North East Anacostia over time (USGS, 2019). These data were used to normalize the cation data from the ICP-OES. Approximate sampling dates are denoted by the red arrows.

Each bottle (250 ml) was rinsed several times with the sample water before a final collection was made by completely submerging the bottle and capping it under water to avoid generation of headspace.

After collection, each sample was kept chilled until returned to the lab and was then frozen, to halt microbial activity, until ready to be analyzed. When that time came, each sample was set out and thawed at room temperature and filtered (pore size of 0.7 µm). Then, using a micropipette,

60 ml of the sample was acidified with 30 µl of 15.8 molarity nitric acid to remove bacteria and other organics which could affect the ions of interest. This process also prevents adsorption by the bottle or precipitation of the ions.

Fifteen ml of each acidified sample was analyzed for major salt cations, sodium, calcium, magnesium, and potassium, via Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) on a Shimadzu ICPE-9820 Plasma Atomic Emission Spectrometer. In this process, the sample was completely ionized within the machine by an ultra-high purity argon plasma torch at a temperature of 7000 K. When the excited ions returned to their stable state, they released characteristic wavelengths. Thus, which ions are present was determined, as well as their concentrations based on the intensity of the light emitted (EPA, 2018; Shimadzu, 2006). Samples runs consisted of three blanks, 15 standards, the samples, and then another blank. The standards used were diluted with deionized water from a stock solution, IV-ICPMS-71A, which contained 10 ug/ml of over 50 different cations, including the cations of interest. The standards were (in ppb) 2.5, 5, ,10, 15, 50, 100, 250, 500, 1000, 5000, 10,000, 25,000, 50,000, 100,000, and 250,000. Each sample was analyzed in triplicate for each ion. After background corrections were applied, a quantitative average concentration was reported, with relative standard deviation, in mg/L. These values were then normalized to discharge and converted into fluxes (Table 1).

Another 25 ml of the initial filtered sample was analyzed using a Shimadzu Total Organic Carbon Laboratory (TOC-L) analyzer with a Total Nitrogen Measuring Unit (TNM-L). To produce the inorganic carbon (IC) data, the sample and acid are mixed and then sparged to isolate $CO_2$. Then the mix was cooled and run through a Non-Dispersive Infrared (NDIR) gas analyzer inside the Shimadzu. The NDIR analyzer drew the gas through a chamber and passes infrared light through it. Any infrared absorbed is attributed to the $CO_2$. The infrared intensity was compared to a control chamber with no $CO_2$ and the difference was converted into a measure of carbon in ppm (EPA, 2008).

The organic carbon (OC) analysis started the same way as the inorganic carbon, but once the sample was acidified and sparged, inorganic carbon was purged. Then purified air was added and the mix was combusted to produce $CO_2$, which was cooled and run through the NDIR gas analyzer.

Total Nitrogen (TN) analysis began by converting the nitrogen in the sample to nitrogen oxide (NO) through combustion. Then the NO was cooled in the carrier gas as it passed through a thermoelectric cooler. This cooled and dehumidified gas entered a chemiluminescence analyzer which converted the NO into an unexcited and excited phase of $NO_2$ by reacting it with ozone ($O_3$). When the excited $NO_2$ returned to ground state, its radiation was measured photoelectrically. This peak was used to determine the nitrogen concentration (Shimadzu, 2008).

## DISCUSSION

All four major salt base cations, potassium, magnesium, calcium, and sodium (Figures 4, 5, 6, 7) increased downstream in both fall and winter. Thus, salts are accumulating as streams enter more urbanized environments. This can be attributed to increased impervious surface weathering. Calcium and magnesium especially, and to a lesser extent sodium, are components of concrete via the limestone in it.

Also, all four cations had noticeably increased slopes and concentrations in the winter season relative to wall. Increased weathering most likely led to the calcium and magnesium increases. The concentrations increase more rapidly as you become more urbanized downstream and as the cations accumulate. Another parameter closely related to the weathering of impervious surface is inorganic carbon. The bicarbonate ion $HCO_3^{2-}$ is the primary source of inorganic carbon in streams and it is also an ion that comes from the weathering of limestone in concrete. Figures 9 and 10 show this relationship and thus inorganic carbon follows the same trends as calcium and magnesium.

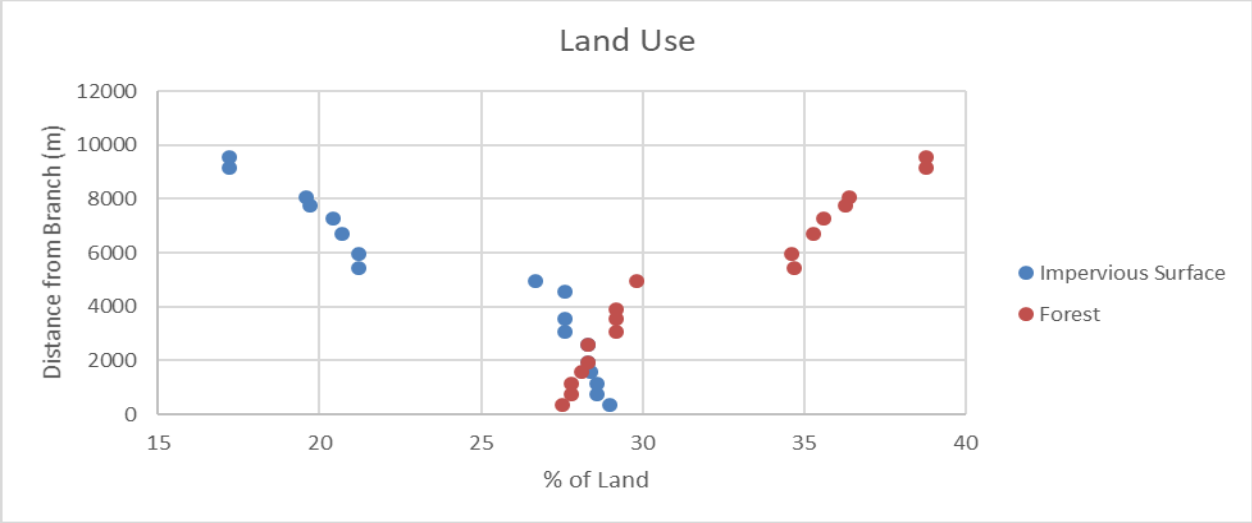


Figure 2. Land use data along the length of the stream. Each point was calculated from Streamstats (2019) by analyzing the drainage basin of each sample site and how much was covered by impervious surface and how much was forested. The discrepancy in percentage is unforested or developed land that isn't impervious. Impervious surface cover increases and forested area decreases from upstream to downstream. This serves as a proxy for urbanization and contributes to cations such as magnesium and calcium from weathering of these impervious surfaces (i.e. concrete).

