

## **Baxter Creek Watershed Water Quality Stage 2 Analysis**

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Completed for: Baxter Creek Watershed Association

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## **Baxter Creek Water Quality Analysis Part 2**

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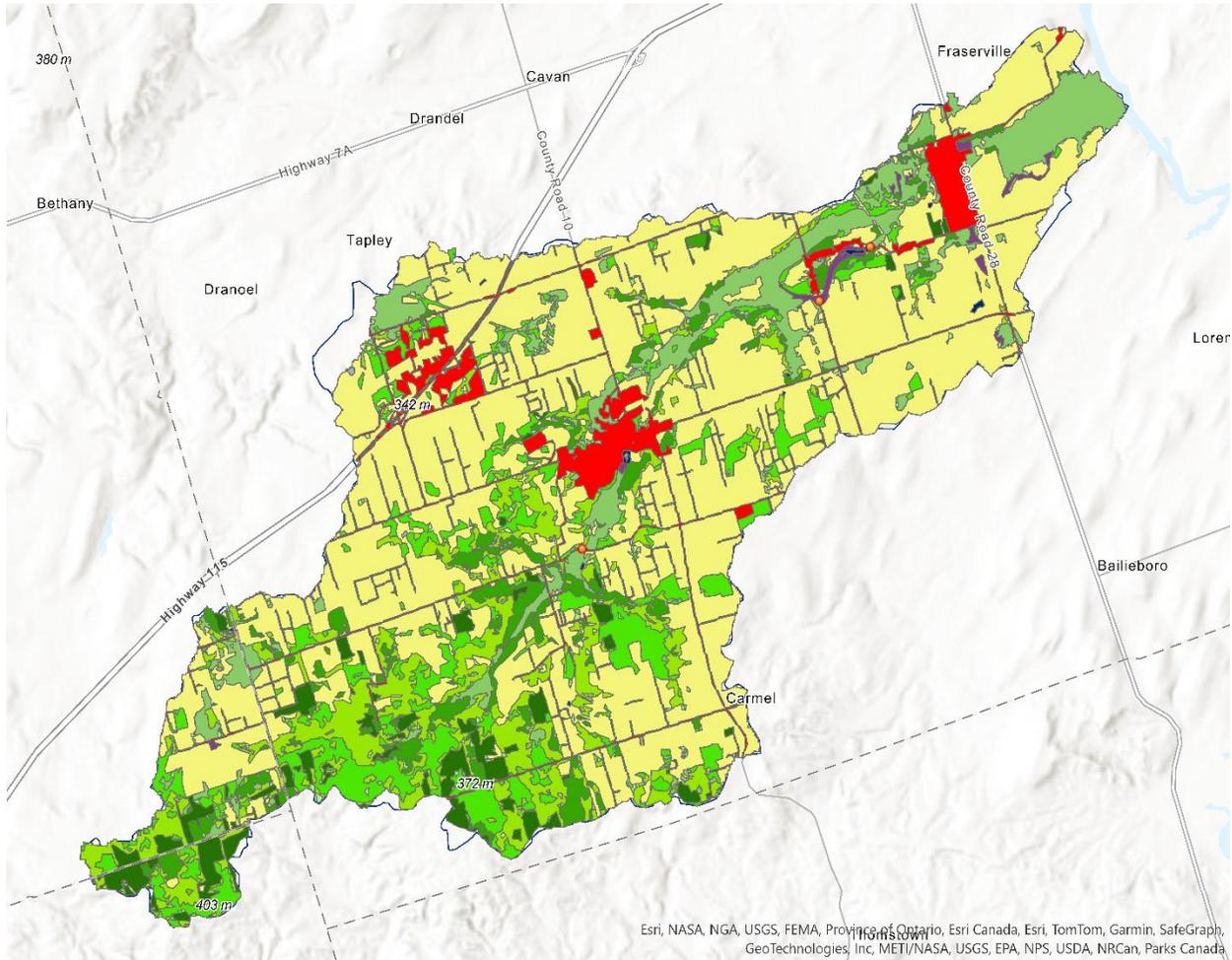
## Abstract

This project examined water quality data for Baxter Creek with the aim of identifying long term trends in several key water quality parameters. This project also looked for trends in the stoichiometric ratio of nitrogen and dissolved organic carbon [DOC] as well as phosphorus and DOC as these ratios provide insight into the bioavailability of these nutrients. This analysis built off a previous project analyzing the same record of water quality data for Baxter Creek with the method of trend identification, incorporating seasonality and stream discharge being the main expansions. This project used a Mann-Kendall test to identify if trends existed over the period of record, and significance was stated if the p value  $<0.05$ . The result of this data analysis was that of the 8 parameters and 3 seasons per parameter, 10 significant trends were observed, and of the 3 ratios with 3 seasons each, 2 significant trends were observed. Some of the trends identified raise concern, such as the trend of DOC: Nitrate molar ratio decreasing over time, but the seasonal analysis performed did not effectively incorporate hydrological parameters such as Discharge.

## Plain Language Abstract

This project looked at the data set for Baxter creek and ran statistical analysis to check if any increasing or decreasing trends existed over time. The data was classified by season due to seasonal events such as snowmelt in spring. This was done to ensure these seasonal events were not confused for long-term trends. The data set was also modified to look at the ratio of nutrients such as nitrogen and phosphorus, to organic matter in the form of dissolved organic carbon. This ratio can be evaluated to better understand what biological communities can access the nutrients. This is important because eutrophication caused by algae communities can happen when this ratio gets too low. This project identified a total of 12 significant trends, out of the 33 parameter seasons examined. There were trends of concern but there is a limitation on this project by the limited record for some parameters.

## Introduction



*Figure 1 Showing the Baxter Creek sub-watershed with the land use shown by colour. The yellow represents agricultural land, the red represents the build up areas, and the various greens represents the natural areas.*

The sub-watershed of Baxter Creek contains a single developed settlement of Millbrook, which is experiencing growth and new development. The rest of the watershed consists of either agricultural or natural areas, and Baxter Creek flows through the center of the town before joining the Otonabee River. The contents of Baxter Creek along with the contents of the Otonabee river flow into Rice Lake. To understand what is affecting water quality, stream monitoring programs are quite useful as streams are transport mechanisms which deliver nutrients and possible pollutants to downstream areas such as Rice Lake. Streams act largely as transport pathways for delivering nutrients and other debris downstream, and when nutrients are

too concentrated eutrophication can occur in those downstream area (Stutter et al. 2018). The provincial government of Ontario's Ministry of the Environment Conservation and Parks has sampled streams across the province as a part of the Provincial Water Quality Monitoring Network [PWQMN]. This network is publicly available and allows researchers to access and analyze this dataset, which for streams is often done to assess the eutrophication risk for downstream communities. On Baxter Creek, there have been 3 sampling sites for the PWQMN, but only one is active to this day and it is station 17002107702 which was first sampled in 1977. The key nutrients associated with eutrophication are phosphorus and nitrogen, but there are other parameters of biological importance such as dissolved organic carbon, sodium and chloride (Stutter et al. 2018, Hintz and Relyea 2017). While these chemicals on their own can be analyzed to assess the water quality, researchers have found that the molar ratio of nitrogen and phosphorus to organic carbon can provide a clearer insight for the bioavailable fraction (Stutter et al. 2018).

This study is not the first to examine the PWQMN data for Baxter Creek as in March of 2023 Trent student Brooke Ceci did a brief analysis of this data (Ceci 2023). This 2023 study examined the annual average concentrations of the parameters and used a pivot table to generate trend lines (Ceci 2023). Then, the strength of the relationship between concentration and time was assessed using the  $R^2$  value (Ceci 2023). That study was limited as it did not account for differences in units within the dataset, nor did it account for seasonality, but it did reduce the impact of the variable sampling regime by using the average annual concentration (Ceci 2023). This study will analyze some parameters in common including sodium, chloride, nitrogen and phosphorus but this study will not be analyzing dissolved oxygen. This study will compare results with trends found in the previous study, but as methodologies between these studies vary, the results are not directly comparable.

This study aimed to resolve these limitations by ensuring units were consistent, and sample events were classified into a season to account for seasonality. This study will use a Mann-Kendall test as this non-parametric test is robust against data gaps which were an issue in the previous study (Ceci 2023). This study will also categorize each sample event into a season as streams are subject to seasonal variability due to seasonal hydrological events (Meals et al.

2011). This study will also do a brief inspection on the seasonal relationship between concentration and the discharge of Baxter Creek.

Within this study the water quality parameters being examined are sodium, chloride, dissolved organic carbon [DOC], nitrate, total nitrogen [TN], total nitrogen by the Kjeldahl method [TKN], total phosphorus [TP] and soluble reactive phosphorus [SRP]. This study sought to (1) investigate if any linear seasonal trends are present in the period of record of water quality for Baxter Creek. This study also sought to determine (2) if seasonal trends are present in the stoichiometric ratio of N:C or P:C for Baxter Creek.

## Materials and Methods

This project began by comparing the data analyzed within the previous study (Ceci, 2023) and the data publicly available from the provincial water quality monitoring network [PWQMN]. I then downloaded the data for Baxter creek sample station 17002107702 from PWQMN and filtered the parameters. The parameters being examined were sodium, chloride, DOC, nitrate, total nitrogen [TN], total nitrogen of the Kjeldahl method [TKN], total phosphorus [TP], and soluble reactive phosphorus [SRP]. The naming of these parameters was consistent in the PWQMN data from 1980-2020, but for the 2021-2023 data the exact naming code was slightly different. The values and ranges of the parameters were briefly compared between 2020 and 2021-2023 and the naming code was altered to match 1980-2020. The PWQMN data was organized by decade and these files were compiled into a single CSV file.

