Analysis of Water Quality Conditions and Trends for Indicators Triggered in 2012 under the Surface Water Quality Management Framework for the Lower Athabasca River

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Prepared by:

Hannah McKenzie, M.Sc., Kim Westcott, M.Sc., Colin Cooke, Ph.D.

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Comments or questions regarding *Analysis of Water Quality Conditions and Trends for Indicators Triggered in 2012 under the Surface Water Quality Management Framework for the Lower Athabasca River* are welcome and may be directed to:

Operations Division
Lower Athabasca Region
Alberta Environment and Parks
Address: #111 Main Floor, Twin Atria Building
4999-98 Avenue, Edmonton, AB T6B 2X3
Phone: (780) 427-7617 (outside Edmonton dial 310-0000 for a toll-free connection)
Fax: (780) 427-7824

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EXECUTIVE SUMMARY

This report presents the results of a technical assessment of water quality trigger exceedances for total nitrogen, dissolved uranium and dissolved lithium at the Athabasca River at Old Fort monitoring station for the year 2012. The assessment was initiated under the *Lower Athabasca Region Surface Water Quality Management Framework for the Lower Athabasca River* and helps fulfill a commitment made in the *Lower Athabasca Regional Plan* to initiate a management response when annual assessments indicate triggers or limits have been exceeded. The monitoring results are found in the *2012 Status of Ambient Environmental Conditions Report*. This water quality assessment completes the first two steps (verification and preliminary assessment) in the management response and identifies which water quality indicators will be moved into the investigation phase. The key findings of the assessment are described below.

Total nitrogen varied significantly between seasons and these differences could not be explained by seasonal variability in flow alone, suggesting other natural or anthropogenic factors may also be important. Examination of the relationship between total nitrogen and flow revealed a nonlinear association, with total nitrogen initially decreasing with increasing flow at lower flows (<500 m^3/sec), and then increasing with increasing flow at higher flows (>500 m^3/sec).

In 2012, a mean trigger was exceeded for total nitrogen at the Athabasca River at Old Fort monitoring station. Examination of 2012 flow conditions suggests that flow may have contributed to this exceedance, since total nitrogen concentrations increase at higher flows, and 2012 exhibited higher than normal mean flow.

Trend analyses on total nitrogen concentrations at the Athabasca River at Old Fort monitoring station indicate that significant increasing annual and/or seasonal trends exist for the non-flow and flow-adjusted data. Significant annual (non-flow-adjusted) and seasonal (flow-adjusted) trends were also detected at the Athabasca River upstream of Fort McMurray. Consequently, we cannot rule out the potential influence of the upstream station on trends in total nitrogen at the Athabasca River at Old Fort monitoring station, particularly given that a majority of water at the Old Fort station originates from sources upstream of Fort McMurray.

Although the magnitude of the total nitrogen trends detected at the Athabasca River at Old Fort are small relative to in-stream concentrations, total nitrogen again exceeded the mean trigger in 2013 (AEP 2016). The potential effects of increasing total nitrogen concentrations in the lower Athabasca River are primarily related to nutrient enrichment. Nutrient enrichment is an ongoing concern within the lower Athabasca River.

Dissolved uranium did not exhibit significant differences between seasons, although it appeared to be slightly higher in the winter. This pattern disappeared following flow adjustment, suggesting that the marginal seasonality observed was due to flow. Dissolved uranium was negatively related to flow during low flow, and not strongly related to flow during high flow. In 2012, both mean and peak triggers were exceeded for dissolved uranium. Examination of 2012 flow conditions in relation to these trigger exceedances indicates that they are not well explained by flow conditions.

Trend assessment indicated that there was a marginally significant increasing trend in dissolved uranium at the Athabasca River at Old Fort station, but this trend was not significant following flow adjustment. Given the proximity of the non-flow-adjusted trend to statistical significance and because dissolved uranium triggered again in 2013 (AEP 2016), we ran a trend analysis for the same time period at the Athabasca River upstream of Fort McMurray station. This analysis did not reveal any significant trends in dissolved uranium at the Athabasca River upstream of Fort McMurray station either before or after flow adjustment.

Dissolved lithium exhibited a seasonal pattern with higher concentrations in the winter and lower concentrations in the spring, summer, and fall. This seasonal pattern was attributed to variation in flow, as dissolved lithium was strongly, negatively related to flow on a log-log scale and the seasonal pattern disappeared following flow adjustment. Examination of 2012 flow conditions in relation to the 2012 peak trigger exceedance, suggests that the exceedance was due to flow conditions. Trend analysis did not reveal any significant trend in dissolved lithium, even after adjustment for flow.

The following recommendations have emerged from the preliminary assessment step of the 2012 management response:

- Move total nitrogen and dissolved uranium from preliminary assessment into investigation and close the management response for dissolved lithium.
- Use the data collected during AEP's 2015 synoptic survey of the Athabasca River to examine total nitrogen loading within the basin. Compare the 2015 synoptic survey data to earlier surveys to see if changes in total nitrogen loading are apparent.
- Focus future dissolved uranium analyses on the lower Athabasca River and its tributaries downstream of Fort McMurray. Review all existing dissolved uranium monitoring data for the lower Athabasca River and its tributaries collected through AEP's Long-Term River Network program, the Regional Aquatics Monitoring Program, and the Joint Oil Sands Monitoring Program.

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ACKNOWLEDGEMENTS

Our thanks to the Alberta Environment and Sustainable Resource Development team who support the collection and management of the Long-Term River Monitoring Network data. Thanks also to Ernst Kerkhoven and Yaw Okyere for generating the modeled flows for the Old Fort monitoring station, Mary Raven for her assistance in preparing this report, Nathan Ballard and German Rojas for their technical input, and Dr. Dennis Helsel for his expert advice on the trend assessment methodology used in this report.

1.0 INTRODUCTION

The *Surface Water Quality Management Framework for the Lower Athabasca River* (SWQMF) was developed as part of the Lower Athabasca Regional Plan. The Lower Athabasca Regional Plan and the SWQMF came into effect on September 1, 2012, and they focus on the lower Athabasca River downstream of the Grand Rapids to the Athabasca River Delta (Figure 1). The SWQMF includes ambient surface water quality limits and triggers – developed using historic monitoring data – for a suite of water quality indicators. The triggers and limits were designed to protect surface water quality from unacceptable impacts and to safeguard it for current and future uses (ESRD 2012). Under the SWQMF, a management response is required if water quality triggers or limits are exceeded.

As part of the SWQMF, ambient conditions are evaluated annually at Alberta Environment and Park's (AEP) Athabasca River at Old Fort monitoring station. Ambient conditions are then compared to the surface water quality limits and triggers developed for this station. The results of the 2012 annual assessment of ambient surface water quality conditions are presented in the *2012 Status of Ambient Environmental Condition Report* (2012 Status Report). While no surface water quality limits were exceeded, triggers were exceeded for three indicators: total nitrogen, dissolved uranium, and dissolved lithium. Because triggers were exceeded, AEP has initiated a management response to ensure water quality is maintained at acceptable levels.

The management response is a set of six steps that must be undertaken (in full or in part) when an ambient surface water quality trigger or limit is exceeded. A full description of the management system is found in the SWQMF (ESRD 2012). The purpose of this report is to support the preliminary assessment step of the management response to the 2012 annual assessment of ambient surface water quality conditions by examining water quality conditions and trends for the indicators that triggered in 2012. The technical assessment included in this report involved:

- examining 2012 flow conditions;
- establishing relationships between the water quality indicators and flow;
- examining seasonality;
- testing for temporal trends in flow and in water quality for each indicator.

Because flow is an important factor affecting water quality concentrations, trends were examined for both flow-adjusted and non-flow-adjusted concentrations. When increasing trends were found for either the non-flow-adjusted or flow-adjusted concentrations, trends were also examined at the upstream of Ft. McMurray monitoring station (approximately 200 km upstream of the Old Fort station; Figure 2) to provide a broader regional context. The results presented in this report are being used to guide future steps of the management response.

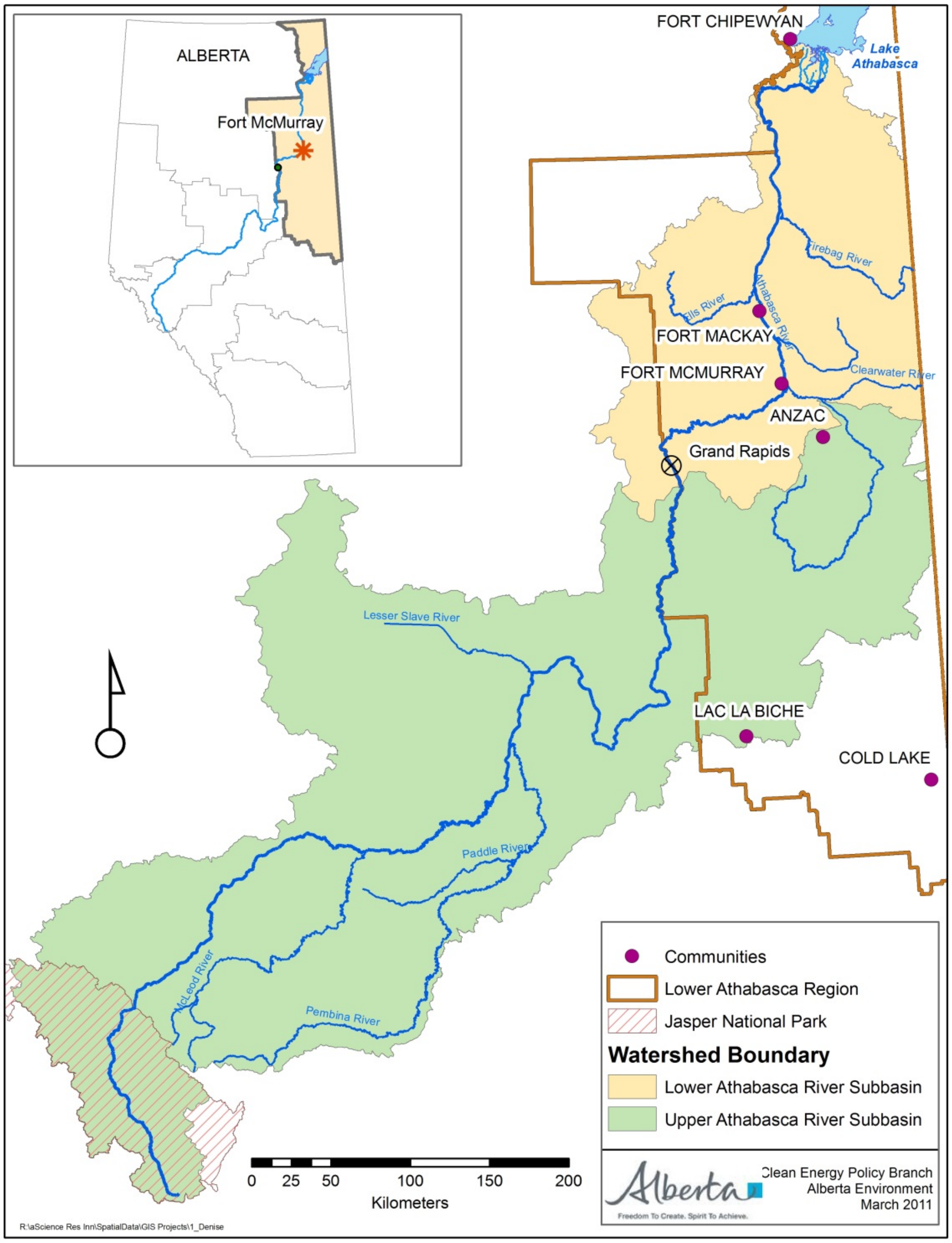


Figure 1. **Map of the Athabasca River Basin and Boundary of the Lower Athabasca Region.** *Note: The Surface Water Quality Management Framework for Lower Athabasca Region focuses on the lower Athabasca River downstream of the Grand Rapids to the Athabasca River Delta.*

2.0 METHODS

2.1 Water Quality Data

2.1.1 Monitoring Stations

The water quality data used in this report were collected by AEP at two Long-Term River Network (LTRN) sites within the lower Athabasca River: Athabasca River at Old Fort (AB07DD010/AB07DD0105) and Athabasca River upstream of Fort McMurray (AB07CC0030).

The Athabasca River at Old Fort monitoring station is located downstream of the second of four breakoff channels formed as the Embarras River breaks off of the main channel and flows toward Mamawi Lake and Lake Athabasca (Figure 2). Due to access issues, water quality samples from the Athabasca River at Old Fort station have been collected at two separate locations since 1997: at Old Fort (AB07DD010) during the open-water season and downstream of Devil's Elbow (AB07DD0105) during the winter (usually December-March). The Devil's Elbow station is located approximately 20 km downstream from the Old Fort station (but upstream of the winter road), and the Richardson River joins the Athabasca River between the sites (Figure 2). In the winter, the flow of the Richardson River ranges by approximately 3-9% of the flow of the Athabasca River where the Richardson River joins the Athabasca River, with an overall average of 5.5% in the winter months. Historically these stations have been combined for water quality analysis (Hebben 2009) and they are treated as a single station in the SWQMF.

The Athabasca River upstream of Fort McMurray monitoring station is located approximately 100 metres upstream of the confluence of the Horse and Athabasca rivers and approximately 3 km upstream of the confluence of the Clearwater and Athabasca rivers (Figure 2).

2.1.2 Water Quality Datasets

The water quality data included in this report were collected using discrete surface water grab samples following the water sampling protocols outlined in AENV (2006). The quality assurance/quality control samples are not included in the water quality datasets. All water quality data used in this report are available through the Oil Sands Information Portal: www.osip.alberta.ca. The water quality datasets used to describe conditions and trends at the Athabasca River at Old Fort monitoring station are briefly described below. The characteristics of the datasets for the Athabasca River upstream of Fort McMurray (used in follow-up trend analyses) are described in Appendix A.

Total nitrogen

Total nitrogen was calculated as sum of total Kjeldahl nitrogen and dissolved nitrate and nitrite. Where values were below the method detection level for nitrate and nitrite, a value of zero was used in the calculation. The period of record for total nitrogen at the Athabasca River at Old Fort monitoring station is 26 years (1988-2012). Total nitrogen was sampled monthly throughout the period of record, although there are 35 monthly observations missing. The occurrences of missing observations are spread relatively evenly between years and months, except there are a higher frequency of missing observations in April (n = 13) and November (n = 7), likely due to ice conditions (see Appendix). Of the 265 observations, none were censored. Censored data are observations for which there is incomplete information, with values being reported as less than the method detection limit. There were two samples taken in each of March 1990, March 1991, February 1994, October 1998, and July 2008. In each case we randomly chose one of the observations to keep and removed the other in order to have a consistent sampling frequency over the period of record (Helsel and Hirsch, 2002). The final dataset consisted of 260 observations.

Dissolved uranium

The period of record for dissolved uranium at the Athabasca River at Old Fort monitoring station is 10 years (2003-2012). Dissolved uranium was generally sampled quarterly in February, May, July, and October, until 2010, after which it was sampled monthly. None of the 61 observations were censored. To account for the systematic trend in sampling frequency (quarterly for eight years followed by monthly for two years), we defined seasons based on quarterly sampling and only used observations from February, May, July, and October (Helsel and Hirsch, 2002). The final data set consisted of 39 observations.

Dissolved lithium

The period of record for dissolved lithium at the Athabasca River at Old Fort monitoring station is 14 years (1999-2012). Dissolved lithium was generally sampled quarterly in February, May, July, and October, from 1999 until 2010, and monthly thereafter. Of the 75 observations, two were censored at a detection limit of 4 µg/L (2.7%). These occurred in November 2002 and February 2003. After May of 2003, improved laboratory analytical methodology reduced the detection limit to 0.02 µg/L. To account for the systematic trend in sampling frequency (quarterly for 12 years followed by monthly for two years), we defined seasons based on quarterly sampling and only used observations from February, May, July, and October (Helsel and Hirsch, 2002). There were two observations in July of 2008, therefore we randomly removed one of these observations to maintain one sample per quarter. The final data set consisted of 52 observations, with only one censored value.

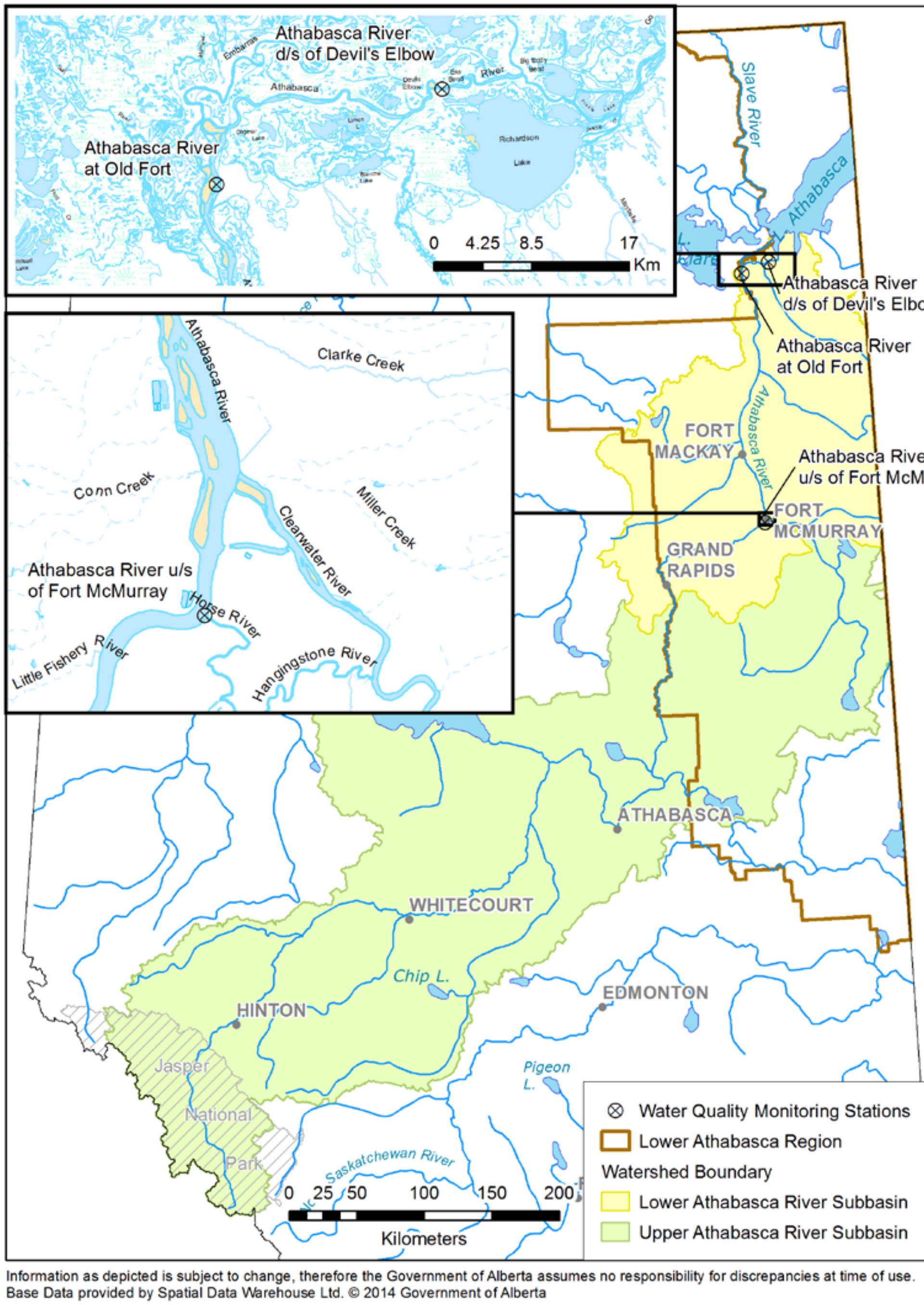


Figure 2. **Location of AEP Long-Term River Network Water Quality Monitoring Stations on the Lower Athabasca River.** *Note: The insets show the monitoring stations in greater detail.*

2.2 Flow Data

2.2.1 Monitoring Stations

There are two Water Survey of Canada (WSC) hydrometric stations close to the two LTRN water quality monitoring stations described in the previous section. These hydrometric stations are the Athabasca River near Old Fort (07DD011) and the Athabasca River below (i.e., downstream) Fort McMurray (07DA001). As with other hydrometric stations, water levels are recorded at the Athabasca River near Old Fort station; however, due to the channel characteristics at that station, a flow-water level relationship (i.e., rating curve) cannot be established. Consequently, flow estimates are not generated for this station, and in turn, there are no flow data available for the Athabasca River at Old Fort water quality monitoring station or for the winter sampling site downstream of Devil's Elbow. In contrast, flow data is available for the Athabasca River below Fort McMurray from 1957 to present. The Clearwater River joins the Athabasca River between the water quality monitoring station upstream of Fort McMurray and the Athabasca River below Fort McMurray hydrometric station. The flow for the Athabasca River upstream of the Fort McMurray water quality station was therefore calculated as the difference between the flow below Fort McMurray and the flow of the Clearwater River at Draper (07CD001).

2.2.2 Flow Modeling

Since there are no flow data available for the Athabasca River at Old Fort water quality monitoring station (or for the winter sampling site downstream of Devil's Elbow), AEP generated modeled flows for these sites. Flows at the Old Fort station and winter sampling site downstream of Devil's Elbow were estimated using a modified version of the lower Athabasca River Hydrol Routing Model (Seneka 2002) and the upper Peace-Athabasca Delta River 1D Routing Model (Andrishak and Hicks 2009). Collectively, these models make use of all available flow data from surrounding WSC and Regional Aquatics Monitoring Program hydrometric stations, and account for reported licensed withdrawals by oil sands mines (Figure 3). Flows were estimated by routing flows either from the Embarras Airport (07DD001), when those data are available, or from the Athabasca River below Fort McMurray (07DA001). The flow at the downstream of Devil's Elbow station was then calculated as the sum of the flow at the Athabasca at Old Fort station and the Richardson River (07DD002). Figure 4 shows the location of the key hydrometric stations supplying data used in the flow modeling.

The final WSC daily flow data for 2012 were not available at the time that the modeled flows were generated for input into the data analyses. Consequently, the model was run with preliminary AEP flow data.

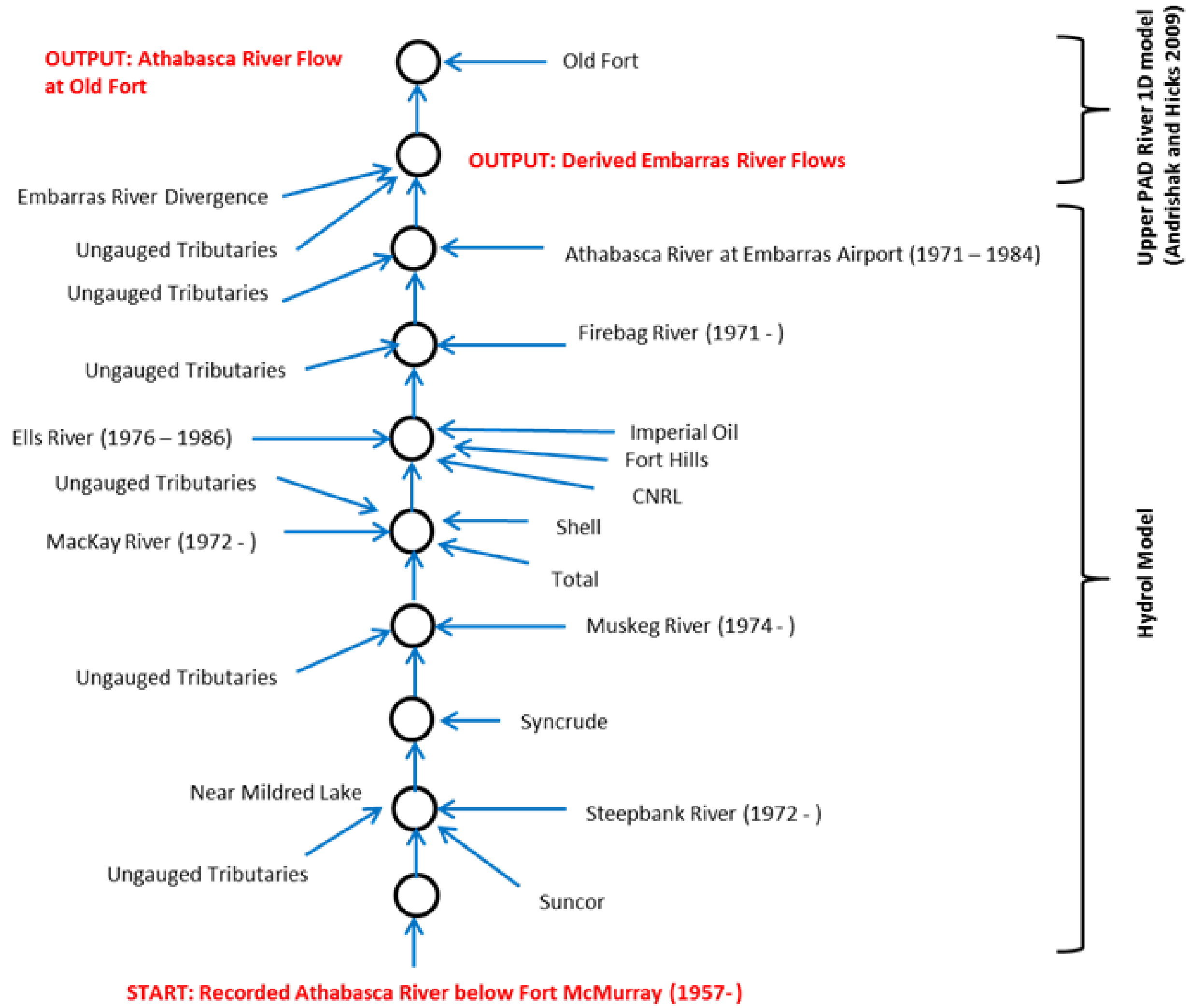
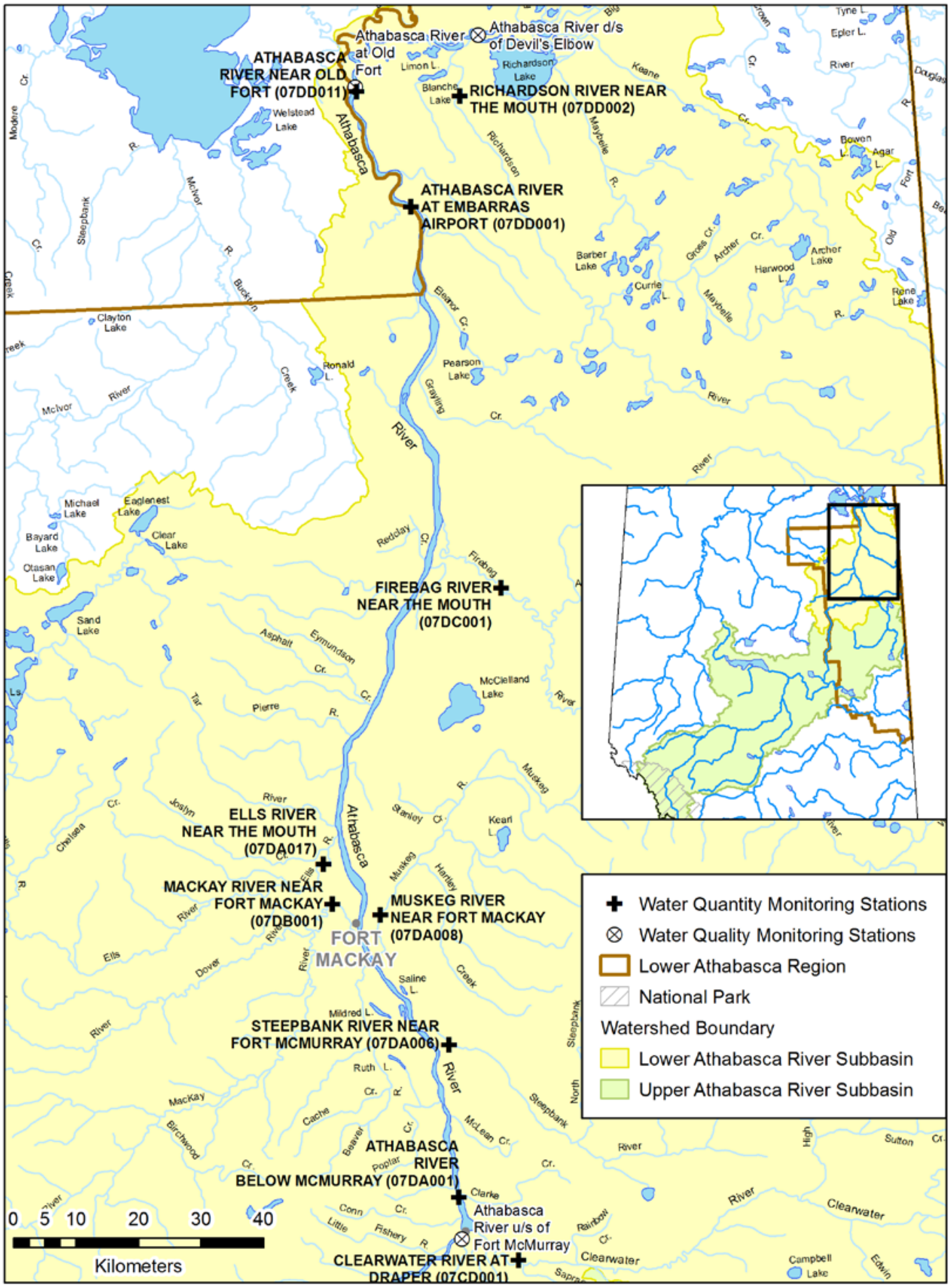


Figure 3. Schematic of the Modeling Approach Used to Estimate Flows at the Athabasca River at Old Fort Monitoring Station. *Note: Arrows indicate where data is being brought into the models.*



Information as depicted is subject to change, therefore the Government of Alberta assumes no responsibility for discrepancies at time of use.
Base Data provided by Spatial Data Warehouse Ltd. © 2014 Government of Alberta

Figure 4. Location of Key Hydrometric Stations from which Data were Obtained to Model Flows at the Athabasca River at Old Fort Monitoring Station.

2.3 Data Analysis

The water quality data were prepared prior to input into the statistical analyses, due to the presence of censored data, varying method detection limits, and varying sampling frequencies over the period of record for each indicator (see section 2.1.2). The details on how each water quality dataset was prepared prior to analysis are described in Appendix A. The datasets used to test for trends in flow included flows for the entire period of record for each water quality indicator, while the datasets used for flow adjustment only included flows that corresponded with water quality sampling dates.

2.3.1 Relationship between Water Quality Indicators and Flow

We tested for a monotonic relationship between the water quality indicators and flow using Kendall's tau. We also fit the Akritas-Theil-Sen (ATS) nonparametric line to the water quality and flow data on both the original and log-log scales to determine if there was a linear relationship on either scale. Both tests were done using 'cenken' in the NADA package. Lastly, we examined the graphical output of a lowess smooth on each water quality indicator and flow using 'loess' in the R base package. This last procedure is particularly useful when the flow-water quality relationship was nonlinear and non-monotonic

2.3.2 Seasonality

We first examined the seasonality of water quality and flow using boxplots (monthly or quarterly depending on the dataset). We then tested for seasonal differences using the Kruskal-Wallis test (implemented using 'kruskal.test' in the R base package) on monthly medians (flow), monthly means (total nitrogen) or quarterly means (dissolved uranium). Because the dissolved lithium dataset contained censored observations, we tested for differences between seasons using the G-rho family of tests (implemented using 'cendiff' in the NADA package).

2.3.3 Trend Assessment

The trend assessment method used follows the approach outlined in Helsel and Hirsh (2002) and Helsel (2012). The methods we used for trend assessment of both censored and uncensored data are described in detail below and all analyses were completed using R statistical software (R Core Team, 2003). The R output from the statistical analyses is provided in Appendix A1-A7.

Trends were assessed for the three water quality indicators that triggered in 2012 at the Athabasca River at Old Fort monitoring station as well as the flows corresponding with the time periods for each indicator. When increasing trends in water quality were detected, additional trend assessment analyses were performed on data from the upstream of Fort McMurray station for comparison. In addition, when increasing trends were detected at the Old Fort monitoring station and the data record exceeded 20 years, we also examined the data from the last decade separately to better understand recent conditions.

Trend analysis method for non-censored data

If the data were not censored, as was the case for flow, total nitrogen, and dissolved uranium, we used a nonparametric Mann-Kendall approach to test for a monotonic trend in concentration in both the original and flow-adjusted concentration. To adjust for flow, in the analysis of water quality indicators, we used the residuals of the lowess smooth of water quality concentration by flow. If there were differences between seasons, we used the seasonal Kendall test rather than the Kendall test. The Mann-Kendall and seasonal Mann-Kendall tests were implemented in the EnvStats package. The technical details are fully explained in the documentation for the EnvStats package, but we briefly describe them here as well.

The Mann-Kendall test for trend is based on Kendall's tau statistic (see Helsel and Hirsch, 1992 for details). The magnitude of the trend (slope) was estimated using the method of Theil (1950) and Sen (1968), and the confidence interval for the slope was obtained using Gilbert's (1987) modification of the Theil/Sen method. The intercept was estimated using Conover's (1980) method.

The seasonal Mann-Kendall test for trend uses the modification of Mann-Kendall's test for trend proposed by Hirsch et al. (1982), which allows for seasonality in observations. This test provides estimates of Kendall's tau, slope, and intercept for each season, as well as combined over all seasons. The overall tau is a weighted average of the seasonal taus. The overall estimate of the slope is the median of all two-point slopes computed within each season (Hirsh et al., 1982), with the confidence interval calculated using Gilbert's (1987) method. The overall intercept is estimated as the median of the seasonal intercepts. The seasonal Mann-Kendall test is only appropriate if there are not opposing trends in each season. Opposing trends between seasons can lead to erroneous conclusions regarding the existence of a trend. Therefore, we used the van Belle and Hughes (1984) heterogeneity test to determine if there were opposing trends in any season.

Trend analysis method for censored data

If non-detects were present in the dataset, as was the case for dissolved lithium, we followed a similar approach as above, with the following modifications. Flow adjustment was done in the same way, but we substituted the detection limit for the non-detect values, and we continued to treat those residuals as non-detects in later analysis. In the case of a single detection limit, as was the case for dissolved Lithium, we used the Mann-Kendall and seasonal Mann-Kendall trend tests as above to test for a significant trend. However, to calculate the nonparametric line we used the Akritas-Theil-Sen (ATS) method to calculate the slope and the Turnbull estimate of intercept instead of the Theil/Sen and Conover approaches outlined above, as the later are affected by the value chosen to represent the censored observations (Helsel, 2012). To obtain a confidence interval for the slope of the ATS line, we use the bootstrap method described by Wilcox (2001). There is no method available at this time for censored data to estimate an overall slope and intercept that takes seasonal differences into account.

3.0 RESULTS

3.1 Flow Conditions

3.1.1 Seasonality in Flow

The modeled daily average flow at the Athabasca River at Old Fort station from 1988-2012 is shown in Figure 5 along with a boxplot by month. The boxplot indicates strong seasonality, with flow increasing beginning in April during the spring freshet, reaching the highest levels in July, and then decreasing throughout the fall, with lowest flows occurring in the winter. The Kruskal-Wallis test for differences between months was highly significant (p-value < 0.001).

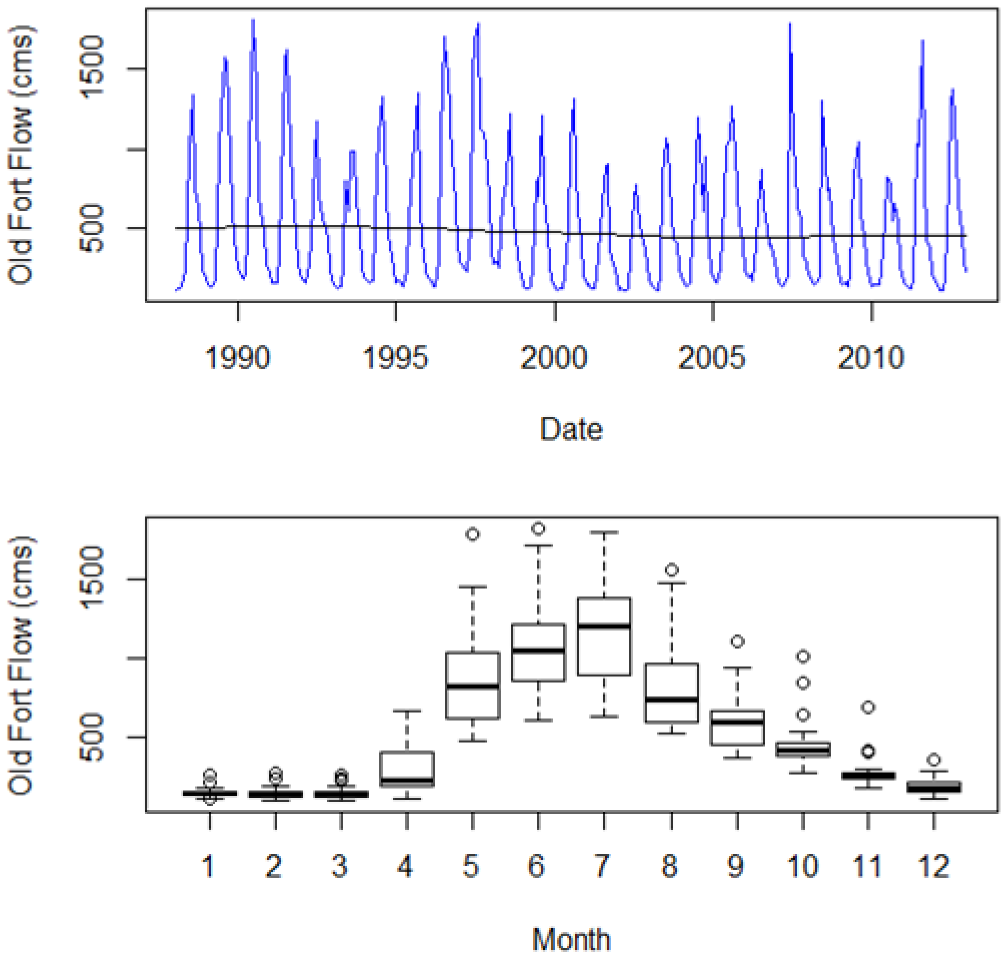


Figure 5. Modeled Average Daily Flow at the Athabasca River at Old Fort Station 1988-2012 (upper panel) and a Boxplot of the Flows by Month (lower panel). *Note: The line in the upper panel is a lowess smooth by date; cms=cubic metre per second.*

3.1.2 2012 Modeled Flow Conditions at Old Fort

The 2012 modeled flows for the Athabasca River at Old Fort Station were compared to modeled historical conditions (1988-2011) for context (Figure 6). The modeled flows indicate that 2012 began with flows near the seasonal median flow. Flows then declined in the third week of January and remained between the lower quartile and minimum of the historical flows until the end of April. The 2012 spring freshet arrived slightly later than in most years peaking in early May just below the upper quartile flow for that time period. The summer of 2012 experienced three high flow events: in mid-June, early July, and late July. Heavy September rains in the Lower Athabasca Region produced a final seasonal high flow peak in mid-September. Flows fluctuated between the median and upper quartile levels for the rest of the year ending at upper quartile levels in December. The average flow rate for 2012 was 580 m^3/s, which lies between the median (507 m^3/s) and upper quartile (603 m^3/s) of modeled annual flows at Old Fort.