Sodium is almost assuredly experiencing the steep increase in concentration as well as slope due to the use of deicing salts on the roadways which permeates streams via runoff. The closer you get to downstream, the more urbanized and road salt needed, as well as just overall accumulation. Sodium also has the effect of mobilizing the other major cations (Figure 11) as well as nitrogen and carbon (Figure 12), so it's large increase increases the other variables as well as seen.

Potassium, as well as nitrogen (Figure 13), can come from fertilizer and sewage, but is also under heavy biologic control. The fact that potassium sees these same increases downstream as the other cations, shows that it is being mobilized by this overall salinity rise. Despite biologic uptake, enough of a concentration of potassium is entering the water for it to accumulate downstream, especially in winter when biologic activity and therefore uptake is much lower.

The same trends are seen in organic carbon and nitrogen (Figures 14 and 15). Once again, these factors are heavily influenced by the presence of biota in the streams (like potassium, Figure 16), and nitrogen can be taken up by soil. The increases they see downstream, as well as in winter,

show their accumulation and mobilization, despite the lower levels of bioactivity. In spring, the beginning renewal of biologic activity brings their overall concentrations back down from uptake.

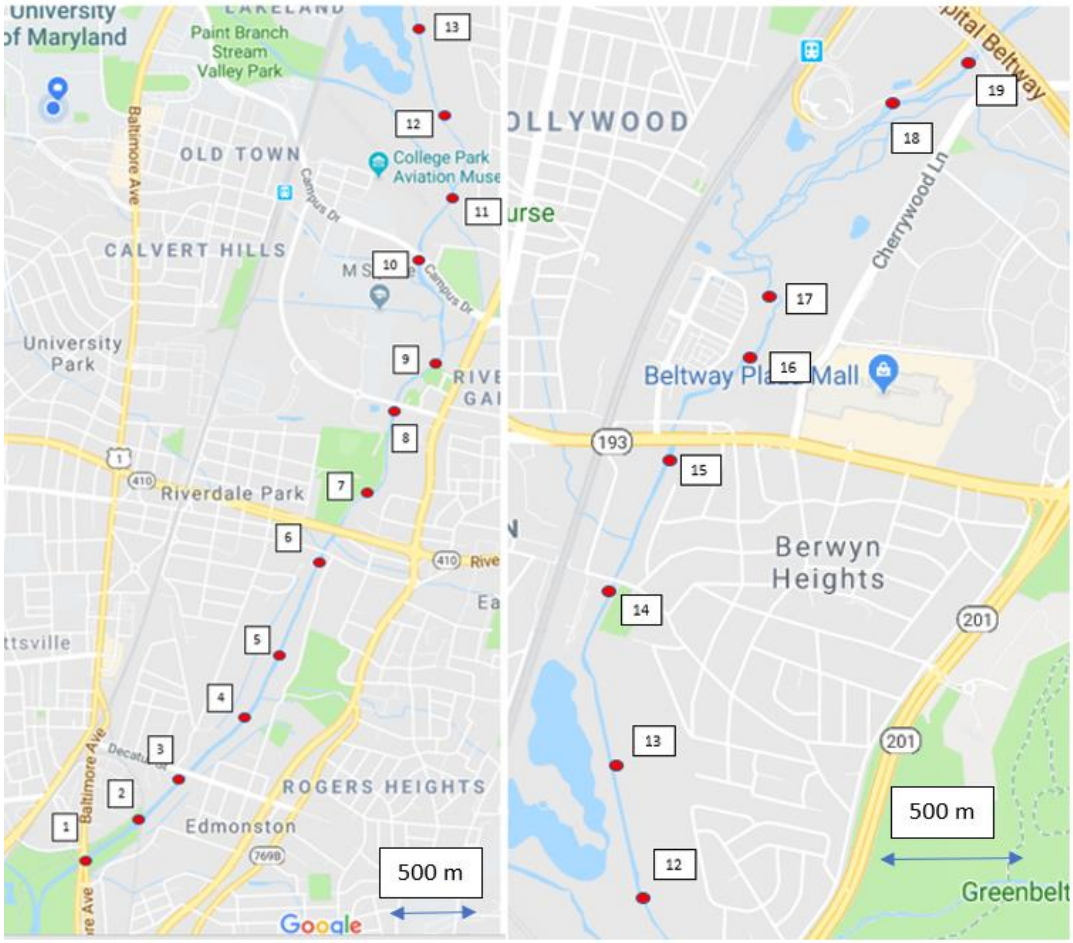


Figure 3. Sample locations – The right picture is Indian Creek, extending from the Capital Beltway past Lake Artemesia next to sample site 12. The left picture is the Northeast Branch of the Anacostia River from where Indian Creek feeds into it near sample site 11 until it merges with the Northwest branch into the Anacostia proper just south of sample site one. (Google Maps, 2018)

Figures 17 and 18 show the effect Paint Branch Creek, the creek that joins Indian Creek to form the Northeast Anacostia River has on the stream system's overall data set. In both Indian Creek and the Northeast Anacostia, the same overall trends of each variable are present. In the less urbanized Indian Creek, the slopes are less pronounced due to less accumulation and input from impervious surfaces or road salts. Then in the Northeast Anacostia, the values are higher due to the input of Paint Branch, but the trends are the same and are accelerated due to the quicker accumulation and larger source of impervious surface weather and road salt usage. I postulate that Paint Branch has a similar accumulation to Indian Creek and that addition leads to the jump at their convergence, but the same overall trending across the whole system. This means that this freshwater salinization syndrome can propagate along stream systems and watersheds in any sort of scale, continental or very localized. A salt map would be required to determine the scale of

each individual case, but I think it's reasonable to assume nearly every water system that has humans near it is experiencing a similar phenomenon and set of stressors.

This freshwater salinization syndrome has numerous potential effects on stream ecosystems. Aquatic life is highly sensitive to salinity levels in their ecosystems. Canedo-Arguelles et al. (2012) found that even short term salinity increases can cause significant declines in density, richness, and diversity of aquatic life as well as biotic quality indices. The increasing inorganic carbon that comes with impervious surface weathering can increase the pH of a stream to a level that is harmful to aquatic life (Finlay, 2003). Naidoo (1987) showed increased salinity and increased nitrogen (which can be mobilized from salinity as shown above) decrease stomatal conductance and tissue water potentials, thus affecting the plants' ability for nutrient uptake. In addition to effects on life, increasing salinity can have effects on agriculture and infrastructure as well (Pitman, 2002).

The process to remediate this continental scale change to freshwater ecosystems will be long and complex, but measures can be taken. Reducing or regulating road salts is an almost immediate thing that can help. Other deicers are available and being able to precisely control how much salt is used in each area can reduce excess salty runoff. Limiting or reducing impervious surface cover is another way to prevent this erosion into freshwater. Some locales offer grants to remove impervious surface cover or when building, utilize materials and designs that aren't impervious and won't erode negatively. For waters affecting drinking supplies, filters and water treatment plants can be put in place, though that only stops the effect at the human level, not at the source. Also, being able to properly contain wastewater, brines, etc. and keeping infrastructure that might shed salts away from areas that are close to the water table to prevent easy entry into the water system can hedge against increasing salinity.