The discharge data of 2007 to 2020 Baxter creek sourced from the Water Survey of Canada accessed by James Kelly was formatted to match the water quality data. In RStudio the discharge data was merged with the water quality data by date. The data was then assigned to a season with March, April, and May being spring months, June, July, and August grouped into the summer season and September, October, and November grouped into the autumn season. The winter season was removed as the period of record did not include consistent data collection in the months December, January, and February.

A simple linear model was performed for each parameter in each of the season with the  $\log(\text{discharge})$  as the x variable, and  $\log(\text{concentration})$  as the y variable. Plots were also

constructed to visualize the relationship between concentration and discharge and the seasonality of this relationship.

A one-way ANOVA Tukey post hoc test was performed on the water quality parameters to determine if the parameters' concentration differed by season across the period of record. The summary statistics were then calculated for the seasons for each parameter by year, and the seasonal mean of the discharge was also calculated. The data was then expanded to ensure missing season-year combinations for each parameter were present. Then the data frame was exported into a .csv file where any blank observations before the first sample event were removed, and this .csv was read back into RStudio.

A Mann-Kendall test was performed on the different water quality parameters for each season across the period of record to determine if any linear trends exist across the period of record. For any years that lacked any observations within a season the seasonal median was used in its place to ensure the Mann-Kendall test could be run on the data set. The  $p$  value was then assessed to determine the significance of the trend, where a  $p$  value of less than 0.05 was labelled significant and greater than 0.05 was non-significant. The Sen slope was calculated as a part of the Mann-Kendall test and from it a y-intercept was calculated for each parameter in the three seasons. The seasonal mean concentration of the water quality parameters was plotted against the year sampled, with a trend line plotted with the slope equal to the Sen's slope and the line type determined by significance.

The seasonal means of the nitrogen, phosphorus and carbon parameters were converted into molar concentrations before the nitrogen and phosphorus parameters were divided by the molar DOC concentration. This ratio data frame was also expanded and any blank rows before the first observation again removed in a .csv file. This seasonal mean molar ratio of N or P to DOC then had a Mann-Kendall test performed on it to determine if any linear trends exist within seasons over years. Plots were constructed as before with the Sen's slope and significance determined line type.

## Results

### Seasonality of Parameters

*Table 1 Showing the Results of the ANOVA and post hoc Tukey test to compare significance of the differences between seasons. The columns note the parameter examined, the seasons being compared, the p value, and the significance where a p-value less than 0.05 is significant.*

Parameter	Comparison	p-value ANOVA	P value Tukey
DOC	Spring-Summer	0.191	not significant
DOC	Spring-Autumn	0.0179	significant
DOC	Summer-Autumn	0.468	not significant
Chloride	Spring-Summer	0.160	not significant
Chloride	Spring-Autumn	0.317	not significant
Chloride	Summer-Autumn	0.610	not significant
Nitrate	Spring-Autumn	0.00150	significant
Nitrate	Summer-Autumn	0.0130	significant
TKN	Autumn-Spring	0.494	not significant
TKN	Autumn-Summer	0.287	not significant
TKN	Spring-Summer	0.761	not significant
TN	Summer-Autumn	0.247	not significant
TN	Summer-Spring	0.0414	significant
TN	Autumn-Spring	0.0104	significant
SRP	Summer-Spring	0.364	not significant
SRP	Summer-Autumn	0.701	not significant
SRP	Spring-Autumn	0.264	not significant
TP	Spring-Summer	0.263	not significant
TP	Spring-Autumn	0.00152	significant
TP	Summer-Autumn	0.320	not significant
Sodium	Autumn-Spring	0.452	not significant
Sodium	Autumn-Summer	0.663	not significant
Sodium	Spring-Summer	0.740	not significant

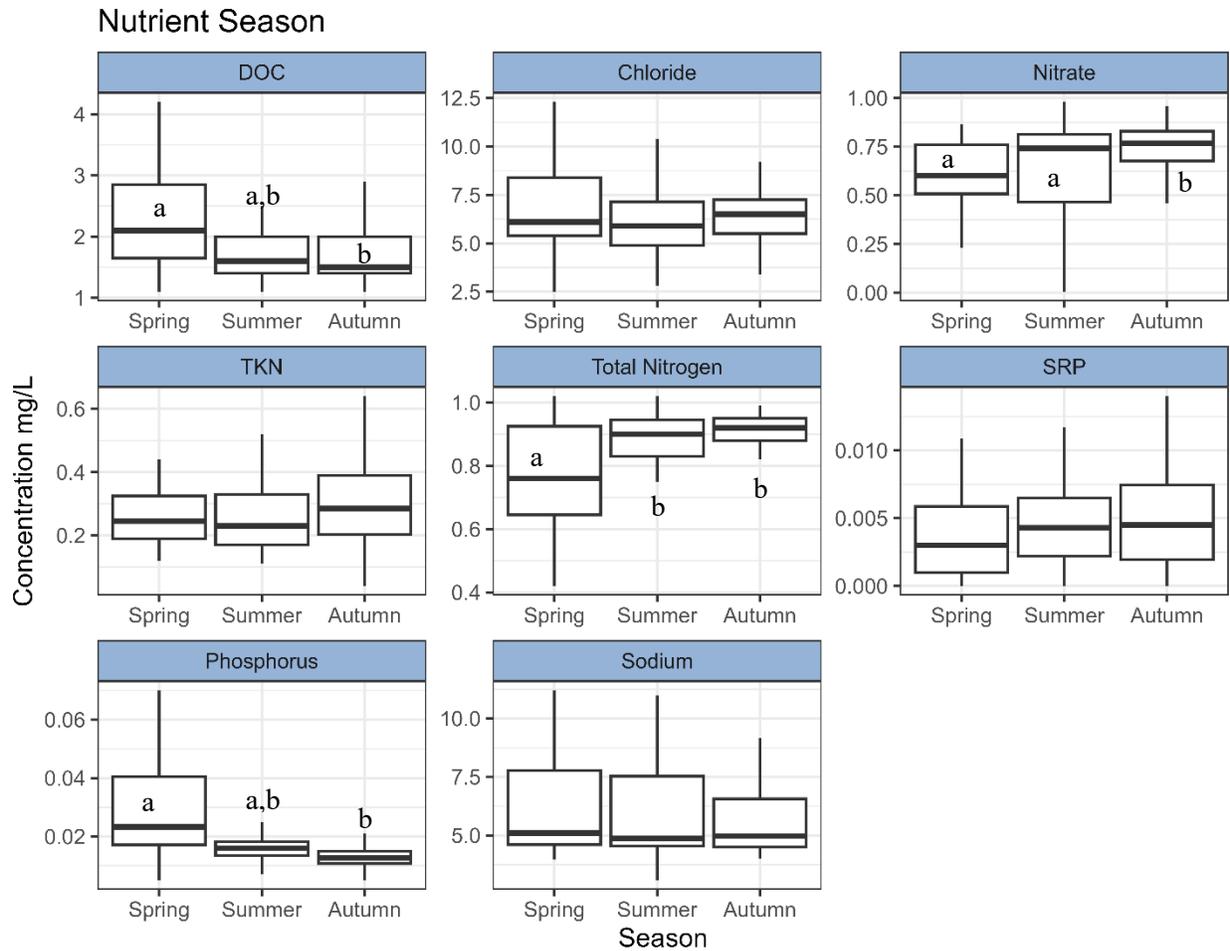


Figure 2 Above is a boxplot of for the concentrations of each parameter within each season. Significant differences are noted with letters above boxes, with boxes sharing a letter having no significant differences, but different letters representing significant differences. Where no significant differences were detected for any season no letter was used.

As Seen above in Table 1 and Figure 2, there is seasonal differences which are statistically significant for some of the parameters. These parameters are Total Phosphorus, Total Nitrogen, DOC, and Nitrate.

#### Trends for Parameters

Table 2 Showing the Results for the Mann-Kendall test on the seasonal mean concentrations (mg/L) for Spring, Summer, and Autumn for the 8 parameters. The columns note the parameter, the season, the Tau value, the Sen slope, the p value, and the significance.

Parameter	season	Tau	Sen slope	P value	significance
-----------	--------	-----	-----------	---------	--------------

DOC	Autumn	-0.412	-0.0469	0.0232	significant
	Spring	0.00735	0.00125	1	non-significant
	Summer	0.0588	0.00468	0.772	non-significant
CHLORIDE	Autumn	0.359	0.102	0.00477	significant
	Spring	0.129	0.05	0.305	non-significant
	Summer	0.153	0.0683	0.224	non-significant
NITRATES	Autumn	0.415	0.00680	0.00107	significant
	Spring	0.284	0.00329	0.0233	significant
	Summer	0.422	0.00807	0.000875	significant
TKN	Autumn	0.309	0.00796	0.00363	significant
	Spring	0.424	0.0103	6.46e-05	significant
	Summer	0.370	0.00925	0.000528	significant
TN	Autumn	0.4	0.0125	0.101	non-significant
	Spring	0.145	0.00786	0.585	non-significant
	Summer	0.2	0.00592	0.436	non-significant
SRP	Autumn	-0.220	-0.00021	0.0405	significant
	Spring	-0.0604	0	0.574	non-significant
	Summer	0.00348	0	0.983	non-significant
TP	Autumn	-0.108	0	0.298	non-significant
	Spring	-0.0743	0	0.469	non-significant
	Summer	-0.0232	0	0.828	non-significant
SODIUM	Autumn	0.249	0.0730	0.0465	significant
	Spring	-0.0444	0	0.724	non-significant
	Summer	-0.0282	0	0.831	non-significant

As seen above in table 2, 10 of the 24 season parameters were found to have p-values <0.05 resulting in those ten being determined to be significant. These were DOC Autumn (p=0.0232), Chloride Autumn (p=0.00477), Nitrate in Autumn (p=0.00107), Summer (p=0.00807), and Spring (p=0.0233), TKN in Autumn (p=0.00363), Spring (p=0.0000646), and Summer (p=0.00925), and lastly SRP in Autumn (p=0.0405).