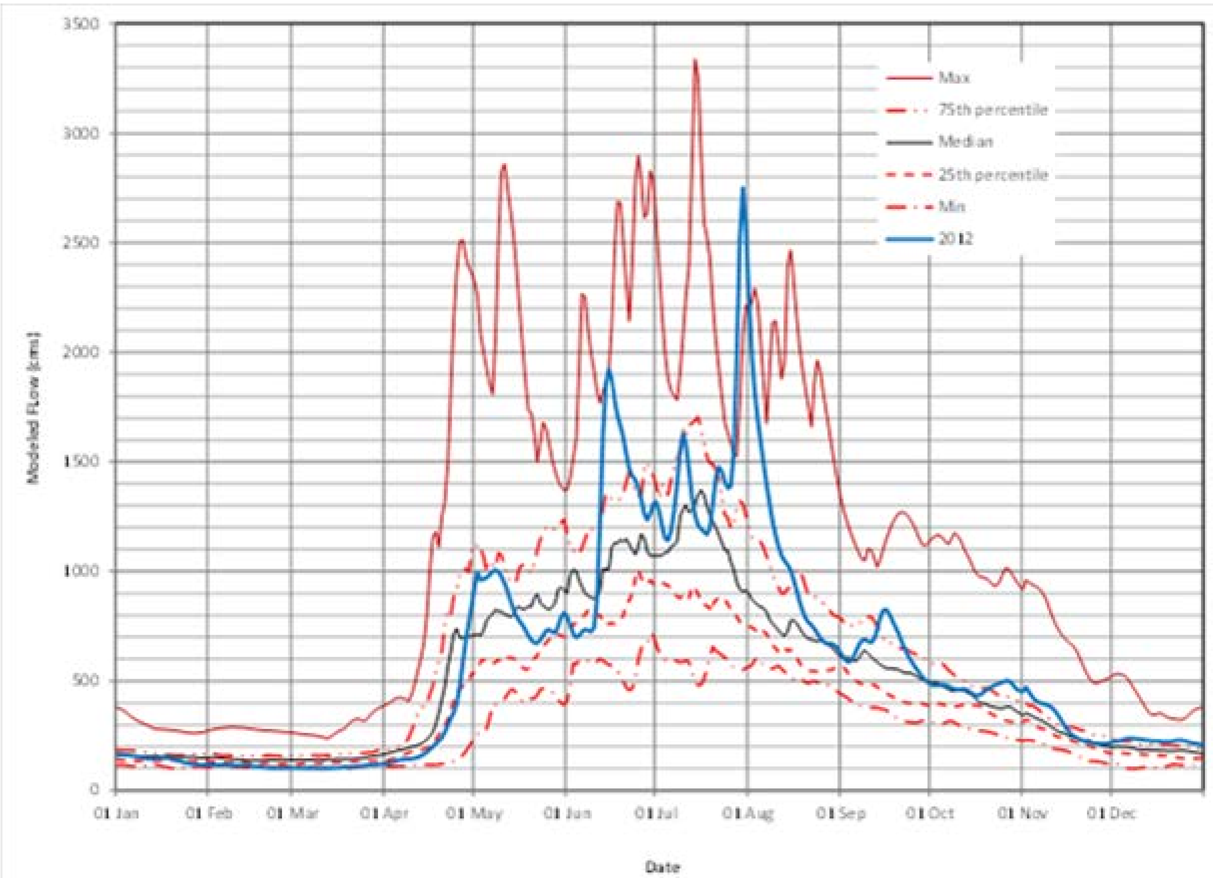


Figure 6. The 2012 Hydrograph for the Athabasca River at Old Fort Station Compared to Historical (1988-2011) Conditions. *Note: cms=cubic metre per second.*

3.2 Relationship between the Water Quality Indicators and Flow

In flowing water systems it is common for water quality concentrations to vary with flow. Understanding the nature and strength of the relationship between a water quality variable and flow can provide important insights into flow-related processes that influence water quality. Hirsch *et al.* (1991) succinctly describe two important processes contributing to flow-related variance in water quality concentrations: dilution and wash-off. Dilution occurs when a solute is delivered to a system at a relatively constant rate but flow varies over time. For water quality variables where this is the case, concentrations are lower at higher flows. Wash-off occurs when a solute, sediment or a constituent attached to sediment is delivered to a system through overland flow. In this case, water quality concentrations tend to increase at higher flows. For some water quality variables, both processes may play a role (Hirsch *et al.* 1991).

3.2.1 Total Nitrogen

The relationship between total nitrogen and flow was not well explained by a linear model on either the original or log-log scale (Appendix A1). In addition, Kendall's tau was not significantly different from zero, meaning there was no strong monotonic relationship between total nitrogen and flow (Appendix A1). The lowess smooth of flow on total nitrogen (Figure 7) illustrates that the relationship is nonlinear, with total nitrogen initially decreasing with increasing flow, and then increasing with flow above about 500 m^3/sec. This relationship suggests that both dilution and wash-off processes may be important in influencing total nitrogen concentrations at Old Fort. It appears that dilution may play an important role when flows are below 500 m^3/sec (often under ice conditions), and wash-off may play an important role at flows above 500 m^3/sec (open water conditions).

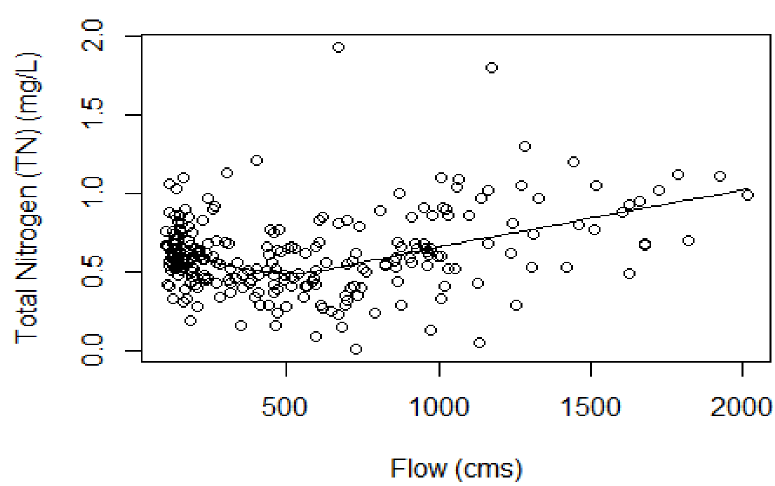


Figure 7. Relationship between Total Nitrogen and Flow at the Athabasca River at Old Fort Monitoring Station (1988-2012). *Note: The solid line is the lowess smooth on flow; cms=cubic metre per second.*

3.2.2 Dissolved Uranium

The relationship between dissolved uranium and flow was not well explained by a linear model on either the original or log-log scale (Appendix A4). In addition, Kendall's tau was not significantly different from zero, meaning there was no strong monotonic relationship between dissolved uranium and flow (Appendix A4). The lowess smooth of flow on dissolved uranium illustrates that the relationship between dissolved uranium and flow is nonlinear (Figure 8). At first glance the relationship appears to resemble a weaker version of the pattern between total nitrogen and flow, with concentrations decreasing with increasing flows up to about 500 m^3/sec. However, unlike total nitrogen, there does not appear to be a strong relationship between concentration and flow above 500 m^3/sec. Overall, it appears that the relationship between dissolved uranium and flow is relatively weak at the Athabasca River at Old Fort station.

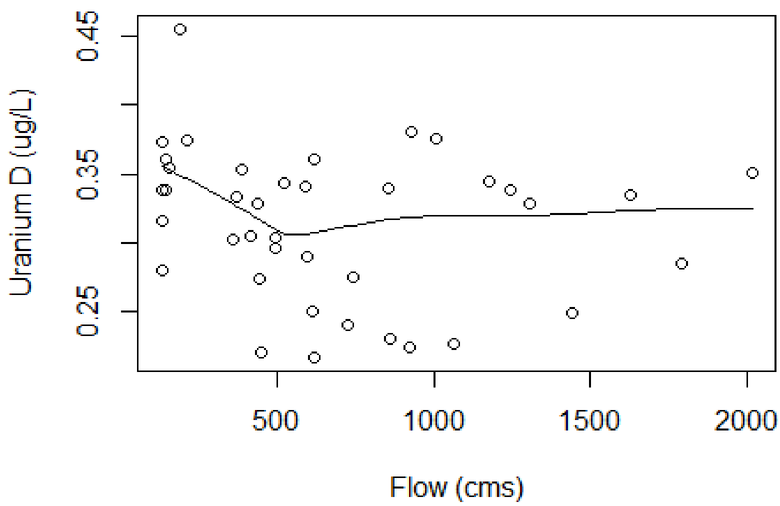


Figure 8. Relationship between Dissolved Uranium and Flow at the Athabasca River at Old Fort Monitoring Station (2003-2012). *Note: The solid line is the lowess smooth on flow; cms= cubic metre per second.*

3.2.3 Dissolved Lithium

There was a strong linear relationship between dissolved lithium and flow on the log-log scale and Kendall's tau was significantly different from zero (-0.48, p-value<0.001), suggesting a strong monotonic relationship between dissolved lithium and flow. The lowess smooth of flow on dissolved lithium shows a negative association, with dissolved lithium concentrations declining with increasing flows (Figure 9). This suggests that dilution plays an important role in explaining the variance in dissolved lithium concentrations and may indicate that the supply of dissolved lithium to the lower Athabasca River is fairly constant.

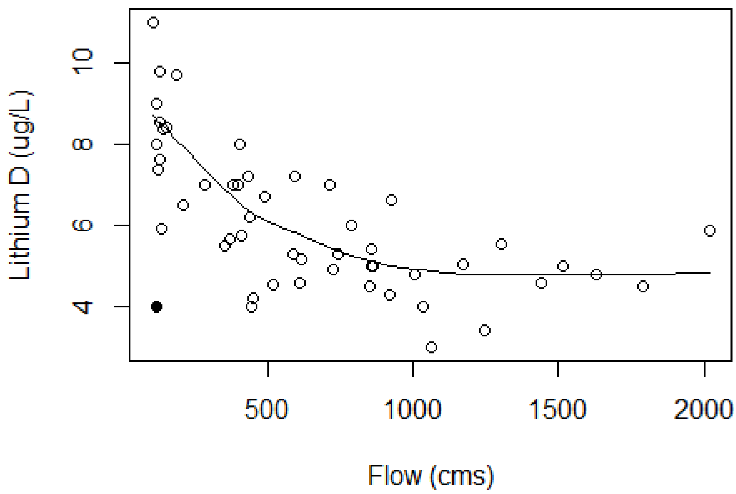


Figure 9. Relationship between Dissolved Lithium and Flow at the Athabasca River at Old Fort Monitoring Station (1999-2012). *Note: The solid line is the lowess smooth on flow and the solid circle represents the one censored valued in the dataset; cms=cubic metre per second.*

3.3 Seasonality in Water Quality

3.3.1 Total Nitrogen

The boxplot of total nitrogen by month showed a seasonal pattern with total nitrogen peaking in May and beginning to decline in August (Figure 10). The Kruskal-Wallis test found a significant difference in total nitrogen between months (p-value <0.001).

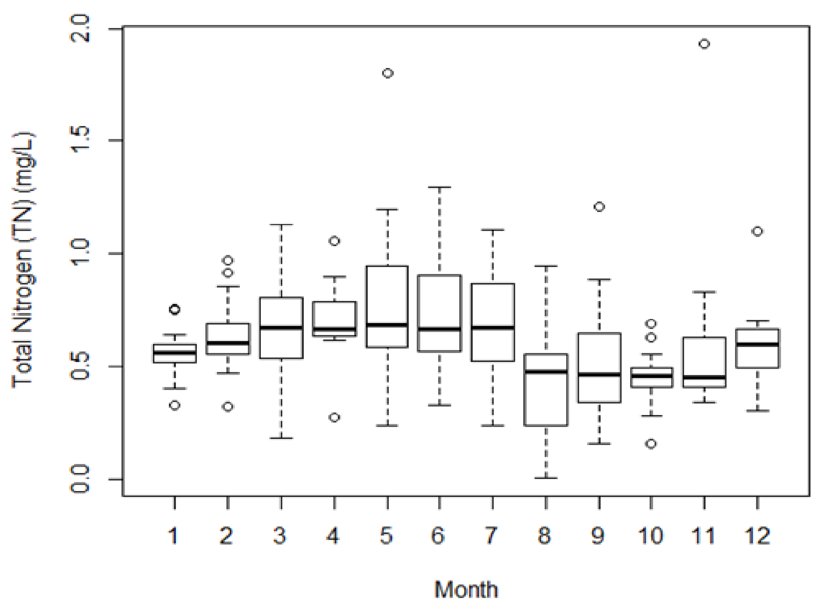


Figure 10. Boxplot of Monthly Total Nitrogen Concentrations at the Athabasca River at Old Fort Station (1988-2012).

The Kruskal-Wallis test also revealed differences between months following flow adjustment (p-value<0.001). This indicates that factors other than flow are contributing to seasonal fluctuations in total nitrogen at the Old Fort station. Interestingly, the seasonal pattern following flow adjustment (Figure 11) was slightly different from the non-flow-adjusted pattern. For example, there is a shift in the timing of the decline in summer total nitrogen concentrations from August to June after adjusting for flow. Given that June coincides with the beginning of the growing season, it is reasonable to hypothesize that flow-related variance may be masking the influence of processes such as biological uptake on total nitrogen concentrations.

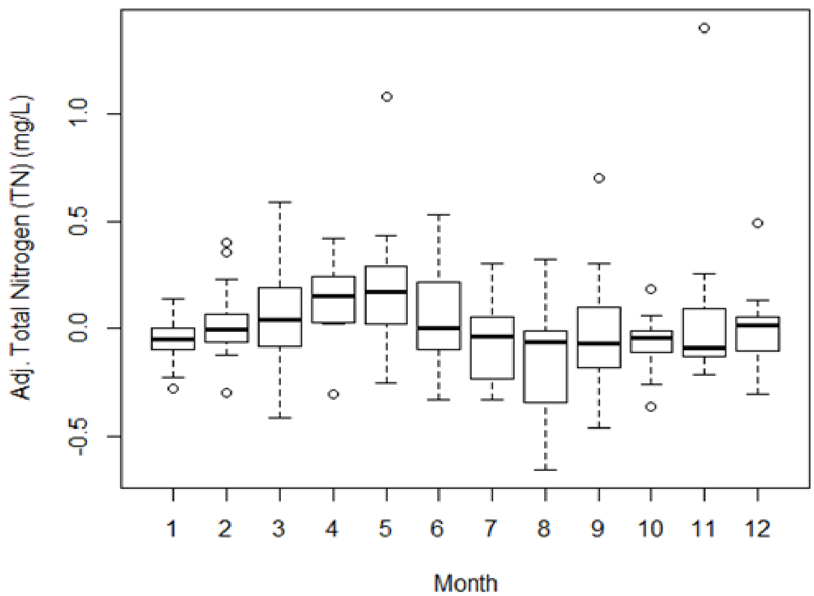


Figure 11. Boxplot of Monthly Total Nitrogen Concentrations Following Flow Adjustment at the Athabasca River at Old Fort Station (1988-2012).

3.3.2 Dissolved Uranium

The plot of dissolved uranium by quarter did not show a clear seasonal pattern (Figure 12). Although concentrations in February appeared to be higher than in other months, the Kruskal-Wallis test was only marginally significant (p-value=0.052). There was no evidence of seasonal differences in dissolved uranium following flow adjustment (Kruskal-Wallis test, p-value=0.5), suggesting that the marginal seasonality detected was likely due to seasonal variance in flow. No changes are evident in quarterly concentration patterns following flow adjustment (Figure 13).

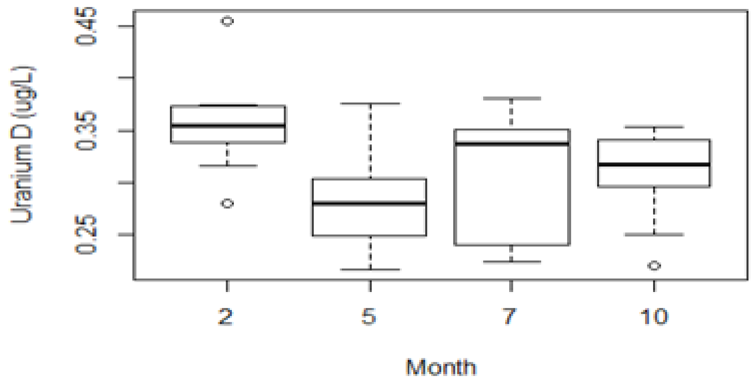


Figure 12. Boxplot of Quarterly Dissolved Uranium Concentrations at the Athabasca River at Old Fort Station (2003-2012).

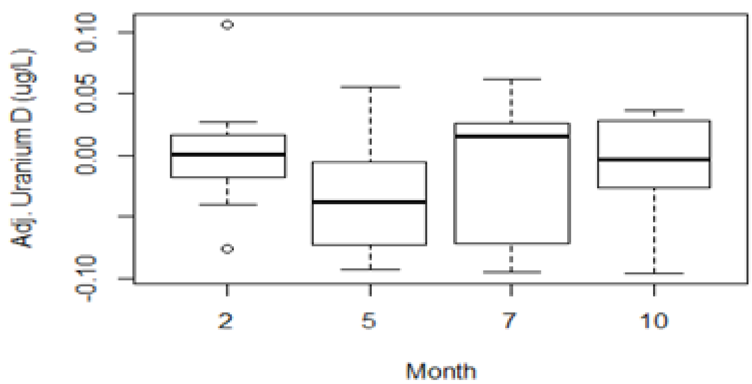


Figure 13. Boxplot of Quarterly Dissolved Uranium Concentrations Following Flow Adjustment at the Athabasca River at Old Fort Station (2003-2012).

3.3.3 Dissolved Lithium

Seasonal differences in dissolved lithium concentrations are apparent with higher concentrations in the winter and lower concentrations in the spring, summer, and fall (Figure 14). The test for differences between months was also significant (G-rho family of tests, p-value<0.001). Seasonal differences were no longer apparent (Figure 15) or significant after adjusting for flow (G-rho family of tests, p-value=0.64). This indicates that the seasonality in dissolved lithium concentrations is largely due to seasonality in flow.

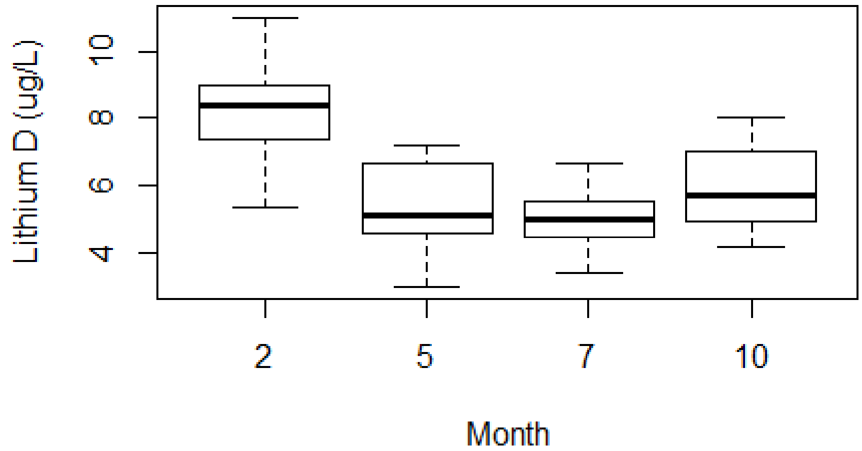


Figure 14. Boxplot of Quarterly Dissolved Lithium Concentrations at the Athabasca River at Old Fort Station (2003-2012).

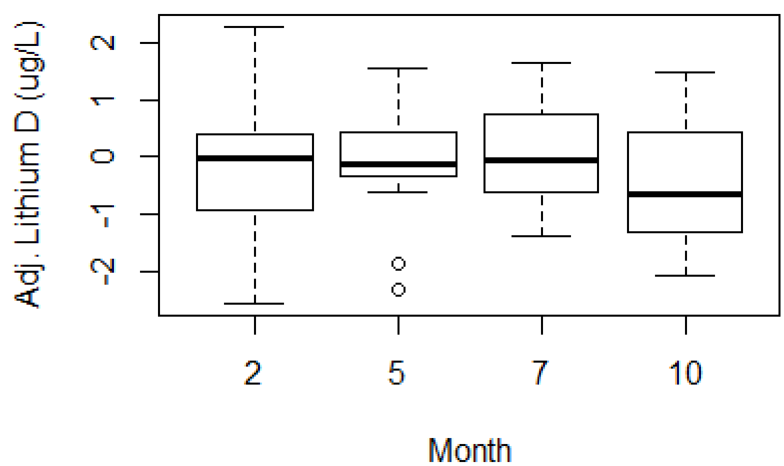


Figure 15. Boxplot of Quarterly Dissolved Lithium Concentrations Following Flow Adjustment at the Athabasca River at Old Fort Station (2003-2012).

3.4 Trends in Flow

We tested for a trend in modeled flow at the Athabasca River at Old Fort station over three different time periods corresponding to the time periods of the water quality indicator datasets: 1988-2012, 1999-2012, and 2003-2012. Our primary reason for doing this was to assess if trends in flow might have an influence on water quality trends. Due to significant seasonal differences in the flow data between months for all time periods (section 3.1.1., Appendix A7), we collapsed the data into a single value for each month by taking the median (Helsel and

Hirsch, 2002) and used the seasonal Mann-Kendall test on the monthly medians of the modeled daily average flow. The results of the trend test for each time period are given in Table 1. There were no opposing seasonal trends in any of the time periods considered.

In addition to examining annual trends in the flow data, we also looked for seasonal trends (Appendix A7). For the time period of 1988-2012, there were marginally significant decreasing trends in July and August. For the time period of 1999-2012 there was a marginally significant increasing trend in May. No seasonal trends were detected for the 2003-2012 time period. Where significant trends were detected, the magnitude the trend (estimated by the slope of the trend line) was very small and therefore we conclude that they are unlikely to influence water quality trends.

Table 1. Results of Trend Tests on Flow for the Time Periods Corresponding with the Water Quality Indicator Datasets. *Note: cms= cubic metre per second.*

Time period	Trend	p-value	Seasonal Mann-Kendall slope (95% confidence interval)
1988-2012 (total nitrogen)	decreasing	<0.001	-2.1 cms/year (-3.4 to -0.9 cms/year) Marginally significant decreasing trends in July and August (p-value<0.1)
1999-2012 (dissolved lithium)	increasing	< 0.01	2.9 cms/year (1.3 to 5.3 cms/year) Marginally significant increasing trend in May (p-value<0.1)
2003-2012 (dissolved uranium)	none	0.15	Not statistically different from zero; no significant seasonal trends

3.5 Trends in Water Quality

3.5.1 Total Nitrogen

The seasonal Mann-Kendall test found a highly significant increasing trend in total nitrogen (p-value<0.001), with a magnitude of 0.005 mg/L/year and a 95% confidence interval of 0.002-0.008 mg/L/year. The test for heterogeneity between seasons was not significant (p-value=0.5), indicating no opposing seasonal trends. Based on Mann-Kendall tests for each season, there were significant increasing trends in May (p-value=0.03) and September (p-value=0.04), and a marginally significant (p-value=0.09) increasing trend in December (Figure 16).

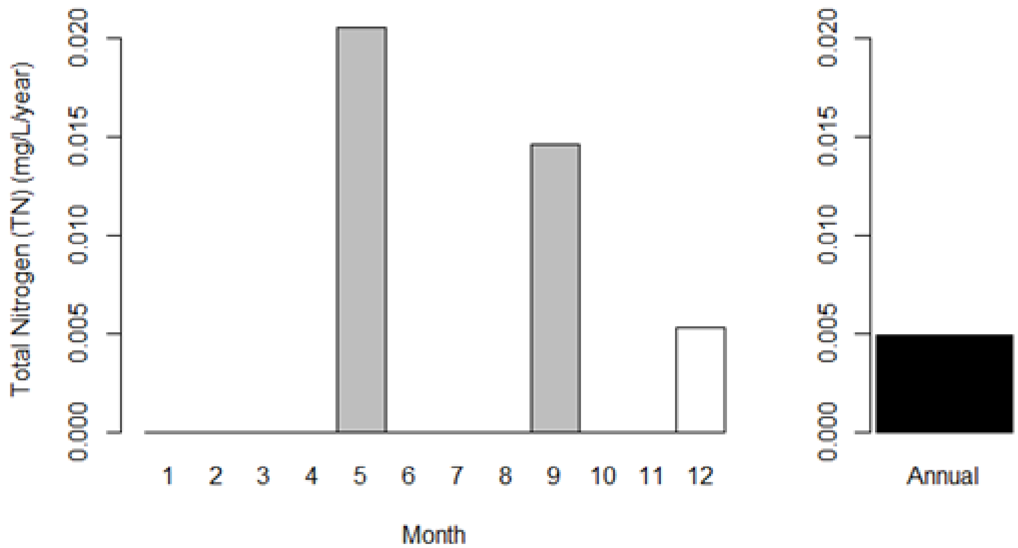


Figure 16. Annual and Seasonal Trends in Total Nitrogen Concentrations at the Athabasca River at Old Fort Station (1988-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

The seasonal Mann-Kendall trend test on total nitrogen after flow adjustment was also significant (Figure 17), with a slightly larger magnitude of 0.006 ug/L/year and a 95% confidence interval of 0.003-0.009 ug/L/year (p-value<0.001). It should be noted that the magnitude of the trend before flow adjustment (0.005 ug/L/year) is included in the confidence interval. The test for heterogeneity between seasons was not significant (p-value=0.43). The results of Mann-Kendall trend tests on the seasons was similar to the results before flow adjustment (Appendix A1), except that the increasing trend in May was highly significant (p-value<0.01) and there was also a marginally significant increasing trend in August (p-value=0.1). Therefore, we conclude that the flow adjustment removed some variability associated with flow, making the trend more apparent.

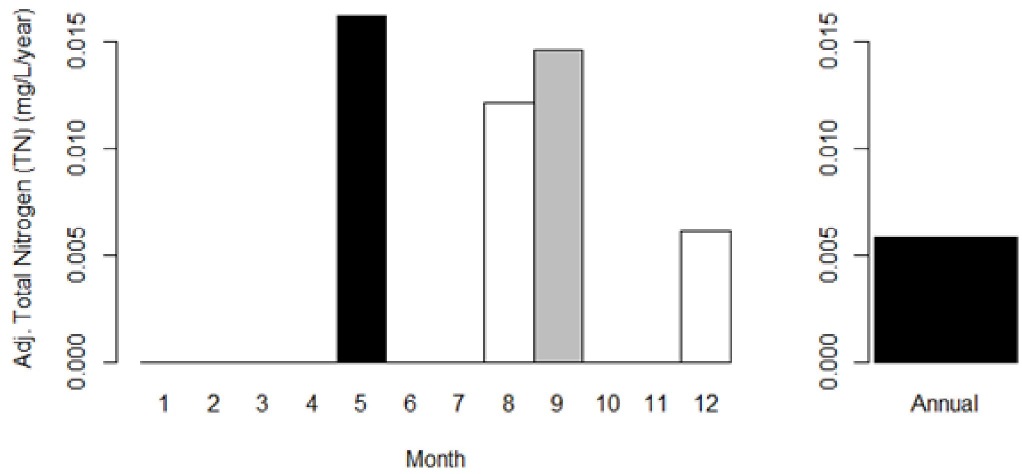


Figure 17. Annual and Seasonal Trends in Total Nitrogen Concentrations Following Flow Adjustment at the Athabasca River at Old Fort Station (1988-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

3.5.1.1 Supplemental Analyses

To investigate the origin and spatial extent of the increasing trend in total nitrogen at the Athabasca River at Old Fort station, additional trend analyses were conducted at both the Athabasca River upstream of Fort McMurray and the Athabasca River at Old Fort monitoring stations for two time periods (1989-2012 and 2002-2012). The trend analyses for the 1989-2012 time period were run on quarterly data, whereas the analyses for 2002-2012 were run on monthly data. The purpose of examining the two time periods was to evaluate whether recent conditions differ from longer-term conditions. The Athabasca River upstream of Fort McMurray is the upstream station and the Athabasca River at Old Fort the downstream station (Figure 2).

Comparison of the Upstream and Downstream Stations (1989-2012)

The seasonal Mann-Kendall test found a significant increasing trend in total nitrogen (p-value=0.03) at the Athabasca River at Old Fort station (Figure 18) with a magnitude of 0.006 mg/L/year and a 95% confidence interval of 0.0005-0.01 mg/L/year. The test for heterogeneity between seasons was not significant (p-value=0.19), indicating no opposing seasonal trends. Based on Mann-Kendall tests for each season, there was a significant increasing trend in May (p-value=0.02) and a marginally significant increasing trend in October (p-value=0.059).

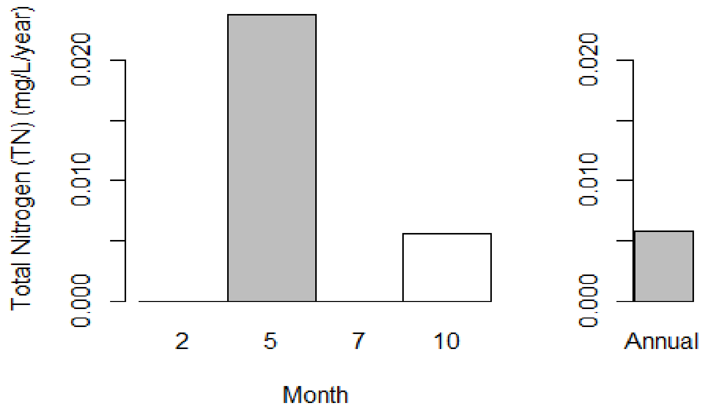


Figure 18. Annual and Seasonal Trends in Total Nitrogen Concentrations at the Athabasca River at Old Fort Station (1989-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

The seasonal Mann-Kendall trend test on total nitrogen after flow adjustment at the Athabasca River at Old Fort station was highly significant (p-value=0.004; Figure 19) with a magnitude of 0.007 mg/L/year and a 95% confidence interval of 0.003-0.012 mg/L/year. The test for heterogeneity between seasons was not significant (p-value=0.27). Based on Mann-Kendall tests for each season, there was a highly significant increasing trend in May (p-value=0.006) and a significant increasing trend in October (p-value=0.04).

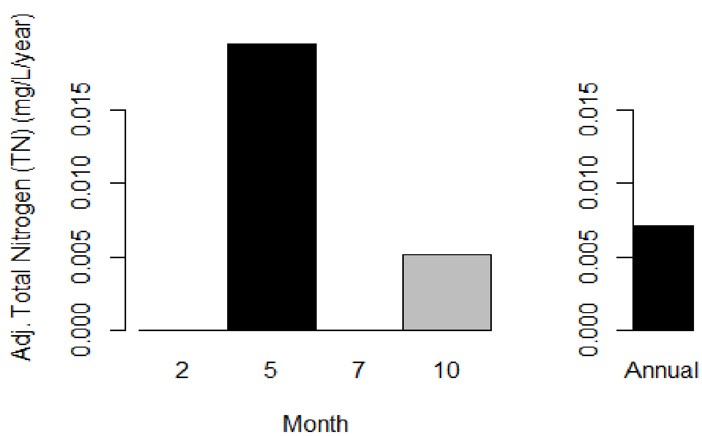


Figure 19. Annual and Seasonal Trends in Total Nitrogen Concentrations Following Flow Adjustment at the Athabasca River at Old Fort Station (1989-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

The seasonal Mann-Kendall test found no significant trend in total nitrogen at the Athabasca River upstream of Fort McMurray monitoring station (p-value=0.92), and no significant heterogeneity between seasons (p-value=0.36) or significant trends within seasons. There was also no significant trend in total nitrogen after flow adjustment (p-value=0.88) and no significant heterogeneity between seasons (p-value=0.25). However, based on Mann-Kendall tests for each season, there was a marginally significant trend in the flow-adjusted concentration in May (p-value=0.09) (Figure 20).

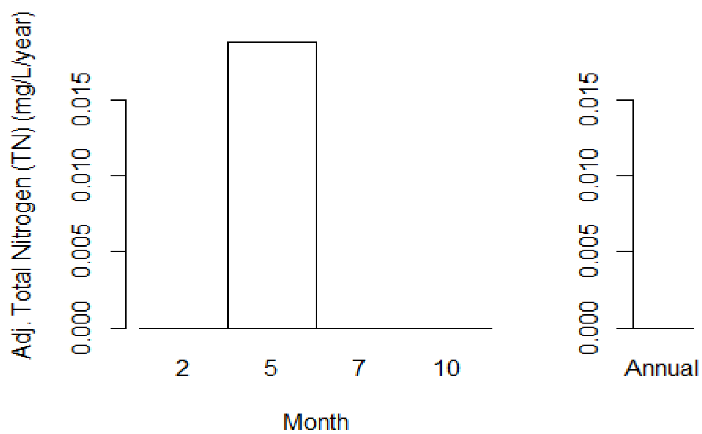


Figure 20. Annual and Seasonal Trends in Total Nitrogen Concentrations Following Flow Adjustment at the Athabasca River Upstream of Fort McMurray Station (1989-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

Comparison of the Upstream and Downstream Station (2002-2012)

The seasonal Mann-Kendall trend test found a significant increasing trend in total nitrogen (p-value=0.04) at the Athabasca River at Old Fort station (Figure 21) with a magnitude of 0.009 mg/L/year and a 95% confidence interval of 0.0003-0.021 mg/L/year. The test for heterogeneity between seasons was not significant indicating no opposing seasonal trends (p-value=0.40). Based on Mann-Kendall trend tests for each season, there was a significant increasing trend in September (p-value=0.01).

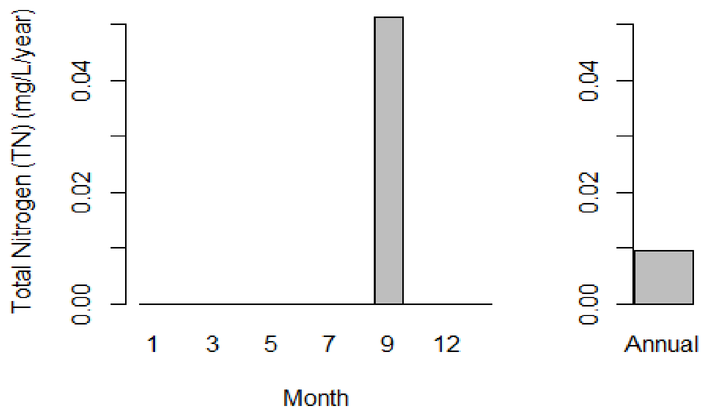


Figure 21. Annual and Seasonal Trends in Total Nitrogen Concentrations at the Athabasca River at Old Fort Station (2002-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

The seasonal Mann-Kendall trend test on total nitrogen after flow adjustment at the Athabasca River at Old Fort station was not significant (p-value=0.17; Figure 22) and the test for heterogeneity between seasons was not significant (p-value=0.39). Based on Mann-Kendall trend tests for each season, there was a highly significant increasing trend in September (p-value=0.008).

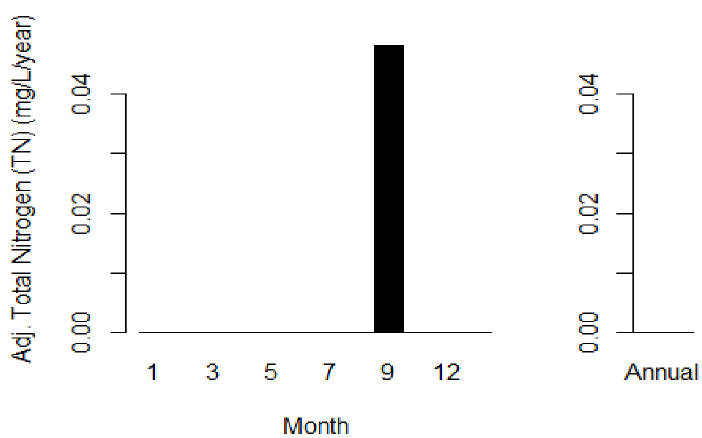


Figure 22. Annual and Seasonal Trends in Total Nitrogen Concentrations Following Flow Adjustment at the Athabasca River at Old Fort Station (2002-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

The seasonal Mann-Kendall trend test found a significant increasing trend in total nitrogen (p-value=0.01) at the Athabasca River upstream of Fort McMurray station (Figure 23) with a magnitude of 0.01 mg/L/year and a 95% confidence interval of 0.002-0.019 mg/L/year. The test for heterogeneity between seasons was not significant indicating no opposing seasonal trends (p-value=0.24). Based on Mann-Kendall trend tests for each season, there were significant increasing trends in August (p-value=0.02) and December (p-value=0.03).

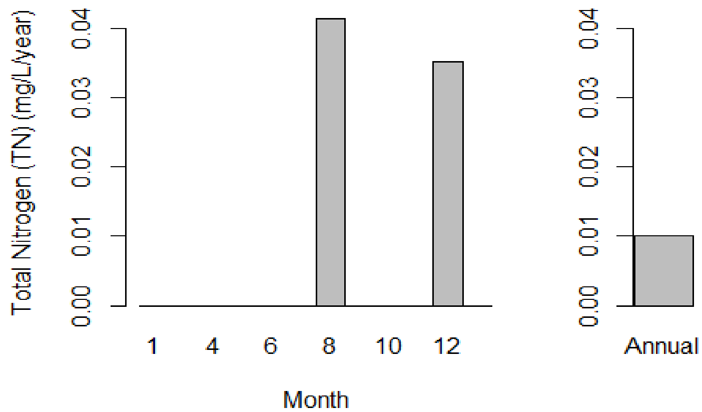


Figure 23. Annual and Seasonal Trends in Total Nitrogen Concentrations at the Athabasca River at Upstream of Fort McMurray Station (2002-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

The seasonal Mann-Kendall trend test on total nitrogen after flow adjustment at the Athabasca River upstream of Fort McMurray station was marginally significant (p-value=0.08; Figure 24) with a magnitude of 0.007 mg/L/year and a 95% confidence interval of 0.0006-0.014 mg/L/year. The test for heterogeneity between seasons was not significant (p-value=0.37). Based on Mann-Kendall trend tests for each season, there were significant increasing trends in August (p-value=0.04) and December (p-value 0.05).

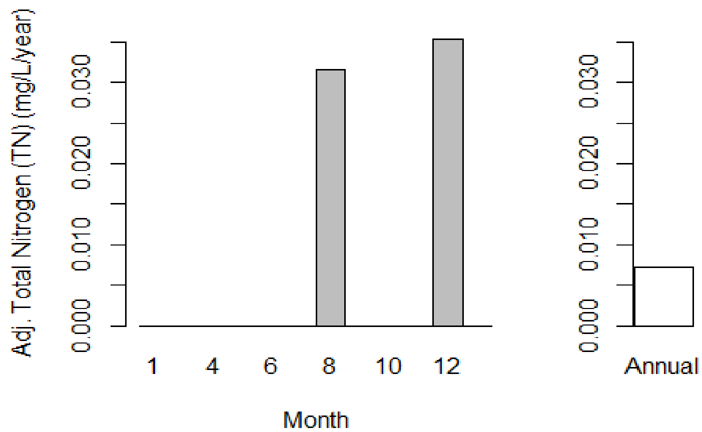


Figure 24. Annual and Seasonal Trends in Total Nitrogen Concentrations Following Flow Adjustment at the Athabasca River Upstream of Fort McMurray Station (2002-2012). *Note: Bar height is the magnitude of the trend and color indicates the significant level. Black is highly significant (p-value < 0.01), gray is significant (p-value<0.05), and white is marginally significant (p-value<0.1).*

3.5.2 Dissolved Uranium

Based on the Mann-Kendall trend test, there was a marginally significant increasing trend in dissolved uranium of 0.006 ug/L/year with a 95% confidence interval of 0.000-0.011 ug/L/year (p-value=0.053). Because the test for seasonality was also marginally significant, we also ran a seasonal Mann-Kendall trend test. There was no heterogeneity between seasons (p-value=0.77) and no significant overall trend (p-value=0.43). Finally, the Mann-Kendall trend test found no significant trend in dissolved uranium concentration after adjustment for flow (p-value=0.17).

3.5.2.1 Supplemental Analyses

Given the proximity of the non-flow-adjusted trend to statistical significance we decided to run a trend assessment for the same time period (2003-2012) at the Athabasca River upstream of Fort McMurray monitoring station to see if it would provide any additional insights. Because the test for seasonality was significant, we ran a seasonal Mann-Kendall trend test. There was no significant overall trend (p-value=0.69) and no heterogeneity between seasons (p-value=0.49). Finally, the Mann-Kendall trend test found no significant trend in dissolved uranium concentration after adjustment for flow (p-value=0.89).

3.5.3 Dissolved Lithium

The seasonal Mann-Kendall trend test found no significant trend in dissolved lithium (p-value=0.90), and there was no heterogeneity between seasons (p-value=0.86). There was also no significant trend in dissolved lithium after flow adjustment (p-value=0.83).

4.0 SYNTHESIS

The results of the analyses conducted in support of the 2012 management response are summarized and briefly discussed below.

Flow conditions and trends

Annual flow patterns at the Athabasca River at Old Fort station (1988-2012) exhibited strong seasonality. Flows typically increase in April during the spring freshet, peak in July, and then decrease throughout the fall, with the lowest flows occurring in the winter. In 2012, flow conditions were characterized by: a higher than normal mean flow relative to historical conditions (1988-2011), unusually low winter flows, a freshet below the upper quartile, three summer high flow events, a seasonal high flow peak in September, and flows between the median and upper quartile for the rest of the year.

For the time period of the total nitrogen dataset (1988-2012) we found a highly significant decrease in flow, with marginally significant decreases in July and August. This indicates the Athabasca River at Old Fort station experienced slightly drier summer conditions from 1988-2012, although the magnitude of the trend was very small in comparison to the flow during these months. There were no trends in flow over the time period of the dissolved uranium dataset (2003-2012). Over the time period of the dissolved lithium dataset (1999-2012), there was a highly significant increase in flow, with a marginally significant increase during the month of May. Again, the magnitude of the trend was small in comparison to the flow during that month. The primary intent of the trend analyses for flow was to provide context in which to interpret the water quality trends. Due to the very small changes detected, we conclude that trends in flow are not likely to substantially influence trends in water quality. The trends in flow reported here may not reflect trends over a longer time period.

Total nitrogen conditions and trends

Our analyses indicate that total nitrogen varied significantly between seasons and these differences could not be explained by seasonal variability in flow alone, suggesting other natural or anthropogenic factors may also be important. Examination of the relationship between total nitrogen and flow revealed a nonlinear association, with total nitrogen initially decreasing with increasing flow at lower flows (<500 m^3/sec), and then increasing with increasing flow at higher flows (>500 m^3/sec).

In 2012, a mean trigger was exceeded for total nitrogen at the Athabasca River at Old Fort station. Examination of 2012 flow conditions suggests that flow conditions may have contributed to this exceedance, since total nitrogen concentrations increase at higher flows, and 2012 exhibited higher than normal mean flow.

Trend analyses on total nitrogen concentrations at the Athabasca River at Old Fort monitoring station indicate that significant increasing annual and/or seasonal trends exist for the non-flow adjusted and flow-adjusted data for both the longer-term and recent datasets (Table 2). Although only a marginally significant increasing seasonal trend was detected in the longer-term dataset from the Athabasca River upstream of Fort McMurray, significant annual (non-flow-adjusted) and significant seasonal trends (flow-adjusted) were detected in the recent data from that station. Consequently, we cannot rule out the potential influence of the upstream station on trends in total nitrogen at the Athabasca River at Old Fort monitoring station, particularly given that a majority of water at the Old Fort station originates from sources upstream of Fort McMurray.