## SUMMARY

Anthropogenic processes such as the use of road salts and urban karst erosion are increasing salinity levels in freshwater on the continental scale. This research examined the spatial effects of this along the northeast branch of the Anacostia River and Indian Creek using synoptic baseflow sampling events to capture a temporal aspect of fluxes as well. The hypotheses of cyclical temporal fluxes and also increasing spatial gradients downstream were both supported. Increases in all major cations as well as other proxies were noted as they accumulated downstream in correlation to impervious surface cover. These trends were even more pronounced in the winter, likely due to road salting's effect. This also shows that this stream system isn't regulating itself over time but is steadily increasing in salinity. These processes are exacerbating the salt levels of freshwater in the Northeast Anacostia River showing that even small localized watersheds experience freshwater salinization syndrome.

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## APPENDIX

| Sample Site | Distance from Branch (m) | Mg normalized flux (mg/s) | K normalized flux (mg/s) | Ca normalized flux (mg/s) | Na normalized flux (mg/s) | IC normalized flux (mg/s) | OC normalized flux (mg/s) | TN normalized flux (mg/s) |
|---|---|---|---|---|---|---|---|---|
| 1 | 349 | 8693.173235 | 4969.11565 | 31793.44687 | 39352.72795 | 27958.22339 | 4049.77367 | 1268.402898 |
| 2 | 765 | 7513.196947 | 3641.43268 | 27968.83535 | 30491.51462 | 24239.6573 | 3486.781474 | 1080.693862 |
| 3 | 1,120 | 8368.343216 | 4217.03159 | 30012.12096 | 35488.78537 | 26003.20261 | 4693.501398 | 1182.959512 |
| 4 | 1,590 | 6444.56466 | 3146.33628 | 24953.70154 | 24736.71283 | 21395.08671 | 2989.019468 | 1001.402892 |
| 5 | 1,940 | 7984.442399 | 4008.38404 | 28554.34866 | 32756.68676 | 25117.05159 | 3773.484113 | 1194.972553 |
| 6 | 2,570 | 6262.543488 | 2894.5433 | 25286.9024 | 22273.99488 | 21423.92454 | 3052.720941 | 928.9439507 |
| 7 | 3,060 | 7910.618743 | 4017.11108 | 27810.76902 | 30900.85447 | 24195.36905 | 3375.403336 | 1173.202441 |
| 8 | 3,540 | 7117.526496 | 3579.33413 | 26022.17057 | 26742.15157 | 22926.25225 | 3101.061038 | 1082.028594 |
| 9 | 3,900 | 7415.373925 | 3666.60456 | 26703.56261 | 29168.50685 | 23273.18188 | 3378.00067 | 1119.495509 |
| 10 | 4,540 | 7135.247735 | 3491.51456 | 24640.38885 | 25972.30176 | 20530.48615 | 3131.898073 | 1172.083361 |
| 11 | 4,960 | 6513.490485 | 3207.60368 | 22962.51104 | 23141.20762 | 19710.23321 | 3153.101224 | 1101.66444 |
| 12 | 5,440 | 2375.892787 | 1480.62884 | 9426.096384 | 7575.310336 | 9370.142387 | 2027.686761 | 555.6662298 |
| 13 | 5,970 | 2338.134971 | 1299.43881 | 9361.088823 | 6582.683464 | 9540.616554 | 1973.522698 | 521.4853134 |
| 14 | 6,710 | 2255.940479 | 1297.47968 | 8580.107573 | 6529.252592 | 8534.067971 | 1948.312232 | 540.3375062 |
| 15 | 7,270 | 2381.013246 | 1349.93099 | 8944.328019 | 7287.970978 | 9035.427656 | 1894.044276 | 554.0514301 |
| 16 | 7,770 | 2549.810276 | 1411.13902 | 9272.037369 | 7970.698791 | 9776.306068 | 1880.840914 | 600.6490875 |
| 17 | 8,050 | 2599.82751 | 1473.50472 | 9527.318203 | 8235.478447 | 10019.83211 | 2045.547514 | 620.8904829 |
| 18 | 9,160 | 2254.485972 | 1319.96517 | 8145.23964 | 6581.644531 | 8796.131558 | 1897.040857 | 561.8033591 |
| 19 | 9,530 | 1665.855862 | 927.085002 | 5540.781455 | 3342.576002 | 6493.216437 | 1601.756626 | 445.0732293 |
| | standard error | 609.6337793 | 296.484501 | 2191.136471 | 2770.754593 | 1735.801 | 203.366 | 68.586 |
| Mg normalized flux (mg/s) | K normalized flux (mg/s) | Ca normalized flux (mg/s) | Na normalized flux (mg/s) | IC normalized flux (mg/s) | OC normalized flux (mg/s) | TN normalized flux (mg/s) | IC normalized flux (mg/s) | OC normalized flux (mg/s) | TN normalized flux (mg/s) |
| 18433.44829 | 11038.31859 | 54647.83342 | 213969.3776 | 24107.57905 | 9542.979866 | 2816.674399 | 15766.66121 | 5477.371376 | 1547.020351 |
| 17650.84111 | 9925.244999 | 53113.47324 | 209234.8946 | 24214.9153 | 8583.995674 | 2948.066014 | 15139.96872 | 4890.81201 | 1505.828664 |
| 17493.0129 | 10715.47498 | 53041.60115 | 210291.1965 | 23603.51251 | 8510.766002 | 2812.812182 | 15234.45866 | 5020.923322 | 1361.856504 |
| 17300.55542 | 10719.97606 | 52538.49653 | 208296.5645 | 23767.03603 | 8530.872038 | 3064.745631 | 15443.92987 | 4999.462498 | 1404.189498 |
| 17024.10198 | 9724.293544 | 51388.54312 | 206081.2344 | 23098.4913 | 8317.038055 | 2830.322836 | 15368.86383 | 5181.546332 | 1431.192008 |
| 17026.9696 | 9105.6128 | 51844.096 | 205534.208 | 23437.74208 | 8426.63936 | 2739.57888 | 15408.74957 | 4882.108518 | 1369.615749 |
| 16626.40975 | 8741.460886 | 49627.31396 | 200272.663 | 22019.91631 | 11643.52513 | 2798.778975 | 14691.44834 | 4721.57288 | 1301.628717 |
| 16250.27916 | 8728.865121 | 49052.70025 | 194953.0394 | 21517.78451 | 9772.807203 | 2724.311506 | 14444.86308 | 4664.433844 | 1356.508404 |
| 14694.57514 | 7384.965967 | 49233.10645 | 187638.421 | 22298.07581 | 8738.876395 | 2472.205274 | 14248.46291 | 4810.677354 | 1339.034996 |
| 14844.78054 | 7538.728678 | 43743.24047 | 174972.9619 | 19386.6319 | 7012.879085 | 2487.31511 | 12597.82058 | 4368.414056 | 1207.622897 |
| 13133.06327 | 6752.273796 | 40644.75489 | 136138.0769 | 18244.25046 | 7071.31327 | 2504.24135 | 12414.35038 | 6255.337038 | 1172.107323 |
| 5737.0624 | 3263.2832 | 19053.3632 | 61370.7776 | 8925.605888 | 3708.563456 | 1332.682752 | 6164.720927 | 2994.441298 | 524.8591012 |
| 5728.858818 | 3157.144823 | 18921.9607 | 61470.23695 | 8904.821061 | 3715.394934 | 1242.995098 | 6175.563448 | 2904.060985 | 532.8204595 |
| 5486.67166 | 3122.079956 | 18015.93679 | 60189.60702 | 8236.149287 | X | 257.7507321 | 6082.528297 | 2978.331206 | 533.6535441 |
| 5590.341703 | 3078.738909 | 18431.92373 | 61574.77817 | 7680.643383 | 4272.762979 | 1284.158203 | 5997.261865 | 2891.138384 | 504.2751529 |
| 4823.778692 | 2824.645667 | 16609.7122 | 57487.50689 | 7098.414129 | 3776.47169 | 1067.198874 | 5866.709484 | 2860.669846 | 513.69762 |
| 4798.441966 | 2942.254539 | 16291.00668 | 57364.09017 | 6910.348832 | 3751.868204 | 1141.357801 | 5724.245066 | 2799.416967 | 512.5249434 |
| 4526.671095 | 2623.512717 | 14584.95206 | 47401.09418 | 6236.845656 | 2973.907297 | 1093.871404 | 4914.63082 | 2644.038369 | 451.1010058 |
| 4499.337922 | 2595.090573 | 14525.42164 | 47207.62033 | 6260.988144 | 2952.026239 | 1096.492194 | 4565.543731 | 2679.47973 | 488.9177211 |
| 1339.490999 | 761.2806983 | 3899.365527 | 16596.60631 | 1804.415 | 654.353 | 188.855 | 1060.657 | 268.334 | 101.471 |