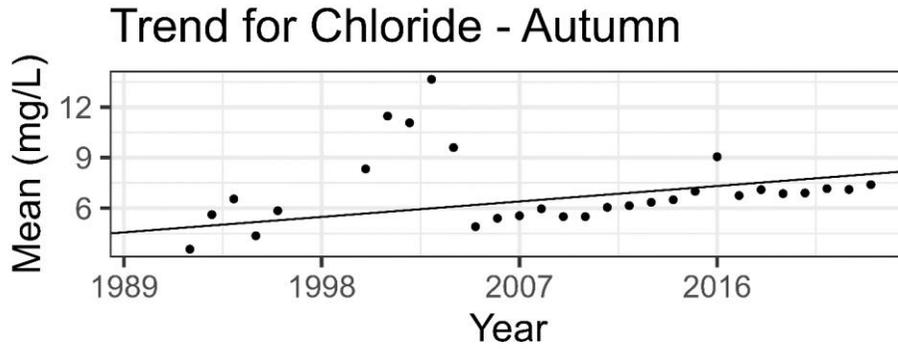


Figure 3 Showing the plot for the mean concentration of Chloride in mg/L in the Autumn season over the years sampled. the Tau value is 0.359, the Sen slope is 0.102, the p value is 0.00477.

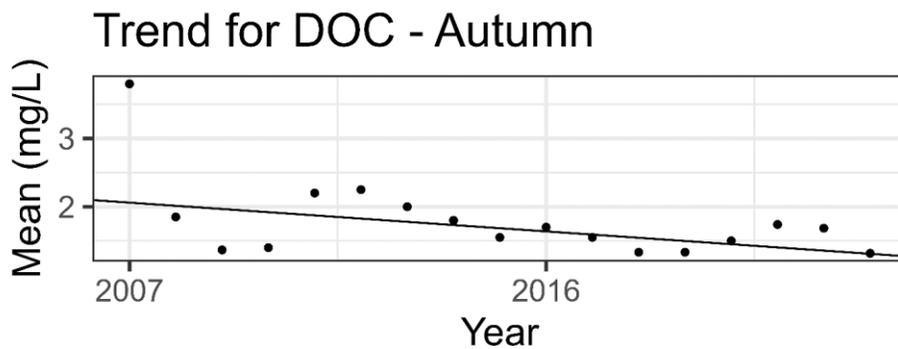


Figure 4 Showing the plot for the mean concentration of DOC in mg/L in the Autumn season over the years sampled. the Tau value is -0.412, the sen slope is -0.0469, the p value is 0.0232.

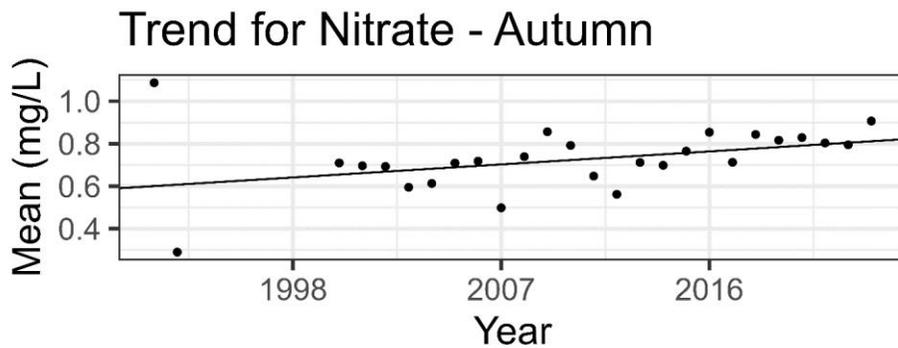


Figure 5 Showing the plot for the mean concentration of Nitrate in mg/L in the Autumn Season over the years sampled. The Tau value is 0.415, the Sen slope is 0.00680, the p value is 0.00107.

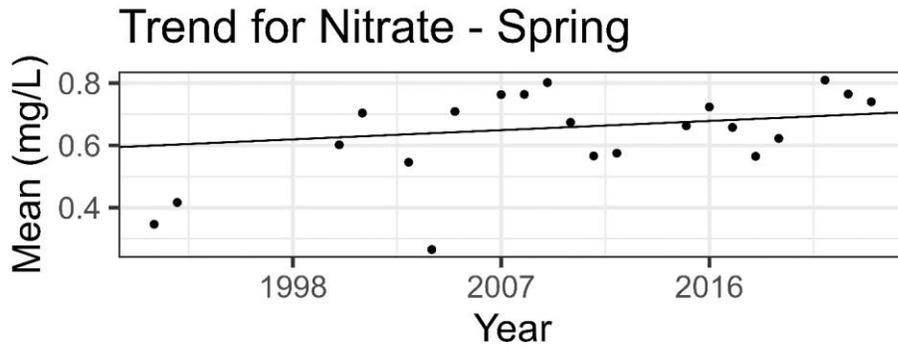


Figure 6 Showing the plot for the mean concentration of Nitrate in mg/L in the Spring Season over the years sampled. The Tau value is 0.284, the Sen slope is 0.00329, the p value is 0.0233.

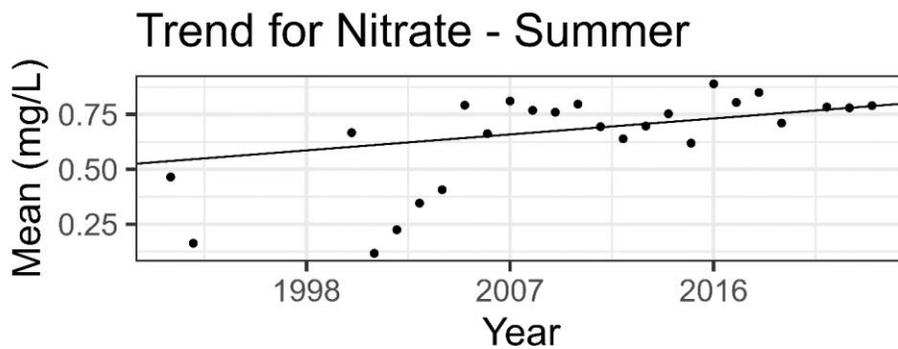


Figure 7 Showing the plot for the mean concentration of Nitrate in mg/L in the Summer Season over the years sampled. The Tau value is 0.422, the Sen slope is 0.00807, the p value is 0.000875.

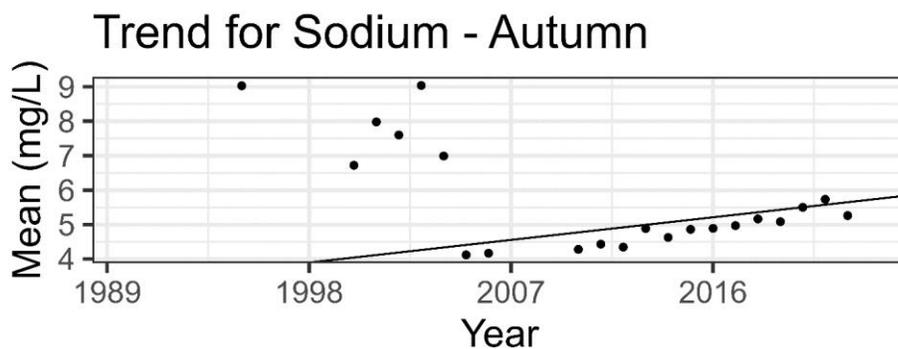


Figure 8 Showing the plot for the mean concentration of Sodium in mg/L in the Autumn Season over the years sampled. The Tau value is 0.249, the Sen slope is 0.0730, the p value is 0.0465.

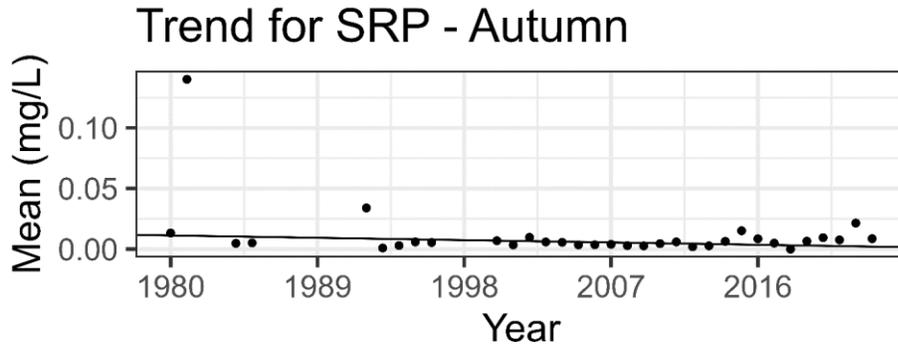


Figure 9 Showing the plot for the mean concentration of SRP in mg/L in the Autumn Season over the years sampled. The Tau value is -0.220, the Sen slope is -0.00021, the p value is 0.0405.