Table 2. Results of the Supplemental Trend Analyses for Total Nitrogen for the Athabasca River at Old Fort and Athabasca River Upstream of Fort McMurray Monitoring Stations. *NFA=non-flow-adjusted, FA=flow-adjusted.*

u/s Fort McMurray (1989-2012)	Old Fort (1989-2012)
NFA concentrations: • Seasonal Mann-Kendall test non-significant (p-value=0.92)	NFA concentrations: • Seasonal Mann-Kendall test revealed a significantly increasing trend (p-value=0.03) • Significant increasing trend in May (p-value=0.02) and marginally significant increasing trend in October (p=0.059)
FA concentrations: • Seasonal Mann-Kendall test non-significant (p-value=0.88) • Marginally significant trend in May (p-value=0.09)	FA concentrations: • Seasonal Mann-Kendall test revealed a highly significantly increasing trend (p-value=0.004) • Highly significant trend in May (p-value=0.006) and significant trend in Oct (p-value=0.04)
u/s Fort McMurray (2002-2012)	**Old Fort (2002-2012)**
NFA concentration: • Seasonal Mann-Kendall test revealed a significantly increasing trend (p-value=0.01) • Significant trend in August (p-value=0.02) and December (p-value=0.03)	NFA concentration: • Seasonal Mann-Kendall test revealed a significantly increasing trend (p-value=0.04) • Significant trend in September (p-value=0.01)
FA concentration: • Seasonal Mann-Kendall trend test marginally significant (p-value=0.08) • Significant trends in August (p-value=0.04) and Dec (p-value=0.05)	FA concentration: • Seasonal Mann-Kendall trend test non-significant (p-value=0.17) • Highly significant increasing trend in September (p-value=0.008)

Although the magnitude of the trends detected at the Athabasca River at Old Fort are small relative to in-stream concentrations, total nitrogen again exceeded the mean trigger in 2013 (AEP 2016). The potential effects of increasing total nitrogen concentrations in the lower Athabasca River are primarily related to nutrient enrichment. Nutrient enrichment is an ongoing concern within the lower Athabasca River as other studies have found increasing trends in nutrients at Old Fort (Hebben 2009) and in the Athabasca River downstream of the Old Fort station (Glozier et. al. 2009).

Since the results of the preliminary assessment step of the 2012 management response indicate increasing trends in total nitrogen within the lower Athabasca River, and total nitrogen triggered again in 2013 (AEP 2016), we recommend moving total nitrogen from preliminary assessment into investigation. We further recommend that AEP capitalize on the synoptic survey being conducted on the Athabasca River this winter to examine total nitrogen loading within the basin. The results from this year's synoptic can be compared to earlier surveys (e.g., Noton and Saffran, 1995) to evaluate changes in total nitrogen loading over time.

Dissolved uranium conditions and trends

Dissolved uranium did not exhibit significant differences between seasons, although it appeared to be slightly higher in the winter. This pattern disappeared following flow adjustment, suggesting that the marginal seasonality observed was due to flow. Dissolved uranium was negatively related to flow during low flow, and not strongly related to flow during high flow.

In 2012, both mean and peak triggers were exceeded for dissolved uranium, and 2012 flow conditions do not shed much light on these exceedances. The three observations above the historical 95th percentile (which collectively produced the peak trigger exceedance), occurred in January, April and August, over a range of flow conditions. In addition, the poor relationship between dissolved uranium and flow at higher flows (>500 m^3/sec), makes it difficult to directly relate the higher 2012 mean flow to the mean trigger exceedance. This leads us to conclude that the 2012 trigger exceedances are not well explained by flow and other factors should be explored.

Trend assessment indicated that there was a marginally significant increasing trend in dissolved uranium, but this trend was not significant following flow adjustment. Given the proximity of the non-flow-adjusted trend result to statistical significance and because dissolved uranium triggered again in 2013 (AEP 2016), we ran a trend analysis for the same time period at the Athabasca River upstream of Fort McMurray station. This trend analysis did not reveal any significant differences in dissolved uranium at the Athabasca River upstream of Fort McMurray station (2003-2012) either before or after flow adjustment.

It should be noted that the supplemental analyses carried out for dissolved uranium at the upstream station were not initiated out of concern for existing concentrations of dissolved uranium in the lower Athabasca River. Current levels at Old Fort are lower than at stations on the upper Athabasca River (AEP, unpublished data), and more than an order of magnitude lower than the most stringent water quality guideline (10 ug/L, adopted as the limit in the SWQMF). Rather, the intent of the additional testing is to better understand temporal and spatial patterns in dissolved uranium within the lower Athabasca River.

Since the results of the dissolved uranium preliminary assessment were largely inconclusive, and given that dissolved uranium triggered again in 2013 (AEP 2016), we recommend moving dissolved uranium from preliminary assessment into investigation. We further recommend that future analyses should focus on the lower Athabasca River and its tributaries downstream of Fort McMurray. The starting point for this analysis is the existing data collected through AEP's LTRN program, the Regional Aquatics Monitoring Program, and the Joint Oil Sands Monitoring Program.

Dissolved lithium conditions and trends

Dissolved lithium exhibited a seasonal pattern with higher concentrations in the winter and lower concentrations in the spring, summer, and fall. We attribute this seasonal pattern to variation in flow, as dissolved lithium was strongly, negatively related to flow on a log-log scale and the seasonal pattern disappeared following adjustment for flow. The timing of the 2012 dissolved lithium 95th percentile exceedances (January, February and April) corresponded well with unusually low flow conditions at the Athabasca River at Old Fort monitoring station. This suggests that the 2012 peak trigger exceedance was due to flow conditions. Trend analysis did not reveal any significant trend in dissolved lithium, even after adjustment for flow.

Given that the 2012 peak trigger exceedance appears to be related to flow and there is no evidence that dissolved lithium concentrations are changing over time, we recommend that dissolved lithium not be moved from preliminary assessment into investigation and conclude that no further management action is required.

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Van Belle, G. and J.P. Hughes. 1984. Nonparametric tests for trends in water quality. *Water Resources Research* 20:127-136.

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6.0 APPENDICES

APPENDIX A – STATISTICAL OUTPUT

A.1 - Total Nitrogen at Old Fort Station

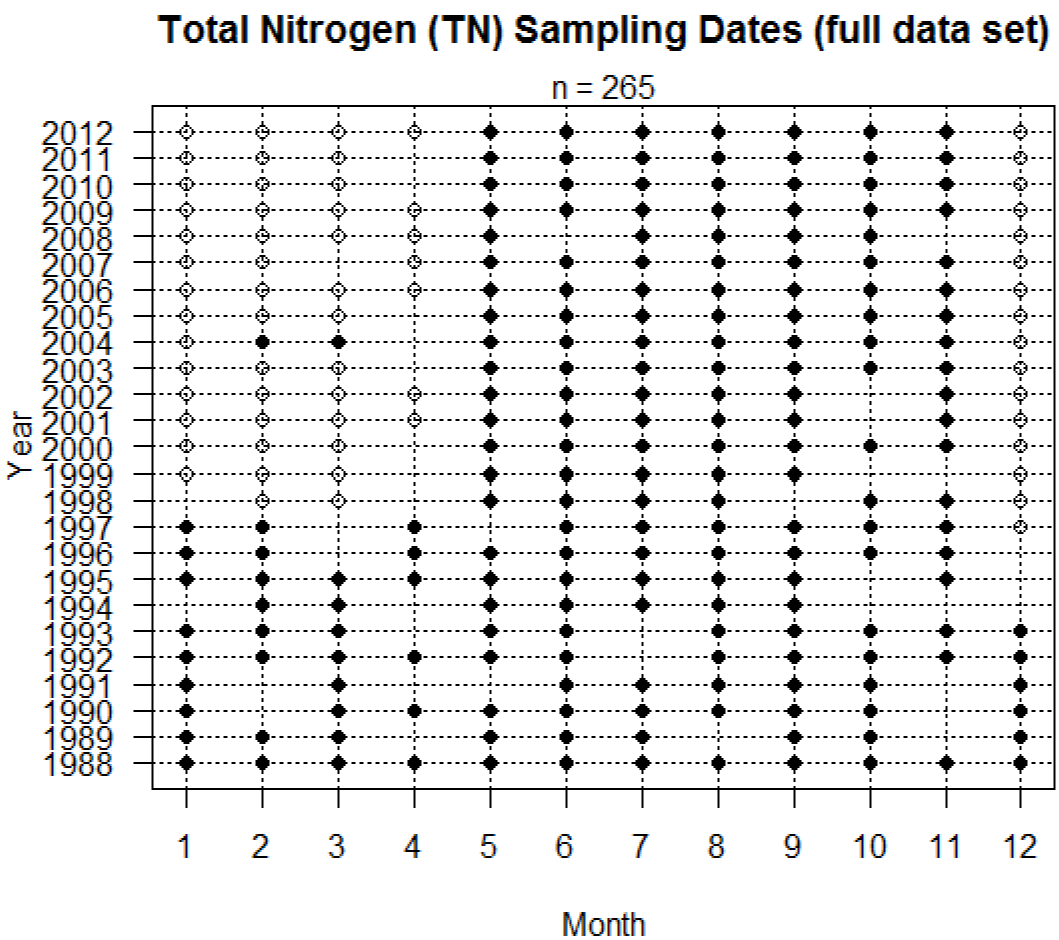
Censoring

```
### Censoring

# Determine level of censoring and detection limits
with(wq, censummary(Value,ValueCen))

## all:
##       n   n.cen pct.cen     min     max
## 265.000   0.000   0.000   0.009   1.931
##
## limits:
##   limit n uncen pexceed
## 1     0 0   265       1
```

- There are no censored values.

Sampling frequency

```
### Investigate sampling frequency and create final data set for analysis (i.
e. subset the data to give equal sampling throughout time period)

# Dot plot of sampling dates for full data set
source("fun_dateplot.r")
dateplot(wq.in=wq,wq.invar=wqvar,type="full data set")
```



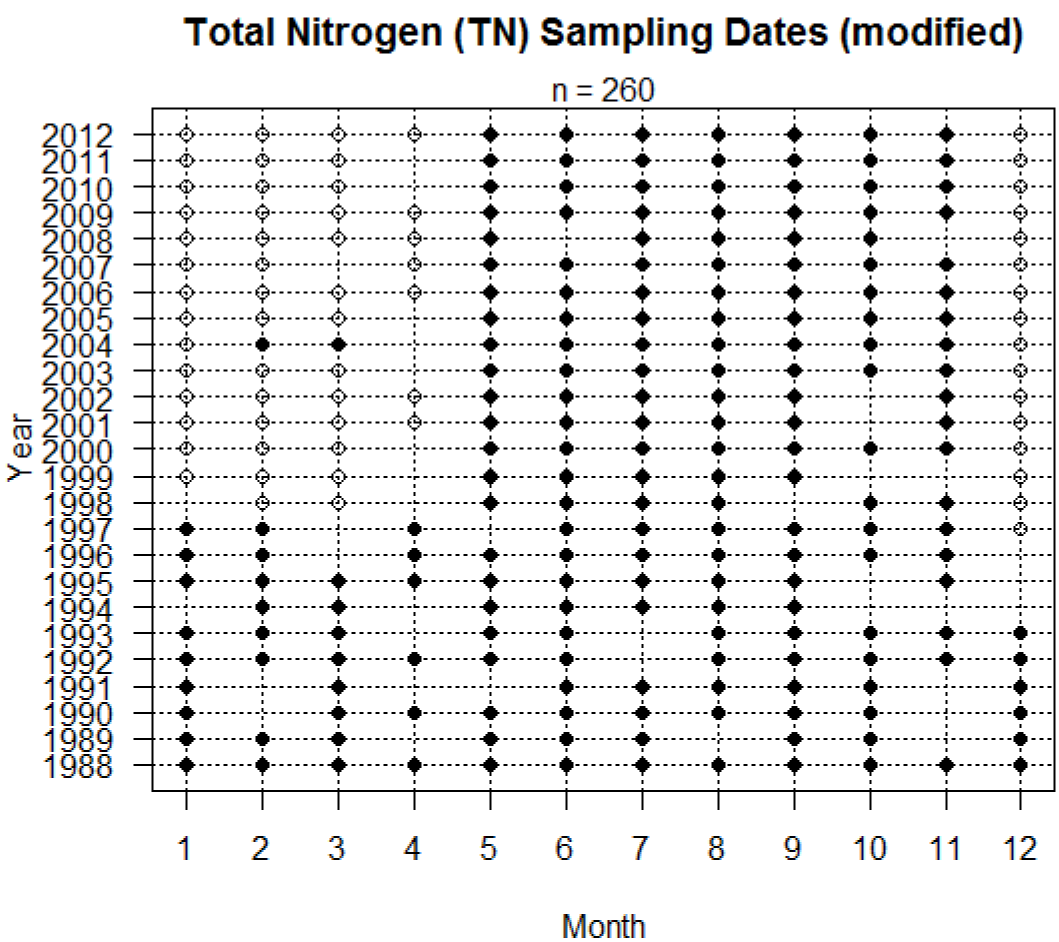

```
# Solid circles correspond to observations made at the Old Fort station and c
losed circles correspond to observations made at the Devil's Elbow station.

# Total number of observations
length(wq[,1])

## [1] 265

# Number of observations by year
table(wq$Year)

##
## 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002
##   12    9   11    9   11   10    8   10   10   10   10    9   11   11   11
## 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##   11   11   11   12   11   11   12   11   11   12

# Number of observtions by month
table(wq$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 23 24 24 13 23 24 24 24 24 21 19 22
```

```
# The data are monthly over the entire time period, so no need to subset the data. Note however that there are some months with missing data over the period of record, as well as several months with multiple samples.
```

- The period of record for total nitrogen is 1988-2012 (26 years).
- Total nitrogen was sampled monthly throughout the period of record (although there are some missing observations). There were two samples taken in each of Mar 1990, Mar 1991, Feb 1994, Oct 1998, and Jul 2008. In each case we randomly chose one of the observations to keep and removed the other.
- Samples were taken at both Athabasca at Old Fort stations over the time period considered.

Final data set for trend analysis

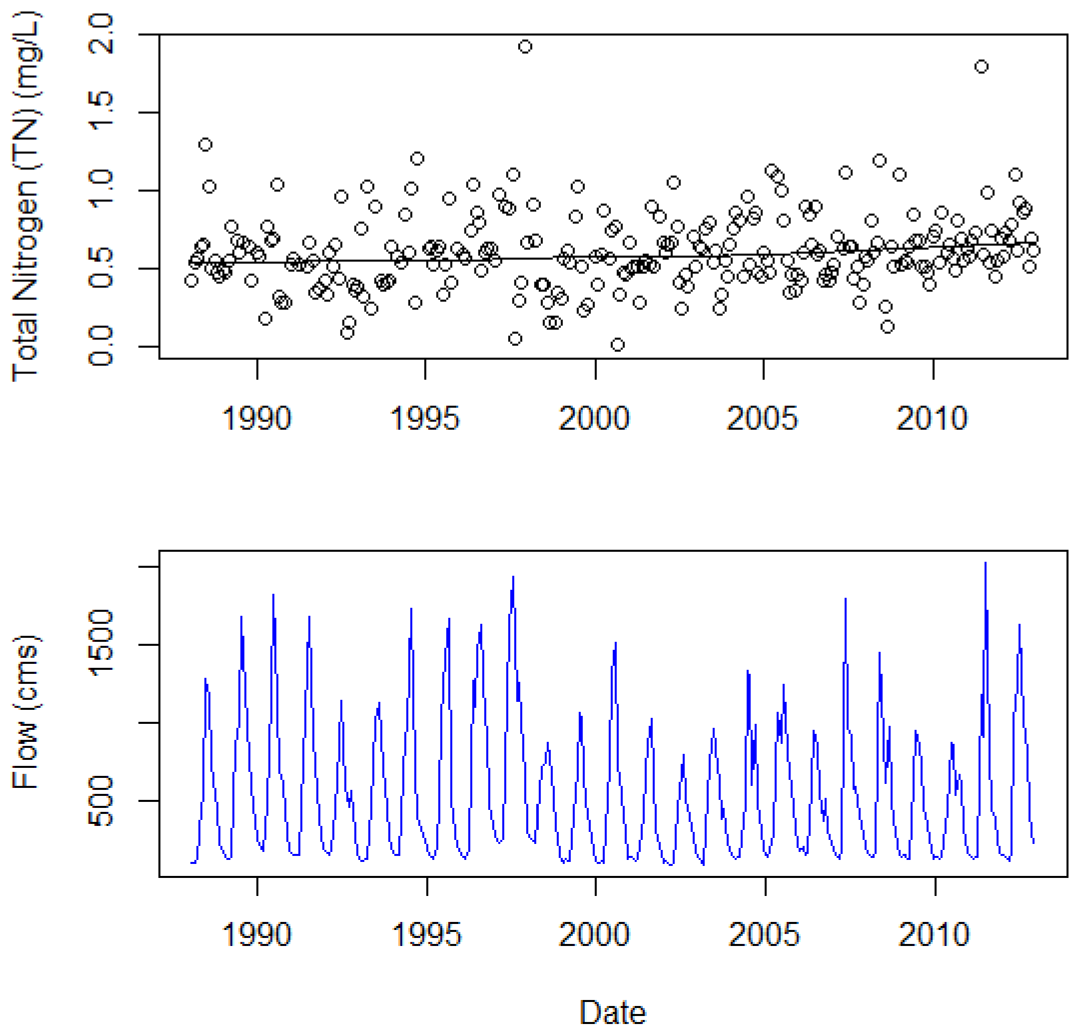
```
### Create final data set for trend analysis (i.e. remove cases of multiple samples per month).


# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq,wq.invar=wqvar,type="modified")
```



```r
# Solid circles correspond to observations made at the Old Fort station and c
losed circles correspond to observations made at the Devil's Elbow station.

# Total number of observations
length(wq[,1])

## [1] 260

# Number of observations by year
table(wq$Year)

##
## 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002
##   12    9   10    8   11   10    7   10   10   10    9    9   11   11   11
## 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##   11   11   11   12   11   10   12   11   11   12

# Number of observvtions by month
table(wq$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 23 23 22 13 23 24 23 24 24 20 19 22
```

Time series plot of data

```r
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The blue line represents flow observations from the same dates as the water quality observations. The black line is the lowess smooth to the concentration data.
```

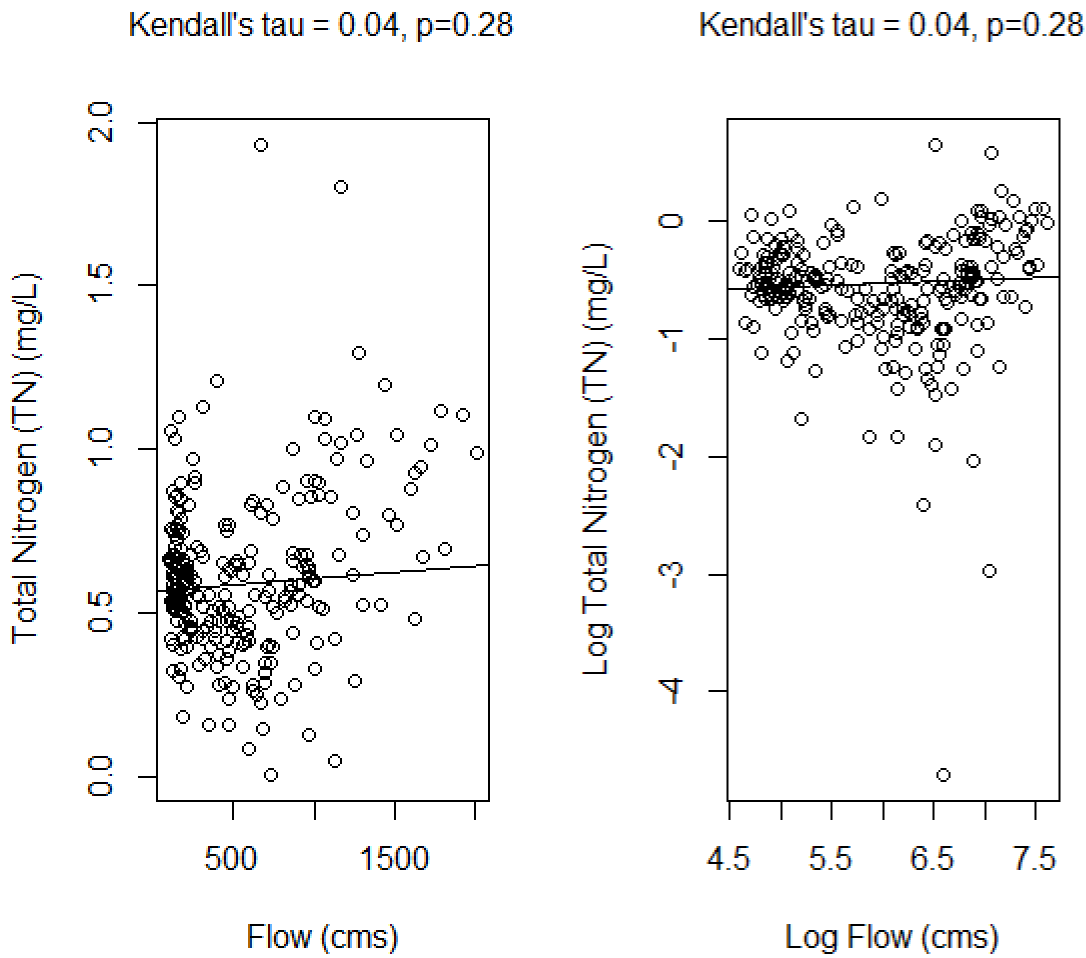
Summary statistics

```
### Calculate summary statistics
# Summary stats were calculated as usual since there was no censoring.

# n
with(wq,length(Value))

## [1] 260

# min
with(wq,min(Value,na.rm=TRUE))

## [1] 0.009
```

```r
# max
with(wq,max(Value, na.rm=TRUE))

## [1] 1.931

# median
with(wq,median(Value, na.rm=TRUE))

## [1] 0.583

# mean
with(wq,mean(Value, na.rm=TRUE))

## [1] 0.6128

# standard deviation
with(wq,sd(Value, na.rm=TRUE))

## [1] 0.249

#variance
with(wq,var(Value, na.rm=TRUE))

## [1] 0.06198
```

Relationship with flow

```r
### Test for a monotonic relationship between concentration and flow
# Determine if there is a monotonic relationship (possibly linear) between fl
ow and concentration (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq,wq.invar=wqvar)
```

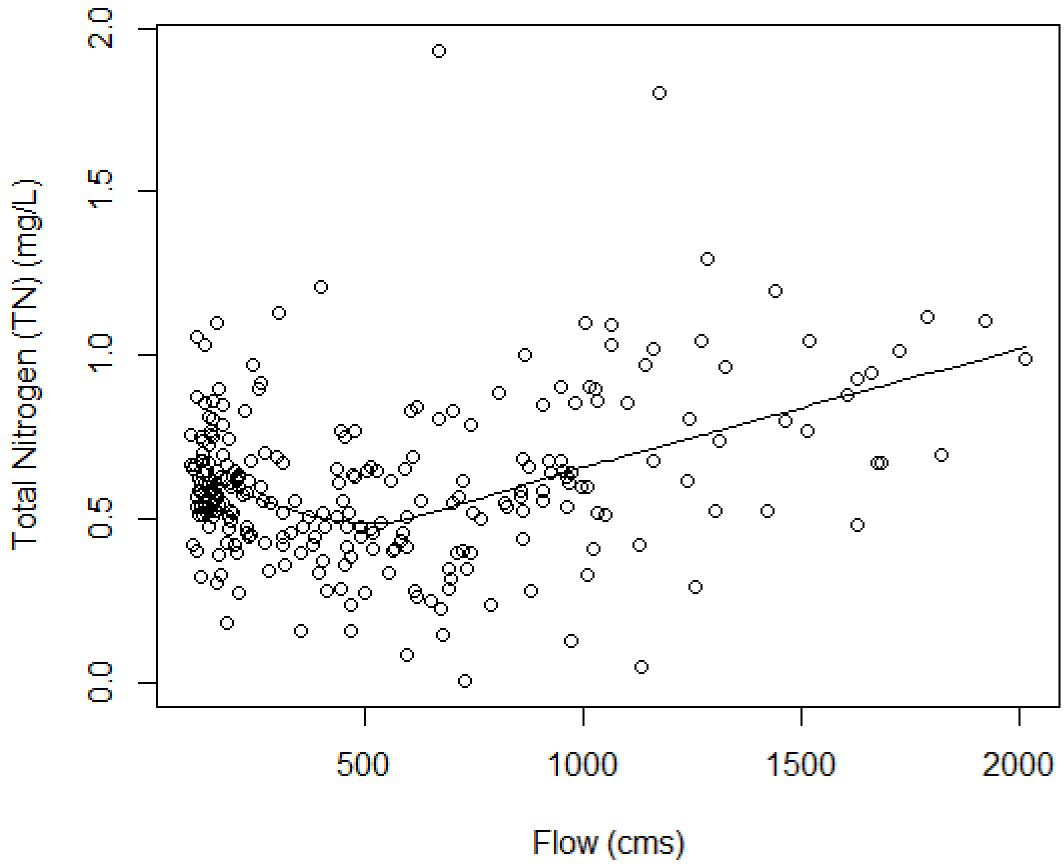



```
# All observations are uncensored observations. The solid line is the ATS slo
pe with Turnbull estimate of intercept.
```

- Kendall's tau is not significantly different from zero, suggesting there is not a monotonic relationship between total nitrogen and flow. This explains the poor fit of the ATS line.

Relationship with flow - lowess smooth

```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq,wq.invar=wqvar)
```

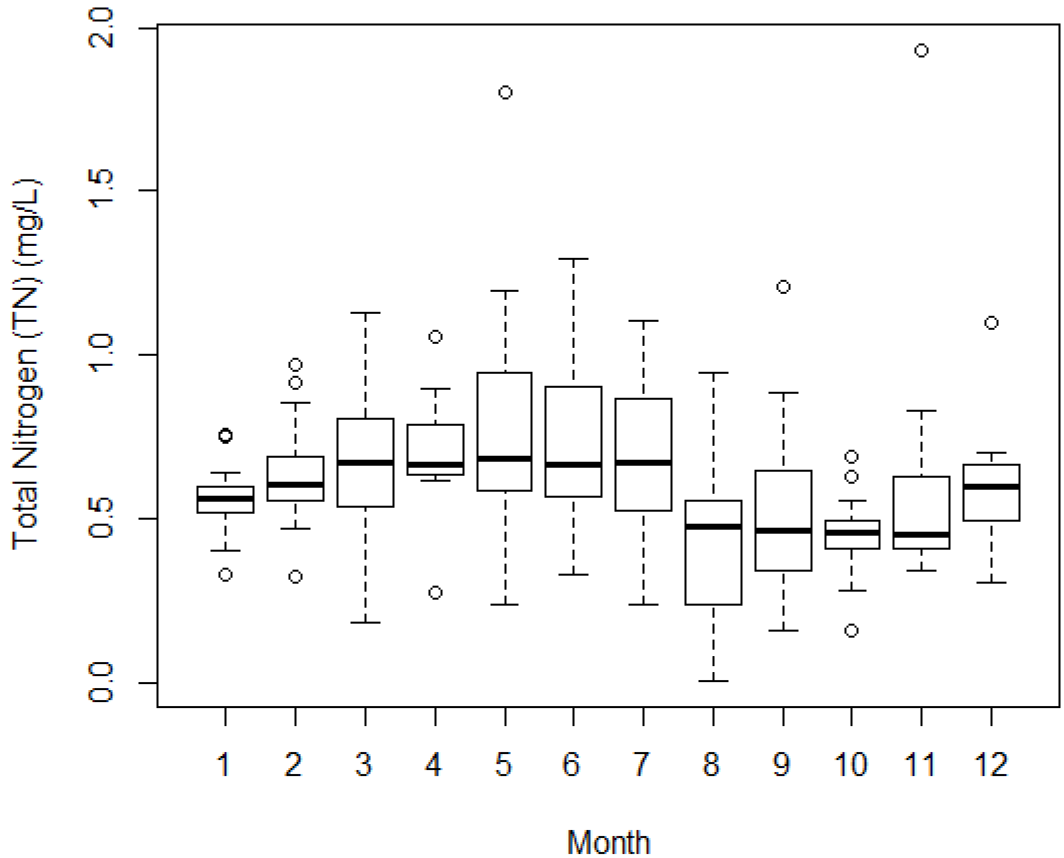



```
# Open circles are uncensored observations. The solid line is the lowess smoo
th.
```

- Based on the lowess smooth, there appears to be a nonlinear, non-monotonic relationship between total nitrogen and flow.

Seasonality in concentration

```
### Test for seasonality non flow-adjusted concentration

# Number of observations per season (month)
table(wq$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 23 23 22 13 23 24 23 24 24 20 19 22

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value~Month,data=wq,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],")
",sep=""))
```

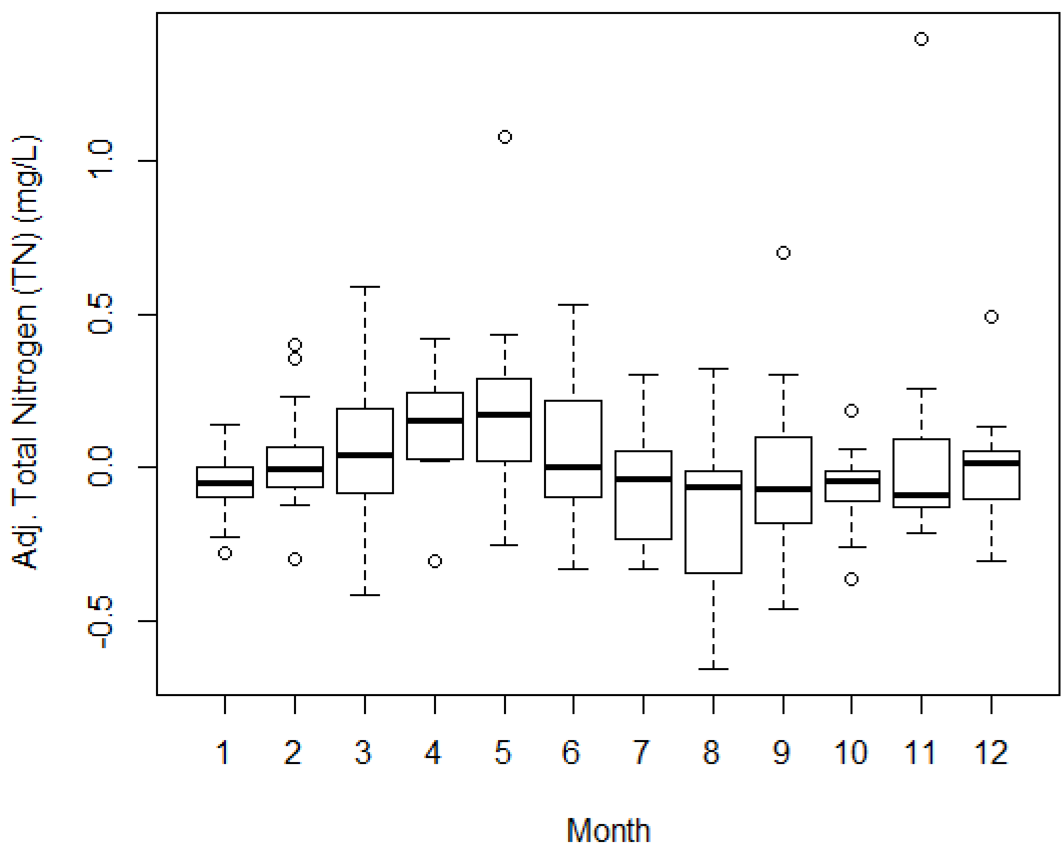



```
# Kruskal-wallis test
kruskal.test(Value ~ Month, data = wq)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 58.42
##
## Test Statistic Parameter:        df = 11
##
## P-value:                         1.822e-08
```

- The boxplot shows evidence of seasonality and the Kruskal-Wallis test is highly significant.

Seasonality in concentration after flow adjustment

```
### Test for seasonality flow-adjusted concentration

# Number of observations per season (month)
table(wq$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 23 23 22 13 23 24 23 24 24 20 19 22

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value.Adj~Month,data=wq,xlab="Month",ylab=paste("Adj. ",wqvar," (",wq
$Units[1],")",sep=""))
```




```
# Kruskal-wallis test
kruskal.test(Value.Adj ~ Month, data = wq)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
```

```
##
## Test Name:                    Kruskal-Wallis rank sum test
##
## Data:                         Value.Adj by Month
##
## Test Statistic:               Kruskal-Wallis chi-squared = 39.74
##
## Test Statistic Parameter:     df = 11
##
## P-value:                      3.964e-05
```

- After adjustment for flow, the boxplot still shows evidence of seasonality, and the Kruskal-Wallis test remains highly significant.

Trend tests - Seasonal Mann-Kendall trend test on non-flow-adjusted concentration

```
### Seasonal Kendall trend test (EnvStats) on un-adjusted concentration
Value.seastrend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,da
ta=wq,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.seastrend
```

```
##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:              All 12 values of tau = 0
##
## Alternative Hypothesis:       The seasonal taus are not all equal
##                               (Chi-Square Heterogeneity Test)
##                               At least one seasonal tau != 0
##                               and all non-zero tau's have the
##                               same sign (z Trend Test)
##
## Test Name:                    Seasonal Kendall Test for Trend
##                               (with continuity correction)
##
## Estimated Parameter(s):       tau       =  0.152988
##                               slope     =  0.004889
##                               intercept = -9.007401
##
## Estimation Method:            tau:        Weighted Average of
##                                           Seasonal Estimates
##                               slope:      Hirsch et al.'s
##                                           Modification of
##                                           Thiel/Sen Estimator
##                               intercept:  Median of
##                                           Seasonal Estimates
##
## Data:                         y      = Value
```

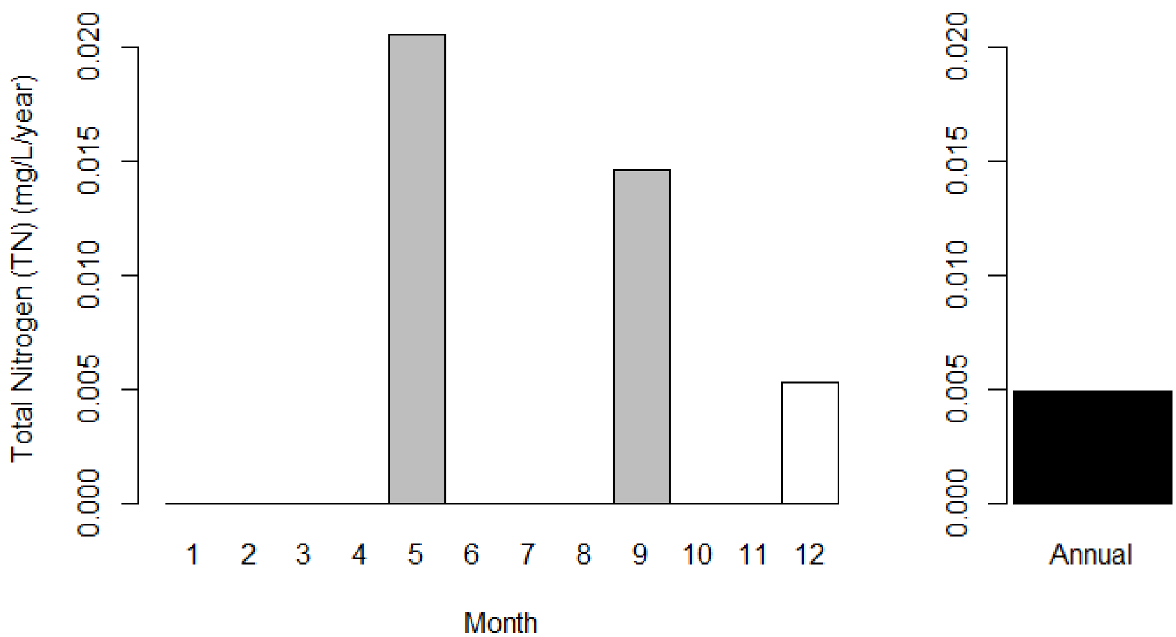
```
##                                   season = as.character(Month)
##                                   year   = Year
##
## Data Source:                      wq
##
## Sample Sizes:                     1     =  23
##                                   2     =  23
##                                   3     =  22
##                                   4     =  13
##                                   5     =  23
##                                   6     =  24
##                                   7     =  23
##                                   8     =  24
##                                   9     =  24
##                                   10    =  20
##                                   11    =  19
##                                   12    =  22
##                                   Total = 260
##
## Test Statistics:                  Chi-Square (Het) = 10.766
##                                   z (Trend)        =  3.422
##
## Test Statistic Parameter:         df = 11
##
## P-values:                         Chi-Square (Het) = 0.4630952
##                                   z (Trend)        = 0.0006225
##
## Confidence Interval for:          slope
##
## Confidence Interval Method:       Gilbert's Modification of
##                                   Theil/Sen Method
##
## Confidence Interval Type:         two-sided
##
## Confidence Level:                 95%
##
## Confidence Interval:              LCL = 0.002367
##                                   UCL = 0.007780
```

- There is no evidence of heterogenous behaviour between seasons.
- There is a highly significant increasing annual trend over time in total nitrogen.