Table 1. Complete data set. Cells highlighted orange are from the fall, blue from the winter, green from the spring, and yellow are standard errors for their respective column.

Figure 4.

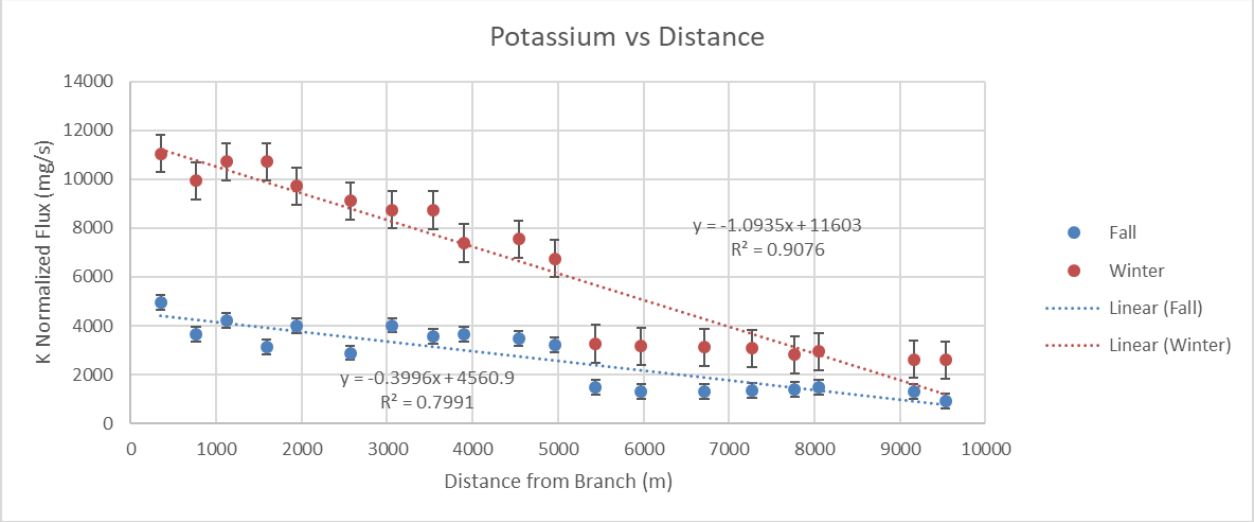



Figure 5.

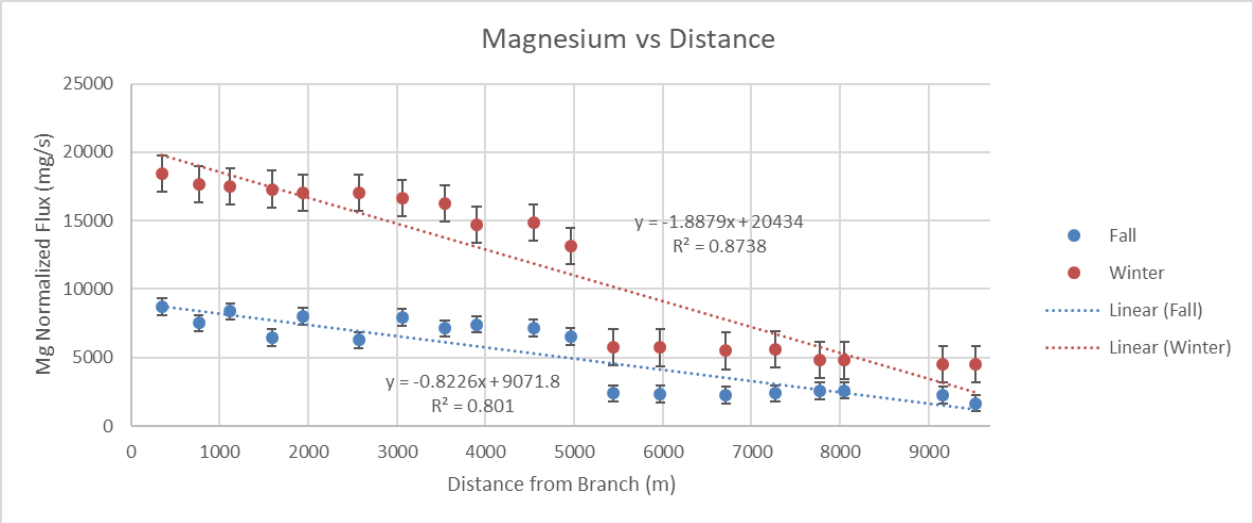



Figure 6.