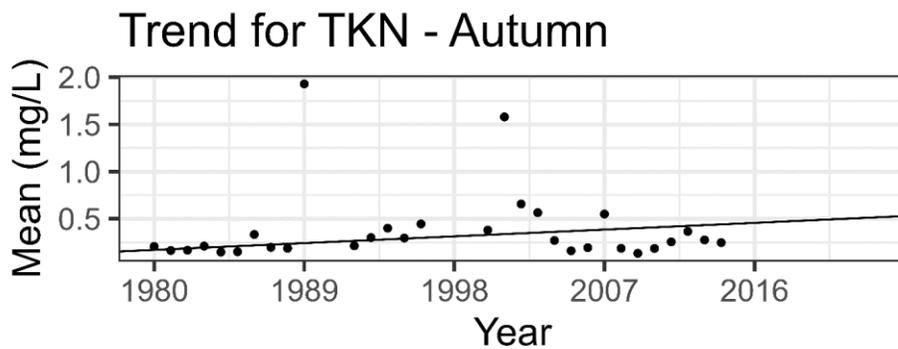


Figure 10 Showing the plot for the mean concentration of TKN in mg/L in the Autumn Season over the years sampled. The Tau value is 0.309, the Sen slope is 0.00796, the p value is 0.00363.

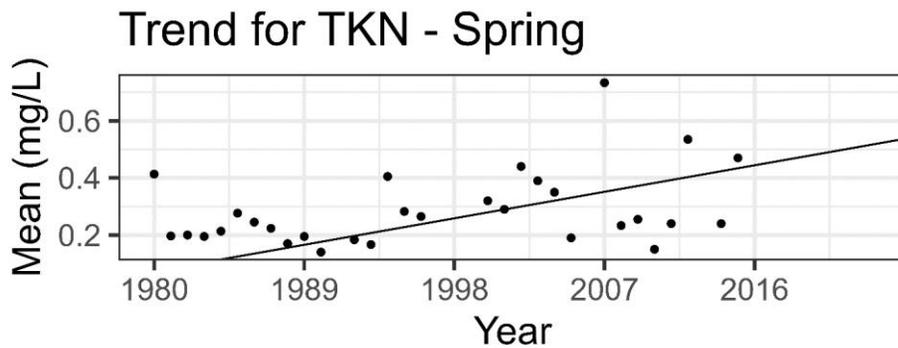


Figure 11 Showing the plot for the mean concentration of TKN in mg/L in the Spring Season over the years sampled. The Tau value is 0.424, the Sen slope is 0.0103, the p value is 0.0000646.

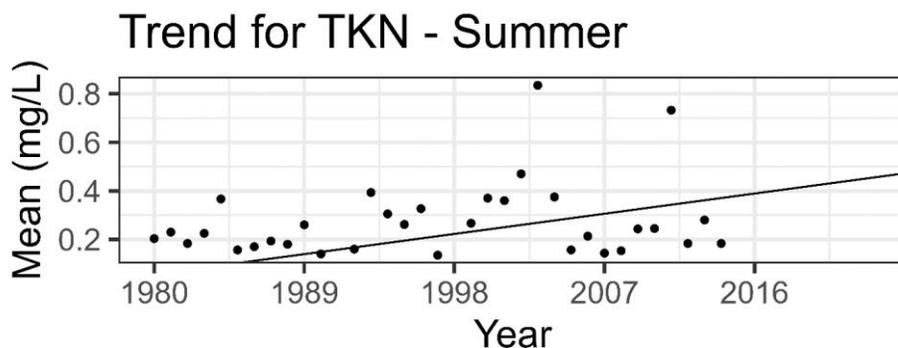


Figure 12 Showing the plot for the mean concentration of TKN in mg/L in the Summer Season over the years sampled. The Tau value is 0.370, the Sen slope is 0.00925, the p value is 0.000528.

### Stoichiometric Ratio

Table 3 Showing the Mann-Kendall results for the stoichiometric molar ratio of DOC: nutrient for Spring, Summer and Autumn. The nutrient ratio being analyzed is denoted in the column "Ratio". The columns show the season, the Tau value, the Sen slope, the p value, and the significance.

Ratio	Season	Tau	Sen slope	P value	significance
NITRATES	Autumn	-0.382	-0.0799	0.0357	significant
	Spring	0.0368	0.00651	0.869	non-significant
	Summer	0.147	0.0303	0.434	non-significant
SRP	Autumn	-0.574	-36.4	0.00151	significant
	Spring	-0.279	-21.0	0.125	non-significant
	Summer	-0.176	-8.90	0.343	non-significant
TP	Autumn	-0.0989	-1.21	0.661	non-significant
	Spring	0.143	3.54	0.510	non-significant
	Summer	-0.0220	-0.0291	0.956	non-significant

As seen above in Table 3, only 2 trends had a p value less than 0.05 and were thus labelled significant. These were DOC: Nitrate in Autumn (p=0.0357), and DOC: SRP in Autumn (p=0.00151).

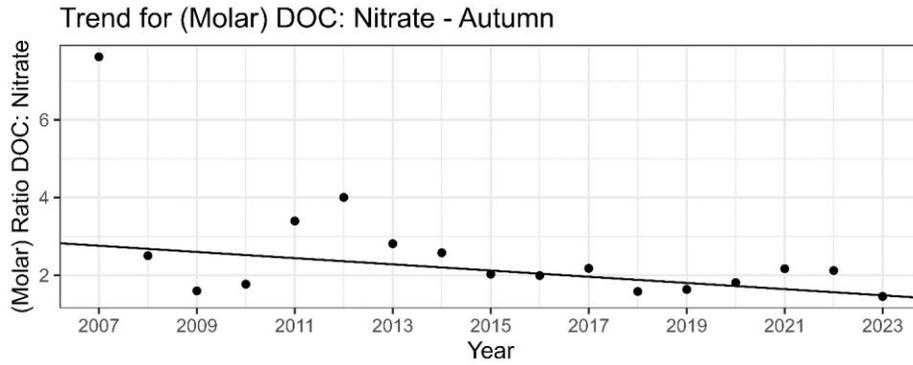


Figure 13 Showing the plot for the molar ratio of DOC: Nitrate in the Autumn Season over the years sampled. The Tau value is -0.382, the Sen slope is -0.0799, the p value is 0.0357.

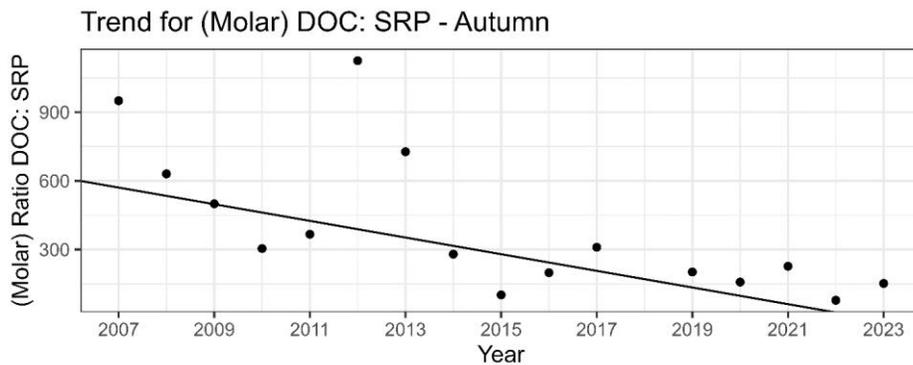


Figure 14 Showing the plot for the molar ratio of DOC: SRP in the Autumn Season over the years sampled. The Tau value is -0.574, the Sen slope is -36.4, the p value is 0.00152.

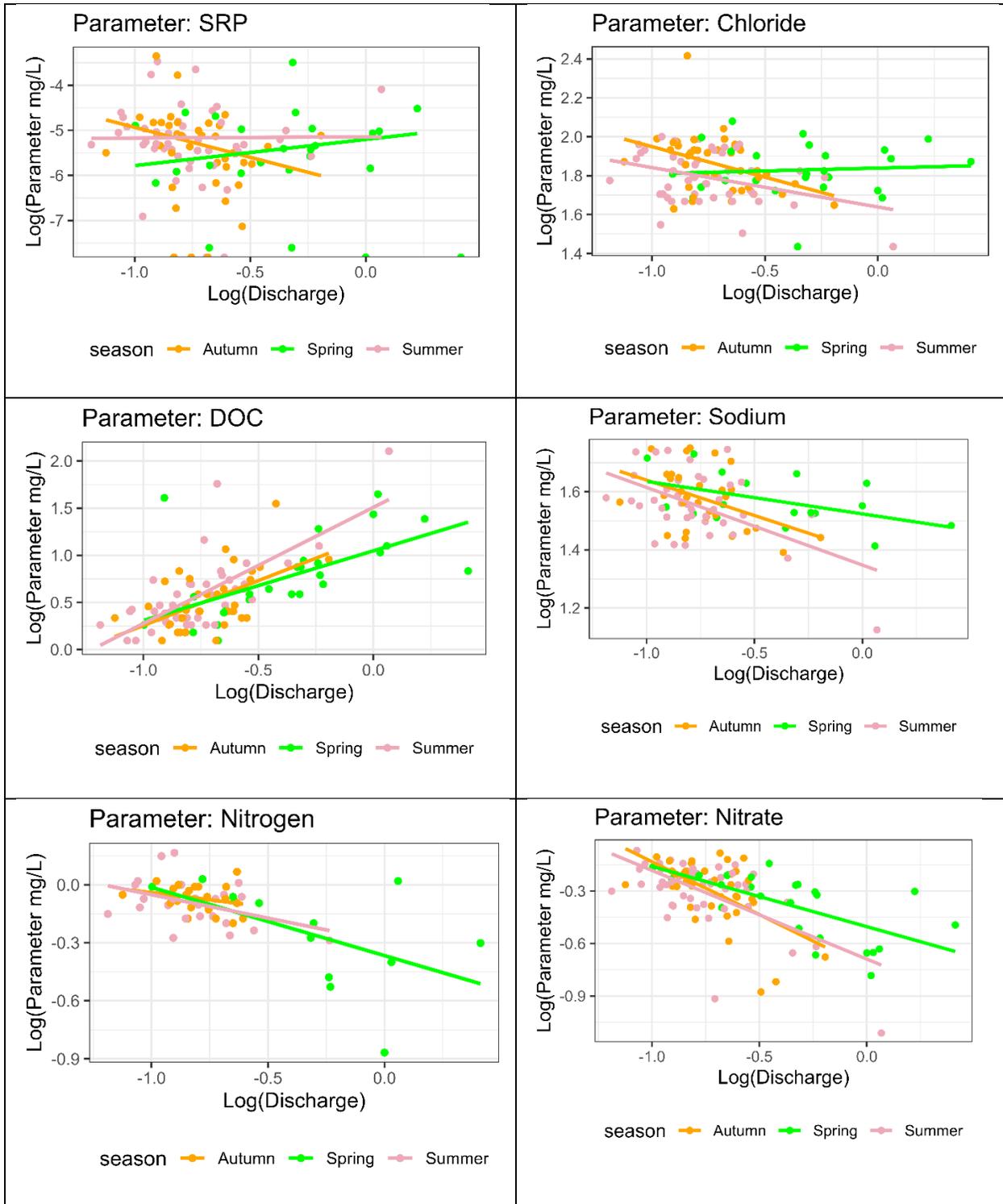
### Concentration-Discharge Relationship