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.seastrend <- seastrends(Value.seastrend,alternative="two.sided")
Value.seastrend$seasonal.estimates

##          tau     slope intercept       z       p
## 1   0.138340  0.002583    -4.605  0.8994 0.36843
```

```
## 2   0.193676  0.005214    -9.826  1.2677 0.20490
## 3   0.242424  0.007900   -15.129  1.5515 0.12078
## 4   0.102564  0.001188    -1.706  0.4271 0.66933
## 5   0.335968  0.020538   -40.409  2.2185 0.02652
## 6  -0.076087 -0.004786    10.238 -0.4962 0.61972
## 7  -0.114625 -0.004810    10.295 -0.7395 0.45961
## 8   0.152174  0.007667   -14.860  1.0170 0.30916
## 9   0.311594  0.014585   -28.711  2.1097 0.03489
## 10  0.257895  0.004321    -8.189  1.5653 0.11751
## 11  0.005848  0.000000     0.454  0.0000 1.00000
## 12  0.264069  0.005250    -9.906  1.6932 0.09041
```

```
# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.seastrend,wq.in=wq,wq.invar=wqvar,adj=FALSE
)
```



- There are significant increasing trends in total nitrogen in May and September, and a marginally significant increasing trend in total nitrogen in December.

Trend tests - Seasonal Mann-Kendall trend test on total nitrogen after flow adjustment

```
### seasonal Kendall trend test (EnvStats) on flow adjusted concentration
Value.Adj.seastrend <- kendallSeasonalTrendTest(Value.Adj~as.character(Month)
+Year,data=wq,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.Adj.seastrend
```

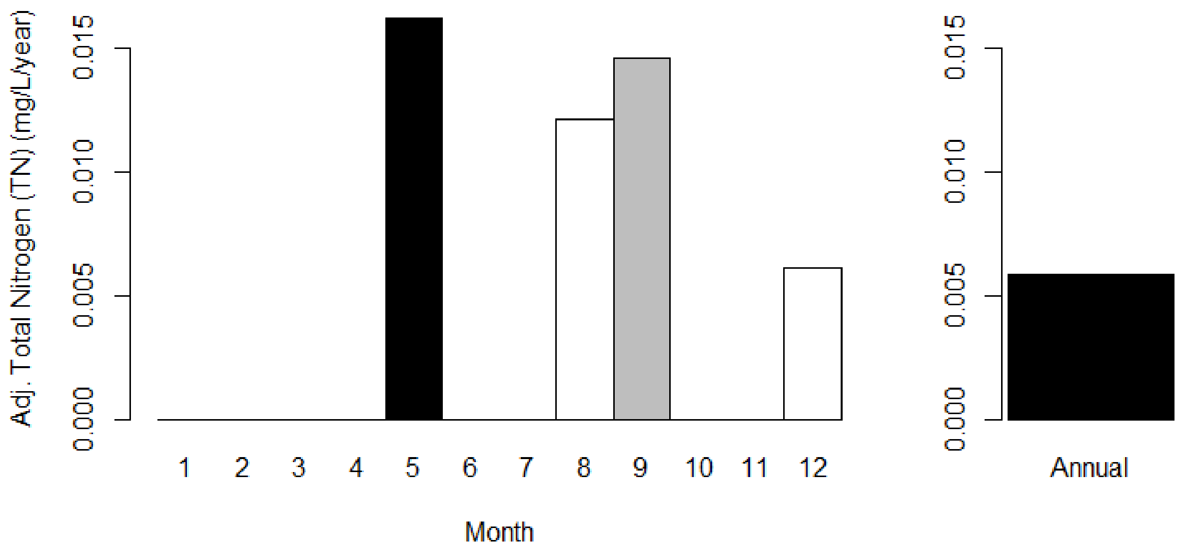
```
##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.176986
##                                  slope     =  0.005842
##                                  intercept = -9.053873
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value.Adj
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq
##
## Sample Sizes:                    1     =  23
##                                  2     =  23
##                                  3     =  22
##                                  4     =  13
##                                  5     =  23
##                                  6     =  24
##                                  7     =  23
##                                  8     =  24
##                                  9     =  24
##                                  10    =  20
##                                  11    =  19
##                                  12    =  22
##                                  Total = 260
##
## Test Statistics:                 Chi-Square (Het) = 11.165
##                                  z (Trend)        =  4.093
##
```

```
## Test Statistic Parameter:        df = 11
##
## P-values:                        Chi-Square (Het) = 4.295e-01
##                                  z (Trend)        = 4.256e-05
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = 0.003176
##                                  UCL = 0.008809
```

- There is no evidence of heterogenous behaviour between seasons.
- There is a highly significant increasing annual trend over time in total nitrogen after flow adjustment.

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.Adj.seastrend <- seastrends(Value.Adj.seastrend,alternative="two.sided"
)
Value.Adj.seastrend$seasonal.estimates
```

```
##          tau      slope intercept       z        p
## 1   0.09091  0.0025281    -5.105  0.5810 0.561220
## 2   0.20158  0.0052977   -10.604  1.3205 0.186661
## 3   0.22078  0.0084713   -16.906  1.4099 0.158570
## 4  -0.10256 -0.0029156     5.985 -0.4271 0.669334
## 5   0.39130  0.0161702   -32.186  2.5882 0.009647
## 6   0.05072  0.0018504    -3.697  0.3225 0.747106
## 7  -0.05138 -0.0008783     1.725 -0.3169 0.751300
## 8   0.24638  0.0121015   -24.274  1.6619 0.096534
## 9   0.35507  0.0145877   -29.253  2.4060 0.016127
## 10  0.26316  0.0037293    -7.504  1.5898 0.111887
## 11  0.06433  0.0007783    -1.648  0.3499 0.726447
## 12  0.26407  0.0060862   -12.165  1.6919 0.090670
```



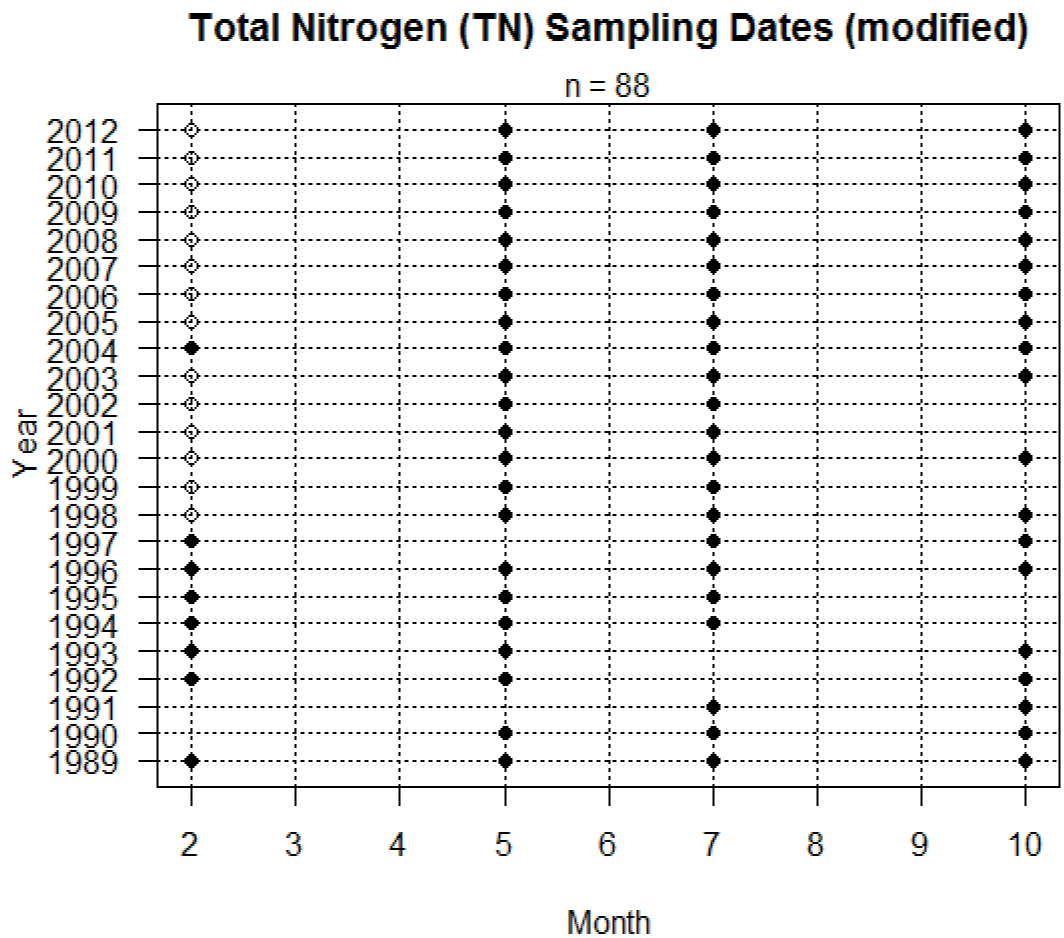
- After flow adjustment, there is a highly significant increasing trend in total nitrogen in May, a significant increasing trend in September, and marginally significant increasing trends in August and December.

A.2 - Supplemental Trend Analysis at Old Fort: Total Nitrogen

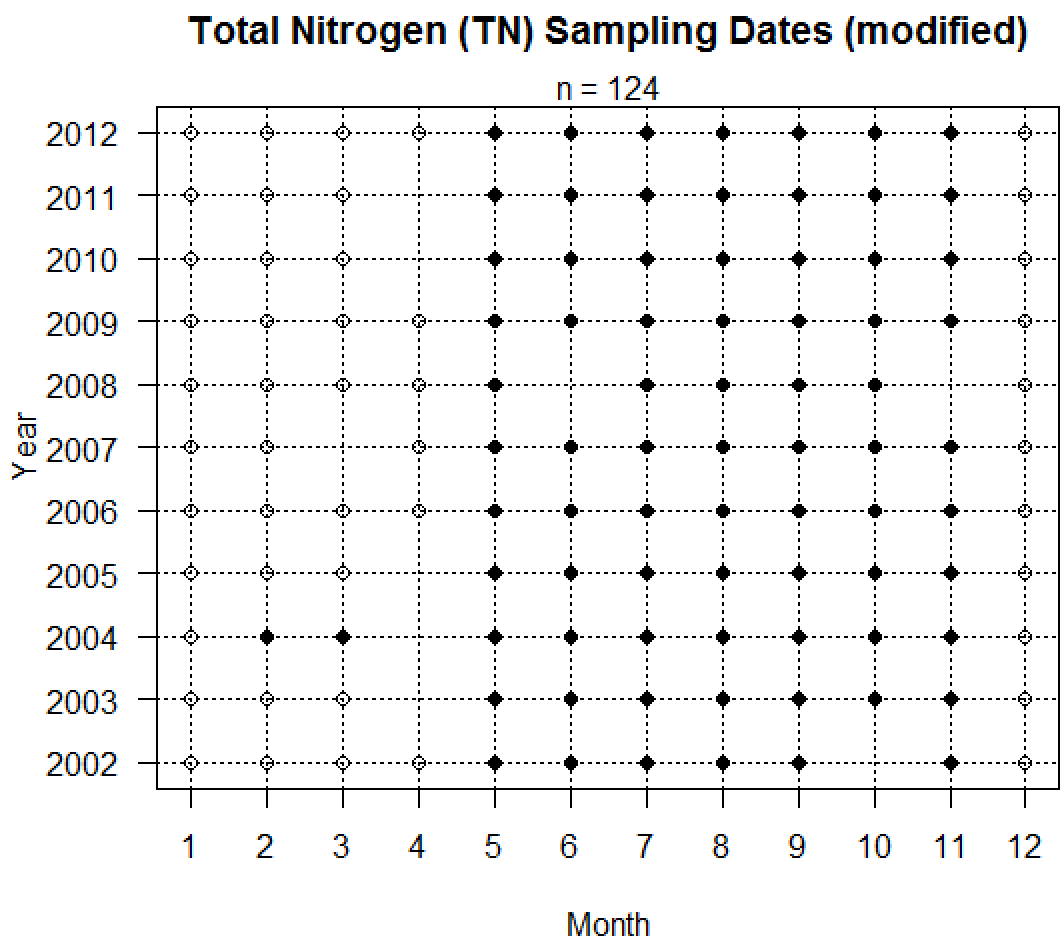
- The period of record for total nitrogen is 1988-2012 (26 years).
- This analysis matches the time periods/sampling frequency with the data available from the upstream of Fort McMurray station to allow for consistent comparisons
- We will look at the trend over two time periods A) quarterly from 1989 -2012 (25 years) and B) monthly 2002-2012 (10 years)

Final data set for trend analysis

```
### Create final data set for trend analysis

# Total occurrences and occurrences by year in modified data set and verify t
hat they are as expected (A: 1989-2012)
length(wq_A[,1])

## [1] 88

table(wq_A$Year)

##
## 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002 2003
##    4    3    2    3    3    4    3    4    3    5    3    4    3    3    4
## 2004 2005 2006 2007 2008 2009 2010 2011 2012
##    4    4    4    4    5    4    4    4    4

table(wq_A$Month)

##
##  2  5  7 10
## 23 22 23 20

# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq_A,wq.invar=wqvar,type="modified")
```



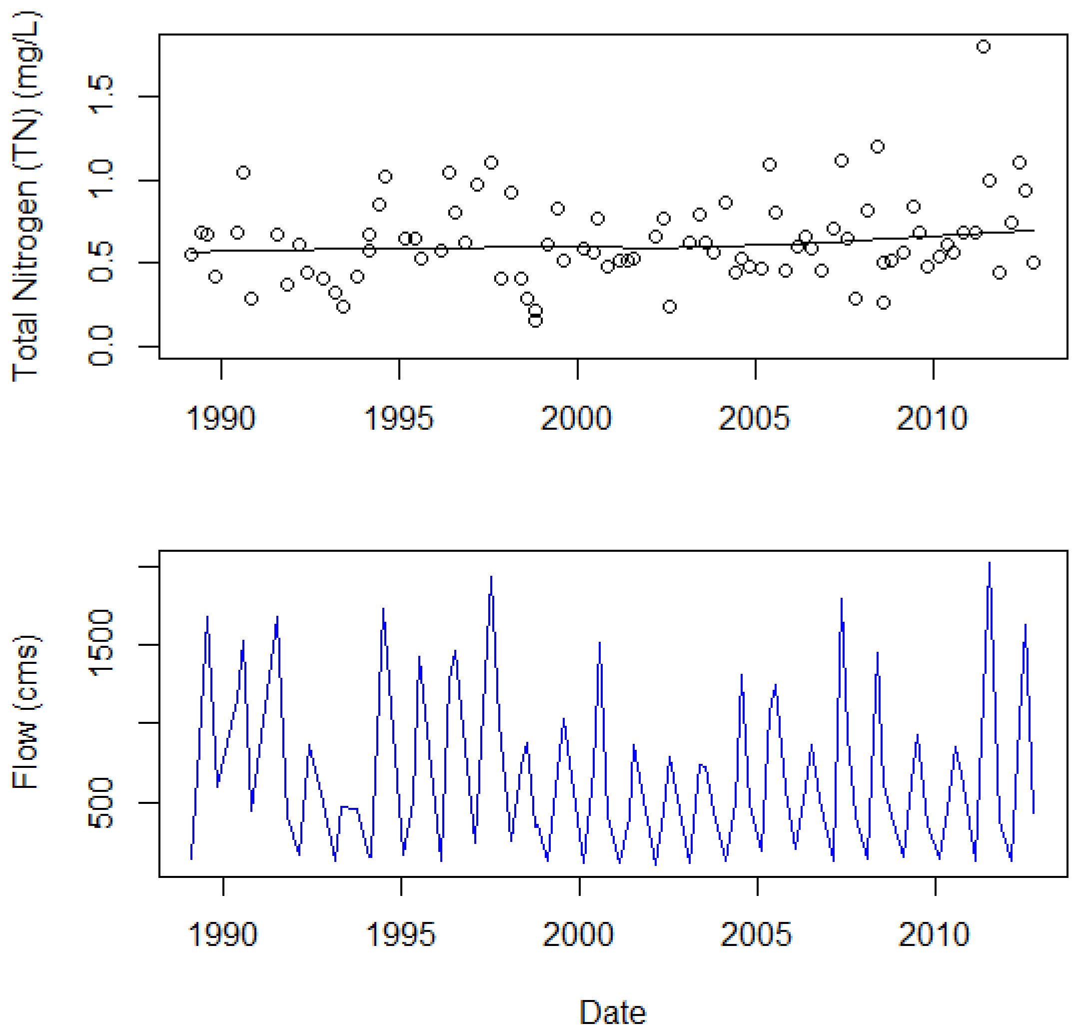

```
# Total occurrences and occurrences by year in modified data set and verify
that they are as expected (B: 2002-2012)
length(wq_B[,1])

## [1] 124

table(wq_B$Year)

##
## 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##   11   11   11   11   12   11   11   12   11   11   12

table(wq_B$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 11 11 10  6 11 10 12 11 11 10 10 11

# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq_B,wq.invar=wqvar,type="modified")
```



Analysis of quarterly data from 1989-2012

Time series plot of data

```
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq_A,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The blue line represents flow
observations from the same dates as the water quality observations. The black
line is the lowess smooth to the concentration data.
```

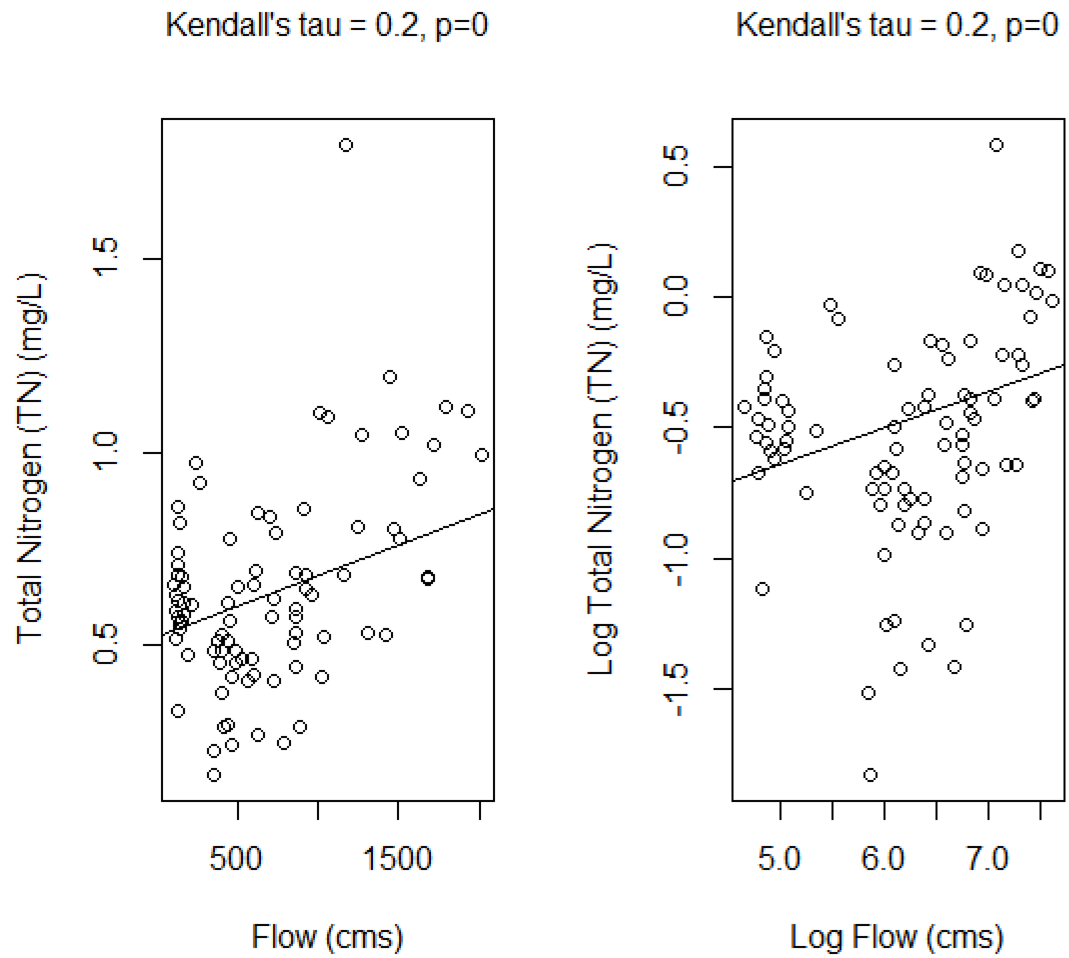
Summary statistics

```
### Calculate summary statistics
# Summary stats were calculated as usual since there was no censoring.

# n
with(wq_A,length(Value))

## [1] 88

# min
with(wq_A,min(Value,na.rm=TRUE))

## [1] 0.16
```

```
# max
with(wq_A,max(Value, na.rm=TRUE))

## [1] 1.8

# median
with(wq_A,median(Value, na.rm=TRUE))

## [1] 0.6045

# mean
with(wq_A,mean(Value, na.rm=TRUE))

## [1] 0.6384

# standard deviation
with(wq_A,sd(Value, na.rm=TRUE))

## [1] 0.2598

#variance
with(wq_A,var(Value, na.rm=TRUE))

## [1] 0.06751
```

Relationship with flow

```
### Test for a relationship between concentration and flow
# Determine if there is a relationship (possibly linear) between flow and con
centration (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq_A,wq.invar=wqvar)
```

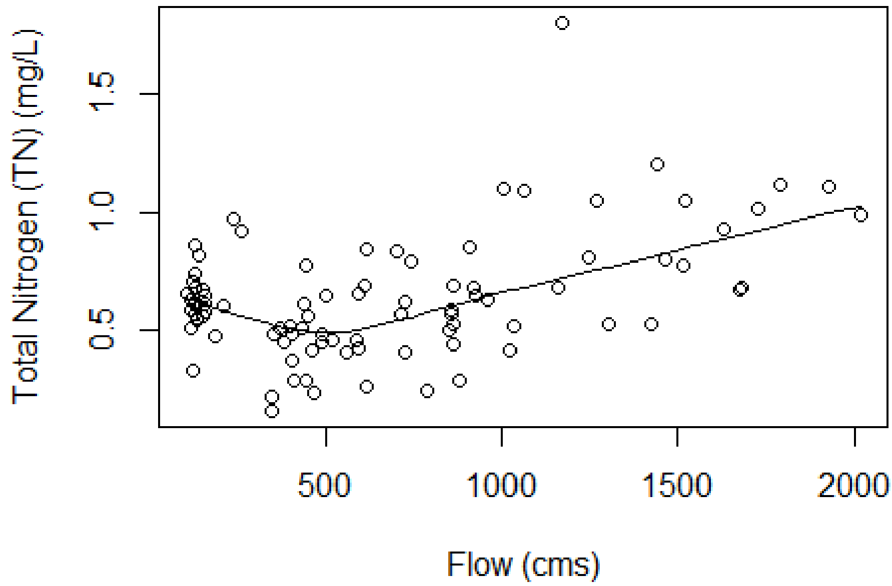



```
# All observations are uncensored observations. The solid line is the ATS slo
pe with Turnbull estimate of intercept.
```

- The relationship between total nitrogen and flow is not fit very well by the ATS line on either the original or log-log scale, but there is some support for a monotonic relationship with flow, as Kendall's tau is significantly different form zero (though still small)

Relationship with flow - lowess smooth

```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq_A,wq.invar=wqvar)
```

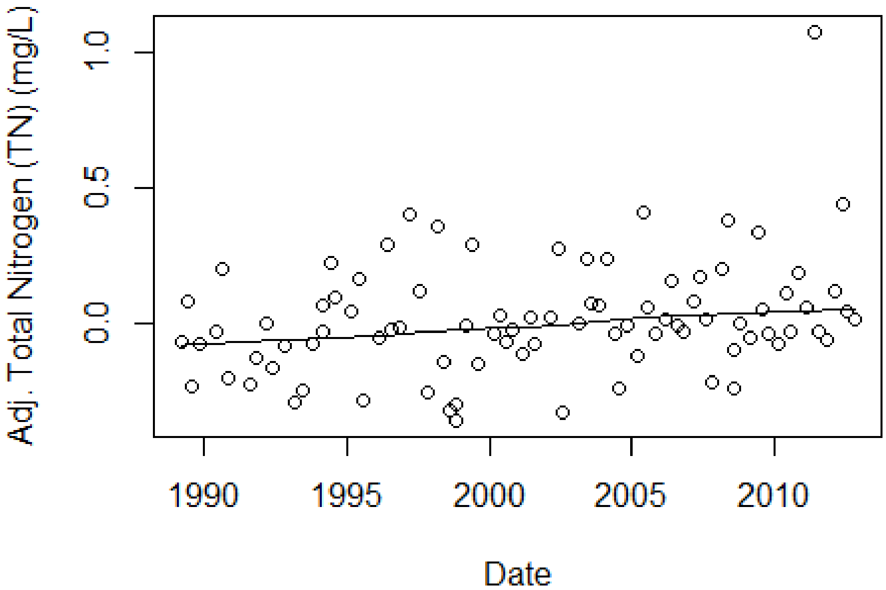



```
# Open circles are uncensored observations and solid circles are censored obs
ervations. The solid line is the lowess smooth.
```

- Based on the lowess smooth, there appears to be a nonlinear, non-monotonic relationship between total nitrogen and flow.
- Initially total nitrogen decreases with increasing flow up to about 500 cms, after which is increases with flow.

Time series plot of data after flow adjustment

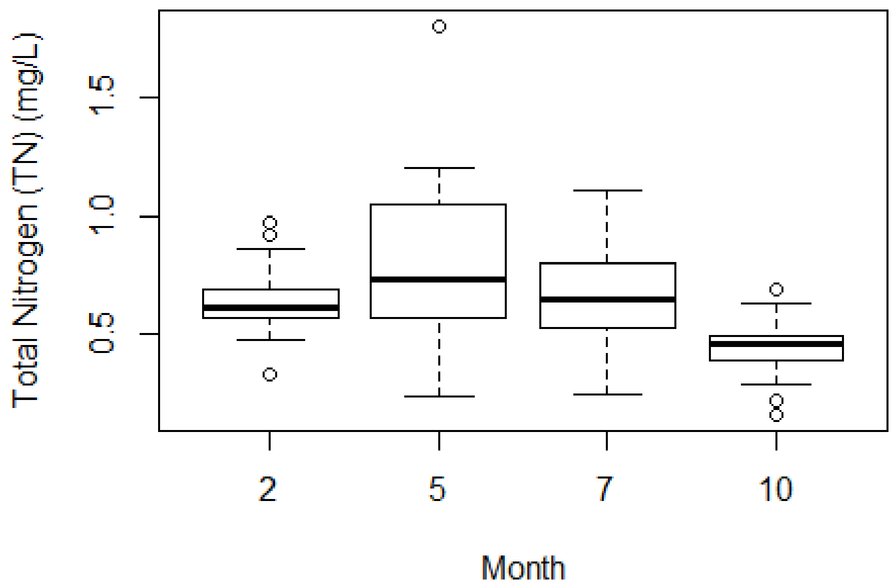
```
### Plot of flow-adjusted water quality data vs Date
source("func_timeseriesplot.r")
timeseriesplot_adj(wq.in=wq_A,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The black line is the lowess smooth to the concentration data.
```

Seasonality in concentration

```
### Test for seasonality un-adjusted data

# Number of observations per season (month)
table(wq_A$Month)

##
##  2  5  7 10
## 23 22 23 20

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value~Month,data=wq_A,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],
")",sep=""))
```



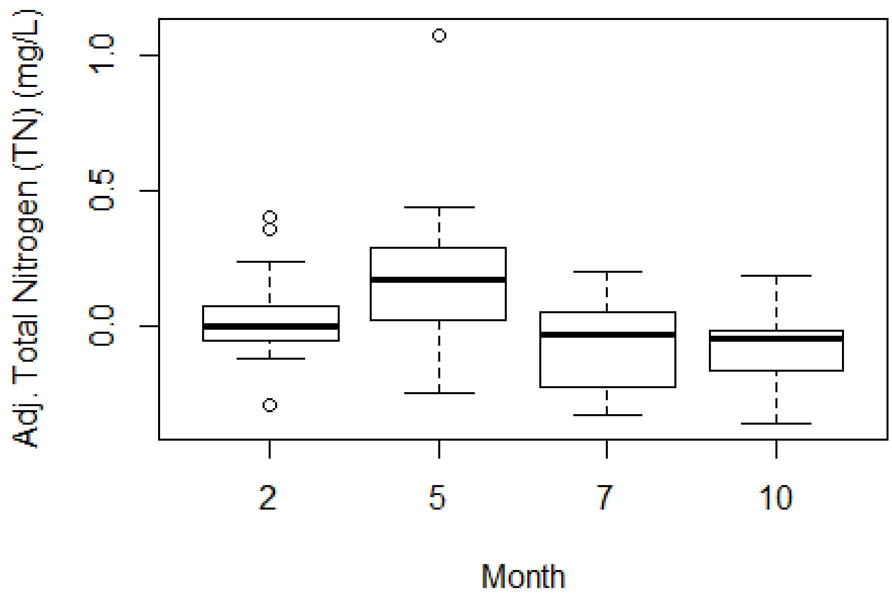

```
# Kruskal-wallis test
kruskal.test(Value ~ Month, data = wq_A)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 24.38
##
## Test Statistic Parameter:        df = 3
##
## P-value:                         2.084e-05
```

- The boxplot shows evidence of seasonality and the Kruskal-Wallis test is highly significant.

Seasonality in concentration after flow adjustment

```
### Test for seasonality flow-adjusted data

# Number of observations per season (month)
table(wq_A$Month)

##
##  2  5  7 10
## 23 22 23 20
```

```
# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value.Adj~Month,data=wq_A,xlab="Month",ylab=paste("Adj. ",wqvar," (",
wq$Units[1],")",sep=""))
```




```
# Kruskal-wallis test
kruskal.test(Value.Adj ~ Month, data = wq_A)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value.Adj by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 20.28
##
## Test Statistic Parameter:        df = 3
##
## P-value:                         0.0001488
```

- After adjustment for flow, the boxplot still shows evidence of seasonality, and the Kruskal-Wallis test is highly significant.

Trend tests - Seasonal Mann-Kendall trend test on total nitrogen

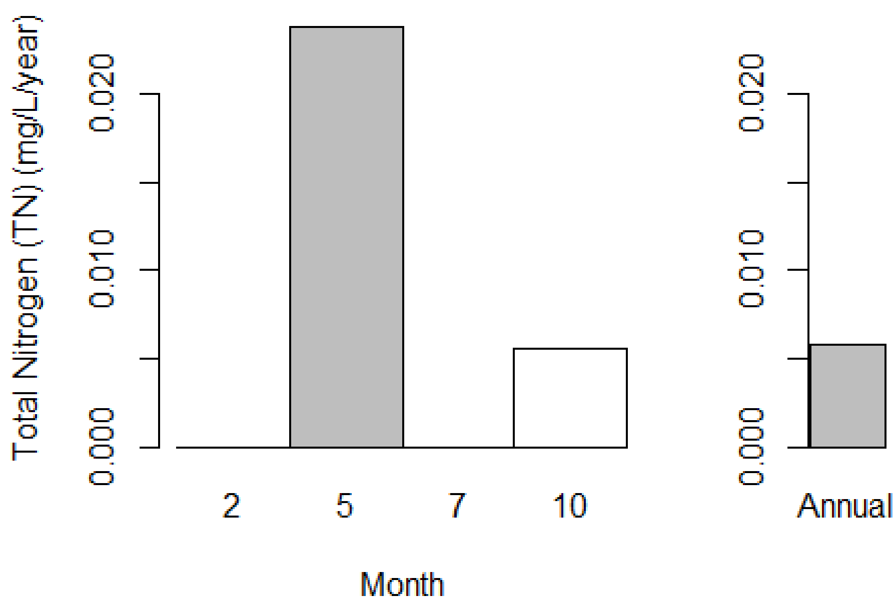
```
### Seasonal Kendall trend test (EnvStats) on un-adjusted concentration
Value.seastrend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,da
```

```
ta=wq_A,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 4 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.17270
##                                  slope     =  0.00575
##                                  intercept = -8.41581
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq_A
##
## Sample Sizes:                    2     = 23
##                                  5     = 22
##                                  7     = 23
##                                  10    = 20
##                                  Total = 88
##
## Test Statistics:                 Chi-Square (Het) = 4.759
##                                  z (Trend)        = 2.149
##
## Test Statistic Parameter:        df = 3
##
## P-values:                        Chi-Square (Het) = 0.19032
##                                  z (Trend)        = 0.03161
##
```

```
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = 0.0004511
##                                  UCL = 0.0100509
```

- There is no evidence of heterogenous behaviour between seasons.
- There is a significant increasing trend in TN

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.seastrend <- seastrends(Value.seastrend,alternative="two.sided")
Value.seastrend$seasonal.estimates

##         tau     slope intercept       z       p
## 2   0.13439  0.003361    -6.112  0.8718 0.38329
## 5   0.35065  0.023765   -46.835  2.2558 0.02408
## 7  -0.07905 -0.003750     8.152 -0.5020 0.61569
## 10  0.31053  0.005583   -10.720  1.8874 0.05911

# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.seastrend,wq.in=wq_A,wq.invar=wqvar,adj=FAL
SE)
```



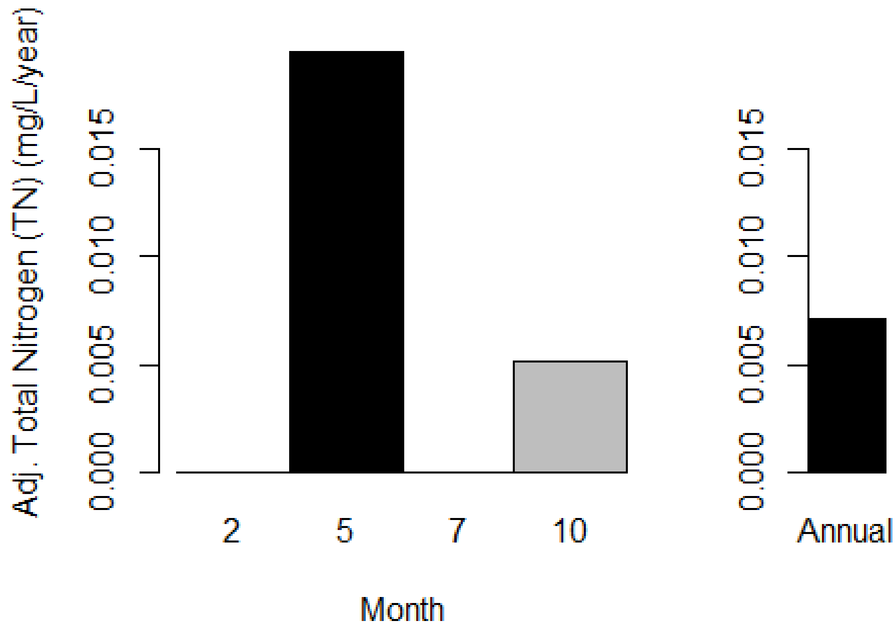
Trend tests - Seasonal Mann-Kendall trend test on total nitrogen after flow adjustment

```
### seasonal Kendall trend test (EnvStats) on flow adjusted concentration
Value.Adj.seastrend <- kendallSeasonalTrendTest(Value.Adj~as.character(Month)
+Year,data=wq_A,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.Adj.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 4 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.225890
##                                  slope     =  0.007144
##                                  intercept = -9.262820
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value.Adj
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq_A
##
## Sample Sizes:                    2     = 23
##                                  5     = 22
##                                  7     = 23
##                                  10    = 20
##                                  Total = 88
##
## Test Statistics:                 Chi-Square (Het) = 3.92
##                                  z (Trend)        = 2.85
##
```

```
## Test Statistic Parameter:        df = 3
##
## P-values:                        Chi-Square (Het) = 0.270204
##                                  z (Trend)        = 0.004366
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = 0.003004
##                                  UCL = 0.012107
```

- There is no evidence of heterogenous behaviour between seasons.
- There is a significant trend in total nitrogen after flow adjustment.

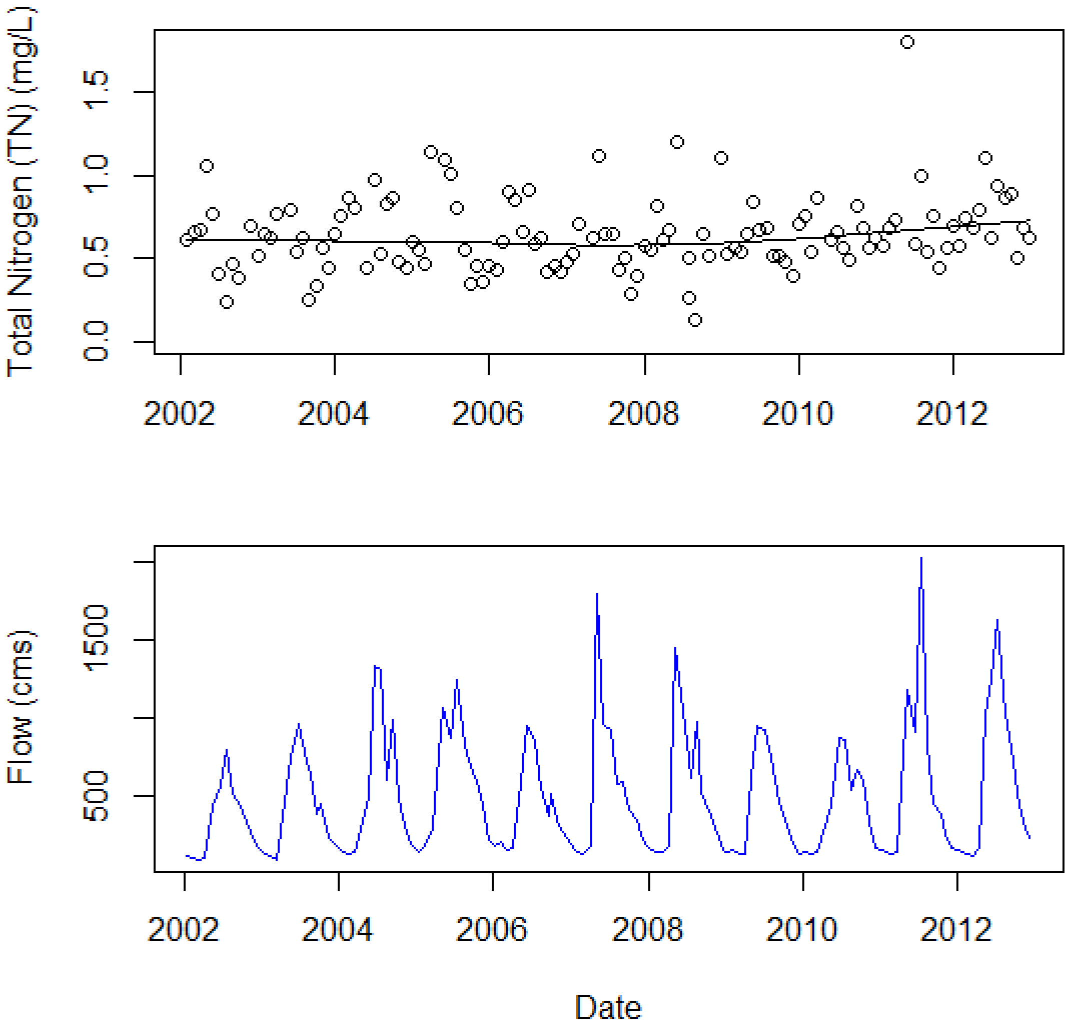
```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.Adj.seastrend <- seastrends(Value.Adj.seastrend,alternative="two.sided"
)
Value.Adj.seastrend$seasonal.estimates

##         tau    slope intercept      z       p
## 2  0.12648 0.004129    -8.263 0.8190 0.41278
## 5  0.42857 0.019542   -38.947 2.7634 0.00572
## 7  0.03953 0.003783    -7.609 0.2378 0.81205
## 10 0.33158 0.005102   -10.263 2.0126 0.04416

# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.Adj.seastrend,wq.in=wq_A,wq.invar=wqvar,adj
=TRUE)
```



Analysis of monthly data from 2002-2012

Time series plot of data

```
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq_B,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The blue line represents flow
observations from the same dates as the water quality observations. The black
line is the lowess smooth to the concentration data.
```

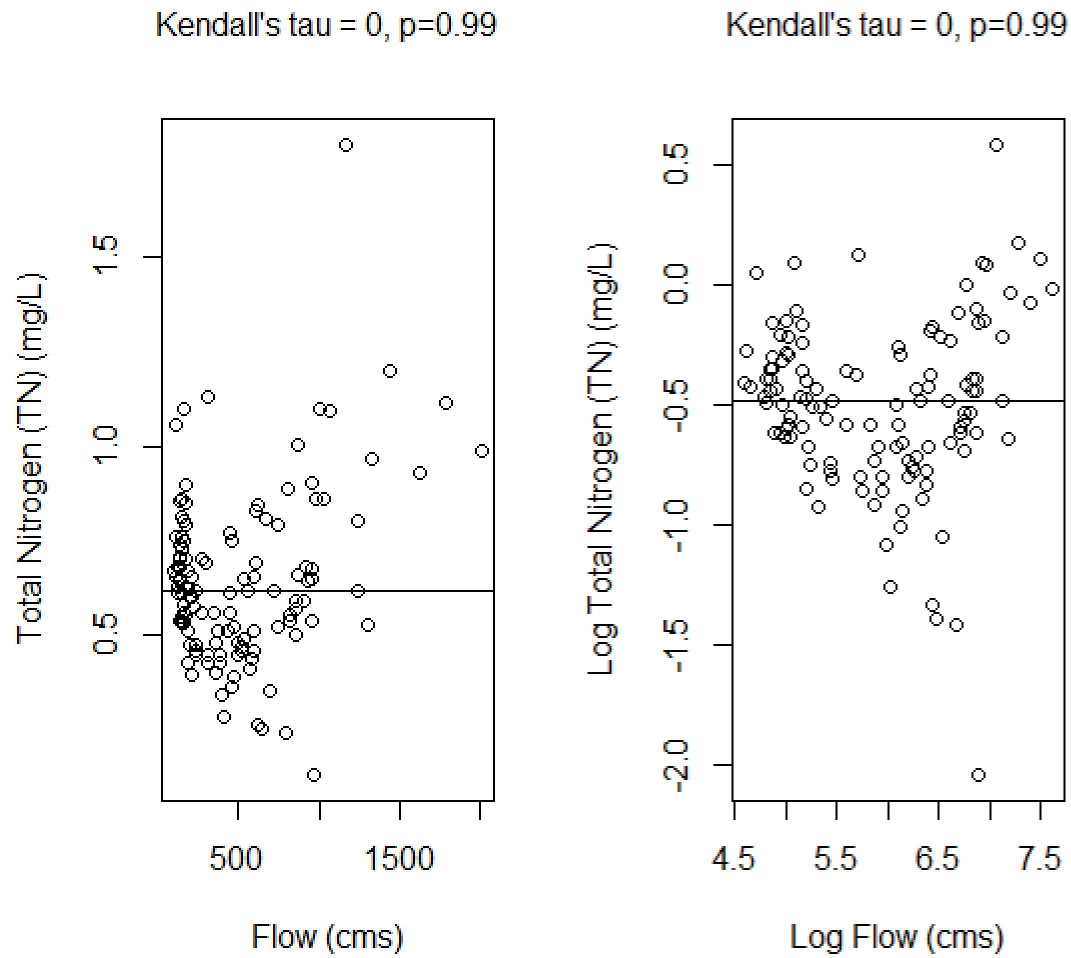
Summary statistics

```
### Calculate summary statistics
# Summary stats were calculated as usual since there was no censoring.