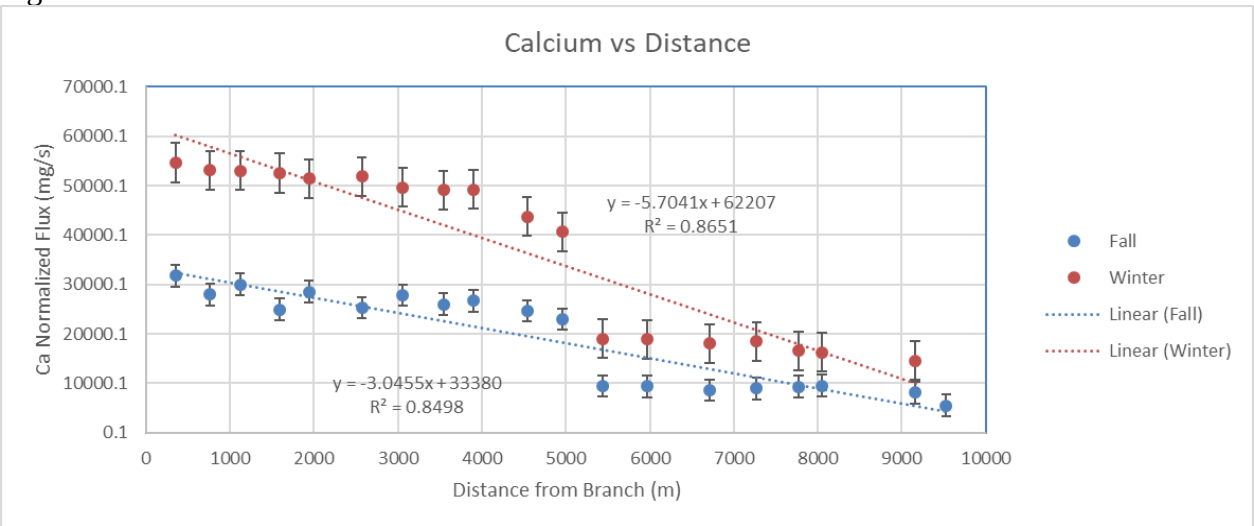


Figure 7.

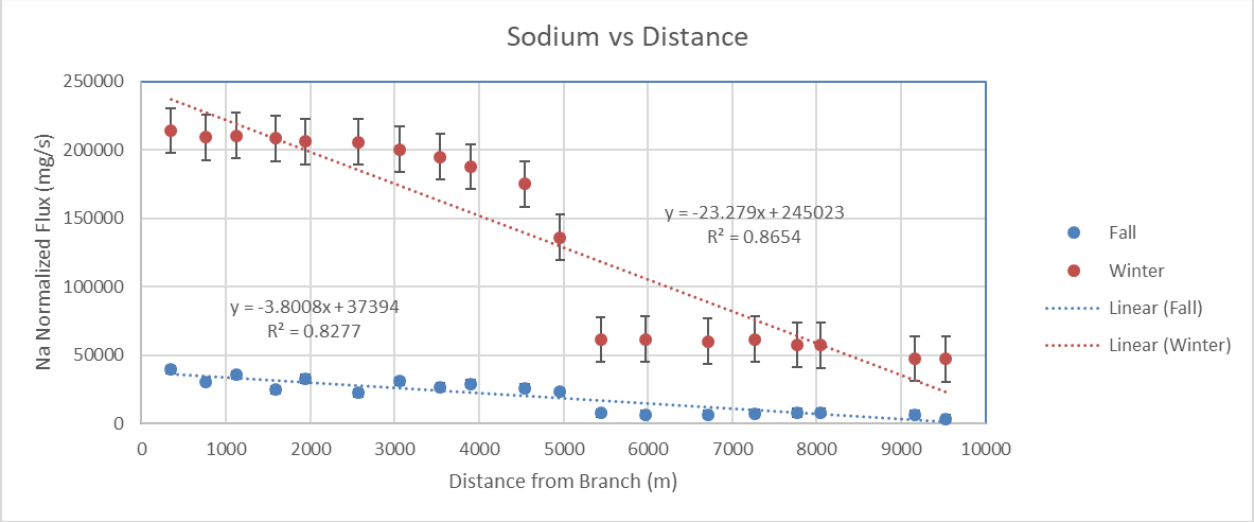



Figure 8.

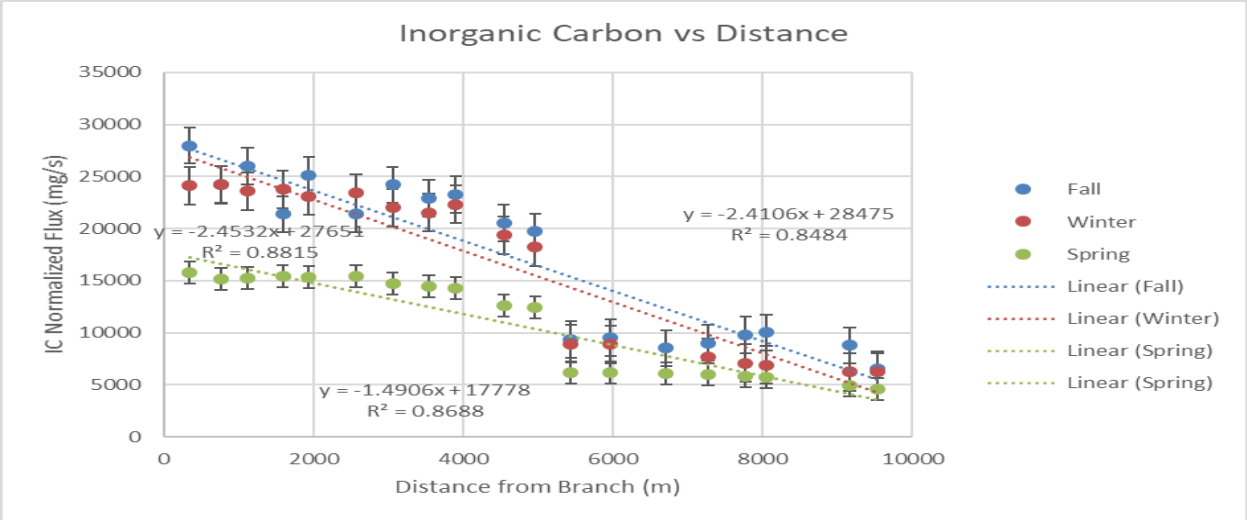



Figure 9.