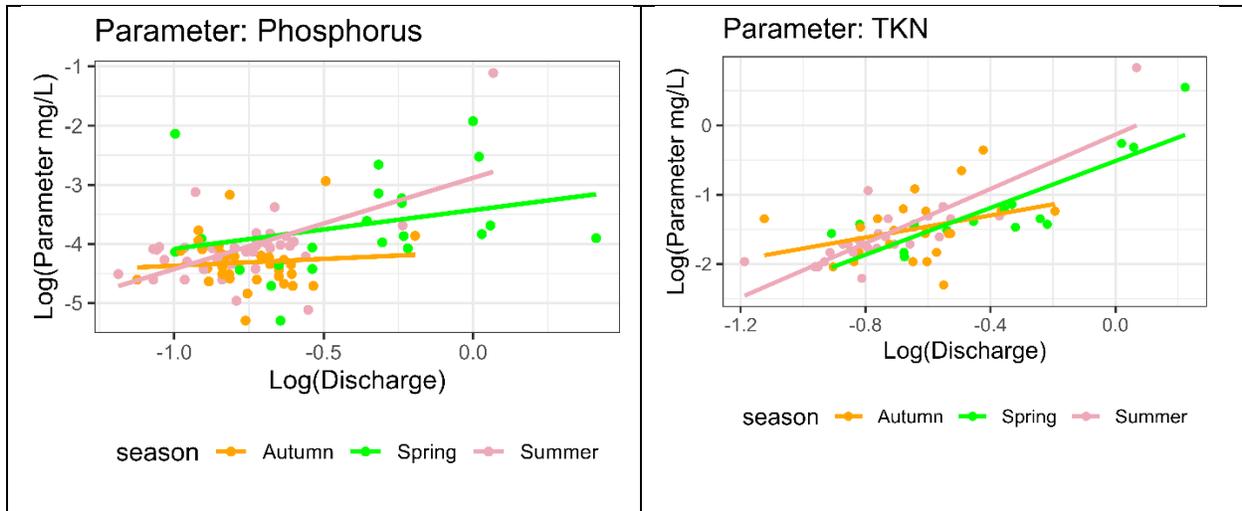
Table 4 Showing the results of the simple linear model on the Log(concentration) against the log(discharge). The columns show the parameter analyzed, the season analyzed and the outputted y Intercept, Slope and R<sup>2</sup> value.

Parameter	Season	Intercept	Slope	R <sup>2</sup>
DOC	Spring	1.05	0.738	0.362
	Summer	1.51	1.23	0.516
	Autumn	1.21	0.951	0.290
Chloride	Spring	1.84	0.0291	0.00550
	Summer	1.64	-0.203	0.126

	Autumn	1.64	-0.313	0.150
Nitrates	Spring	-0.504	-0.344	0.446
	Summer	-0.689	-0.506	0.367
	Autumn	-0.737	-0.604	0.330
TKN	Spring	-0.514	1.69	0.707
	Summer	-0.133	1.96	0.701
	Autumn	-0.981	0.795	0.113
TN	Spring	-0.366	-0.353	0.313
	Summer	-0.294	-0.243	0.182
	Autumn	-0.189	-0.149	0.0721
SRP	Spring	-5.20	0.580	0.0415
	Summer	-5.14	0.0266	8.80e-05
	Autumn	-6.26	-1.33	0.102
TP	Spring	-3.43	0.653	0.0844
	Summer	-2.88	1.54	0.351
	Autumn	-4.14	0.230	0.00786
Sodium	Spring	1.52	-0.112	0.242
	Summer	1.35	-0.267	0.285
	Autumn	1.40	-0.244	0.196

Table 5 Showing the plots of log(concentration) against log(discharge) for the 8 parameters with different colours noting the seasons. Trend lines on plots here do not represent significance.





## Discussion

### Compared trends with previous study.

When comparing results of this study and Ceci's (2023) study the differences between the approaches and methods used are especially important. In both studies the TKN was found to be increasing throughout the period of record, supporting the existence of this trend. This study used Nitrates unfiltered reactive as the nitrate being examined, and in Ceci's study this parameter was found to be increasing overall which this study supported (2023). For the parameter TN, Ceci's study observed a decreasing trend, this study found a nonsignificant trend for this parameter, but the Sen slope was positive further disagreeing with the result of the previous study (2023). As the Ceci study did not evaluate statistical significance, but rather evaluated the  $R^2$  value of the trend line, which is less robust against outliers compared to the Mann-Kendall test (2023). For Sodium, the Ceci observed a decreasing trend, whereas this study observed an increasing trend in the Autumn month and no trend in Spring or Summer (2023). This parameter did have an interesting change in values around 2004, the methodology and units for this parameter did not change at this time. This trend disagreement and abrupt change around 2004 was also found for the Chloride parameter likely due to origins of these parameters being related (Hintz and Relyea 2017). For the parameter TP, the Ceci study did not correct for the values in micrograms and thus that parameter's analysis was not compared (2023). This study found no significant trend for TP in Baxter Creek in Autumn, Spring or Summer. For the parameter SRP, the previous study observed a decreasing trend, which this study did observe a significant decreasing trend for SRP

in Autumn  $p=0.0464$  (2023). This decreasing trend for SRP was not consistent across seasons as the spring and summer seasons had no trends detected within this study. The parameter which was not examined in the Ceci study was DOC, and this study identified a significant ( $p=0.00232$ ) decreasing trend in the Autumn season (2023). The Spring and Summer seasons held no significant trend for DOC ( $p=1$  and  $0.772$  respectively).

### Strength of Statistical analysis

The strength of the trend analysis was not constant across parameters as the length of the period of record is variable between parameters. The DOC parameter was first sampled in 2007 while the SRP had samples taken in 1980, all the parameters did have periods of records greater than seven years which is the accepted minimum for monotonic trend analysis performed in this project (Meals et al. 2011). There were data gaps in all parameters, with parameters such as TP containing a data gap of around 20 years which is large enough that the data is unfit for gradual trend analysis (Meals et al. 2011). The parameter TN showed another concern as sampling began in 2013, and this short period of record leads to a weaker trend analysis. The parameters which did not show serious data gaps and are recommended to use for future analysis are DOC, Sodium, Chloride, TKN, SRP, and possibly Nitrate. The Nitrate parameter has a 30-year period of record (1992-2022) but also contains a 6-year data gap (1994-1999) which is significant but as more samples are taken yearly this data gap becomes less impactful.

### Stoichiometric Trends

The stoichiometric ratios of nitrogen and phosphorus to DOC did reveal two significant trends, both for the Autumn season. The DOC: Nitrate molar ratio had a significant ( $p=0.0357$ ) decreasing trend along with the DOC: SRP trend which was a significant ( $p=0.00151$ ), but these trends had different magnitudes. The DOC: Nitrate ratio decreased gradually as seen with the Sen slope of  $-0.799$  while the DOC: SRP trend was steep with a Sen slope of  $-36.4$ . The other seasons held no significant trends along with the DOC:TP ratio showing no significant trends over time. This type of analysis is useful for understanding the bioavailability of these nutrients but with a DOC's shorter period of record the strength of the trend analysis is not as strong as the parameters on their own. The decreasing nature of the trends for these ratios is concerning as lower ratios of carbon to these nutrients can result in eutrophication (Stutter et al 2018). This ratio is already of some concern as the ratio of DOC: Nitrate has ranged from around 2 to 4 since

2008. This ratio is lower than the ideal carbon: nitrogen ratio of 4-20, as this is the zone which lowers the risk of downstream eutrophication (Stutter et al. 2018). This ratio is using total nitrogen though which includes nitrates along with other forms of nitrogen, but the PWQMN has a period of record for total nitrogen beginning in 2013 making it unsuitable for long term trend analysis currently.