# n
with(wq_B,length(Value))

## [1] 124

# min
with(wq_B,min(Value,na.rm=TRUE))

## [1] 0.13
```

```
# max
with(wq_B,max(Value, na.rm=TRUE))

## [1] 1.8

# median
with(wq_B,median(Value, na.rm=TRUE))

## [1] 0.6195

# mean
with(wq_B,mean(Value, na.rm=TRUE))

## [1] 0.6453

# standard deviation
with(wq_B,sd(Value, na.rm=TRUE))

## [1] 0.2269

#variance
with(wq_B,var(Value, na.rm=TRUE))

## [1] 0.05146
```

Relationship with flow

```
### Test for a relationship between concentration and flow
# Determine if there is a relationship (possibly linear) between flow and con
centration (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq_B,wq.invar=wqvar)
```

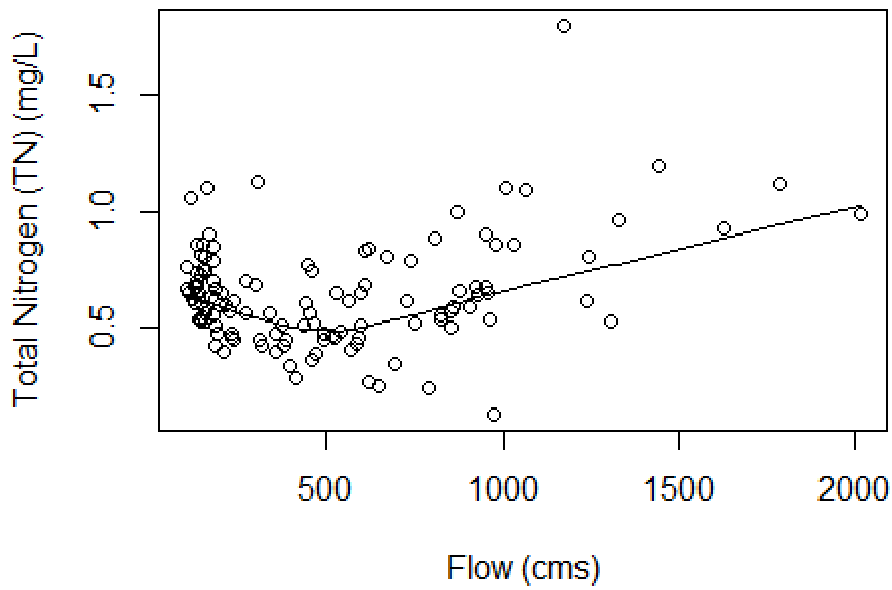



```
# All observations are uncensored observations. The solid line is the ATS slo
pe with Turnbull estimate of intercept and the dashed line is the regression
line.
```

- The relationship between total nitrogen and flow is not fit very well by the ATS line on either the original or log-log scale.
- Additionally, there is no significant monotonic relationship (non-sig Kendall’s tau).

Relationship with flow - lowess smooth

```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq_B,wq.invar=wqvar)
```

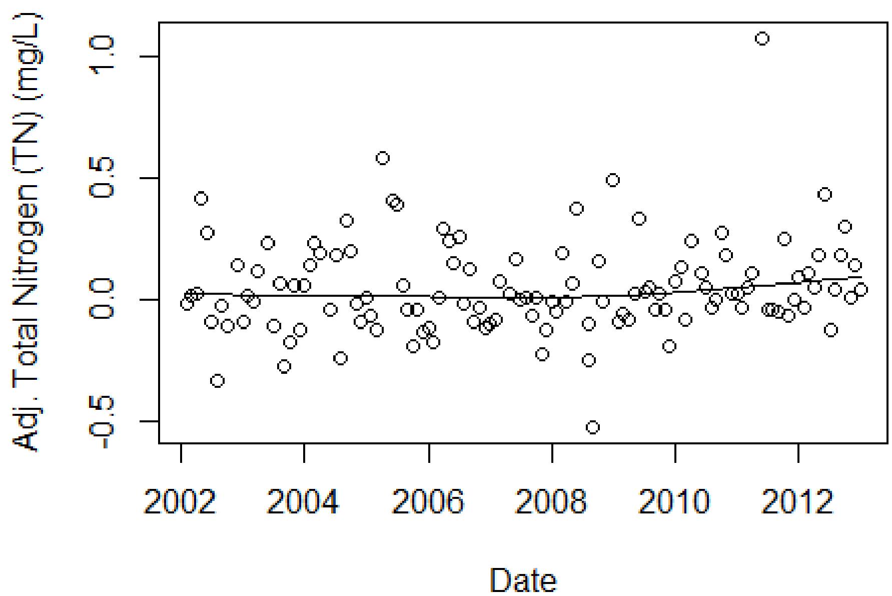



```
# Open circles are uncensored observations and solid circles are censored obs
ervations. The solid line is the lowess smooth.
```

- Based on the lowess smooth, there appears to be a nonlinear, non-monotonic relationship between total nitrogen and flow.
- Initially total nitrogen decreases with increasing flow up to about 500 cms, after which is increases with flow.

Time series plot of data after flow adjustment

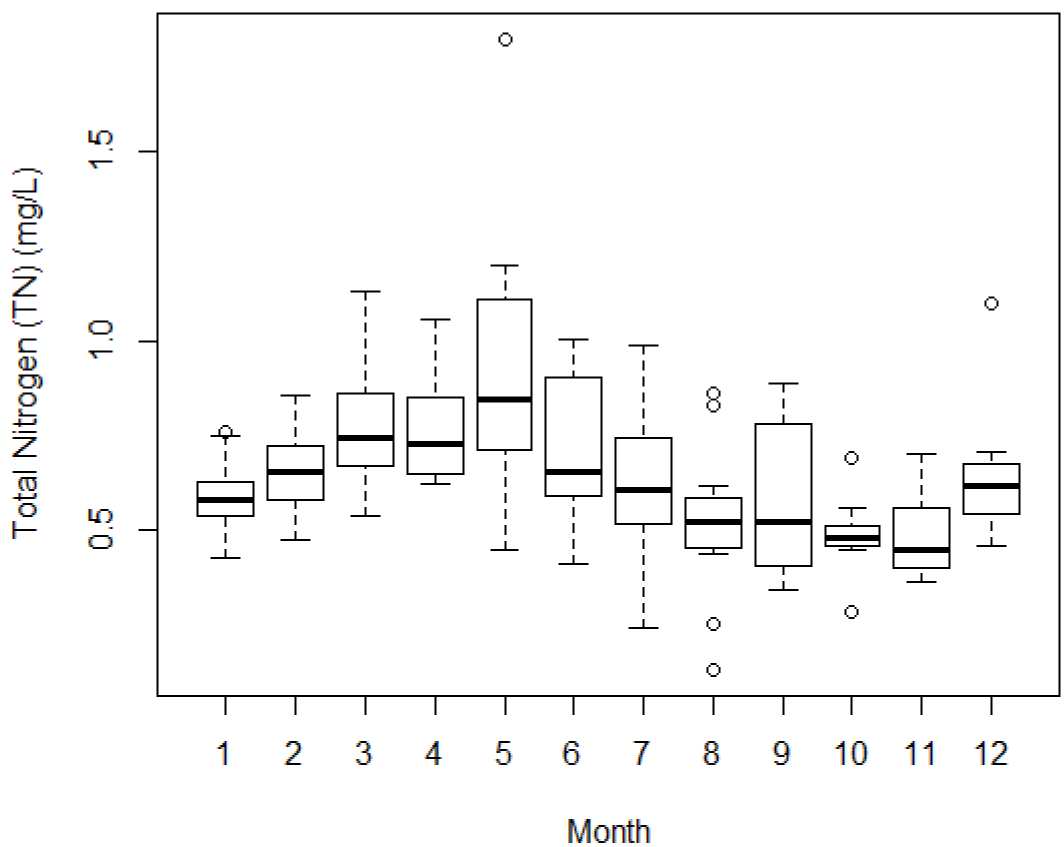
```
### Plot of flow-adjusted water quality data vs Date
source("func_timeseriesplot.r")
timeseriesplot_adj(wq.in=wq_B,wq.invar=wqvar)
```



```
# All observations are uncensored observations. The black line is the lowess
smooth to the concentration data.
```

Seasonality in concentration

```
### Test for seasonality un-adjusted data

# Number of observations per season (month)
table(wq_B$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 11 11 10  6 11 10 12 11 11 10 10 11

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value~Month,data=wq_B,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],
")",sep=""))
```



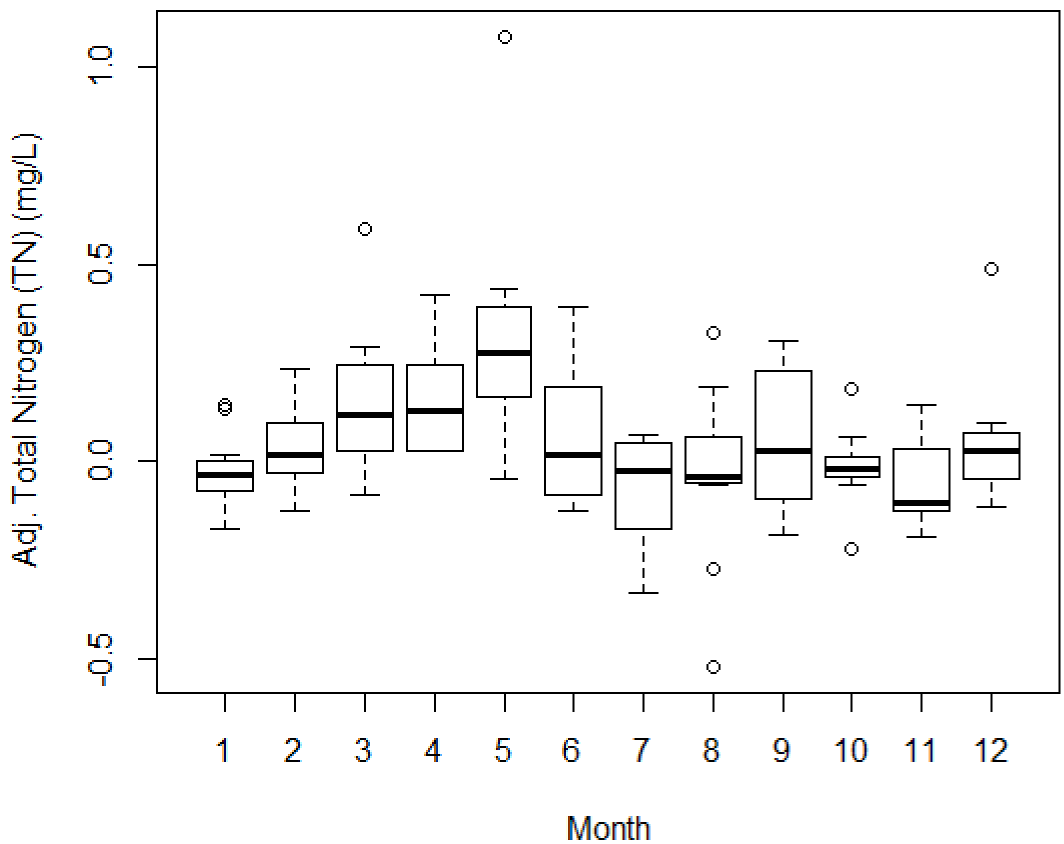

```
# Kruskal-wallis test
kruskal.test(Value ~ Month, data = wq_B)

##
## Results of Hypothesis Test
## --------------------------
```

```
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 37.88
##
## Test Statistic Parameter:        df = 11
##
## P-value:                         8.205e-05
```

- The boxplot shows evidence of seasonality, and the Kruskal-Wallis test is highly significant.

Seasonality in concentration after flow adjustment

```
### Test for seasonality flow-adjusted data

# Number of observations per season (month)
table(wq_B$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 11 11 10  6 11 10 12 11 11 10 10 11

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value.Adj~Month,data=wq_B,xlab="Month",ylab=paste("Adj. ",wqvar," (",
wq$Units[1],")",sep=""))
```




```
# Kruskal-wallis test
kruskal.test(Value.Adj ~ Month, data = wq_B)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                        Kruskal-Wallis rank sum test
##
## Data:                             Value.Adj by Month
##
## Test Statistic:                   Kruskal-Wallis chi-squared = 32.92
##
## Test Statistic Parameter:         df = 11
##
## P-value:                          0.0005413
```

- After adjustment for flow, the boxplot still shows evidence of a similar seasonal pattern, and the Kruskal-Wallis test is highly significant.

Trend tests - Seasonal Mann-Kendall trend test on total nitrogen

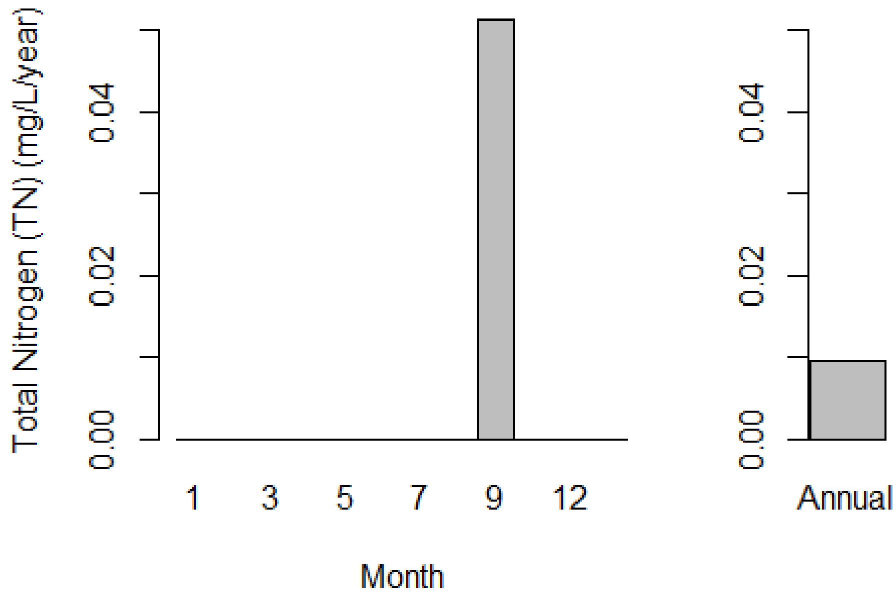
```
### Seasonal Kendall trend test (EnvStats) on un-adjusted concentration
Value.seastrend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,da
ta=wq_B,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.seastrend
```

```
##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =   0.127990
##                                  slope     =   0.009483
##                                  intercept = -10.261750
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq_B
##
## Sample Sizes:                    1     =  11
##                                  2     =  11
##                                  3     =  10
##                                  4     =   6
##                                  5     =  11
##                                  6     =  10
##                                  7     =  12
##                                  8     =  11
##                                  9     =  11
##                                  11    =  10
```

```
##                                    12    =  11
##                                    10    =  10
##                                    Total = 124
##
## Test Statistics:                   Chi-Square (Het) = 11.540
##                                    z (Trend)        =  2.071
##
## Test Statistic Parameter:          df = 11
##
## P-values:                          Chi-Square (Het) = 0.39921
##                                    z (Trend)        = 0.03839
##
## Confidence Interval for:           slope
##
## Confidence Interval Method:        Gilbert's Modification of
##                                    Theil/Sen Method
##
## Confidence Interval Type:          two-sided
##
## Confidence Level:                  95%
##
## Confidence Interval:               LCL = 0.0002983
##                                    UCL = 0.0210000
```

- There is no evidence of heterogenous behaviour between seasons.
- There is a significant increasing trend in TN.

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.seastrend <- seastrends(Value.seastrend,alternative="two.sided")
Value.seastrend$seasonal.estimates

##          tau     slope intercept       z       p
## 1  -0.05455 -0.001333     3.256 -0.1567 0.87552
## 2   0.01818  0.002778    -4.920  0.0000 1.00000
## 3  -0.11111 -0.009833    20.482 -0.3578 0.72051
## 4  -0.33333 -0.026600    54.130 -0.7515 0.45237
## 5   0.34545  0.063000  -125.597  1.4013 0.16112
## 6  -0.06667 -0.014250    29.246 -0.1789 0.85803
## 7   0.34848  0.034444   -68.542  1.5122 0.13049
## 8   0.16364  0.010000   -19.550  0.6228 0.53342
## 9   0.60000  0.051250  -102.339  2.4912 0.01273
## 11  0.08889  0.008000   -15.604  0.2694 0.78762
## 12  0.27273  0.014000   -27.478  1.0899 0.27576
## 10 -0.02222  0.000000     0.480  0.0000 1.00000

# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.seastrend,wq.in=wq_B,wq.invar=wqvar,adj=FAL
SE)
```



Trend tests - Seasonal Mann-Kendall trend test on total nitrogen after flow adjustment

```
### seasonal Kendall trend test (EnvStats) on flow adjusted concentration
Value.Adj.seastrend <- kendallSeasonalTrendTest(Value.Adj~as.character(Month)
+Year,data=wq_B,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.Adj.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.083252
##                                  slope     =  0.007246
##                                  intercept = -6.564824
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
```

```
##                                                Modification of
##                                                Thiel/Sen Estimator
##                                    intercept:  Median of
##                                                Seasonal Estimates
##
## Data:                              y      = Value.Adj
##                                    season = as.character(Month)
##                                    year   = Year
##
## Data Source:                       wq_B
##
## Sample Sizes:                      1     =  11
##                                    2     =  11
##                                    3     =  10
##                                    4     =   6
##                                    5     =  11
##                                    6     =  10
##                                    7     =  12
##                                    8     =  11
##                                    9     =  11
##                                    11    =  10
##                                    12    =  11
##                                    10    =  10
##                                    Total = 124
##
## Test Statistics:                   Chi-Square (Het) = 11.66
##                                    z (Trend)        =  1.37
##
## Test Statistic Parameter:          df = 11
##
## P-values:                          Chi-Square (Het) = 0.3895
##                                    z (Trend)        = 0.1706
##
## Confidence Interval for:           slope
##
## Confidence Interval Method:        Gilbert's Modification of
##                                    Theil/Sen Method
##
## Confidence Interval Type:          two-sided
##
## Confidence Level:                  95%
##
## Confidence Interval:               LCL = -0.001978
##                                    UCL =  0.016211
```

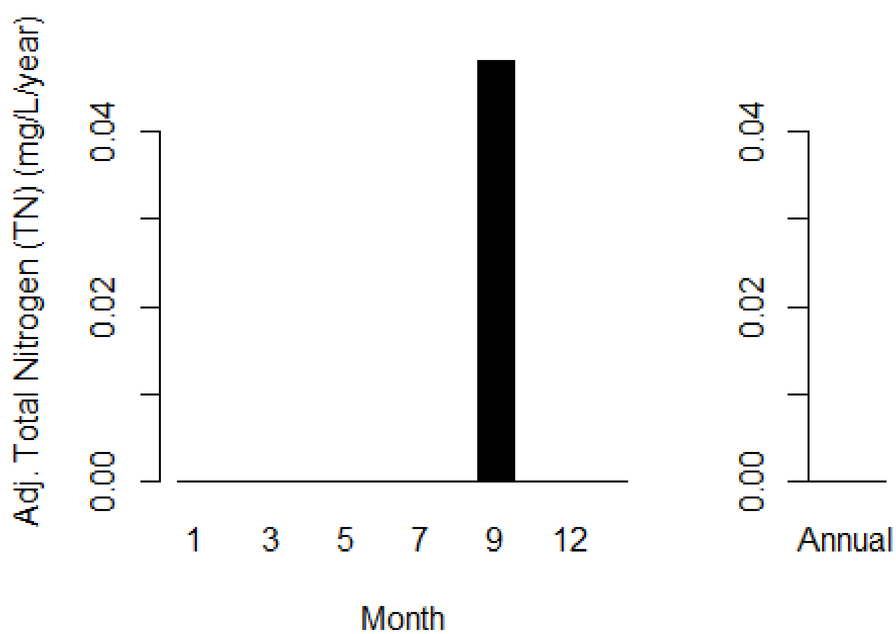
- There is no evidence of heterogenous behaviour between seasons.
- There is no significant trend in total nitrogen after flow adjustment.

```
# Look at trend by season
# calculate p-value of trend by season
```

```
source("func_seastrends.r")
Value.Adj.seastrend <- seastrends(Value.Adj.seastrend,alternative="two.sided"
)
Value.Adj.seastrend$seasonal.estimates
```

```
##           tau     slope intercept       z        p
## 1  -0.05455 -0.001492     2.963 -0.1557 0.876270
## 2   0.05455  0.006329   -12.684  0.1557 0.876270
## 3  -0.11111 -0.007865    15.904 -0.3578 0.720515
## 4  -0.33333 -0.042894    86.239 -0.7515 0.452370
## 5   0.27273  0.022344   -44.568  1.0899 0.275758
## 6  -0.15556 -0.022845    45.858 -0.5367 0.591505
## 7   0.04545  0.009305   -18.704  0.1375 0.890660
## 8   0.01818  0.002451    -4.955  0.0000 1.000000
## 9   0.63636  0.048186   -96.683  2.6469 0.008123
## 11  0.11111  0.004024    -8.175  0.3578 0.720515
## 12  0.34545  0.013268   -26.603  1.4013 0.161125
## 10 -0.06667 -0.003537     7.081 -0.1789 0.858028
```

```
# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.Adj.seastrend,wq.in=wq_B,wq.invar=wqvar,adj
=TRUE)
```



A.3 - Supplemental Trend Analysis at Upstream of Fort McMurray: Total Nitrogen

Last Updated: 2015-02-11

Censoring

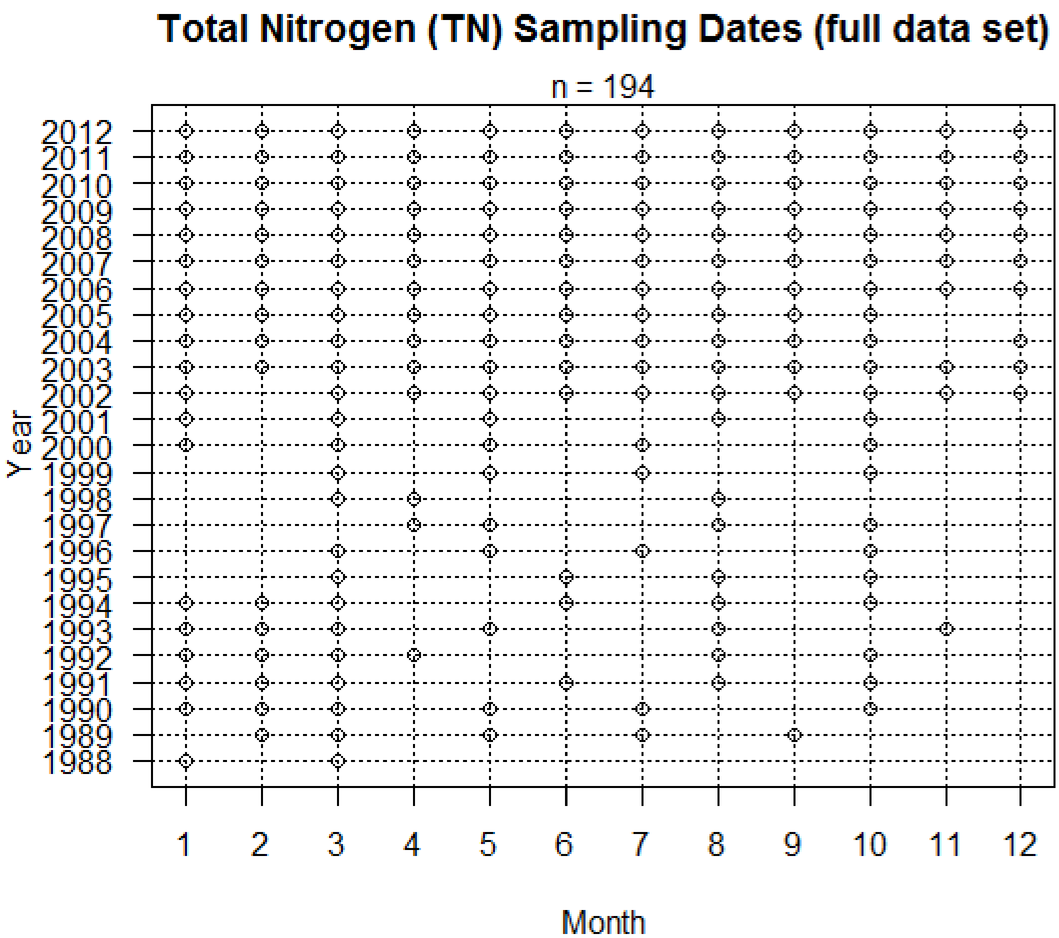
```
### Censoring

# Determine level of censoring and detection limits
with(wq, censummary(Value,ValueCen))
```

```
## all:
##       n   n.cen pct.cen     min     max
##  194.00    0.00    0.00    0.13    1.90
##
## limits:
##   limit n uncen pexceed
## 1     0 0   194       1
```

- There are no censored values.

Sampling frequency

```
### Investigate sampling frequency and create final data set for analysis (i.
e. subset the data to give equal sampling throughout time period)

# Dot plot of sampling dates for full data set
source("fun_dateplot.r")
dateplot(wq.in=wq,wq.invar=wqvar,type="full data set")
```



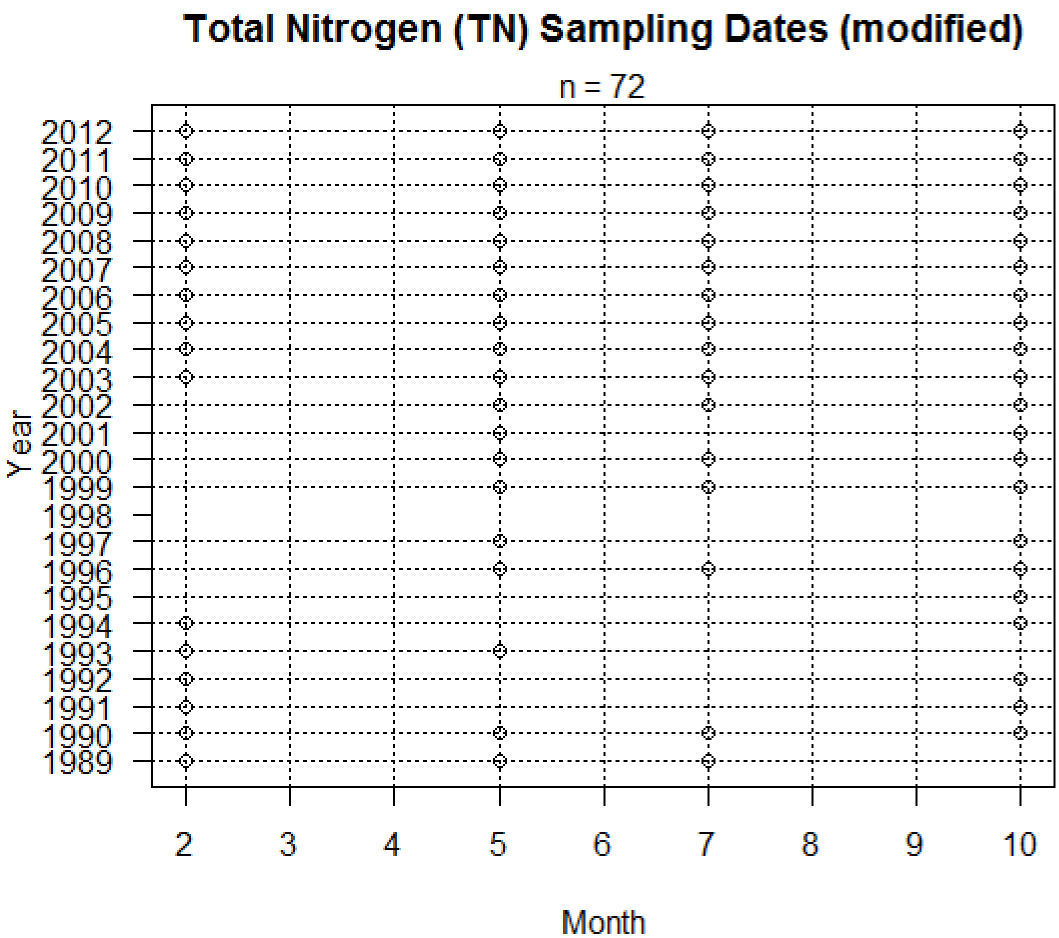

```
# Solid circles correspond to observations made at the Old Fort station and c
losed circles correspond to observations made at the Devil's Elbow station.

# Total number of observations
length(wq[,1])

## [1] 194

# Number of observations by year
table(wq$Year)

##
## 1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002
##    2    5    6    6    6    6    6    4    4    4    3    4    5    5   11
## 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##   12   11   10   12   12   12   12   12   12   12

# Number of observtions by month
table(wq$Month)
```

```
##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 19 16 24 14 19 14 16 19 12 21 10 10

# The data are monthly over the entire time period, so no need to subset the
data. Note however that there are some months with missing data over the peri
od of record, as well as several months with multiple samples.
```

- The period of record for total nitrogen is 1988-2012 (26 years).
- Total nitrogen was sampled ~ 6 times a year form 1988-2001, and then monthly.
- We will look at the trend over two time periods A) quarterly from 1989 -2012 (25 years) and B) monthly 2002-2012 (10 years)

Final data set for trend analysis

```
### Create final data set for trend analysis

# Total occurrences and occurrences by year in modified data set and verify t
hat they are as expected (A: 1989-2012)
length(wq_A[,1])

## [1] 72

table(wq_A$Year)

##
## 1989 1990 1991 1992 1993 1994 1995 1996 1997 1999 2000 2001 2002 2003 2004
##    3    4    2    2    2    2    1    3    2    3    3    2    3    4    4
## 2005 2006 2007 2008 2009 2010 2011 2012
##    4    4    4    4    4    4    4    4

table(wq_A$Month)

##
##  2  5  7 10
## 16 19 16 21

# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq_A,wq.invar=wqvar,type="modified")
```




```r
# Save data set for later reference
write.csv(wq_A,file=paste(wqvar,"upstream_data_used_A_",format(Sys.Date()),".
csv",sep=""),row.names=FALSE)


# Total occurrences and occurrences by year in modified data set and verify
that they are as expected (B: 2002-2012)
length(wq_B[,1])
```

```
## [1] 128
```

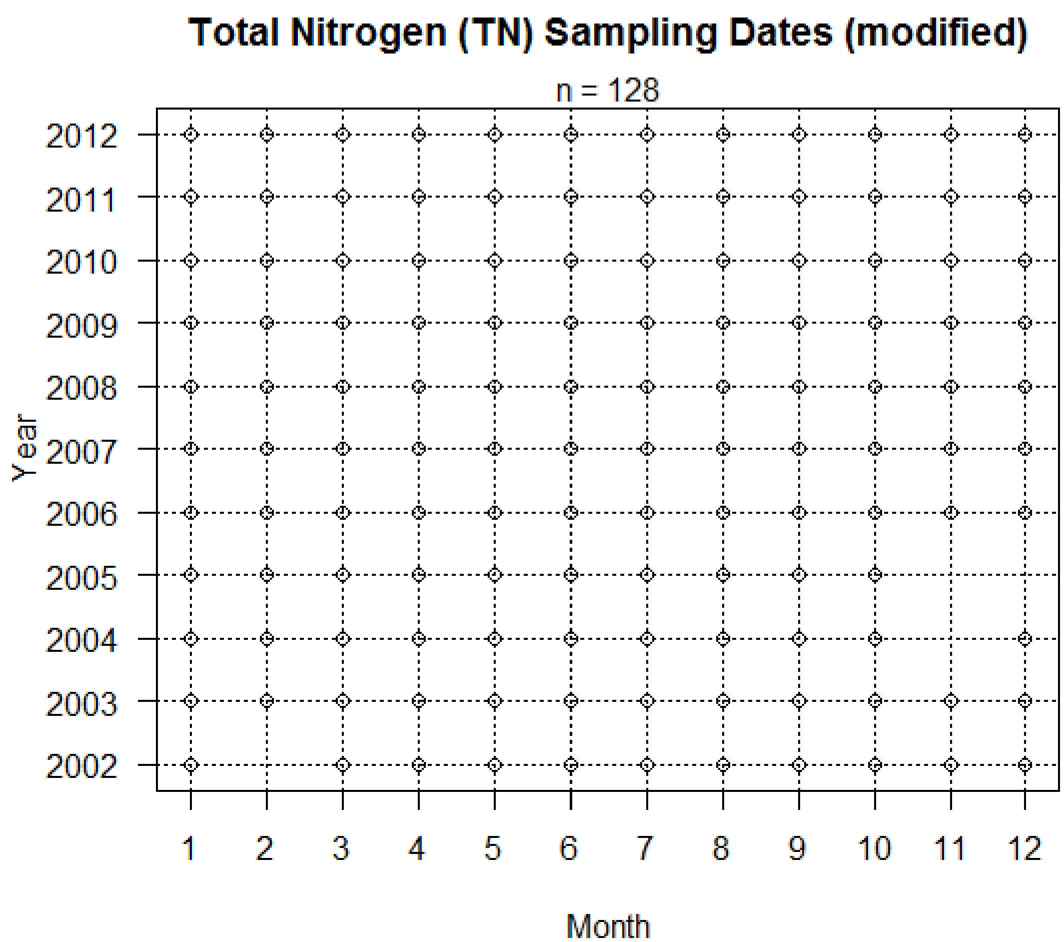
```r
table(wq_B$Year)
```

```
##
## 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##   11   12   11   10   12   12   12   12   12   12   12
```

```r
table(wq_B$Month)
```

```
##
##   1   2   3   4   5   6   7   8   9 10 11 12
## 11 10 11 11 11 11 11 11 11 11   9 10
```

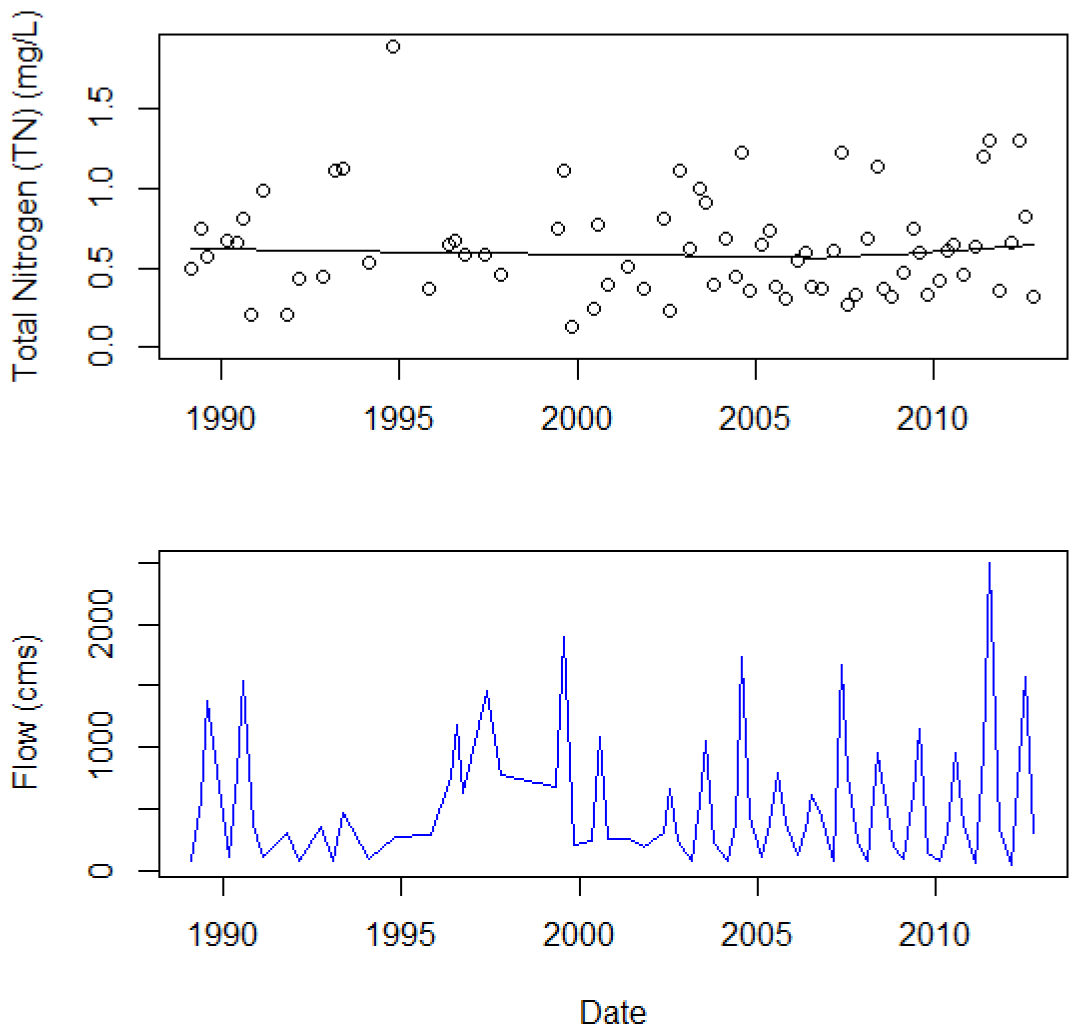
```
# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq_B,wq.invar=wqvar,type="modified")
```



Analysis of quarterly data from 1989-2012

Time series plot of data

```
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq_A,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The blue line represents flow
observations from the same dates as the water quality observations. The black
line is the lowess smooth to the concentration data.
```

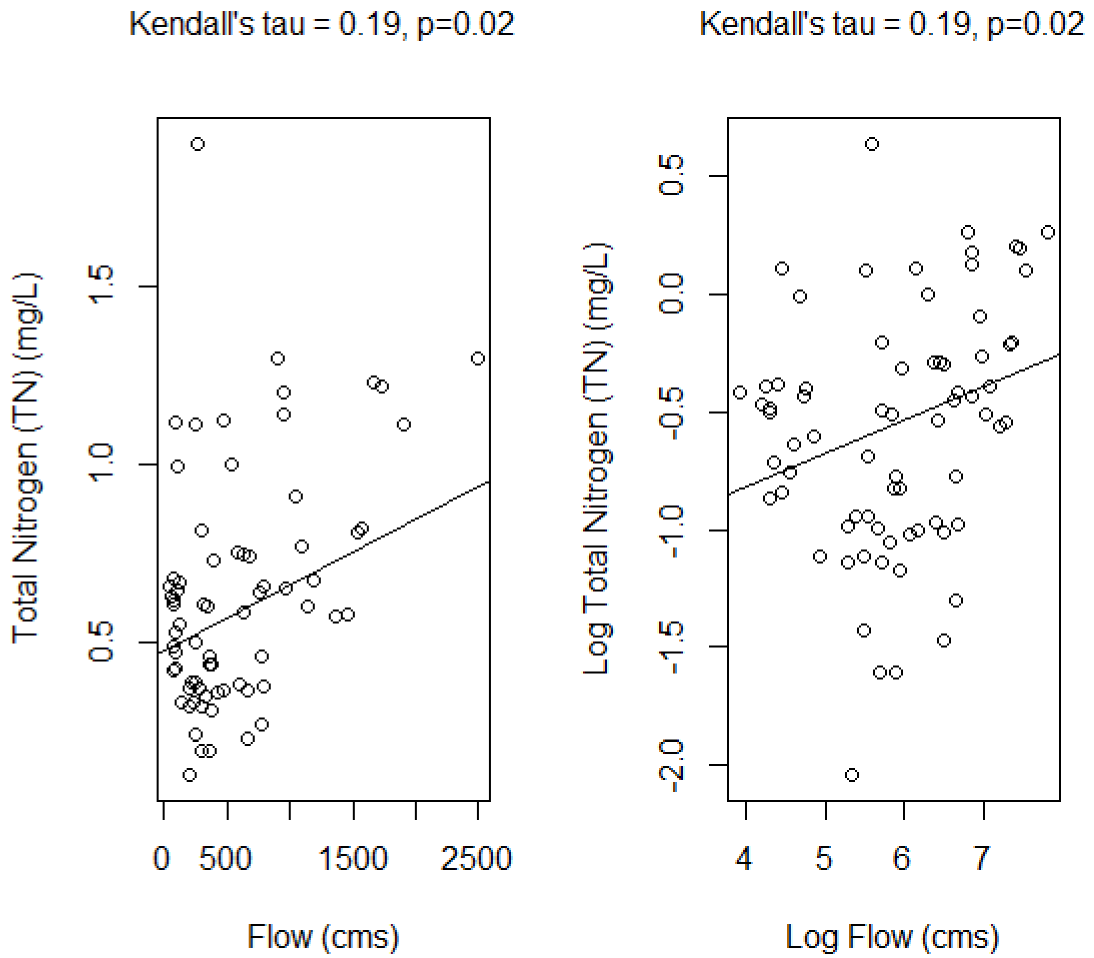
Summary statistics

```
### Calculate summary statistics
# Summary stats were calculated as usual since there was no censoring.

# n
with(wq_A,length(Value))

## [1] 72

# min
with(wq_A,min(Value,na.rm=TRUE))

## [1] 0.13
```

```r
# max
with(wq_A,max(Value, na.rm=TRUE))

## [1] 1.9

# median
with(wq_A,median(Value, na.rm=TRUE))

## [1] 0.6

# mean
with(wq_A,mean(Value, na.rm=TRUE))

## [1] 0.639

# standard deviation
with(wq_A,sd(Value, na.rm=TRUE))

## [1] 0.3311

#variance
with(wq_A,var(Value, na.rm=TRUE))

## [1] 0.1096
```

Relationship with flow – monotonic/linear model

```r
### Test for a relationship between concentration and flow
# Determine if there is a relationship (possibly linear) between flow and con
centration (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq_A,wq.invar=wqvar)
```

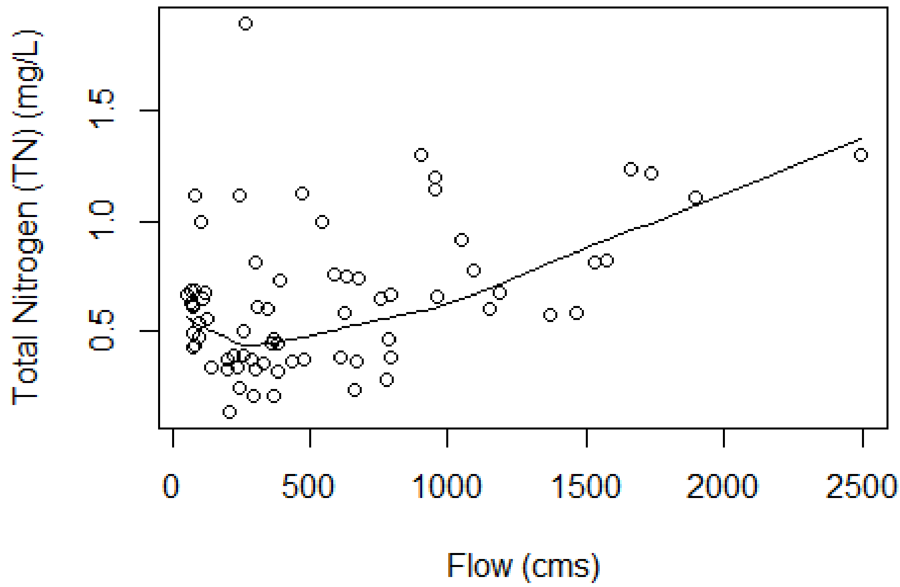



```
# All observations are uncensored observations. The solid line is the ATS slo
pe with Turnbull estimate and the dashed line is the regression line.
```

- The relationship between total nitrogen and flow is not fit very well by a linear model on either the original or log-log scale.