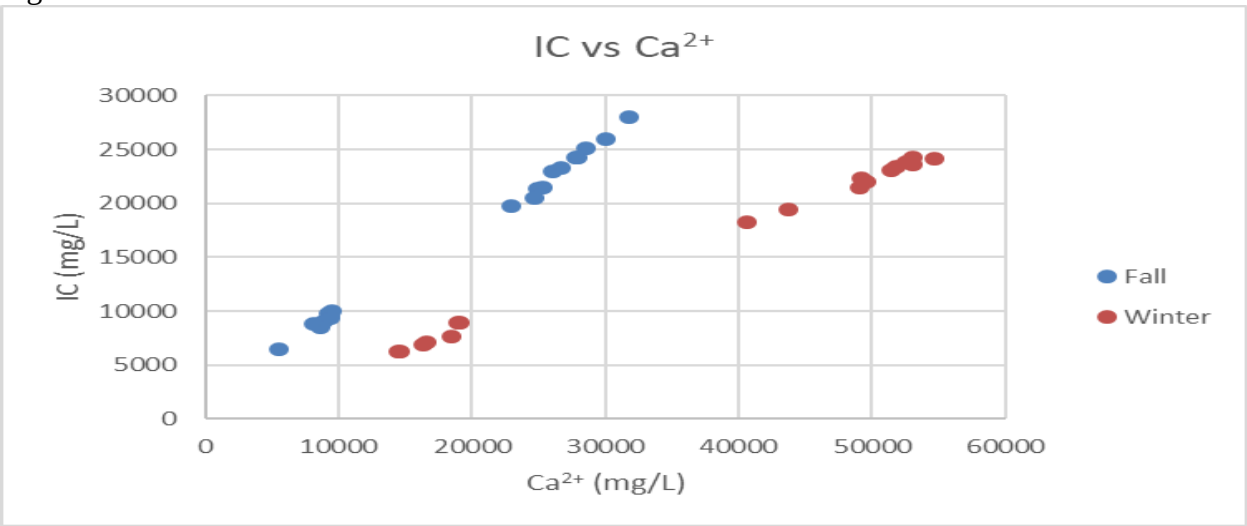


Figure 10.

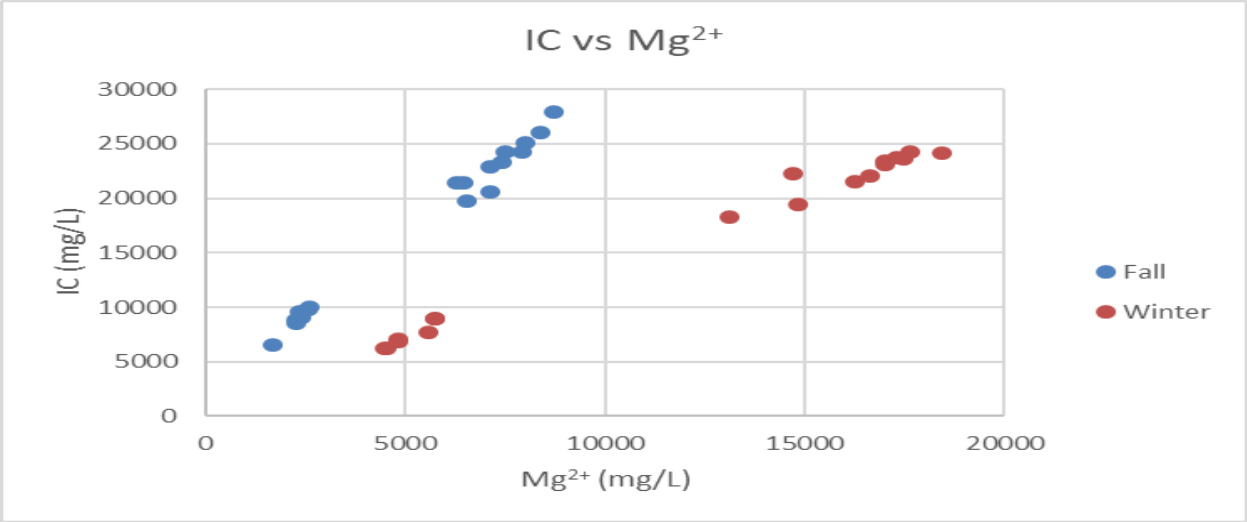



Figure 11.

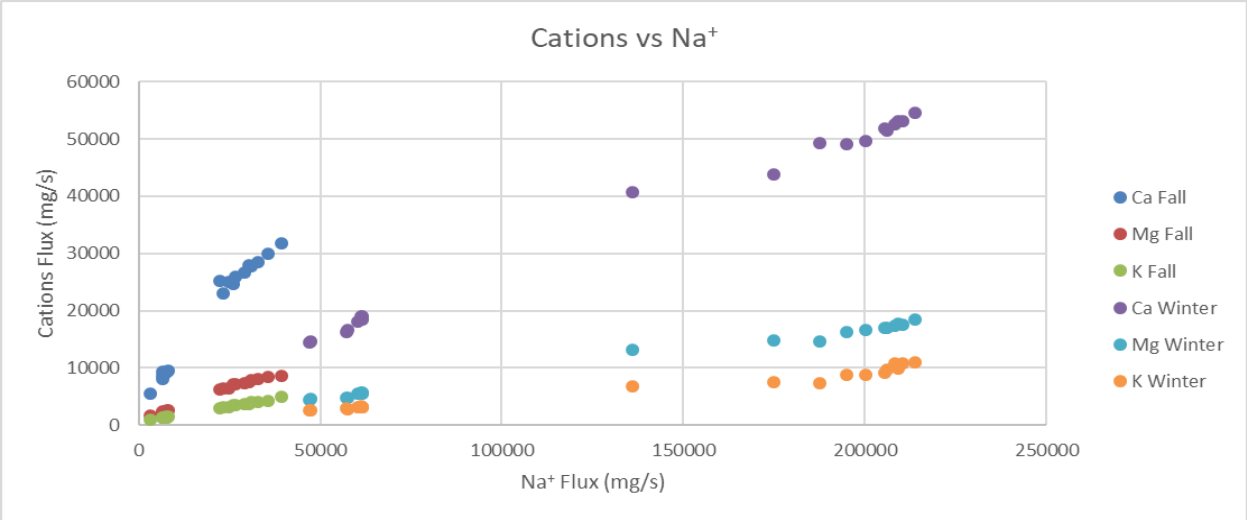



Figure 12.

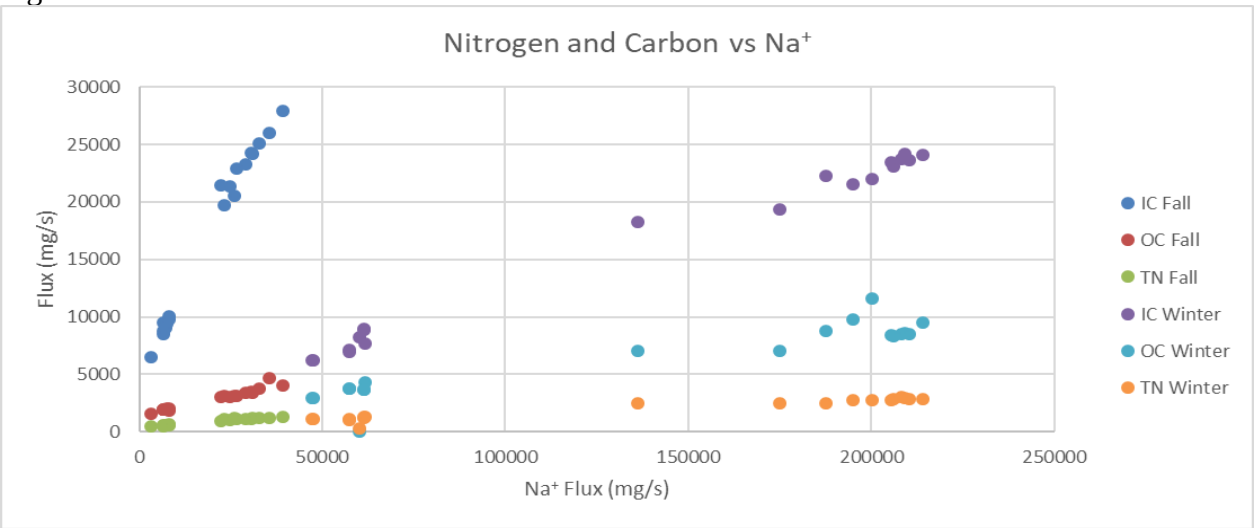


Figure 13.