### Discharge-Concentration relationship

The relationship between concentration and discharge is variable between parameters and for some parameters between seasons as well. For parameters DOC, TKN, sodium, nitrogen [TN], Nitrate, and phosphorus [TP] the direction of the relationship did not differ between seasons only the range of discharge and steepness. For chloride and SRP, the relationships did differ in the direction of relationships between seasons. For chloride, this was observed in Table 4 top right corner with the log(concentration) increasing with log(discharge) in spring but decreasing in Autumn and Summer. This could be due to road salt chloride being added to the Creek from the snowmelt in spring as a loading effect, where that salt is then diluted and flushed downstream in summer and autumn with rainfall runoff. For SRP this was observed in Table 4 top left corner with the log(concentration) decreasing with log(discharge) in Autumn but increasing in Summer and Spring. This is an interesting relationship that could be of interest to examine in further detail in future studies. It is vital to note that these plots are not showing significance with the trend lines, and the simple linear model run does not provide the statistical significance of these relationships.

### Areas for Future Research

Explore non-linear trends in the data which could use a model such as GAMS to generate trend curves. The concentration-discharge relationship should be investigated further as that can provide insight into the origins of some parameters and their proximity to Baxter Creek (D'Amario et al. 2021). Future researchers may decide to classify data not by season but by discharge rates, or pre- and post-snow melt etc. Future researchers should inquire about accessing data from Dr. Xenopoulos but as the sampling location is different an analysis to confirm the data is comparable should be conducted. As the PWQMN data set includes micronutrients and trace metal parameters, an analysis of those parameters could prove interesting, including investigating possible sources. The dissolved oxygen [DO] analysis of the

Ceci study could be expanded upon if more frequent sample events were available for dissolved oxygen, as it varies greatly within a day and season (2023). With more frequent sample events for DO, any long-term trends could be investigated once the daily and seasonal fluctuations are defined. Lastly, the abrupt change in the concentrations of Sodium and Chloride around 2004 should be investigated, as this study found that no unit or methodology changes occurred at 2004. One consideration for this area of research should be to contact the local public works department to learn more about what road de-icing agents are used and if they have changed in recent years. By comparing changes in applications of various de-icing agents with changes in chloride and sodium concentrations researchers may identify additional step trends due to changes in winter road management.

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Appendices

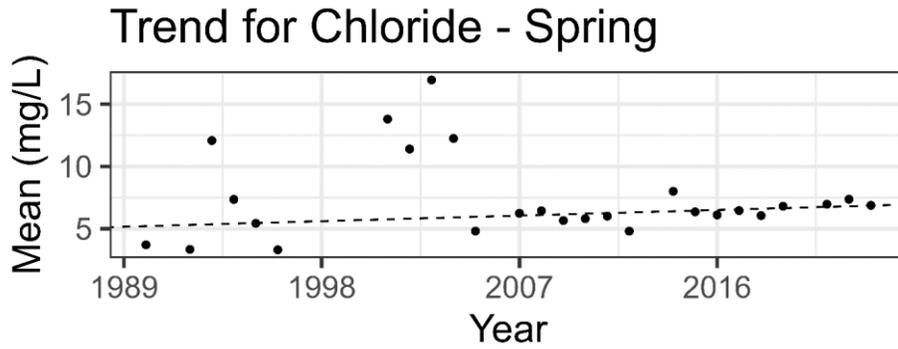


Figure 15 Showing the plot for the mean concentration of Chloride in mg/L in the Spring season over the years sampled. the Tau value is 0.129, the Sen slope is 0.05, the p value is 0.305.

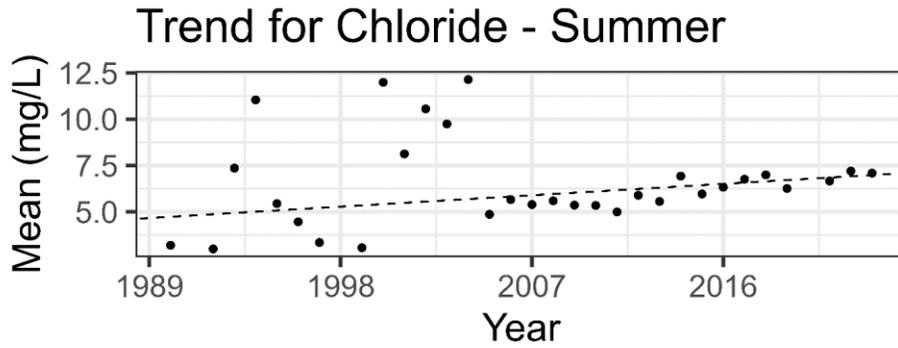


Figure 16 Showing the plot for the mean concentration of Chloride in mg/L in the Summer season over the years sampled. the Tau value is 0.153, the Sen slope is 0.0683, the p value is 224.

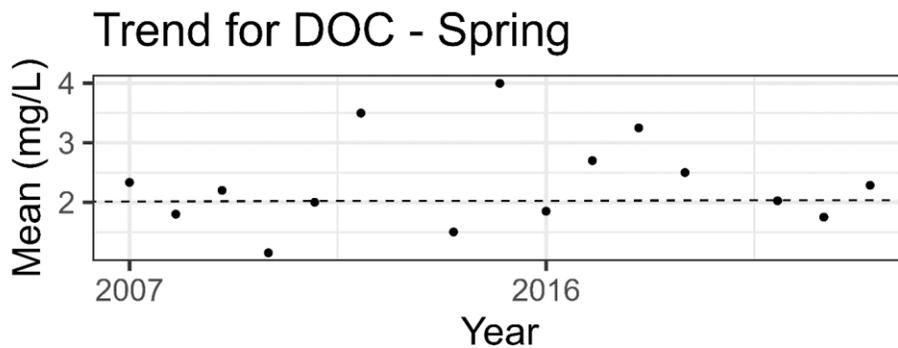


Figure 17 Showing the plot for the mean concentration of DOC in mg/L in the Spring season over the years sampled. the Tau value is 0.0074, the Sen slope is 0.00125, the p value is 1.

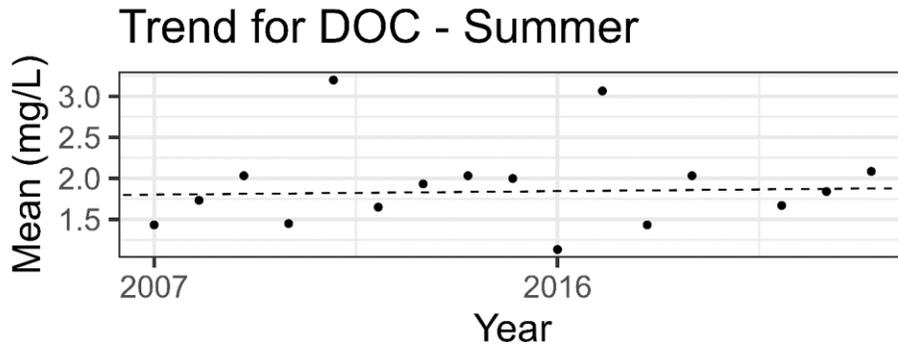


Figure 18 Showing the plot for the mean concentration of DOC in mg/L in the Summer season over the years sampled. the Tau value is 0.0588, the Sen slope is 0.00477, the p value is 0.772.

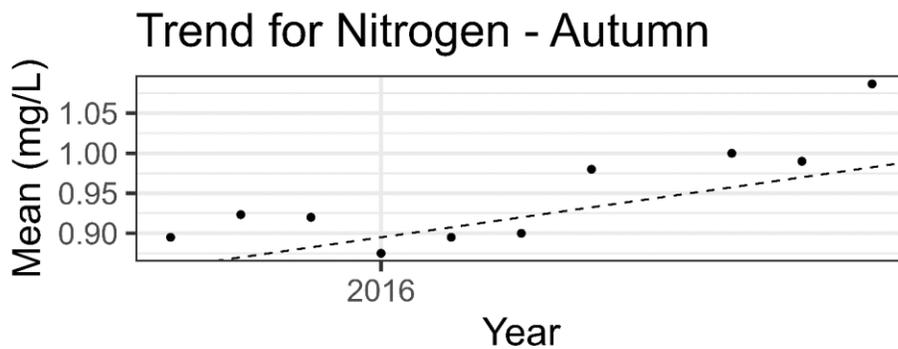


Figure 19 Showing the plot for the mean concentration of TN in mg/L in the Autumn Season over the years sampled. The Tau value is 0.4, the Sen slope is 0.0125, the p value is 0.101.

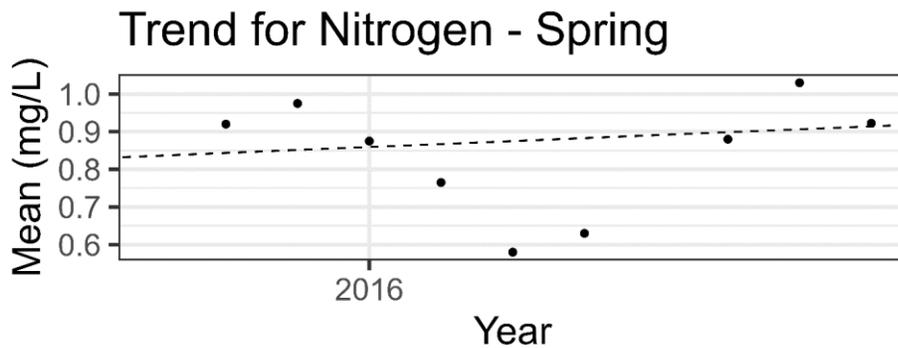


Figure 20 Showing the plot for the mean concentration of TN in mg/L in the Spring Season over the years sampled. The Tau value is 0.145, the Sen slope is 0.00786, the p value is 0.585.