Relationship with flow - lowess smooth

```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq_A,wq.invar=wqvar)
```

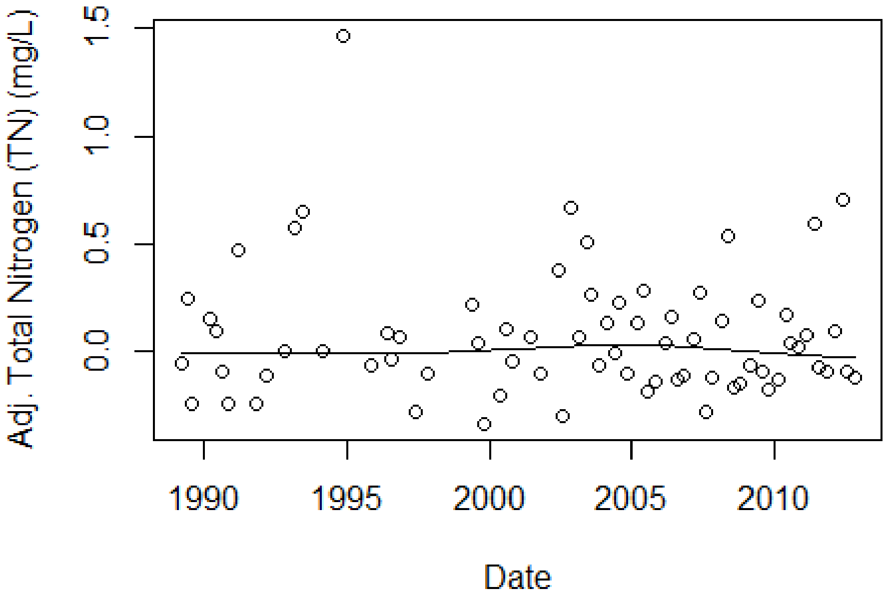



```
# Open circles are uncensored observations and solid circles are censored obs
ervations. The solid line is the lowess smooth.
```

- Based on the lowess smooth, there appears to be a nonlinear, non-monotonic relationship between total nitrogen and flow.
- Initially total nitrogen decreases with increasing flow up to about 500 cms, after which is increases with flow.

Time series plot of data after flow adjustment

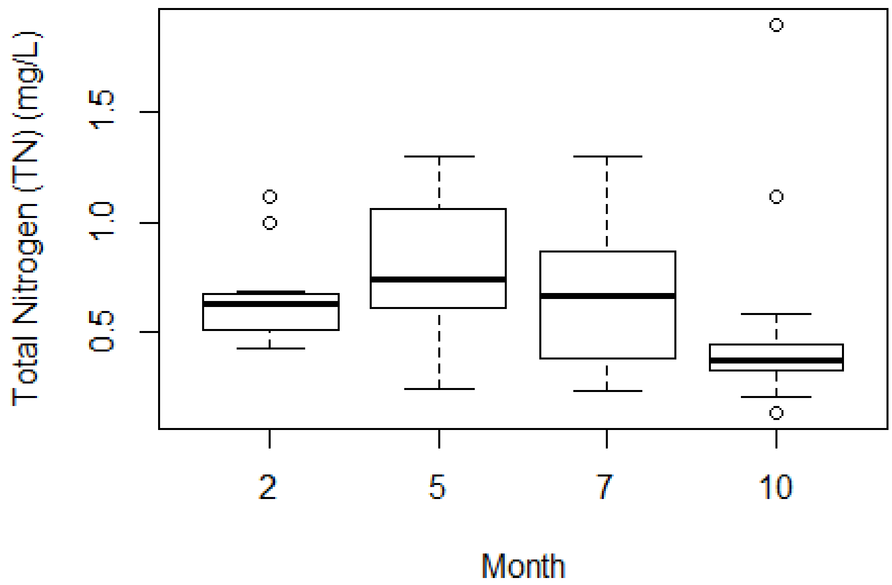
```
### Plot of flow-adjusted water quality data vs Date
source("func_timeseriesplot.r")
timeseriesplot_adj(wq.in=wq_A,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The black line is the lowess
smooth to the concentration data.
```

Seasonality in concentration

```
### Test for seasonality un-adjusted data

# Number of observations per season (month)
table(wq_A$Month)

##
##  2  5  7 10
## 16 19 16 21

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value~Month,data=wq_A,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],
")",sep=""))
```



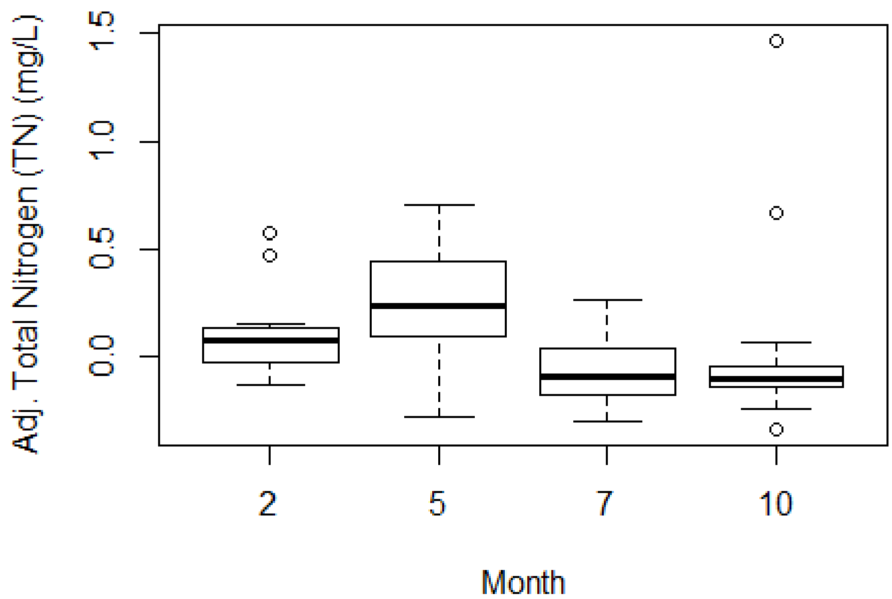

```
# Kruskal-wallis test
kruskal.test(Value ~ Month, data = wq_A)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                        Kruskal-Wallis rank sum test
##
## Data:                             Value by Month
##
## Test Statistic:                   Kruskal-Wallis chi-squared = 21.03
##
## Test Statistic Parameter:         df = 3
##
## P-value:                          0.0001038
```

- The boxplot shows evidence of seasonality and the Kruskal-Wallis test is hightly significant.

Seasonality in concentration after flow adjustment

```
### Test for seasonality flow-adjusted data

# Number of observations per season (month)
table(wq_A$Month)

##
##  2  5  7 10
## 16 19 16 21
```

```r
# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value.Adj~Month,data=wq_A,xlab="Month",ylab=paste("Adj. ",wqvar," (",
wq$Units[1],")",sep=""))
```




```r
# Kruskal-wallis test
kruskal.test(Value.Adj ~ Month, data = wq_A)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value.Adj by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 21.55
##
## Test Statistic Parameter:        df = 3
##
## P-value:                         8.092e-05
```

- After adjustment for flow, the boxplot still shows evidence of seasonality and the Kruskal-Wallis test is hightly significant.

Trend tests - Seasonal Mann-Kendall trend test on total nitrogen

```r
### Seasonal Kendall trend test (EnvStats) on un-adjusted concentration
Value.seastrend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,da
```

```
ta=wq_A,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 4 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.01373
##                                  slope     =  0.00050
##                                  intercept = -0.58784
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq_A
##
## Sample Sizes:                    2     = 16
##                                  5     = 19
##                                  7     = 16
##                                  10    = 21
##                                  Total = 72
##
## Test Statistics:                 Chi-Square (Het) = 3.22793
##                                  z (Trend)        = 0.09292
##
## Test Statistic Parameter:        df = 3
##
## P-values:                        Chi-Square (Het) = 0.3578
##                                  z (Trend)        = 0.9260
##
```

```
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.005577
##                                  UCL =  0.007679
```

- There is no evidence of heterogenous behaviour between seasons.
- There is no significant trend in TN

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.seastrend <- seastrends(Value.seastrend,alternative="two.sided")
Value.seastrend$seasonal.estimates

##          tau     slope intercept       z      p
## 2  -0.06667 -0.001652     3.936 -0.3152 0.7526
## 5   0.23977  0.018750   -36.814  1.3994 0.1617
## 7   0.05000  0.002881    -5.111  0.2251 0.8219
## 10 -0.15714 -0.003923     8.220 -0.9685 0.3328
```

Trend tests - Seasonal Mann-Kendall trend test on total nitrogen after flow adjustment

```
### seasonal Kendall trend test (EnvStats) on flow adjusted concentration
Value.Adj.seastrend <- kendallSeasonalTrendTest(Value.Adj~as.character(Month)
+Year,data=wq_A,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.Adj.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 4 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
```

```
## Estimated Parameter(s):          tau       = 0.0154321
##                                  slope     = 0.0006973
##                                  intercept = 1.3538315
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value.Adj
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq_A
##
## Sample Sizes:                    2     = 16
##                                  5     = 19
##                                  7     = 16
##                                  10    = 21
##                                  Total = 72
##
## Test Statistics:                 Chi-Square (Het) = 4.1571
##                                  z (Trend)        = 0.1485
##
## Test Statistic Parameter:        df = 3
##
## P-values:                        Chi-Square (Het) = 0.2450
##                                  z (Trend)        = 0.8819
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.004214
##                                  UCL =  0.007249
```

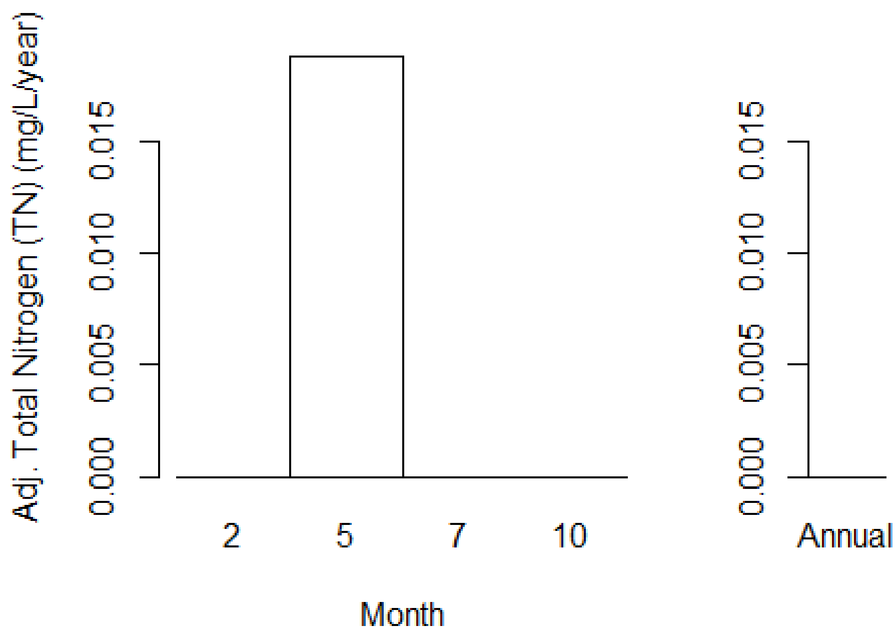
- There is no evidence of heterogenous behaviour between seasons.
- There is no significant trend in total nitrogen after flow adjustment.

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
```

```
Value.Adj.seastrend <- seastrends(Value.Adj.seastrend,alternative="two.sided"
)
Value.Adj.seastrend$seasonal.estimates
```

```
##          tau     slope intercept       z       p
## 2  -0.11667 -0.002719     5.528 -0.5853 0.55835
## 5   0.28655  0.018805   -37.429  1.6793 0.09309
## 7   0.03333  0.001363    -2.820  0.1351 0.89256
## 10 -0.14286 -0.003449     6.808 -0.8757 0.38119
```

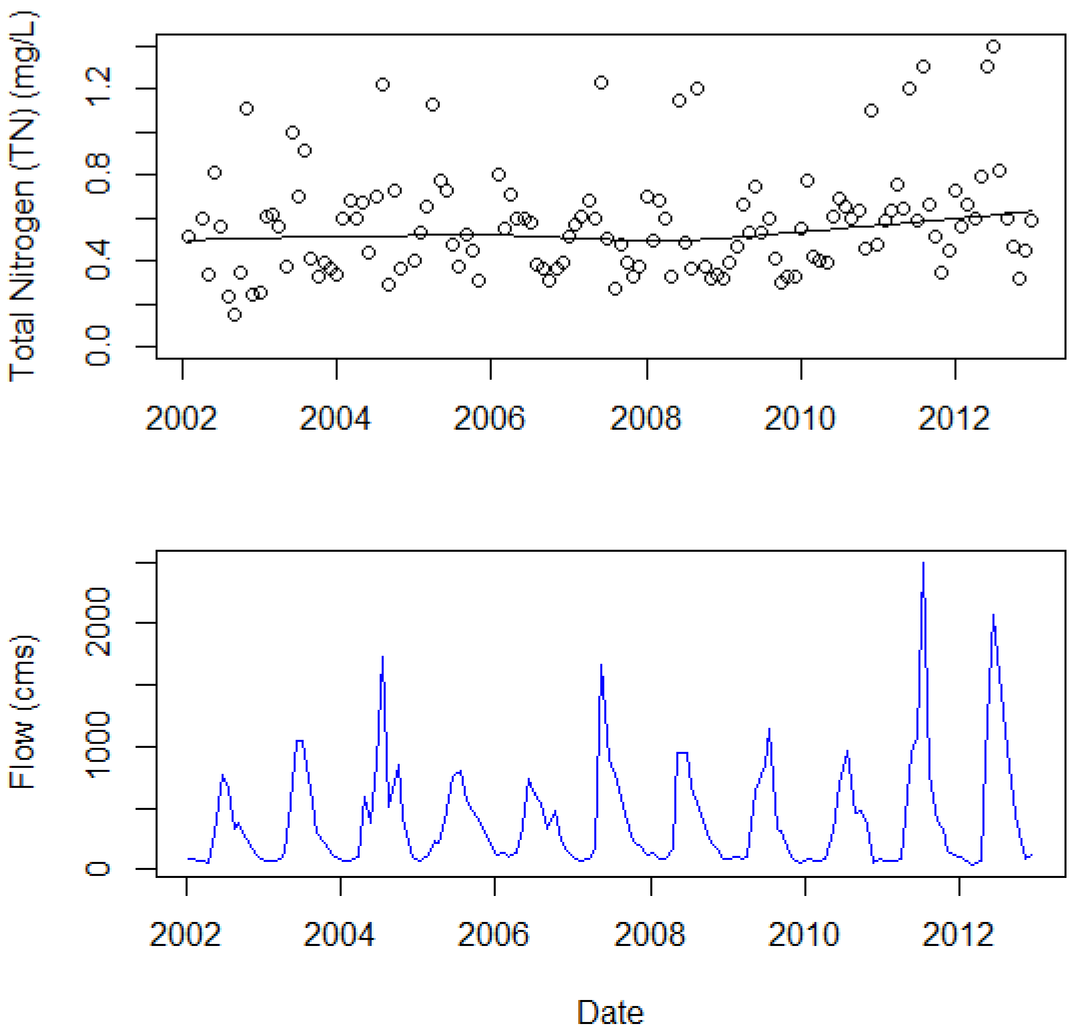
```
# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.Adj.seastrend,wq.in=wq_A,wq.invar=wqvar,adj
=TRUE)
```



Analysis of monthly data from 2002-2012

Time series plot of data

```
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq_B,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The blue line represents flow
observations from the same dates as the water quality observations. The black
line is the lowess smooth to the concentration data.
```

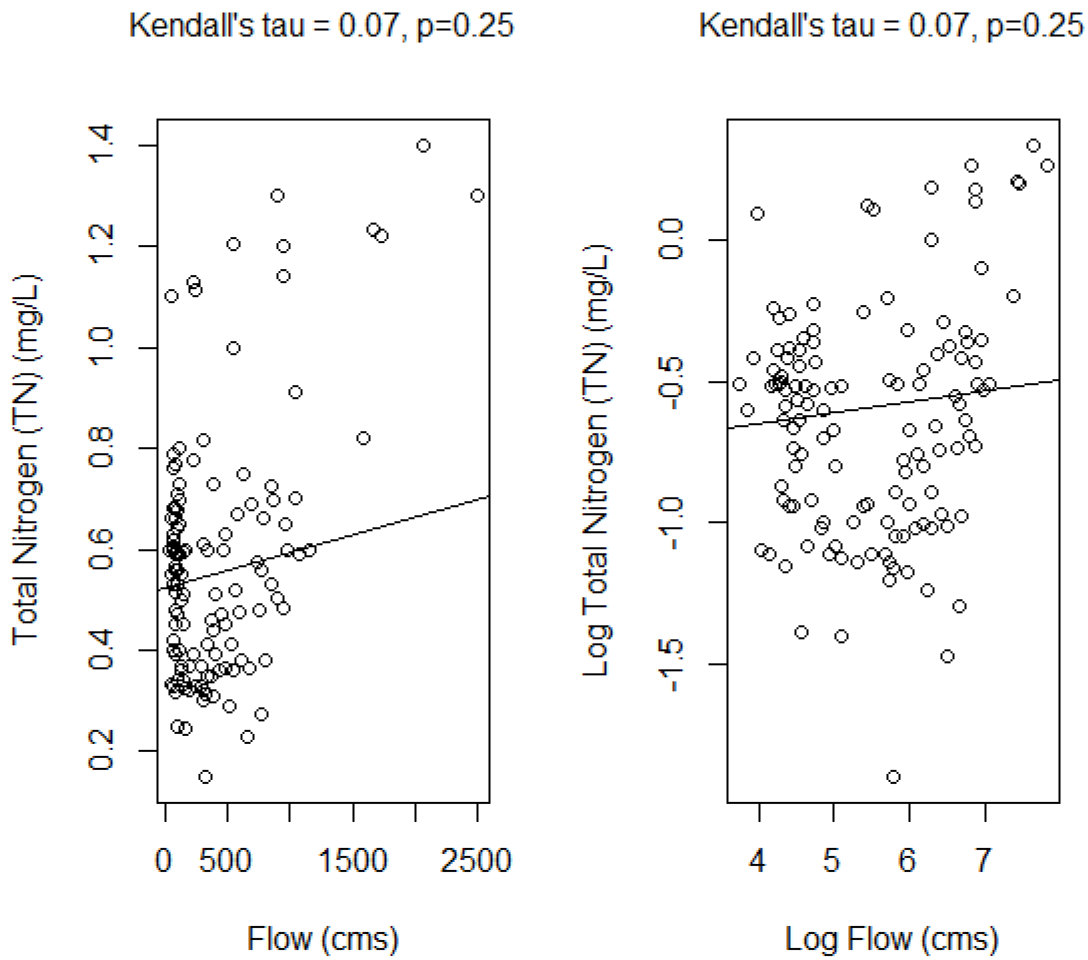
Summary statistics

```
### Calculate summary statistics
# Summary stats were calculated as usual since there was no censoring.

# n
with(wq_B,length(Value))

## [1] 128

# min
with(wq_B,min(Value,na.rm=TRUE))

## [1] 0.15
```

```
# max
with(wq_B,max(Value, na.rm=TRUE))

## [1] 1.4

# median
with(wq_B,median(Value, na.rm=TRUE))

## [1] 0.5535

# mean
with(wq_B,mean(Value, na.rm=TRUE))

## [1] 0.5774

# standard deviation
with(wq_B,sd(Value, na.rm=TRUE))

## [1] 0.2516

#variance
with(wq_B,var(Value, na.rm=TRUE))

## [1] 0.06329
```

Relationship with flow - linear model

```
### Test for a relationship between concentration and flow
# Determine if there is a relationship (possiblylinear) between flow and conc
entration (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq_B,wq.invar=wqvar)
```

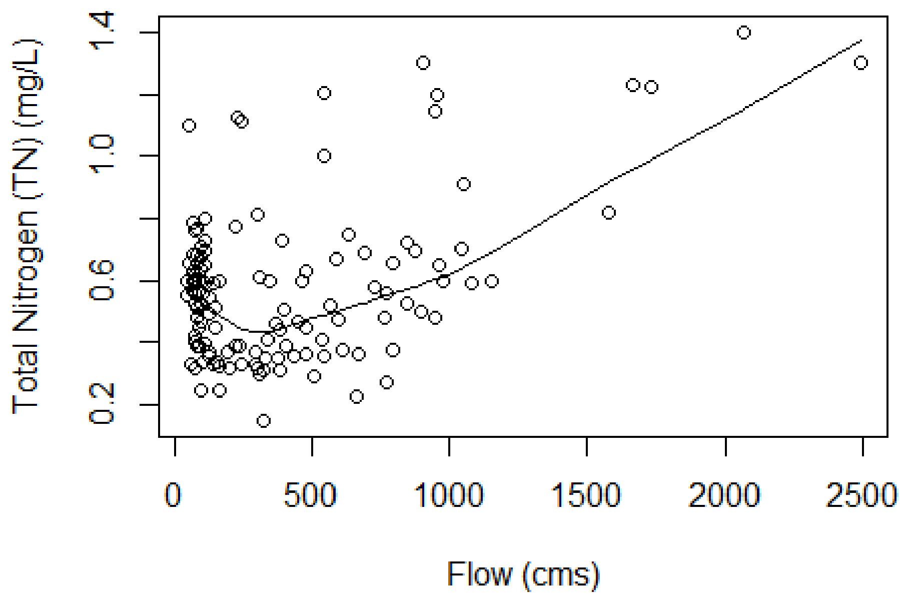



```
# All observations are uncensored observations. The solid line is the ATS slo
pe with Turnbull estimate and the dashed line is the regression line.
```

- The relationship between total nitrogen and flow is not fit very well by a linear model on either the original or log-log scale, and there is no significant monotonic relationship.

Relationship with flow - lowess smooth

```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq_B,wq.invar=wqvar)
```

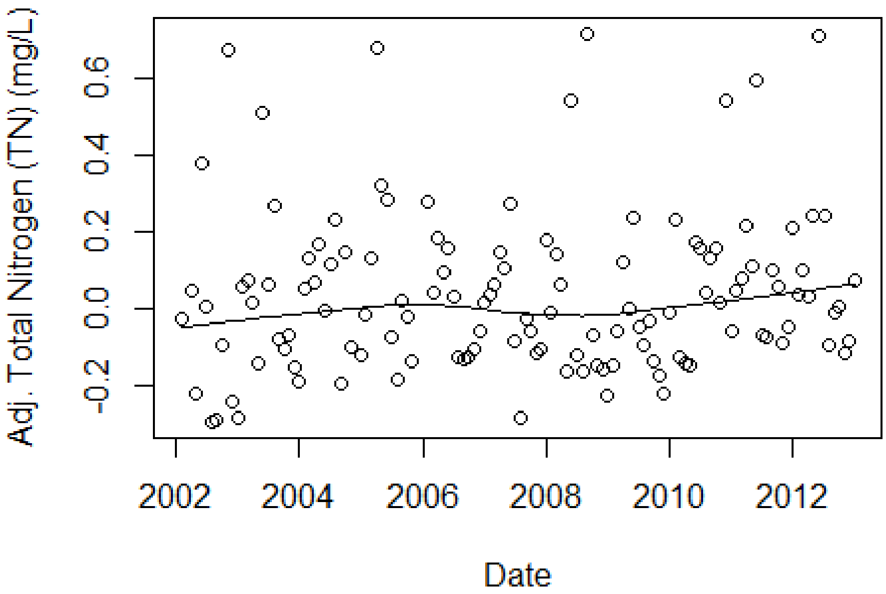



```
# Open circles are uncensored observations and solid circles are censored obs
ervations. The solid line is the lowess smooth.
```

- Based on the lowess smooth, there appears to be a nonlinear, non-monotonic relationship between total nitrogen and flow.
- Initially total nitrogen decreases with increasing flow up to about 500 cms, after which is increases with flow.

Time series plot of data after flow adjustment

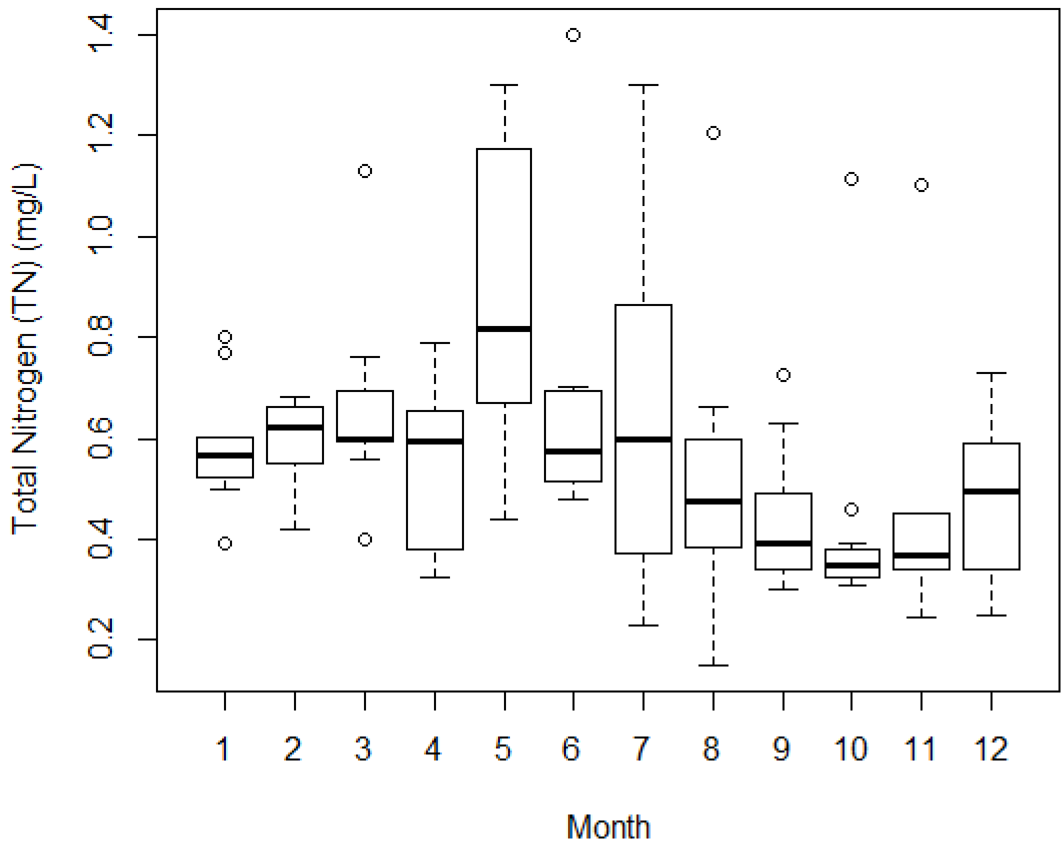
```
### Plot of flow-adjusted water quality data vs Date
source("func_timeseriesplot.r")
timeseriesplot_adj(wq.in=wq_B,wq.invar=wqvar)
```




```
# All observations are uncensored observations. The black line is the lowess
smooth to the concentration data.
```

Seasonality in concentration

```
### Test for seasonality un-adjusted data

# Number of observations per season (month)
table(wq_B$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 11 10 11 11 11 11 11 11 11 11  9 10

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value~Month,data=wq_B,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],
")",sep=""))
```

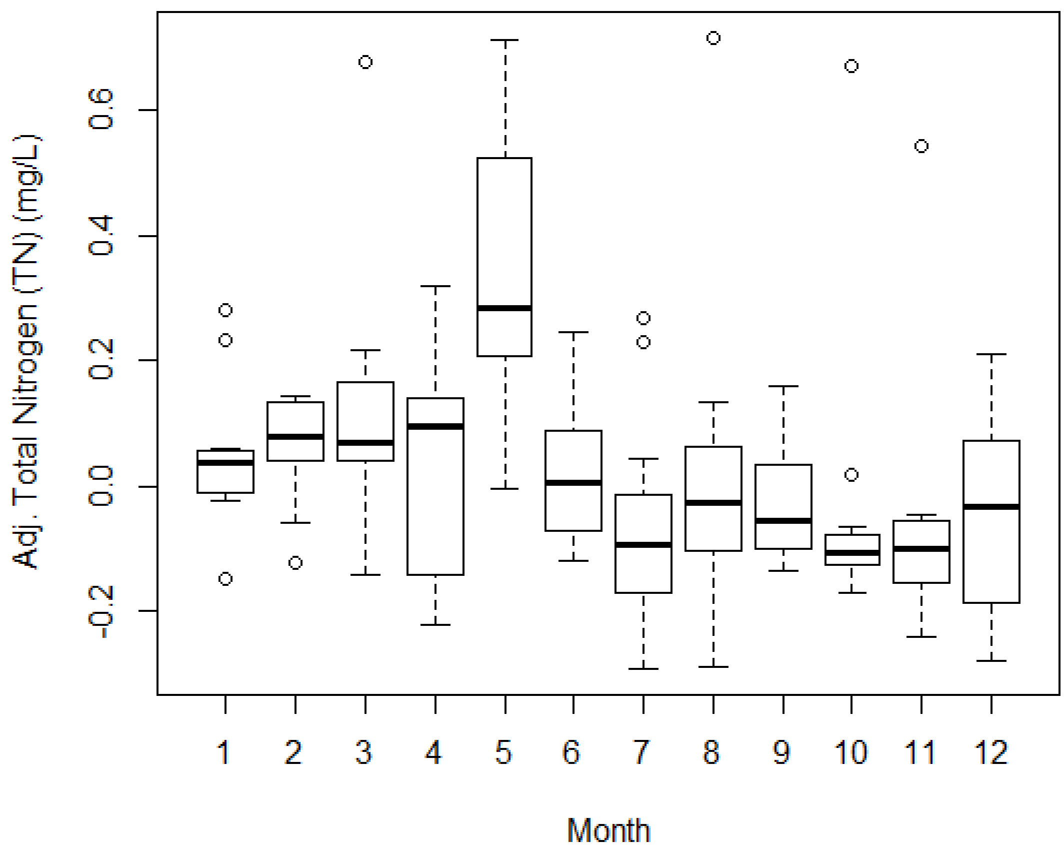



```r
# Kruskal-wallis test
kruskal.test(Value ~ Month, data = wq_B)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 39.98
##
## Test Statistic Parameter:        df = 11
##
## P-value:                         3.608e-05
```

- The boxplot shows evidence of seasonality, and the Kruskal-Wallis test is hightly significant.

Seasonality in concentration after flow adjustment

```
### Test for seasonality flow-adjusted data

# Number of observations per season (month)
table(wq_B$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
## 11 10 11 11 11 11 11 11 11 11  9 10

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value.Adj~Month,data=wq_B,xlab="Month",ylab=paste("Adj. ",wqvar," (",
wq$Units[1],")",sep=""))
```




```
# Kruskal-wallis test
kruskal.test(Value.Adj ~ Month, data = wq_B)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
```

```
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value.Adj by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 37.76
##
## Test Statistic Parameter:        df = 11
##
## P-value:                         8.598e-05
```

- After adjustment for flow, the boxplot still shows evidence of a similar seasonal patter, and the Kruskal-Wallis test is hightly significant.

Trend tests - Seasonal Mann-Kendall trend test on total nitrogen

```
### Seasonal Kendall trend test (EnvStats) on un-adjusted concentration
Value.seastrend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,da
ta=wq_B,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =   0.17652
##                                  slope     =   0.01017
##                                  intercept = -21.98189
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value
##                                  season = as.character(Month)
```

```
##                                  year    = Year
##
## Data Source:                     wq_B
##
## Sample Sizes:                    1      =  11
##                                  3      =  11
##                                  4      =  11
##                                  5      =  11
##                                  6      =  11
##                                  7      =  11
##                                  8      =  11
##                                  9      =  11
##                                  10     =  11
##                                  11     =   9
##                                  12     =  10
##                                  2      =  10
##                                  Total = 128
##
## Test Statistics:                 Chi-Square (Het) = 13.928
##                                  z (Trend)        =  2.484
##
## Test Statistic Parameter:        df = 11
##
## P-values:                        Chi-Square (Het) = 0.23701
##                                  z (Trend)        = 0.01299
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = 0.00188
##                                  UCL = 0.01866
```

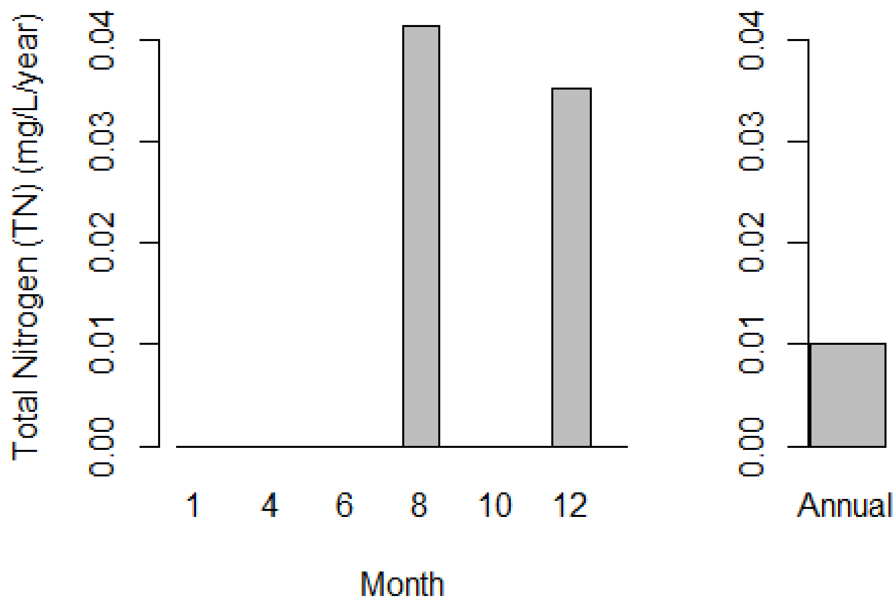
- There is no evidence of heterogenous behaviour between seasons.
- There is a significant increasing trend in TN.

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.seastrend <- seastrends(Value.seastrend,alternative="two.sided")
Value.seastrend$seasonal.estimates
```

```
##           tau     slope intercept        z       p
## 1  -0.09091 -0.001625    3.8294 -0.31140 0.75550
## 3   0.03636  0.000300   -0.0021  0.07809 0.93776
```

```
## 4   0.23636  0.015125  -29.7619  0.93420 0.35020
## 5   0.30909  0.039250  -77.9598  1.24560 0.21291
## 6   0.12727  0.004000   -7.4520  0.46710 0.64043
## 7   0.30909  0.052500 -104.7675  1.24560 0.21291
## 8   0.56364  0.041333  -82.4800  2.34978 0.01878
## 9   0.12727  0.008600  -16.8672  0.46710 0.64043
## 10 -0.30909 -0.007667   15.7370 -1.25322 0.21013
## 11  0.41667  0.013679  -27.0966  1.46760 0.14221
## 12  0.55556  0.035167  -70.1016  2.14663 0.03182
## 2  -0.11111 -0.003167    6.9806 -0.35777 0.72051
```

```
# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.seastrend,wq.in=wq_B,wq.invar=wqvar,adj=FAL
SE)
```



Trend tests - Seasonal Mann-Kendall trend test on total nitrogen after flow adjustment

```
### seasonal Kendall trend test (EnvStats) on flow adjusted concentration
Value.Adj.seastrend <- kendallSeasonalTrendTest(Value.Adj~as.character(Month)
+Year,data=wq_B,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.Adj.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
```

```
##                                   (Chi-Square Heterogeneity Test)
##                                   At least one seasonal tau != 0
##                                   and all non-zero tau's have the
##                                   same sign (z Trend Test)
##
## Test Name:                        Seasonal Kendall Test for Trend
##                                   (with continuity correction)
##
## Estimated Parameter(s):           tau       =   0.127778
##                                   slope     =   0.007289
##                                   intercept = -17.840918
##
## Estimation Method:                tau:        Weighted Average of
##                                               Seasonal Estimates
##                                   slope:      Hirsch et al.'s
##                                               Modification of
##                                               Thiel/Sen Estimator
##                                   intercept:  Median of
##                                               Seasonal Estimates
##
## Data:                             y      = Value.Adj
##                                   season = as.character(Month)
##                                   year   = Year
##
## Data Source:                      wq_B
##
## Sample Sizes:                     1     =  11
##                                   3     =  11
##                                   4     =  11
##                                   5     =  11
##                                   6     =  11
##                                   7     =  11
##                                   8     =  11
##                                   9     =  11
##                                   10    =  11
##                                   11    =   9
##                                   12    =  10
##                                   2     =  10
##                                   Total = 128
##
## Test Statistics:                  Chi-Square (Het) = 11.890
##                                   z (Trend)        =  1.778
##
## Test Statistic Parameter:         df = 11
##
## P-values:                         Chi-Square (Het) = 0.3720
##                                   z (Trend)        = 0.0754
##
## Confidence Interval for:          slope
##
```

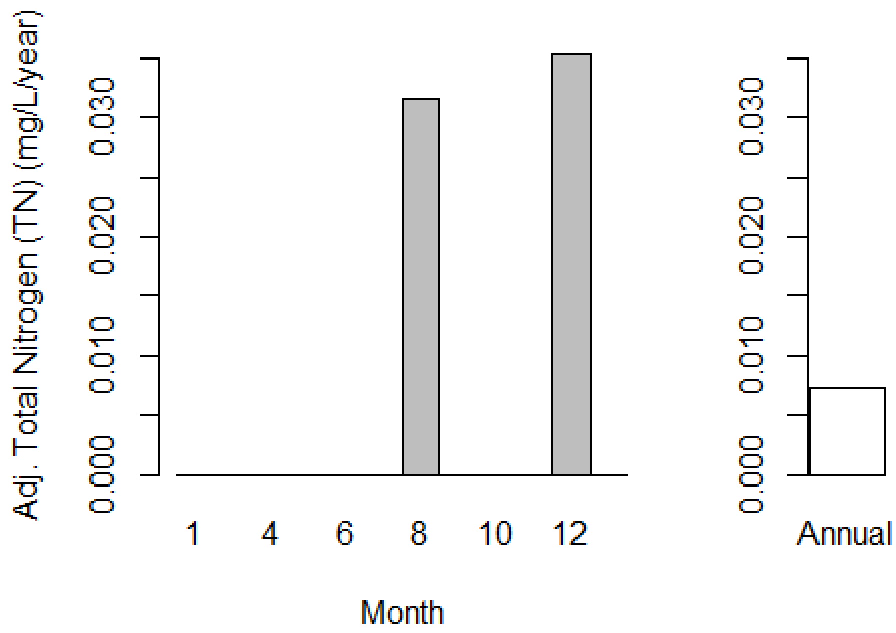
```
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.0006404
##                                  UCL =  0.0140322
```

- There is no evidence of heterogenous behaviour between seasons.
- There is no significant trend in total nitrogen after flow adjustment.

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.Adj.seastrend <- seastrends(Value.Adj.seastrend,alternative="two.sided"
)
Value.Adj.seastrend$seasonal.estimates
```

```
##          tau      slope intercept       z       p
## 1  -0.01818 -0.0001518    0.3412  0.0000 1.00000
## 3  -0.01818 -0.0012366    2.5521  0.0000 1.00000
## 4   0.20000  0.0097766  -19.5280  0.7785 0.43627
## 5   0.23636  0.0249978  -49.8881  0.9342 0.35020
## 6   0.05455  0.0039981   -8.0186  0.1557 0.87627
## 7   0.12727  0.0110293  -22.2301  0.4671 0.64043
## 8   0.49091  0.0315921  -63.4324  2.0241 0.04296
## 9   0.16364  0.0080203  -16.1538  0.6228 0.53342
## 10 -0.34545 -0.0090688   18.0954 -1.4013 0.16112
## 11  0.33333  0.0135658  -27.3418  1.1468 0.25145
## 12  0.51111  0.0353090  -70.9165  1.9677 0.04910
## 2  -0.15556 -0.0044728    9.0569 -0.5367 0.59151
```

```
# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas(test.trend=Value.Adj.seastrend,wq.in=wq_B,wq.invar=wqvar,adj
=TRUE)
```


Adj. Total Nitrogen (TN) (mg/L/year)
0.000
0.010
0.020
0.030
1
4
6
8
10
12
Month
0.000
0.010
0.020
0.030
Annual

A.4 - Uranium D at Old Fort Station

Censoring

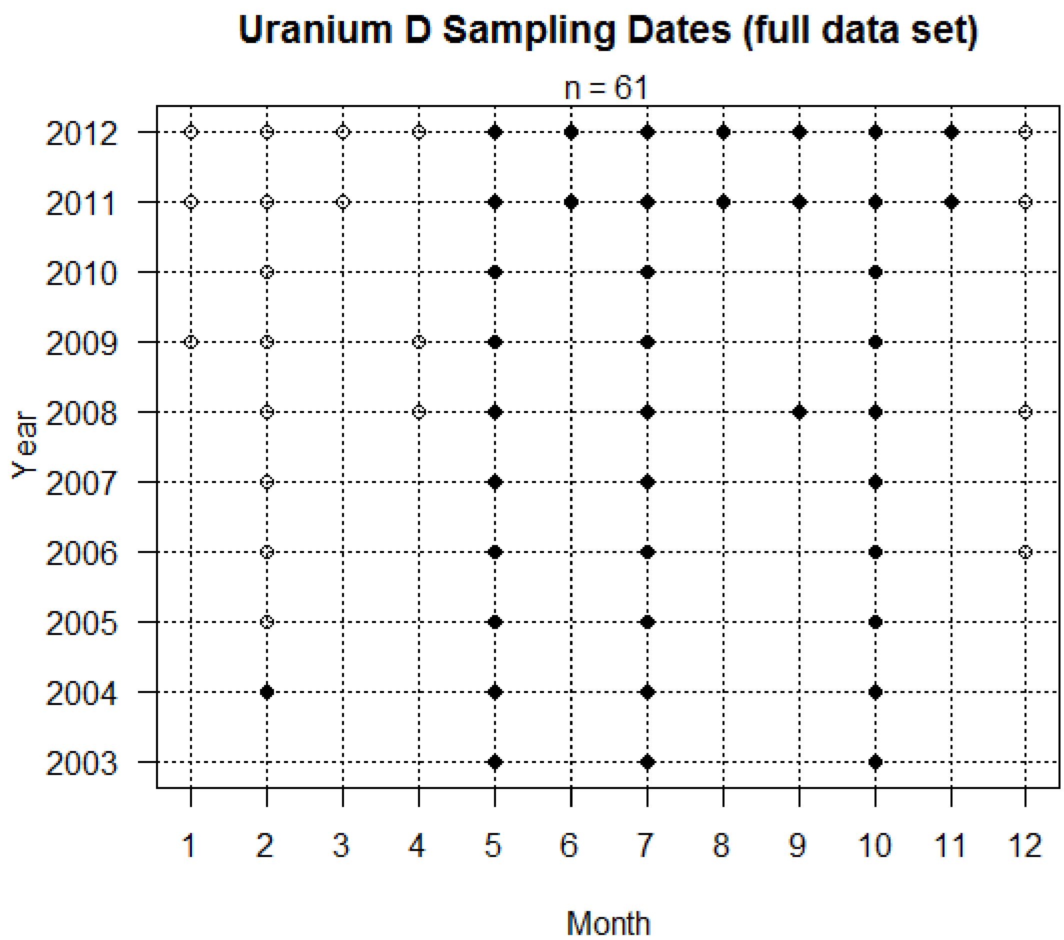
```
### Censoring

# Determine level of censoring and detection limits
with(wq, censummary(Value,ValueCen))
```

```
## all:
##        n   n.cen pct.cen     min     max
##  61.000   0.000   0.000   0.217   0.473
##
## limits:
##   limit n uncen pexceed
## 1     0 0    61       1
```

- There are no censored values.