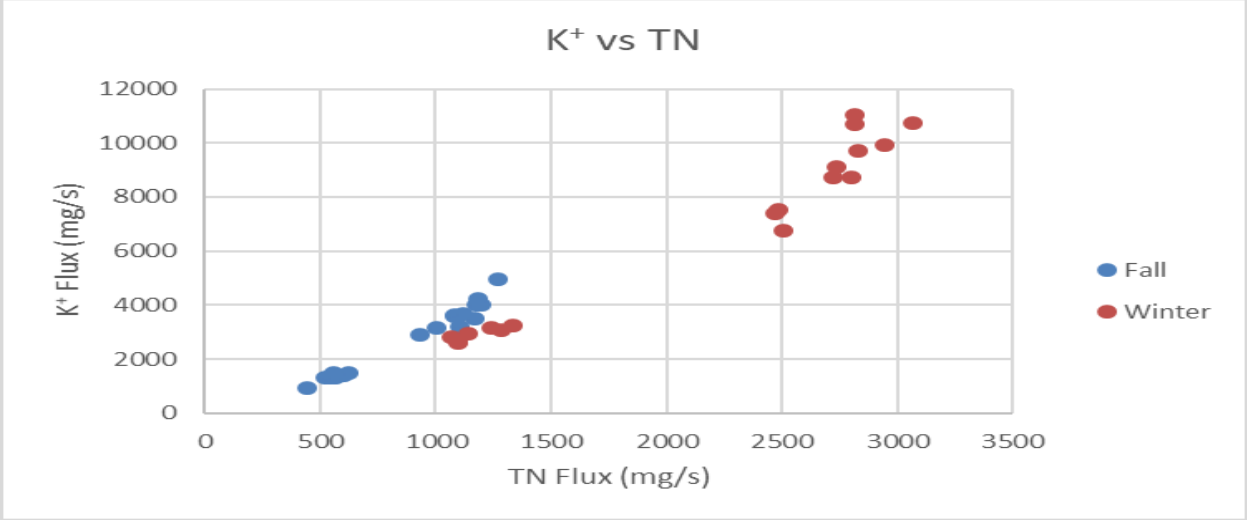



Figure 14

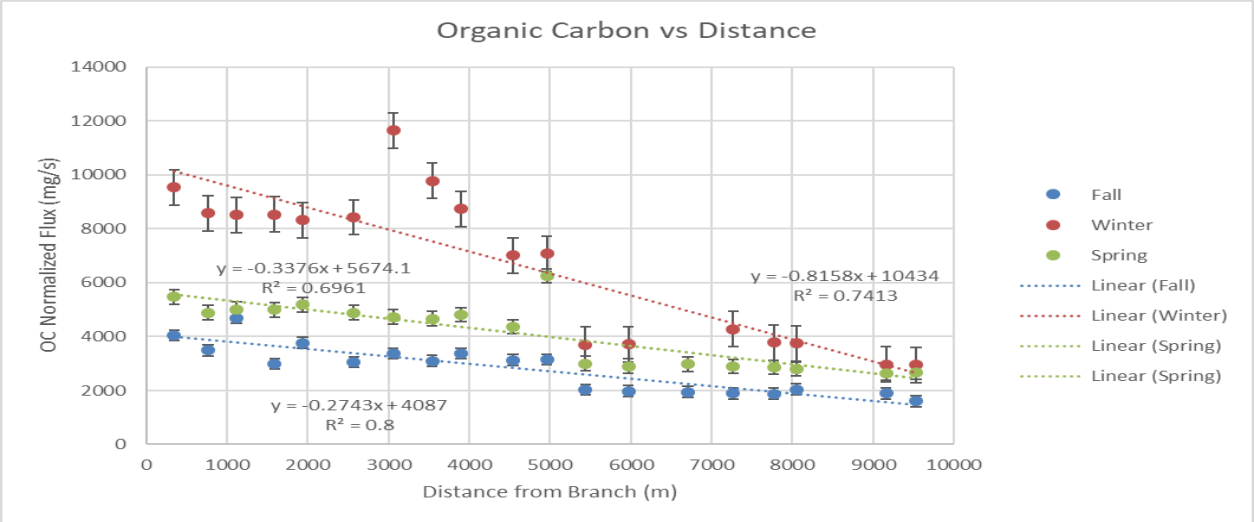



Figure 15

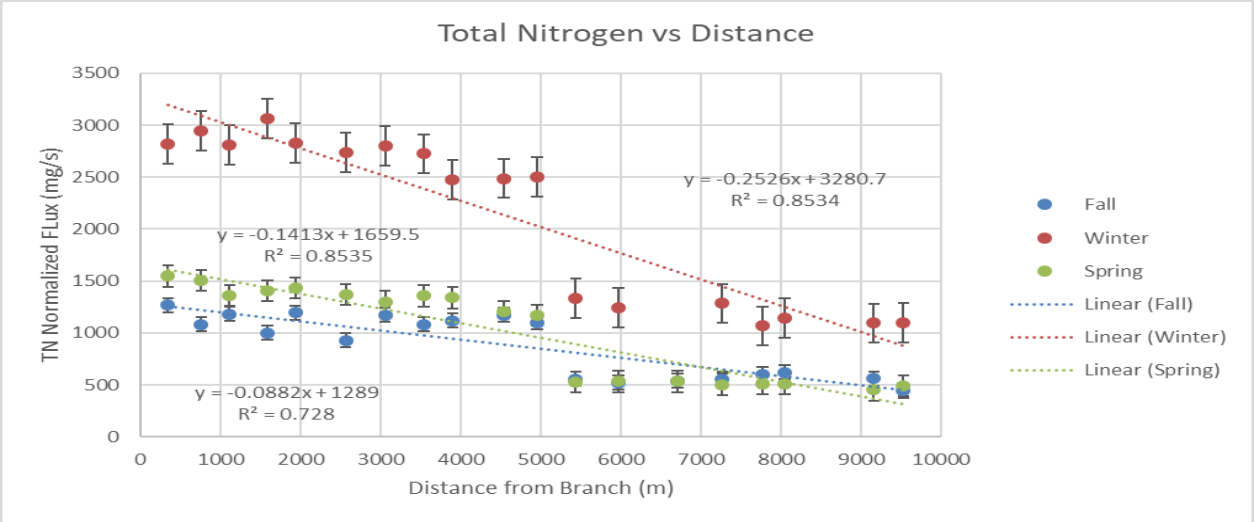


Figure 16

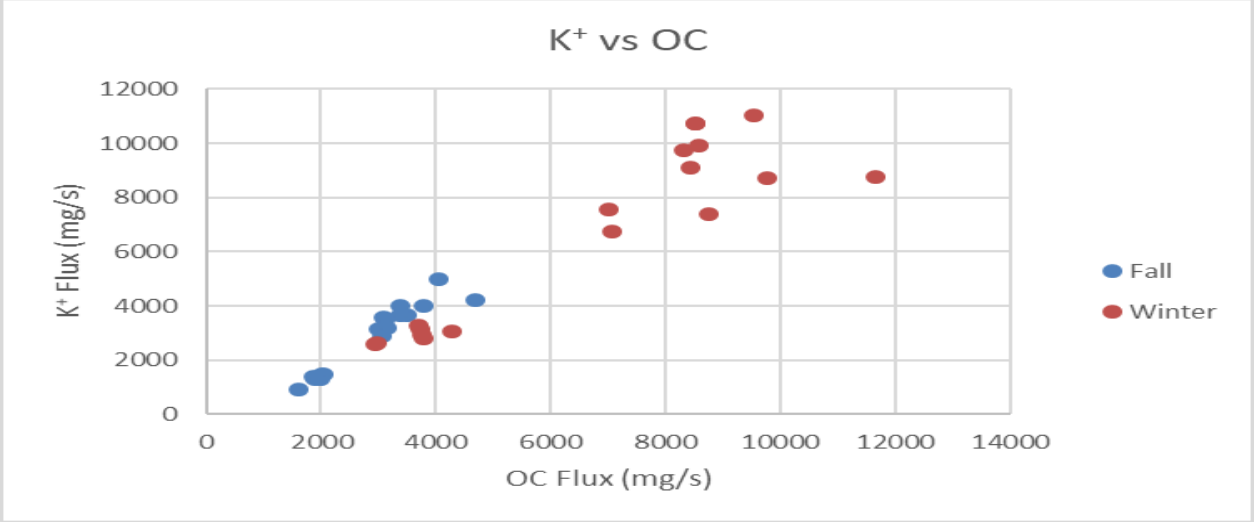