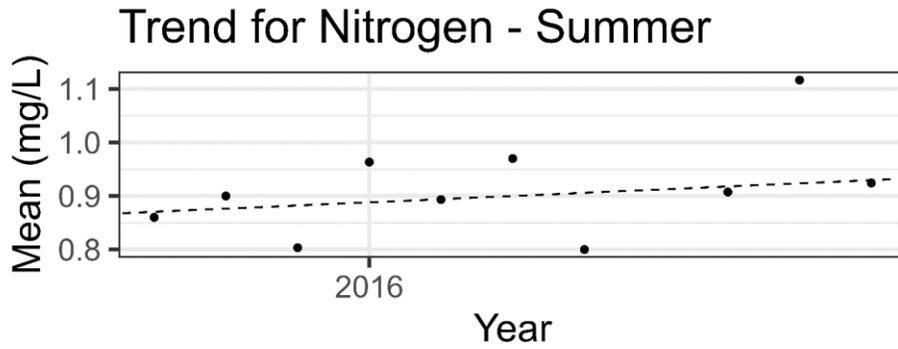


Figure 21 Showing the plot for the mean concentration of TN in mg/L in the Summer Season over the years sampled. The Tau value is 0.2, the Sen slope is 0.00592, the p value is 0.436.

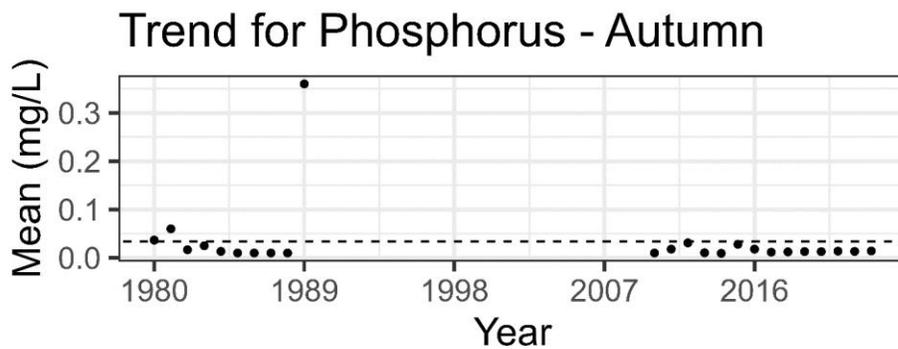


Figure 22 Showing the plot for the mean concentration of TP in mg/L in the Autumn Season over the years sampled. The Tau value is -0.108, the Sen slope is 0, the p value is 0.298.

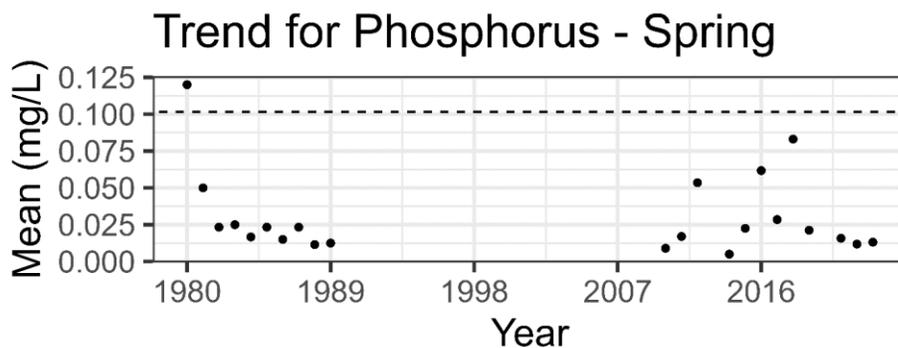


Figure 23 Showing the plot for the mean concentration of TP in mg/L in the Spring Season over the years sampled. The Tau value is -0.0743, the Sen slope is 0, the p value is 0.469.

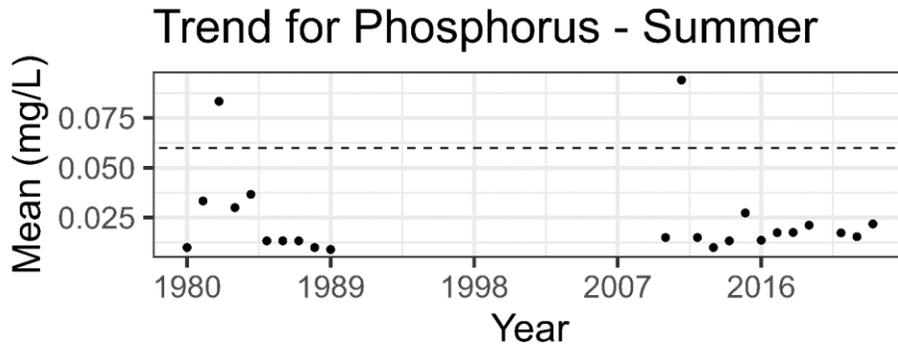


Figure 24 Showing the plot for the mean concentration of TP in mg/L in the Summer Season over the years sampled. The Tau value is -0.0232, the Sen slope is 0, the p value is 0.828.

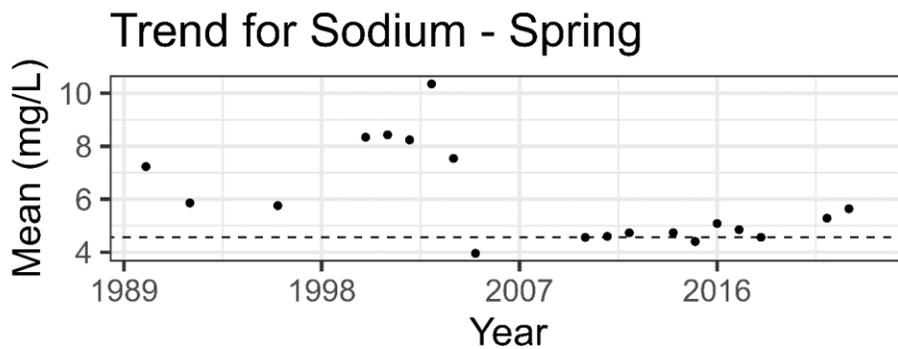


Figure 25 Showing the plot for the mean concentration of Sodium in mg/L in the Spring Season over the years sampled. The Tau value is -0.0444, the Sen slope is 0, the p value is 0.724.

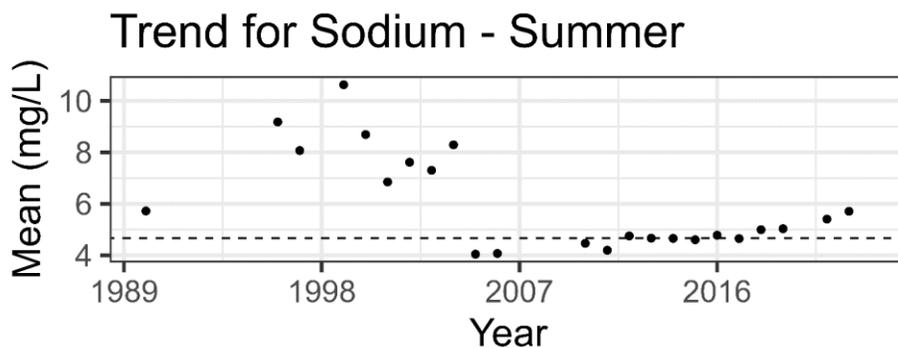


Figure 26 Showing the plot for the mean concentration of Sodium in mg/L in the Summer Season over the years sampled. The Tau value is -0.0282, the Sen slope is 0, the p value is 0.831.

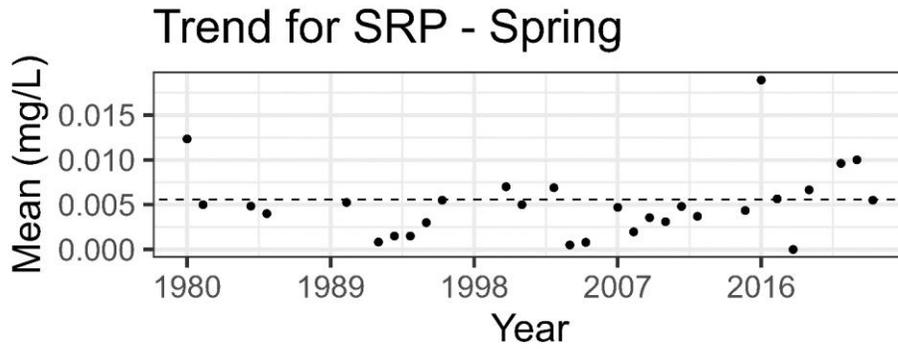


Figure 27 Showing the plot for the mean concentration of SRP in mg/L in the Spring Season over the years sampled. The Tau value is -0.0604, the Sen slope is 0, the p value is 0.574.

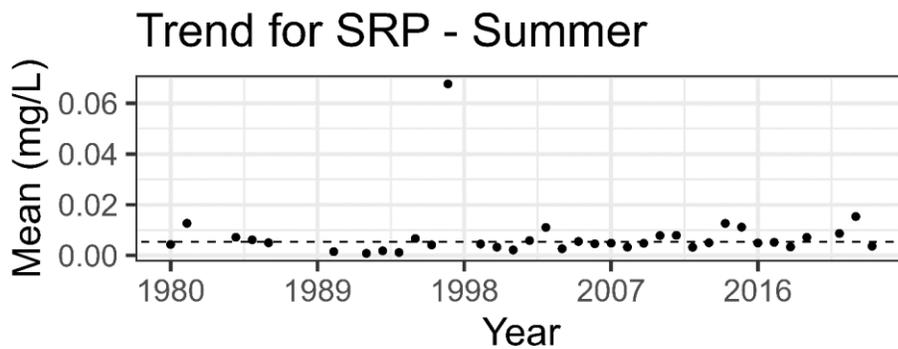


Figure 28 Showing the plot for the mean concentration of SRP in mg/L in the Summer Season over the years sampled. The Tau value is 0.00348, the Sen slope is 0, the p value is 0.983.