Sampling frequency

```
### Investigate sampling frequency and create final data set for analysis (i.
e. subset the data to give equal sampling throughout time period)

# Dot plot of sampling dates for full data set
source("fun_dateplot.r")
dateplot(wq.in=wq,wq.invar=wqvar,type="full data set")
```




```
# Solid circles correspond to observations made at the Old Fort station and o
pen circles correspond to observations made at the Devil's Elbow station.

# Total number of observations
length(wq[,1])

## [1] 61

# Number of observations by year
table(wq$Year)

##
## 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##    3    4    4    5    4    8    6    4   11   12
```

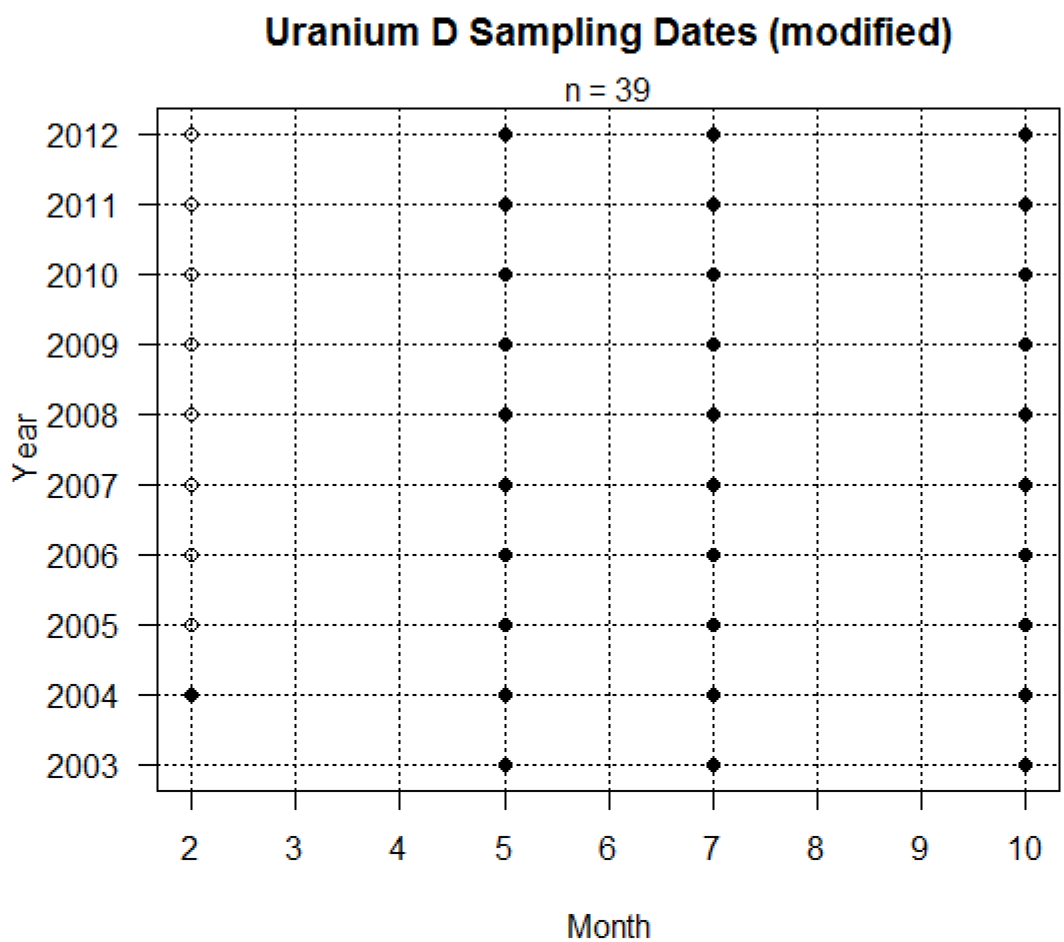
- The period of record for dissolved uranium is 2003-2012 (10 years).
- Dissolved uranium was sampled quarterly (in Feb, May, July, and Oct) from 2003 until 2010, after which it was sampled monthly.
- As there is variation in sampling frequency over the period of record, we modified the data set (Helsel, 2002). Due to the systematic trend in sampling frequency (quarterly for 8 years followed by monthly for two years), we defined the seasons based on quarterly sampling. For the years 2011 and 2012, we used only the observations from

Feb, May, July, and Oct. There were two samples taken in July 2008. We used the later sample (23 Jul), as the timing was more consistent with other July samples.

- All samples in the modified data set used for trend analysis were taken at the Old Fort - Right Bank station, with the exception of the Feb samples from 2005 onwards.

Final data set for trend analysis

```
### Create final data set for trend analysis

# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq,wq.invar=wqvar,type="modified")
```

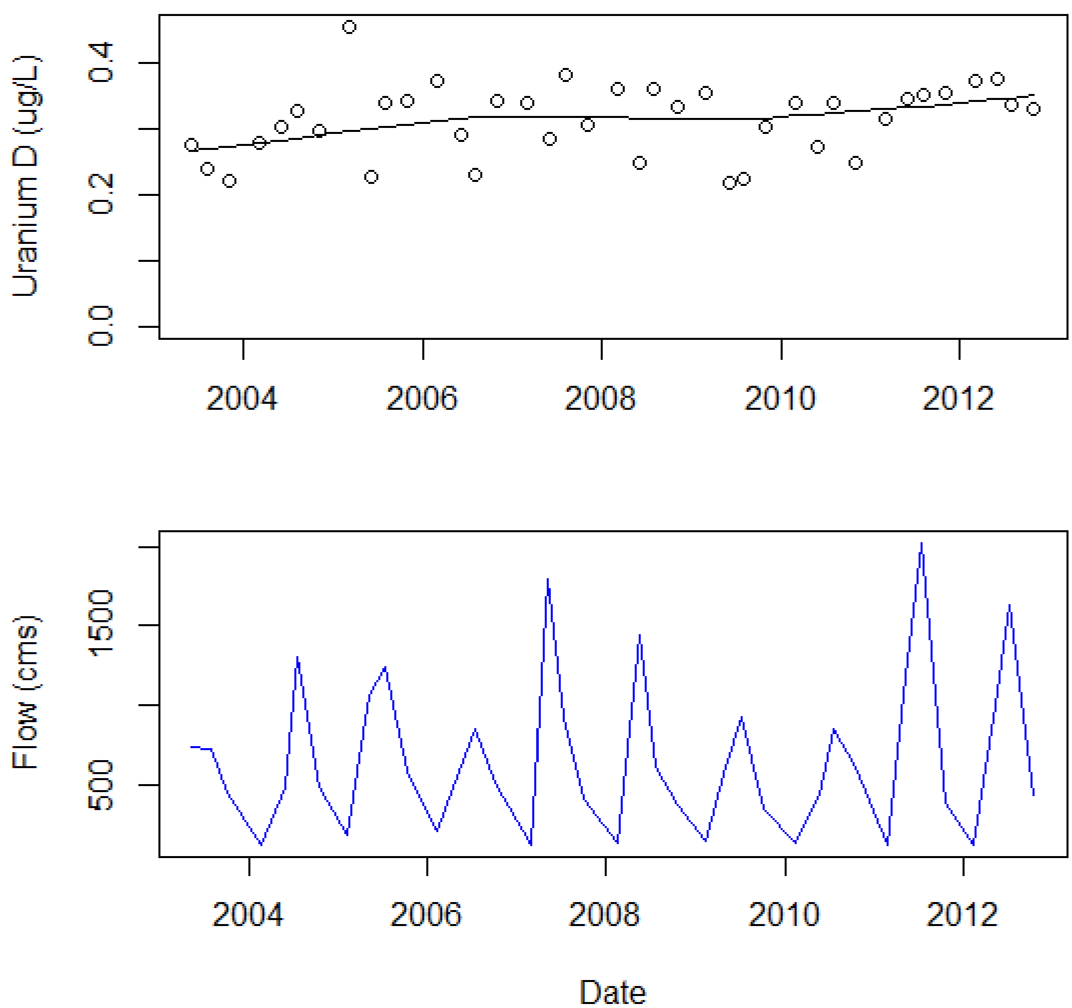



```
# Total occurrences and occurrences by year in modified data set and verify t
hat they are as expected
length(wq[,1])

## [1] 39

table(wq$Year)
```

```
##
## 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##    3    4    4    4    4    4    4    4    4    4
```

Time series plot of data

```
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq,wq.invar=wqvar)
```




```
# The black line is the lowess smooth to the concentration data (open circles
). The blue line is the flow based on observations from the same date as the
water quality observations.
```

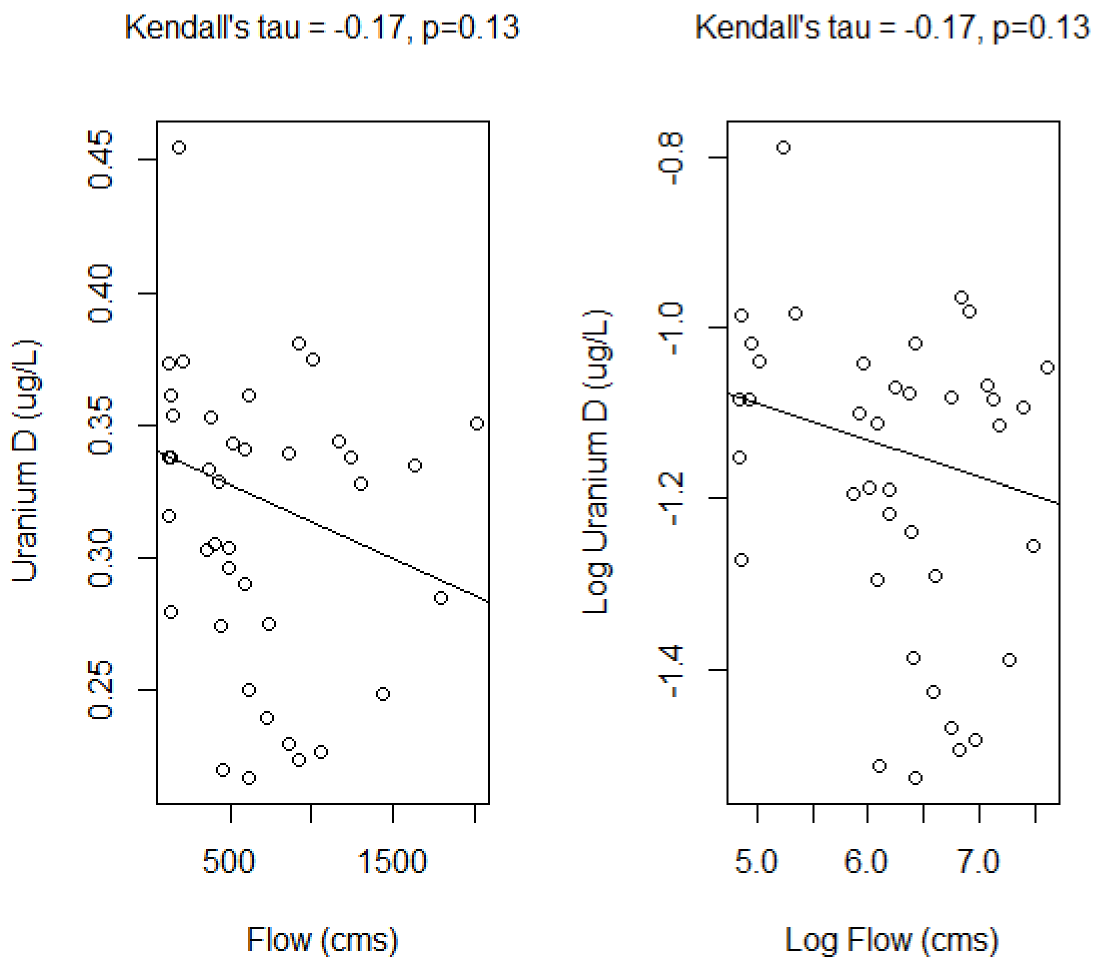
Summary statistics

```
### Calculate summary statistics
# Summary stats were calculated as usual since there was no censoring.
```

```r
# n
with(wq,length(Value))

## [1] 39

# min
with(wq,min(Value,na.rm=TRUE))

## [1] 0.217

# max
with(wq,max(Value, na.rm=TRUE))

## [1] 0.455

# median
with(wq,median(Value, na.rm=TRUE))

## [1] 0.329

# mean
with(wq,mean(Value, na.rm=TRUE))

## [1] 0.3136

# standard deviation
with(wq,sd(Value, na.rm=TRUE))

## [1] 0.0541

#variance
with(wq,var(Value, na.rm=TRUE))

## [1] 0.002927
```

Relationship with flow

```r
### Test for a relationship between dissolved uranium and flow
# Determine if there is a relationship (possibly linear) between flow and con
centration (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq,wq.invar=wqvar)
```

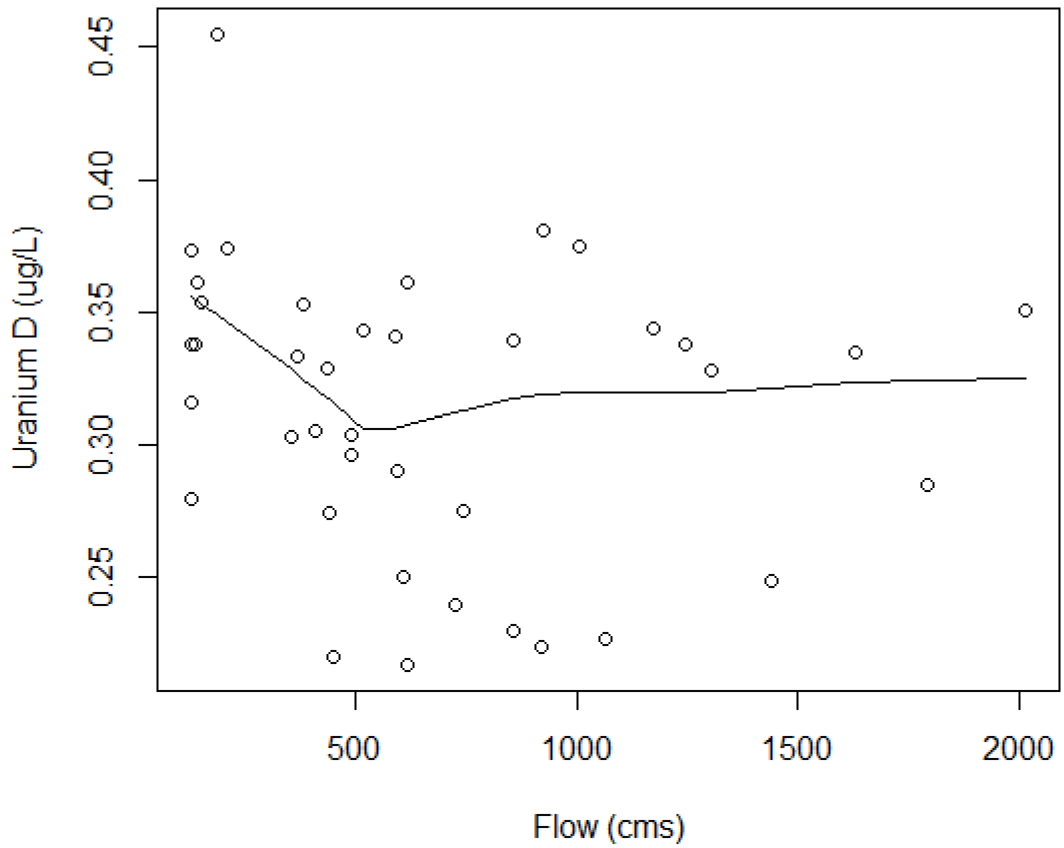



```
# All observations are uncensored observations. The solid line is the ATS slo
pe with Turnbull estimate and the dashed line is the regression line.
```

- The relationship between dissolved uranium and flow is not fit very well by the ATS line on either the original or log-log scale.
- In addition, Kendall's tau is not significantly different from zero (alpha=0.05), suggesting that there is not a strong monotonic relationship (linear or otherwise) between dissolved uranium and flow.

Relationship with flow - lowess smooth

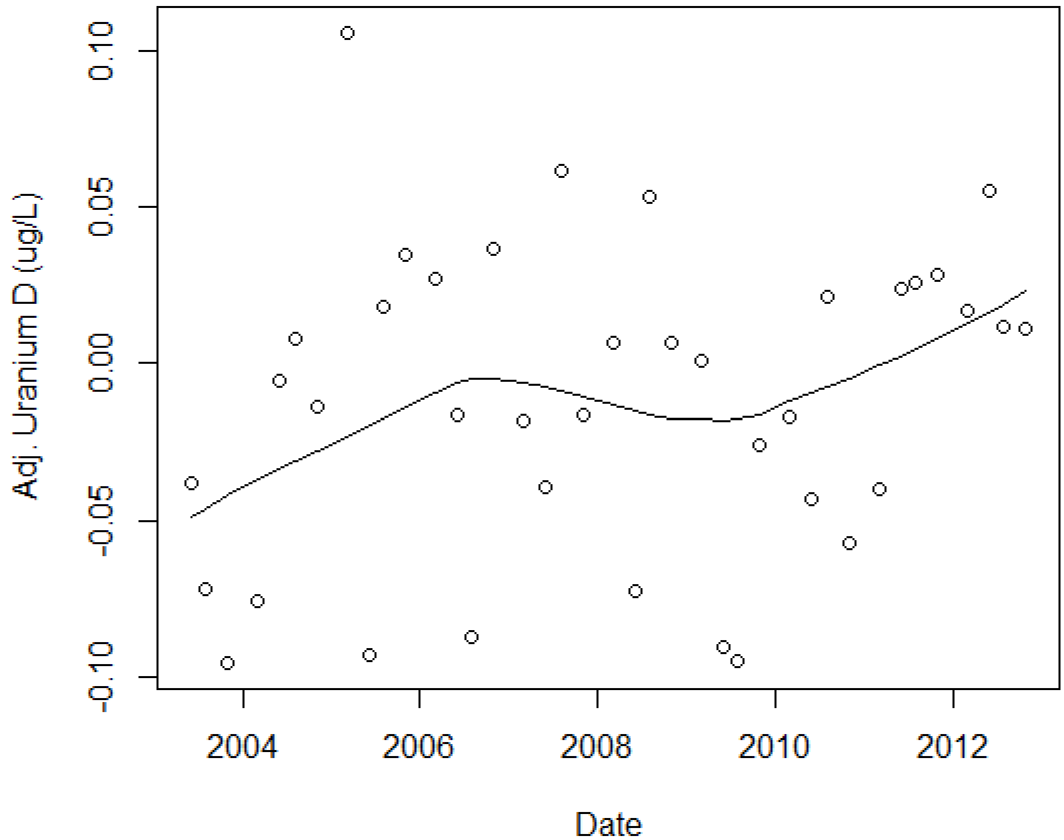
```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq,wq.invar=wqvar)
```




```
# Open circles are uncensored observations. The solid line is the lowess smoo
th.
```

Time series plot of data after flow adjustment

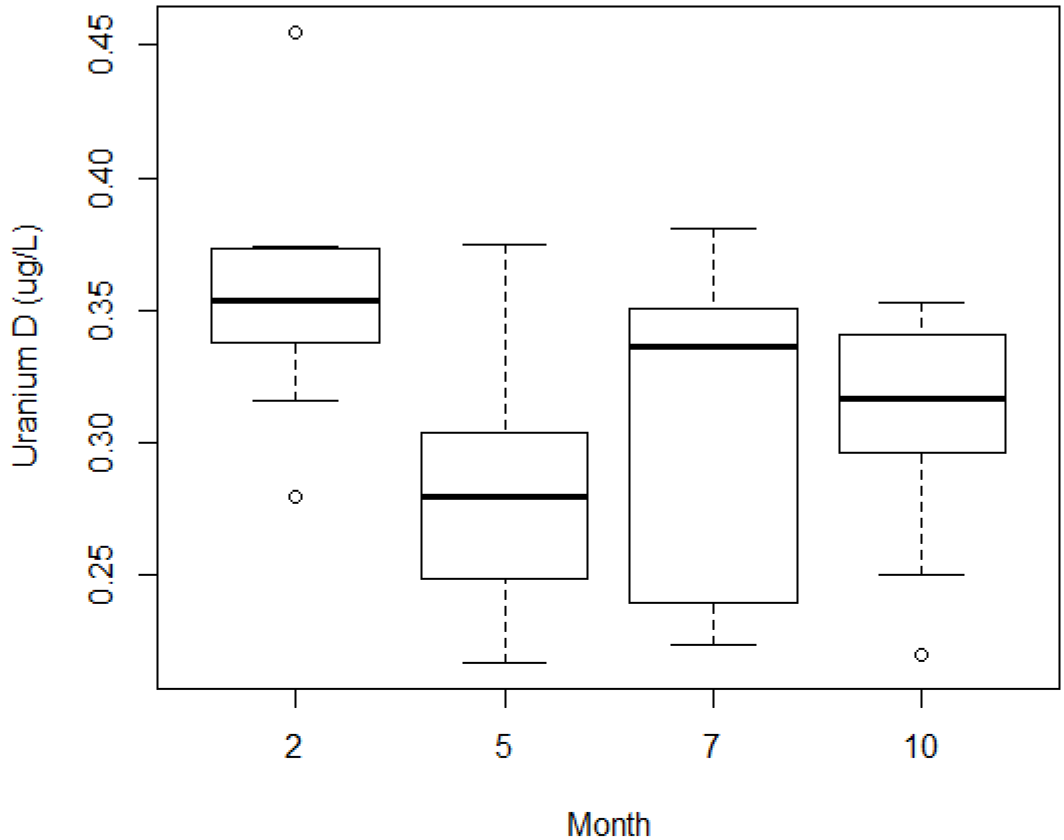
```
### Plot of flow-adjusted water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot_adj(wq.in=wq,wq.invar=wqvar)
```



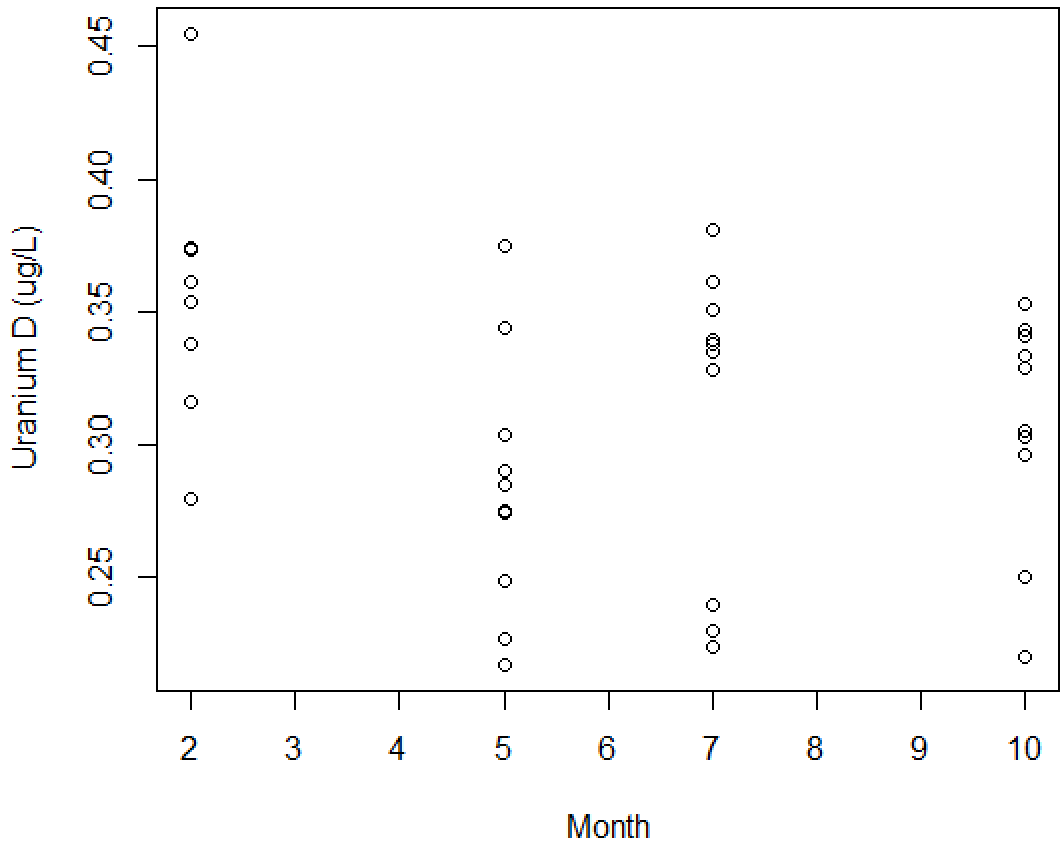

```
# The black line is the lowess smooth to the concentration data (open circles
).
```

Seasonality in concentration

```
### Test for seasonality - concentration

# Number of observations per season (month)
table(wq$Month)

##
##  2  5  7 10
##  9 10 10 10

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value~Month,data=wq,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],")
",sep=""))
```




```
# Points
with(wq,plot(Value~Month,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],")",s
ep=""),xaxp=c(1,12,11)))
```



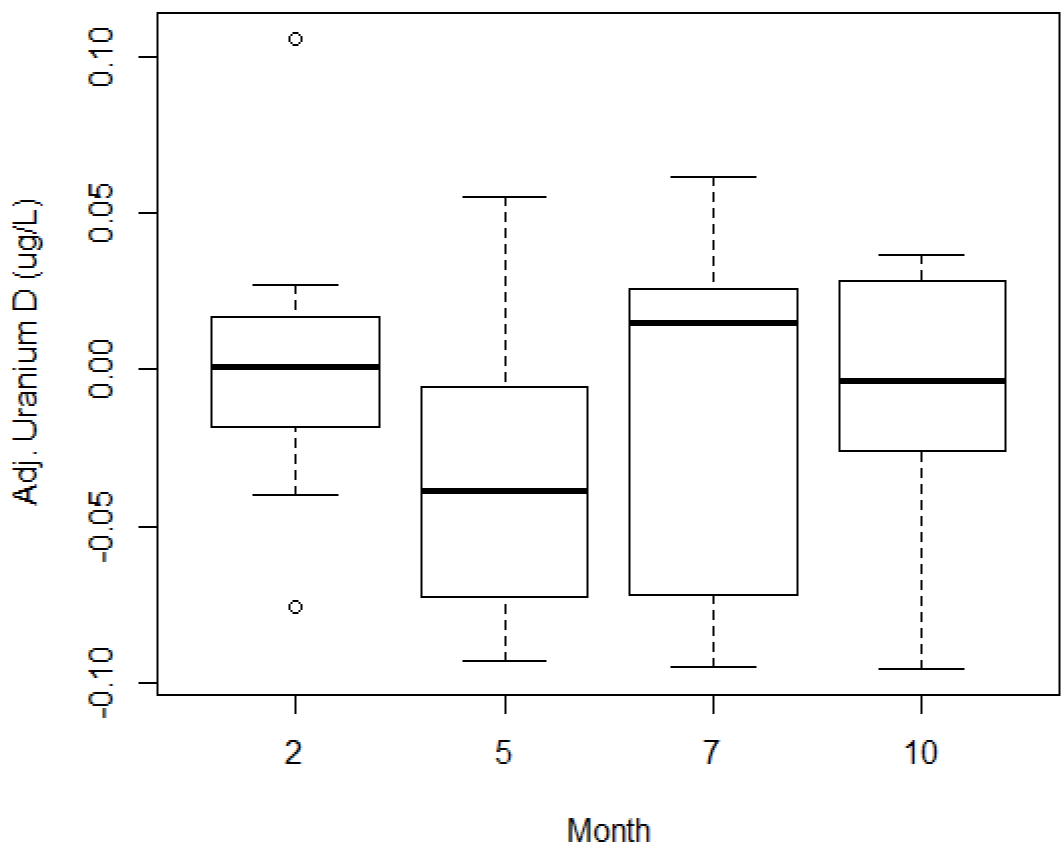

```
# Plot of concentration data (open circles) by month.
```

```
# Kruskal-wallis test
kruskal.test(Value ~ Month, data = wq)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 7.708
##
## Test Statistic Parameter:        df = 3
##
## P-value:                         0.05244
```

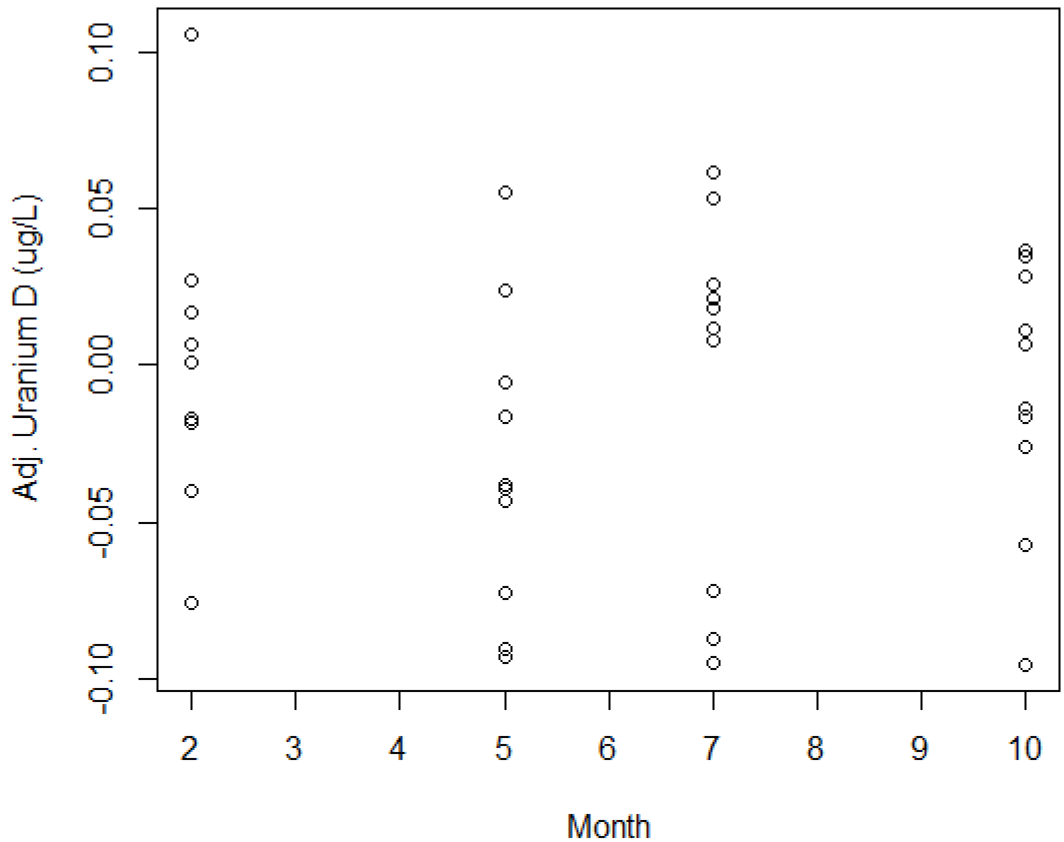
- The boxplot shows some evidence of seasonal differences, with higher dissolved uranium concentrations in February, although there are only 10 obs per season which may skew the interpretation. The dot plot shows less clear seasonal variability.
- The Kruskal-Wallis test for seasonality is non-significant (alpha=0.05), but it is very close to being significant.

Seasonality in concentration after flow adjustment

```
### Test for seasonality - flow-adjusted concentration

# Number of observations per season (month)
table(wq$Month)

##
##  2  5  7 10
##  9 10 10 10

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value.Adj~Month,data=wq,xlab="Month",ylab=paste("Adj. ", wqvar," (",w
q$Units[1],")",sep=""))
```



```
# Points
with(wq,plot(Value.Adj~Month,xlab="Month",ylab=paste("Adj. ",wqvar," (",wq$Units[1],")",sep=""),xaxp=c(1,12,11)))
```




```
# Plot of concentration data (open circles) by month.
```

```
# Kruskal-wallis test
kruskal.test(Value.Adj ~ Month, data = wq)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value.Adj by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 2.422
##
## Test Statistic Parameter:        df = 3
```

```
##
## P-value:                         0.4895
```

- There is no evidence of seasonality in dissovled uranium after flow adjustment and the Kruskal-Wallis test is not significant.
- Therefore, some of the seasonality in concentration was likely related to flow (in particular in February).

Trend tests – Mann-Kendall trend test on dissolved uranium

```
### Kendall trend test (EnvStats) on concentration
Value.trend <- kendallTrendTest(Value~DateDec,data=wq,alternative="two.sided"
,ci.slope=TRUE)
Value.trend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 tau = 0
##
## Alternative Hypothesis:          True tau is not equal to 0
##
## Test Name:                       Kendall's Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =   0.217274
##                                  slope     =   0.005673
##                                  intercept = -11.062782
##
## Estimation Method:               slope:      Theil/Sen Estimator
##                                  intercept:  Conover's Estimator
##
## Data:                            y = Value
##                                  x = DateDec
##
## Data Source:                     wq
##
## Sample Size:                     39
##
## Test Statistic:                  z = 1.936
##
## P-value:                         0.05285
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification
##                                  of Theil/Sen Method
##
## Confidence Interval Type:        two-sided
```

```
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = 0.00000
##                                  UCL = 0.01099
```

- There is no significant trend over time in dissolved uranium (alpha=0.05), but the p-value is marginally significant.

Trend tests - Seasonal Mann-Kendall trend test on dissolved uranium

```
### Seasonal Kendall trend test (EnvStats) on concentration
Value.seastrend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,da
ta=wq,alternative="two.sided",ci.slope=TRUE)
Value.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 4 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.0990
##                                  slope     =  0.0025
##                                  intercept = -4.8593
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq
##
## Sample Sizes:                    5     = 10
##                                  7     = 10
```

```
##                                   10    = 10
##                                   2     =  9
##                                   Total = 39
##
## Test Statistics:                  Chi-Square (Het) = 1.1192
##                                   z (Trend)        = 0.7875
##
## Test Statistic Parameter:         df = 3
##
## P-values:                         Chi-Square (Het) = 0.7724
##                                   z (Trend)        = 0.4310
##
## Confidence Interval for:          slope
##
## Confidence Interval Method:       Gilbert's Modification of
##                                   Theil/Sen Method
##
## Confidence Interval Type:         two-sided
##
## Confidence Level:                 95%
##
## Confidence Interval:              LCL = -0.003103
##                                   UCL =  0.009348
```

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.seastrend <- seastrends(Value.seastrend,alternative="two.sided")
# plot trend by season
Value.seastrend$seasonal.estimates
```

```
##        tau     slope intercept       z      p
## 5   0.1556  0.007333   -14.442  0.5367 0.5915
## 7   0.1556  0.002167    -4.013  0.5367 0.5915
## 10  0.2000  0.003000    -5.706  0.7155 0.4743
## 2  -0.1389 -0.006000    12.402 -0.4193 0.6750
```

- There is no significant annual trend or any significant trends in any of the seasons.

Trend tests – Mann-Kendall trend test on flow-adjusted dissolved uranium

```
### Kendall trend test (EnvStats) on flow-adjusted concentration
Value.Adj.trend <- kendallTrendTest(Value.Adj~DateDec,data=wq,alternative="tw
o.sided",ci.slope=TRUE)
Value.Adj.trend
```

```
##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                  tau = 0
```

```
##
## Alternative Hypothesis:          True tau is not equal to 0
##
## Test Name:                       Kendall's Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.15520
##                                  slope     =  0.00444
##                                  intercept = -8.92105
##
## Estimation Method:               slope:      Theil/Sen Estimator
##                                  intercept:  Conover's Estimator
##
## Data:                            y = Value.Adj
##                                  x = DateDec
##
## Data Source:                     wq
##
## Sample Size:                     39
##
## Test Statistic:                  z = 1.379
##
## P-value:                         0.1679
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification
##                                  of Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.001595
##                                  UCL =  0.010009
```

- There is no significant trend over time in dissolved uranium after adjusting for flow.

A.5 - Supplemental Analysis at Upstream of Fort McMurray: Uranium D

Censoring

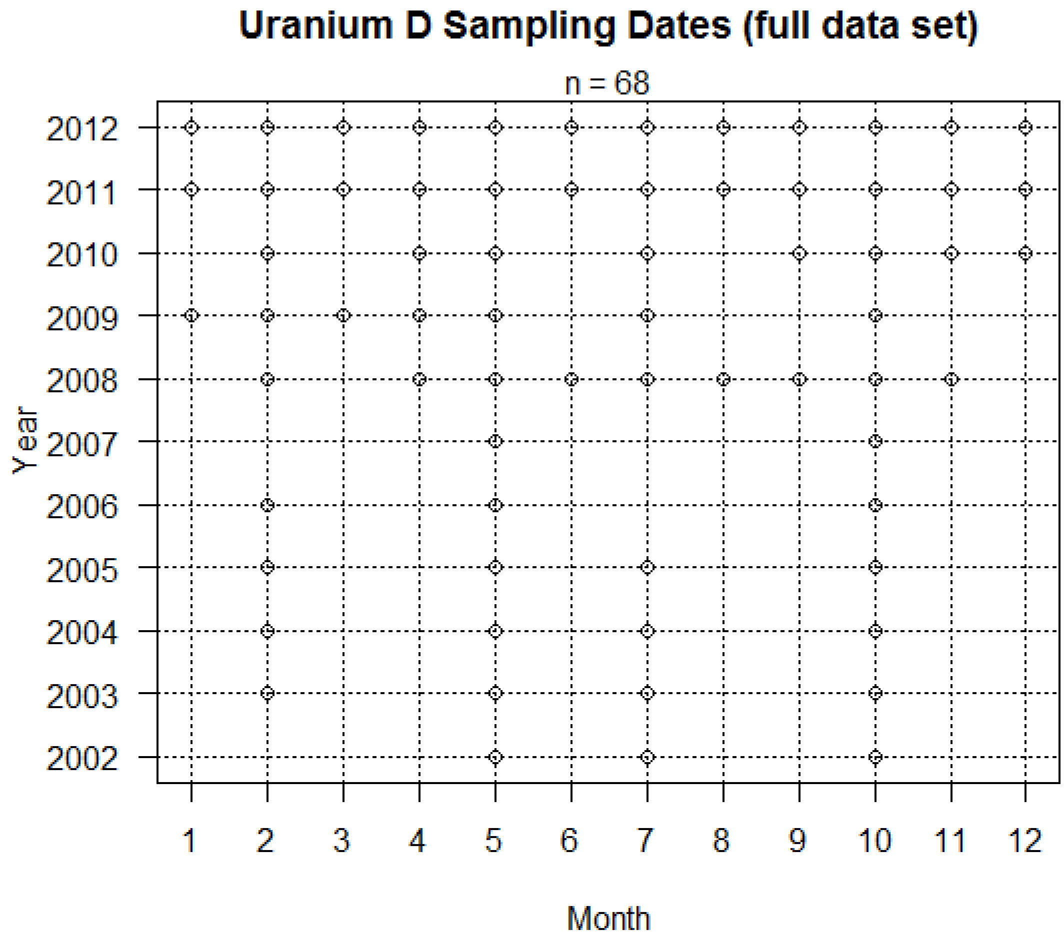
```
### Censoring

# Determine level of censoring and detection limits
with(wq, censummary(Value,ValueCen))
```

```
## all:
##       n   n.cen pct.cen     min     max
## 68.0000  1.0000  1.4706  0.0864  0.8000
##
## limits:
##   limit n uncen pexceed
## 1   0.0 0    19  1.0000
## 2   0.4 1    48  0.7059
```

- There is one censored value in July 2002.

Sampling frequency

```
### Investigate sampling frequency and create final data set for analysis (i.
e. subset the data to give equal sampling throughout time period)

# Dot plot of sampling dates for full data set
source("fun_dateplot.r")
dateplot(wq.in=wq,wq.invar=wqvar,type="full data set")
```



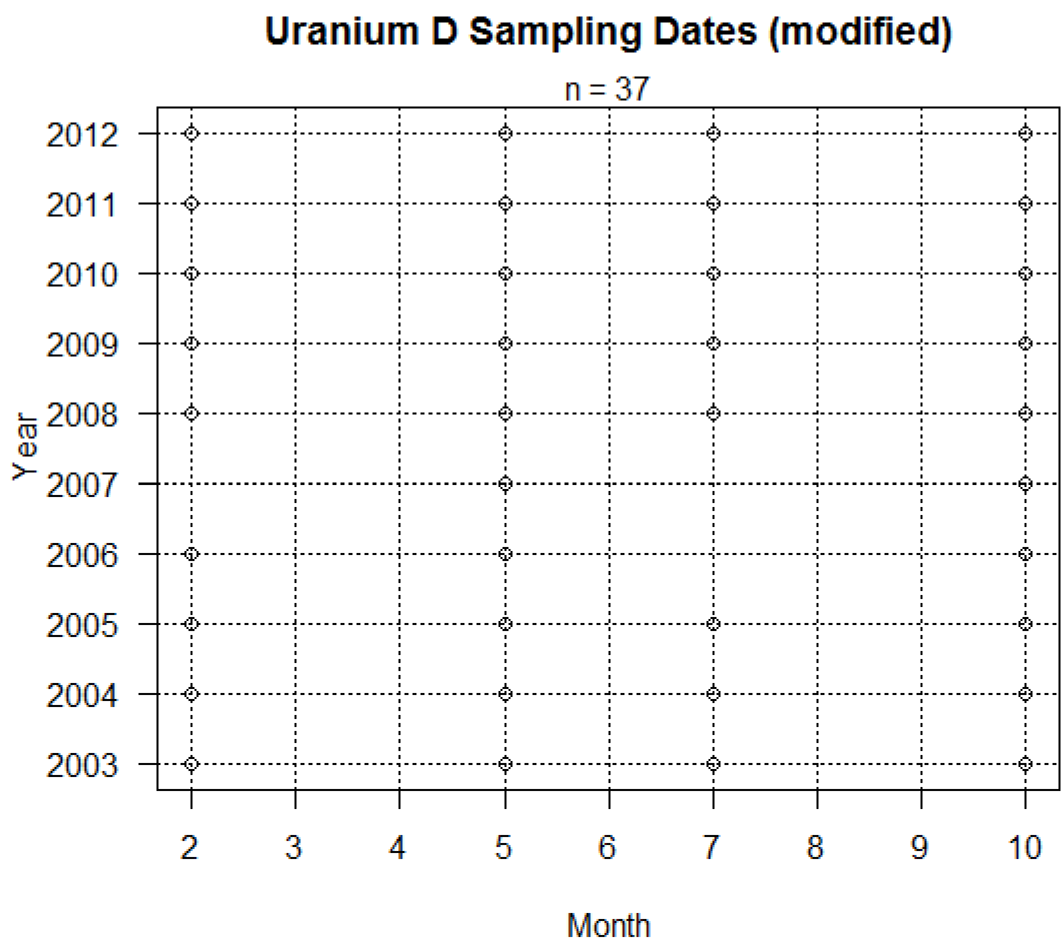

```
# Open circles correspond to observations made at the upstream Fort McMurray
station.