Figure 16

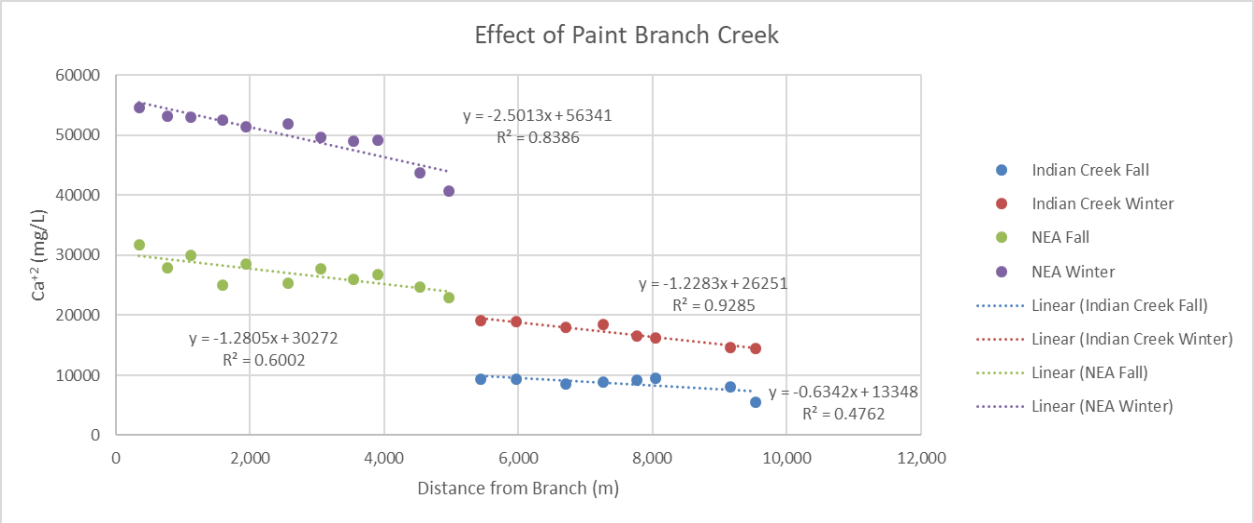
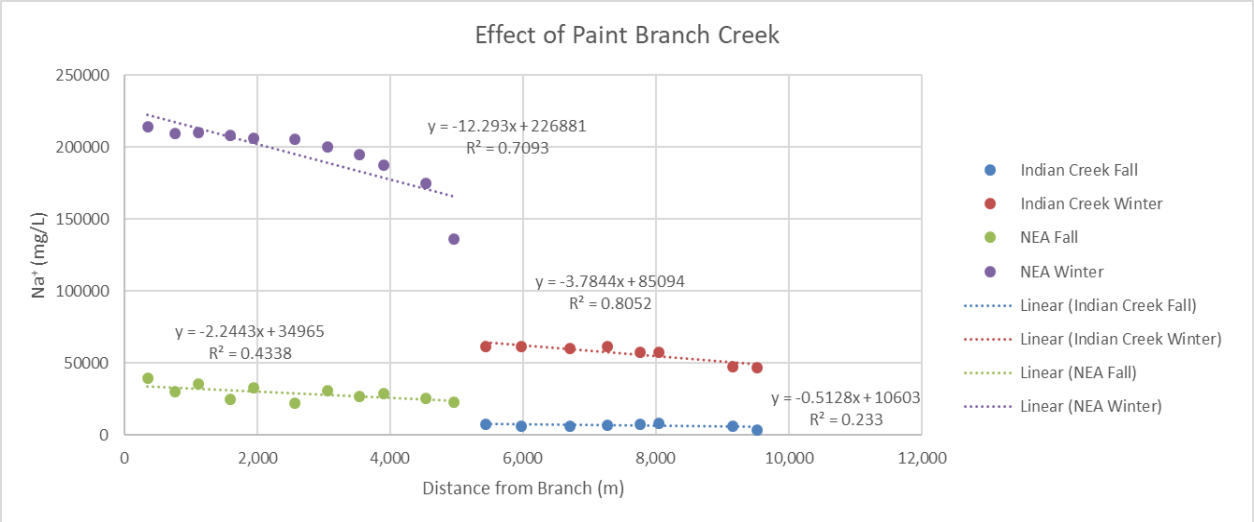



Figure 17



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

*Julian Leal*
*4/25/2019*