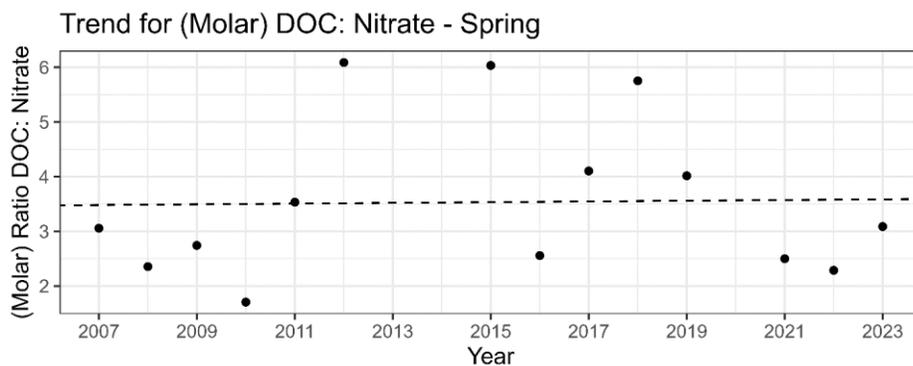


Figure 29 Showing the plot for the molar ratio of DOC: Nitrate in the Spring Season over the years sampled. The Tau value is 0.0368, the Sen slope is 0.00651, the p value is 0.869.

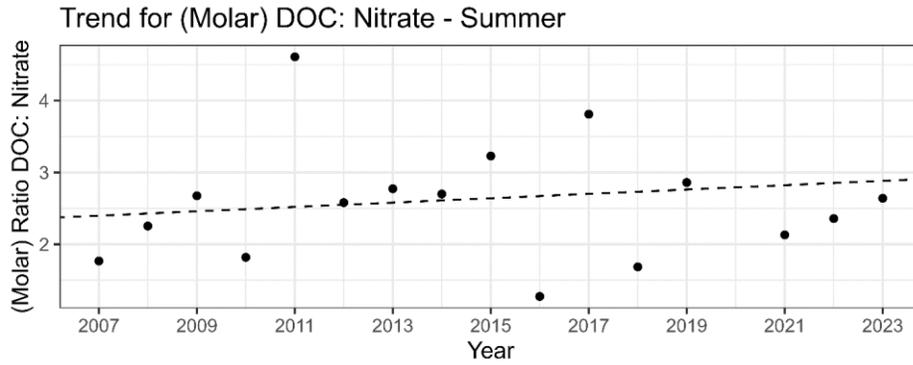


Figure 30 Showing the plot for the molar ratio of DOC: Nitrate in the Summer Season over the years sampled. The Tau value is 0.147, the Sen slope is 0.0303, the p value is 0.434.

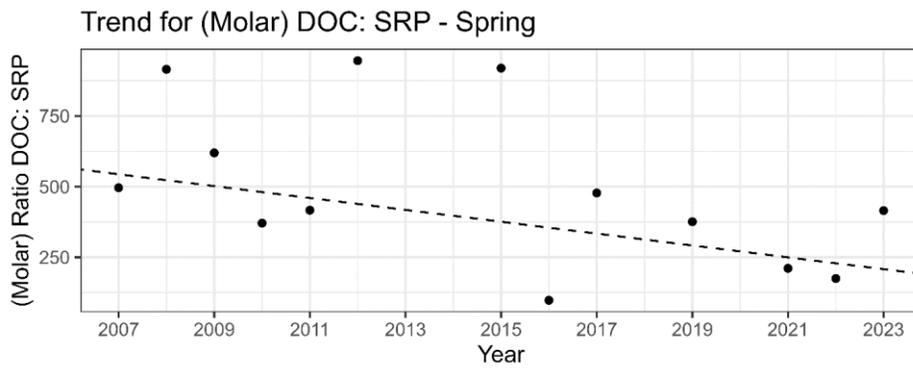


Figure 31 Showing the plot for the molar ratio of DOC:SRP in the Spring Season over the years sampled. The Tau value is -0.279, the Sen slope is -21.0, the p value is 0.125.

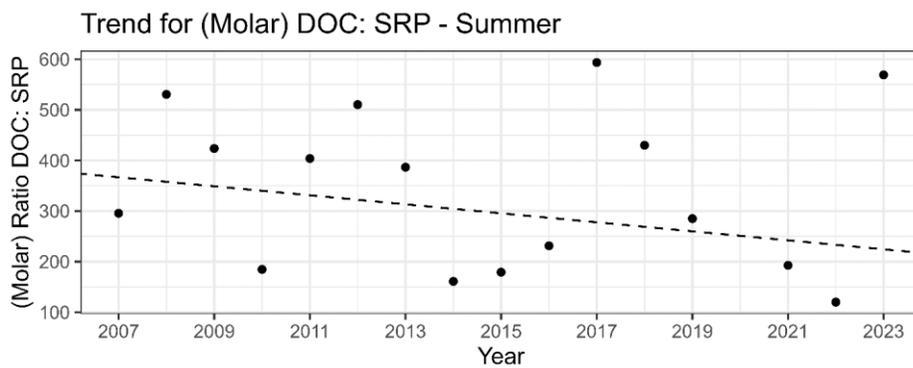


Figure 32 Showing the plot for the molar ratio of DOC: SRP in the Summer Season over the years sampled. The Tau value is -0.176, the Sen slope is -8.90, the p value is 0.343.

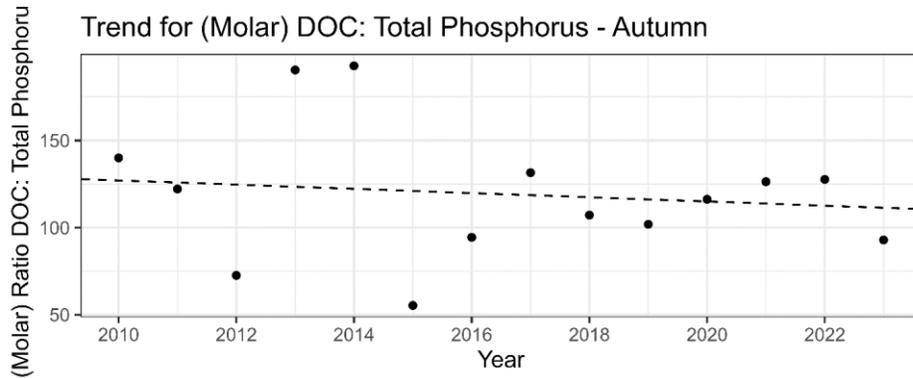


Figure 33 Showing the plot for the molar ratio of DOC: TP in the Autumn Season over the years sampled. The Tau value is -0.0989, the Sen slope is -1.21, the p value is 0.661.

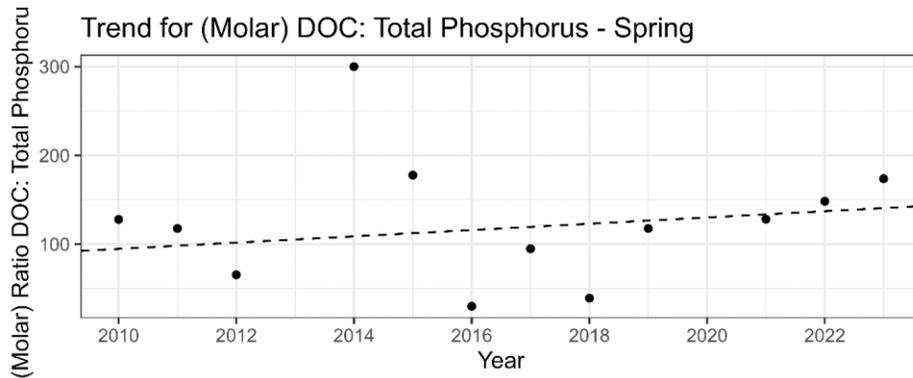


Figure 34 Showing the plot for the molar ratio of DOC: TP in the Spring Season over the years sampled. The Tau value is 0.143, the Sen slope is 3.54, the p value is 0.510.

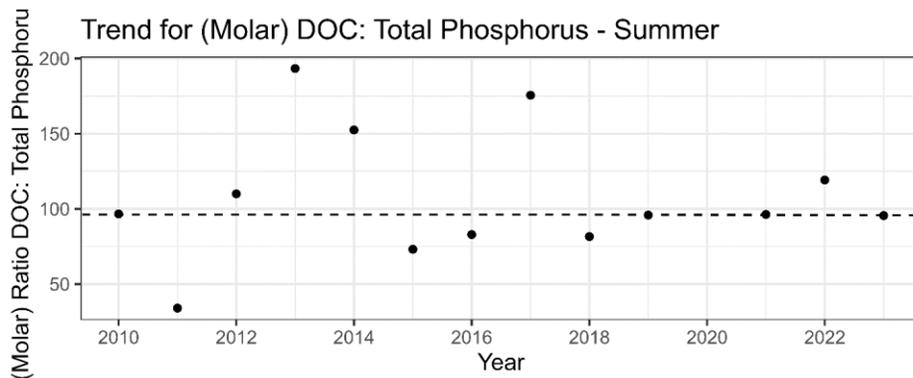


Figure 35 Showing the plot for the molar ratio of DOC: TP in the Summer Season over the years sampled. The Tau value is -0.0220, the Sen slope is -0.00291, the p value is 0.956.