# Total number of observations
length(wq[,1])

## [1] 68

# Number of observations by year
table(wq$Year)

##
## 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##    3    4    4    4    3    2    9    7    8   12   12
```

- The period of record for dissolved uranium is 2002-2012 (11 years).
- Dissolved uranium was sampled quarterly (in Feb, May, July, and Oct) from 2002 until 2008, after which it was sampled more frequently (but not montly) until 2011, after which it was sampled monthly.
- As there is variation in sampling frequency over the period of record, we modified the data set (Helsel, 2002). Due to the systematic trend in sampling frequency (quarterly

for 6 years followed by almost monthly for 5 years), we defined the seasons based on quarterly sampling. For the years 2008-2012, we used only the observations from Feb, May, July, and Oct.

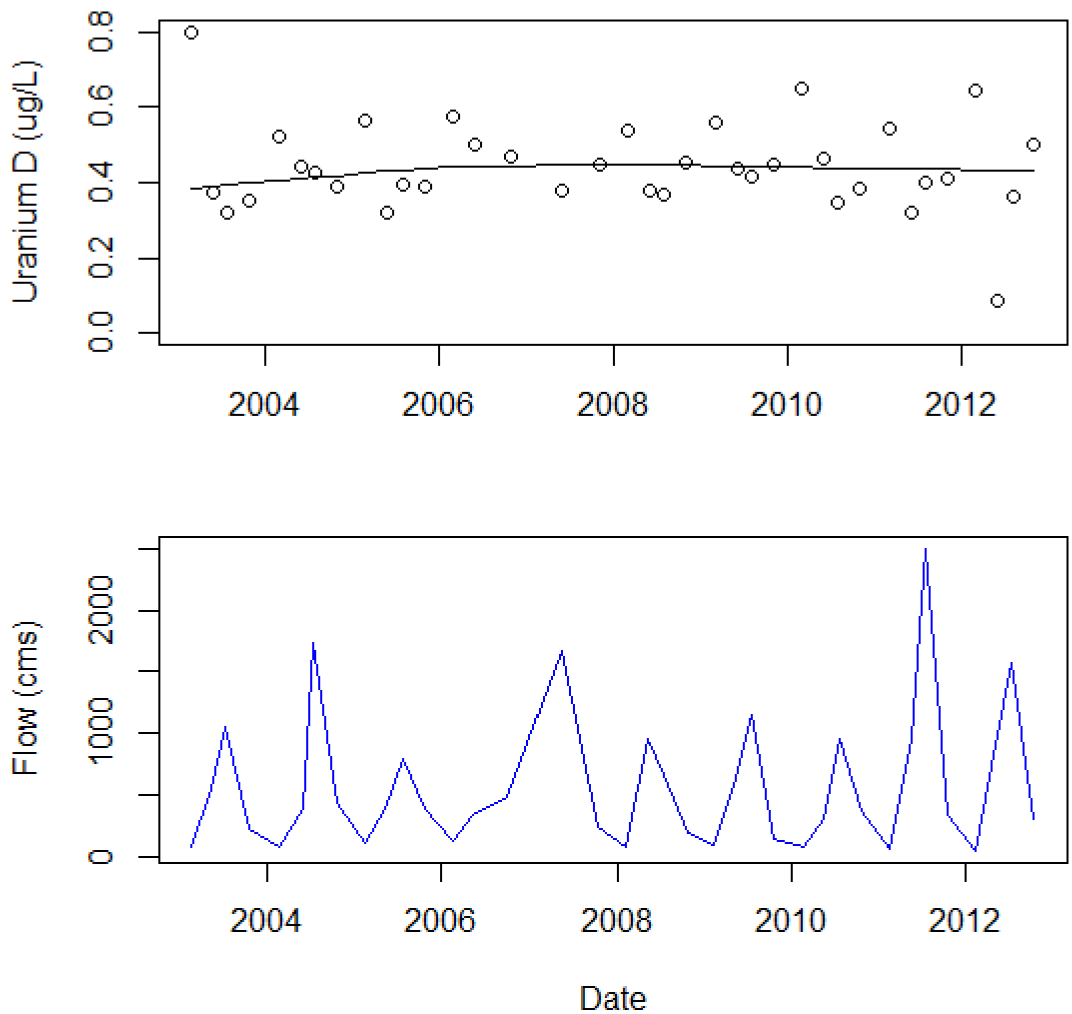
Final data set for trend analysis

```
# Total occurrences and occurrences by year in modified data set and verify t
hat they are as expected
length(wq[,1])

## [1] 37

table(wq$Year)

##
## 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##    4    4    4    3    2    4    4    4    4    4

# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq,wq.invar=wqvar,type="modified")
```



Time series plot of data

```
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq,wq.invar=wqvar)
```




```
# The black line is the lowess smooth to the concentration data (open circles
). The blue line is the flow based on observations from the same date as the
water quality observations.
```

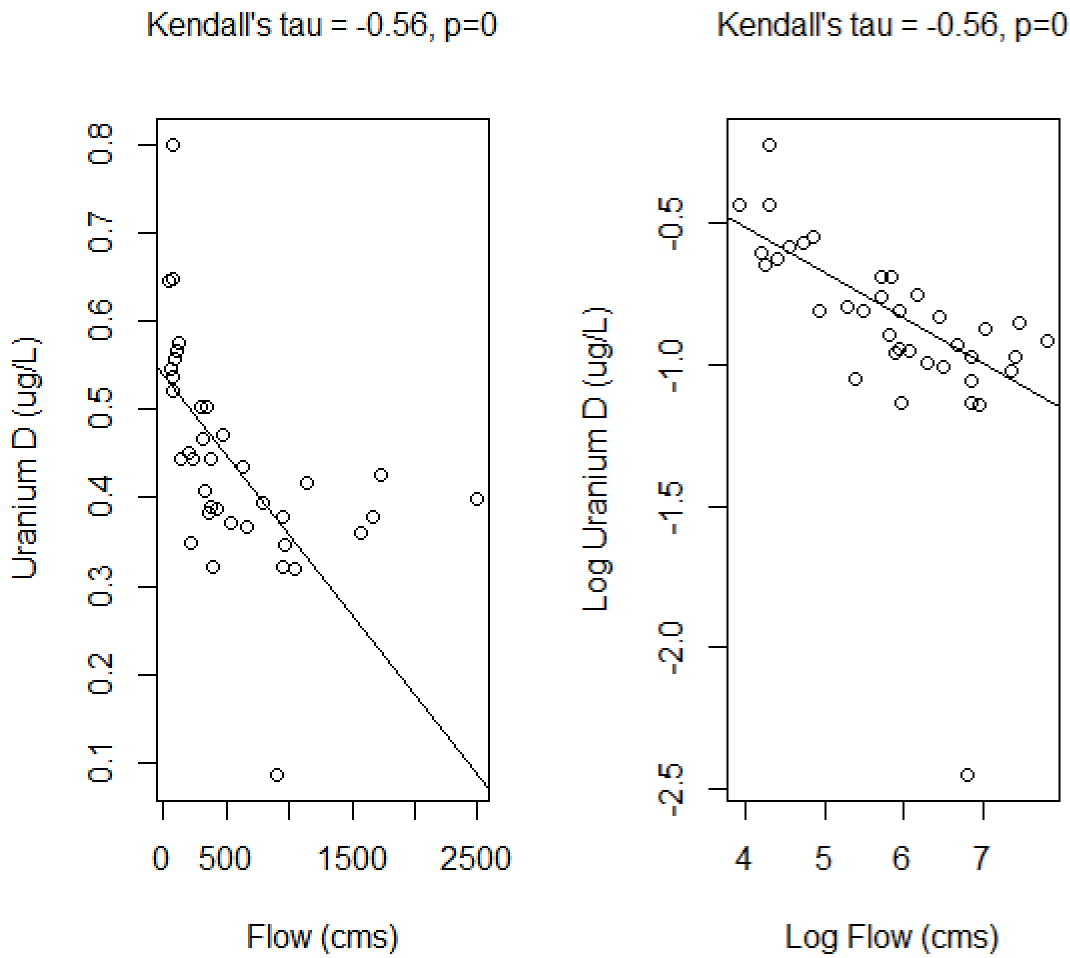
Summary statistics

```
### Calculate summary statistics
# Summary stats were calculated as usual since there was no censoring.

# n
with(wq,length(Value))

## [1] 37
```

```
# min
with(wq,min(Value,na.rm=TRUE))

## [1] 0.0864

# max
with(wq,max(Value, na.rm=TRUE))

## [1] 0.8

# median
with(wq,median(Value, na.rm=TRUE))

## [1] 0.427

# mean
with(wq,mean(Value, na.rm=TRUE))

## [1] 0.4423

# standard deviation
with(wq,sd(Value, na.rm=TRUE))

## [1] 0.1204

#variance
with(wq,var(Value, na.rm=TRUE))

## [1] 0.0145
```

Relationship with flow

```
### Test for a relationship between dissolved uranium and flow
# Determine if there is a relationship (possibly linear) between flow and con
centration (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq,wq.invar=wqvar)
```

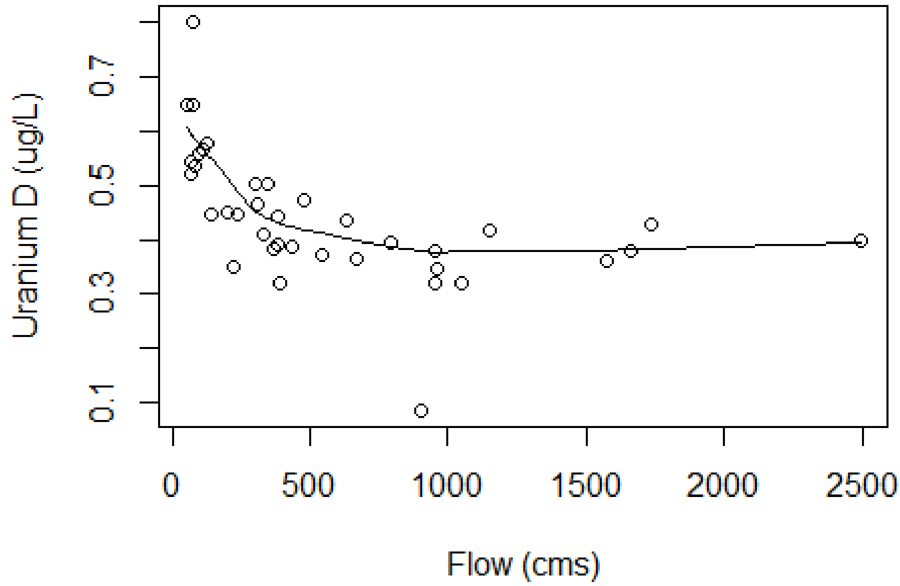



```
# All observations are uncensored observations. The solid line is the ATS slo
pe with Turnbull estimate and the dashed line is the regression line.
```

- The relationship between dissolved uranium and flow is not fit very well by the ATS line on the original, but the fit is good on the log-log scale.
- In addition, Kendall's tau is significantly different from zero (alpha=0.05), suggesting that there is a strong monotonic relationship (linear or otherwise) between dissolved uranium and flow.

Relationship with flow - lowess smooth

```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq,wq.invar=wqvar)
```

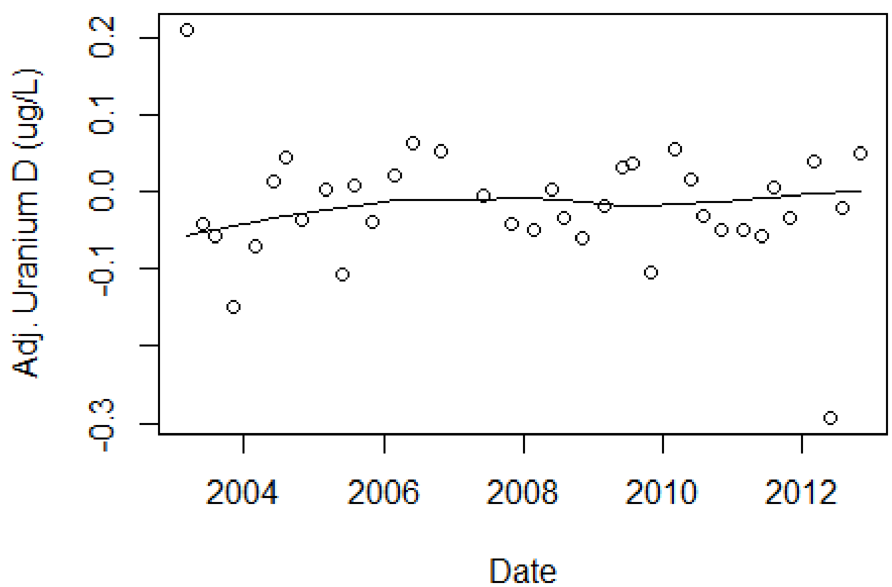



```
# Open circles are uncensored observations and solid circles are censored obs
ervations. The solid line is the lowess smooth.
```

- The lowess smooth suggests that dissolved uranium may decrease with increasing flow up to ~500 cms, and then remain relatively constant.

Time series plot of data after flow adjustment

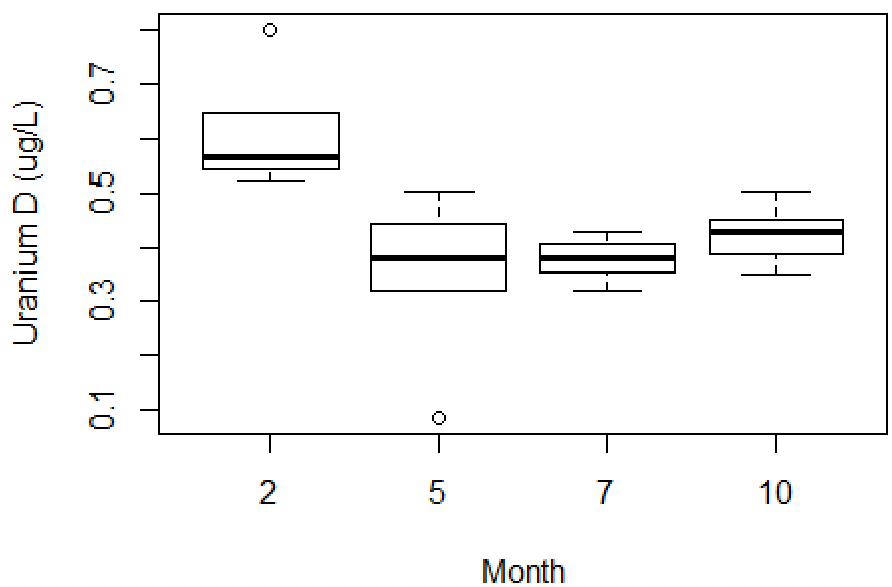
```
### Plot of flow-adjusted water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot_adj(wq.in=wq,wq.invar=wqvar)
```



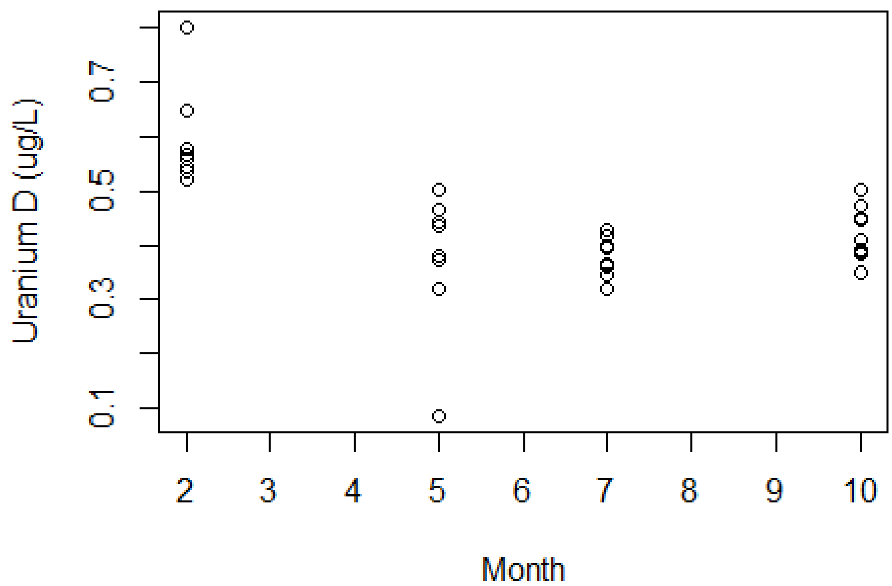
```
# The black line is the lowess smooth to the concentration data (open circles
).
```

Seasonality in concentration

```
### Test for seasonality - concentration

# Number of observations per season (month)
table(wq$Month)

##
##  2  5  7 10
##  9 10  8 10

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value~Month,data=wq,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],")
",sep=""))
```




```
# Points
with(wq,plot(Value~Month,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],")",s
ep=""),xaxp=c(1,12,11)))
```



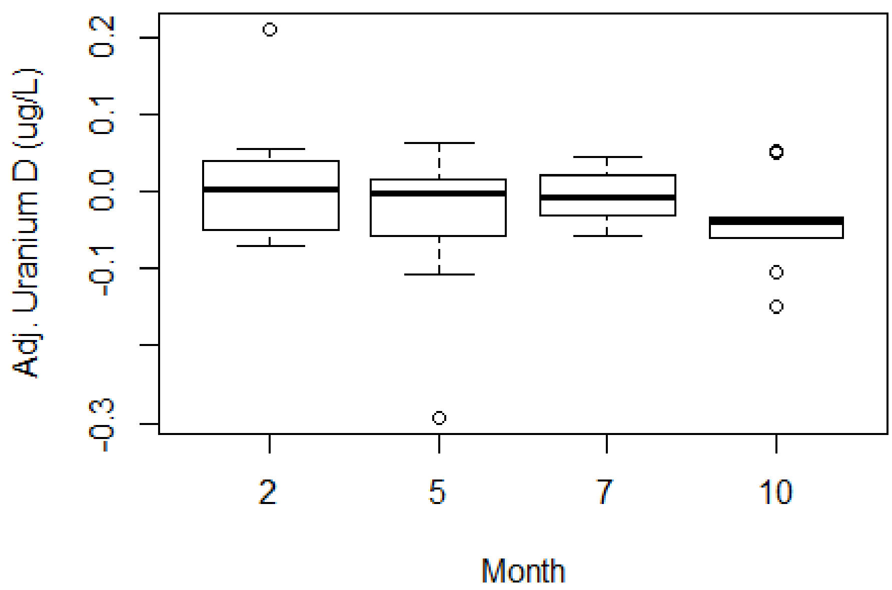

```
# Kruskal-wallis test
kruskal.test(Value ~ Month, data = wq)

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                        Kruskal-Wallis rank sum test
##
## Data:                             Value by Month
##
## Test Statistic:                   Kruskal-Wallis chi-squared = 22.15
##
## Test Statistic Parameter:         df = 3
##
## P-value:                          6.067e-05
```

- The boxplot shows some evidence of seasonal differences, and the Kruskal-Wallis test for seasonality is highly significant (alpha=0.001).

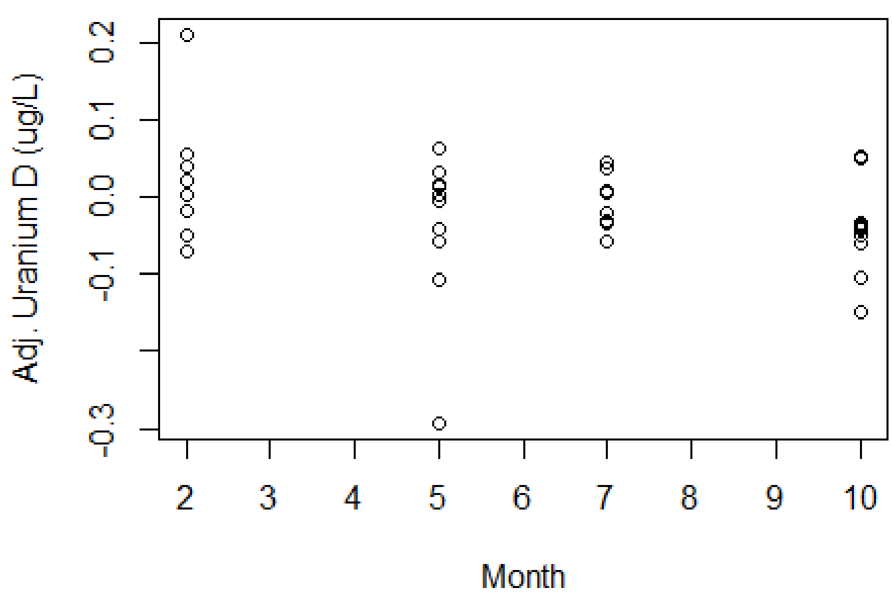
Seasonality in concentration after flow adjustment

```
### Test for seasonality - flow-adjusted concentration

# Number of observations per season (month)
table(wq$Month)

##
##  2  5  7 10
##  9 10  8 10
```

```
# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
boxplot(Value.Adj~Month,data=wq,xlab="Month",ylab=paste("Adj. ", wqvar," (",wq$Units[1],")",sep=""))
```




```
# Points
with(wq,plot(Value.Adj~Month,xlab="Month",ylab=paste("Adj. ",wqvar," (",wq$Units[1],")",sep=""),xaxp=c(1,12,11)))
```




```
# Kruskal-wallis test
kruskal.test(Value.Adj ~ Month, data = wq)
```

```
##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            Value.Adj by Month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 2.836
##
## Test Statistic Parameter:        df = 3
##
## P-value:                         0.4176
```

- There is no evidence of seasonality in dissovled uranium after flow adjustment and the Kruskal-Wallis test is not significant.

Trend tests – Mann-Kendall trend test on dissolved uranium

```
### Kendall trend test (EnvStats) on concentration
Value.trend <- kendallTrendTest(Value~DateDec,data=wq,alternative="two.sided"
,ci.slope=TRUE)
Value.trend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 tau = 0
##
## Alternative Hypothesis:          True tau is not equal to 0
##
## Test Name:                       Kendall's Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       = -0.0105105
##                                  slope     = -0.0005833
##                                  intercept =  1.5985764
##
## Estimation Method:               slope:      Theil/Sen Estimator
##                                  intercept:  Conover's Estimator
##
## Data:                            y = Value
##                                  x = DateDec
##
## Data Source:                     wq
##
## Sample Size:                     37
##
```

```
## Test Statistic:                  z = -0.07848
##
## P-value:                         0.9374
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification
##                                  of Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.01474
##                                  UCL =  0.01116
```

- There is no significant annual trend.

Trend tests - Seasonal Mann-Kendall trend test on dissolved uranium

```
### Seasonal Kendall trend test (EnvStats) on concentration
This was done to compare with the results of the seasonal Kendall trend test
at the Old Fort station.

Value.seastrend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,da
ta=wq,alternative="two.sided",ci.slope=TRUE)
Value.seastrend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 4 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.052124
##                                  slope     =  0.002375
##                                  intercept = -0.824316
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
```

```
##                                                Thiel/Sen Estimator
##                                  intercept:    Median of
##                                                Seasonal Estimates
##
## Data:                            y      = Value
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq
##
## Sample Sizes:                    2     =  9
##                                  5     = 10
##                                  7     =  8
##                                  10    = 10
##                                  Total = 37
##
## Test Statistics:                 Chi-Square (Het) = 2.4123
##                                  z (Trend)        = 0.3969
##
## Test Statistic Parameter:        df = 3
##
## P-values:                        Chi-Square (Het) = 0.4914
##                                  z (Trend)        = 0.6915
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.006313
##                                  UCL =  0.010918
```

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
Value.seastrend <- seastrends(Value.seastrend,alternative="two.sided")
# plot trend by season
Value.seastrend$seasonal.estimates
```

```
##           tau     slope intercept       z      p
## 2   0.05556  0.003143    -5.745  0.1043 0.9170
## 5  -0.15556 -0.009000    18.446 -0.5367 0.5915
## 7  -0.07143 -0.001850     4.096 -0.1237 0.9015
## 10  0.35556  0.011600   -22.860  1.3470 0.1780
```

- There is no significant annual trend or any significant trends in any of the seasons.

Trend tests – Mann-Kendall trend test on flow-adjusted dissolved uranium

```
### Kendall trend test (EnvStats) on flow-adjusted concentration
Value.Adj.trend <- kendallTrendTest(Value.Adj~DateDec,data=wq,alternative="tw
o.sided",ci.slope=TRUE)
Value.Adj.trend
```

```
##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 tau = 0
##
## Alternative Hypothesis:          True tau is not equal to 0
##
## Test Name:                       Kendall's Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =  0.0180180
##                                  slope     =  0.0005391
##                                  intercept = -1.1037108
##
## Estimation Method:               slope:      Theil/Sen Estimator
##                                  intercept:  Conover's Estimator
##
## Data:                            y = Value.Adj
##                                  x = DateDec
##
## Data Source:                     wq
##
## Sample Size:                     37
##
## Test Statistic:                  z = 0.1439
##
## P-value:                         0.8856
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification
##                                  of Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.007395
##                                  UCL =  0.006862
```

- There is no significant trend over time in dissolved uranium after adjusting for flow.

A.6 - Trend Analysis: Lithium D at Old Fort Station

Censoring

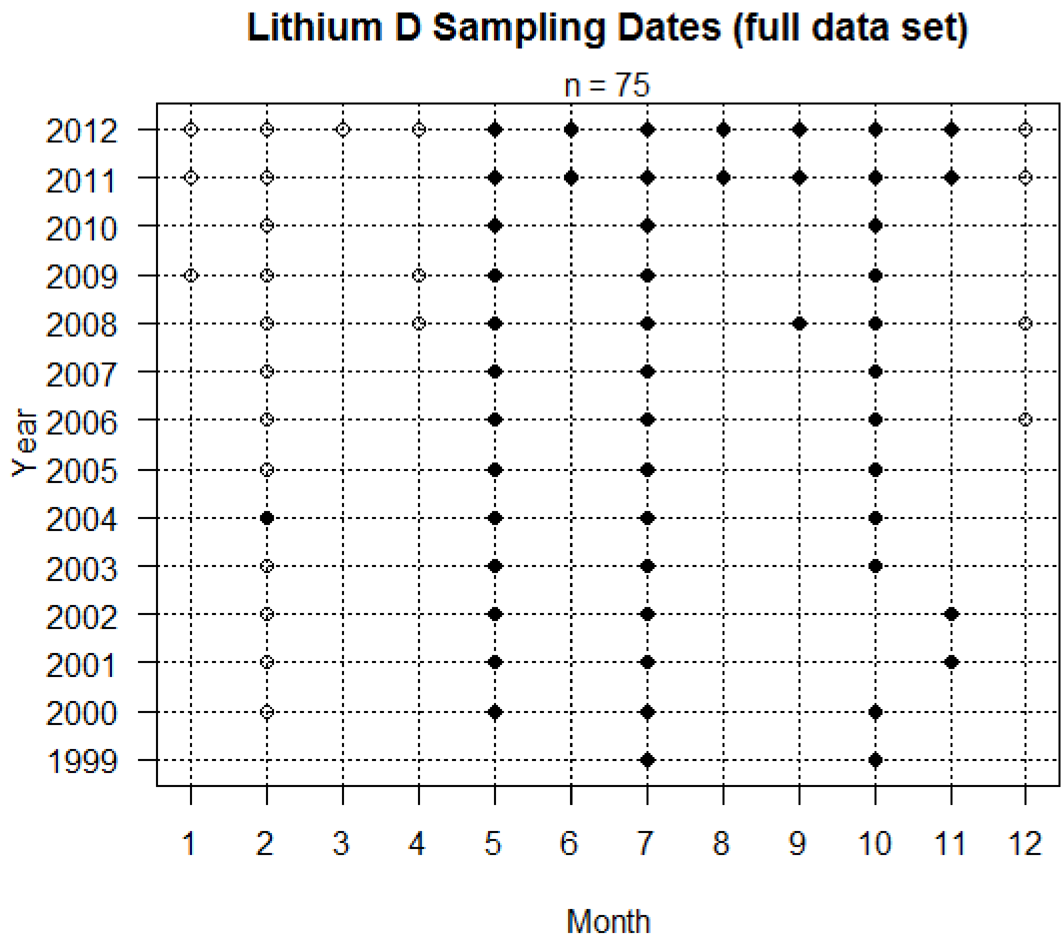
```
### Censoring

# Determine level of censoring and detection limits
with(wq, censummary(Value,ValueCen))
```

```
## all:
##       n   n.cen pct.cen     min     max
##  75.000   2.000   2.667   3.000  11.000
##
## limits:
##   limit n uncen pexceed
## 1     0 0     3  1.0000
## 2     4 2    70  0.9333
```

- Of the 75 observations, there were 2 censored values (2.7% nondetects. Censored values occurred in Nov 2002 and Feb 2003). The detection limit at that time was 4 ug/L.

Sampling frequency

```
### Investigate sampling frequency and create final data set for analysis (i.
e. subset the data to give equal sampling throughout time period)

# Dot plot of sampling dates for full data set
source("fun_dateplot.r")
dateplot(wq.in=wq,wq.invar=wqvar,type="full data set")
```



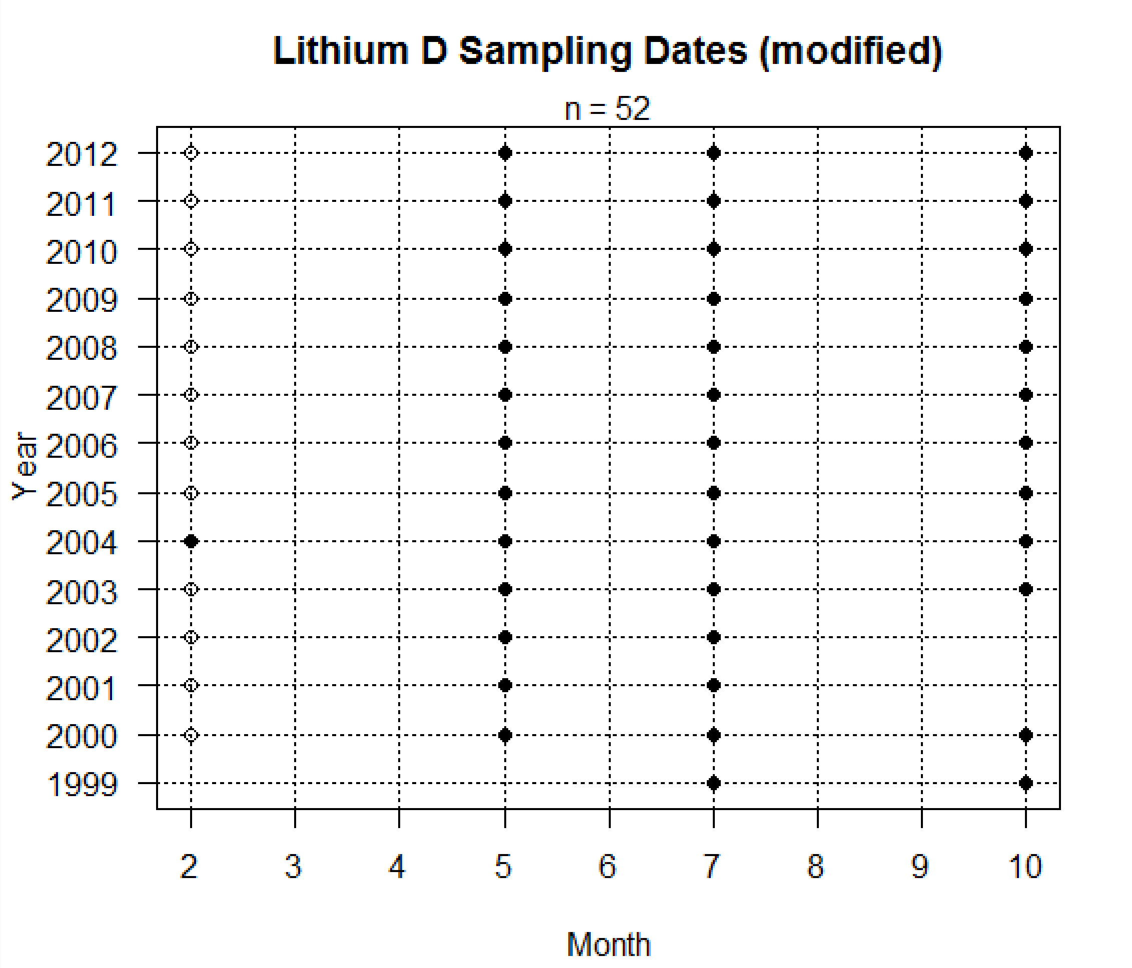

```
# Solid circles correspond to observations made at the Old Fort station and c
losed circles correspond to observations made at the Devil's Elbow station.

# Total number of observations
length(wq[,1])

## [1] 75

# Number of observations by year
table(wq$Year)

##
## 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##    2    4    4    4    4    4    4    5    4    8    6    4   10   12

# Number of observtions by month
table(wq$Month)

##
##  1  2  3  4  5  6  7  8  9 10 11 12
##  3 13  1  3 13  2 15  2  3 12  4  4
```

```
# The data are monthly over the entire time period, so no need to subset the
data. Note however that there are some months with missing data over the peri
od of record, as well as several months with multiple samples.
```

- The period of record for dissolved lithium is 1999-2012 (14 years).
- Dissolved lithium was sampled quarterly (in Feb, May, July, and Oct) from 1999 until 2010, after which it was sampled monthly (see below), with several exceptions.
- Samples were taken at both Athabasca at Old Fort stations (at Old Fort (spring/summer/fall) and d/s Devil's Elbow (winter)).

Final data set for trend analysis

```
### Create final data set for trend analysis


# Dot plot of sampling dates in modified data set
dateplot(wq.in=wq,wq.invar=wqvar,type="modified")
```



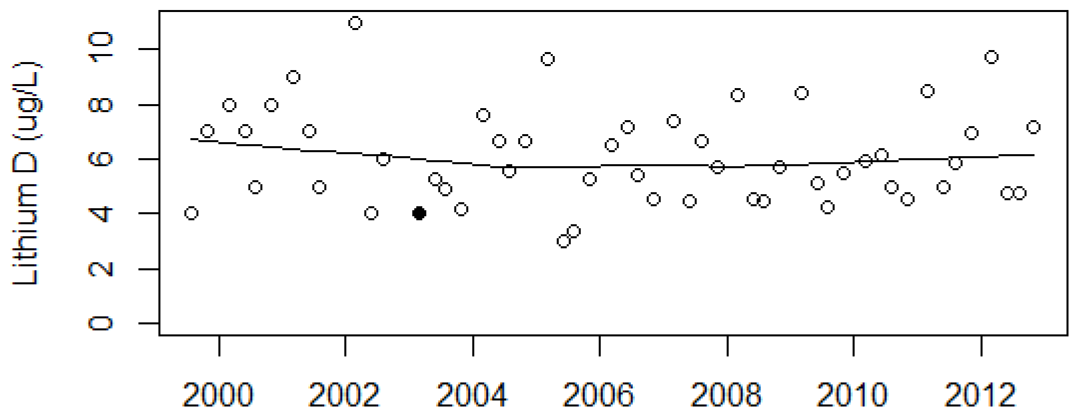

```
# Total occurrences and occurrences by year in modified data set and verify t
hat they are as expected
length(wq[,1])
```

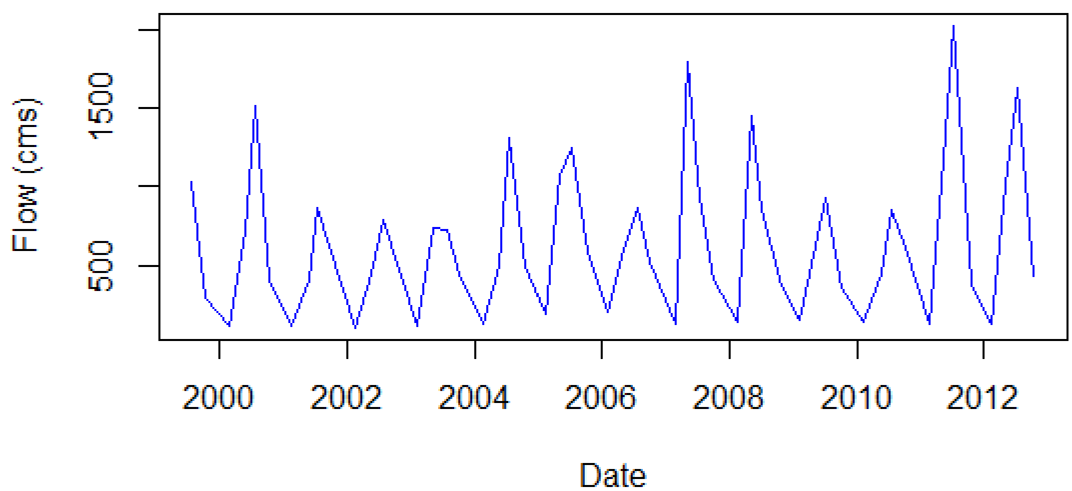
```
## [1] 52

table(wq$Year)

##
## 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012
##    2    4    3    3    4    4    4    4    4    4    4    4    4    4

table(wq$Month)

##
##  2  5  7 10
## 13 13 14 12

# Determine level of censoring and detection limits in final dataset
with(wq, censummary(Value,ValueCen))

## all:
##       n   n.cen pct.cen     min     max
##  52.000   1.000   1.923   3.000  11.000
##
## limits:
##   limit n uncen pexceed
## 1     0 0     2  1.0000
## 2     4 1    49  0.9423
```

- There was only 1 nondetect in the final dataset.

Time series plot of data

```
### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot(wq.in=wq,wq.invar=wqvar)
```






```
# Open circles are uncensored values, solid circles are censored values. The blue line is flow observations from the same date as the water quality observ ations. The black line is the lowess smooth to the concentration data.
```

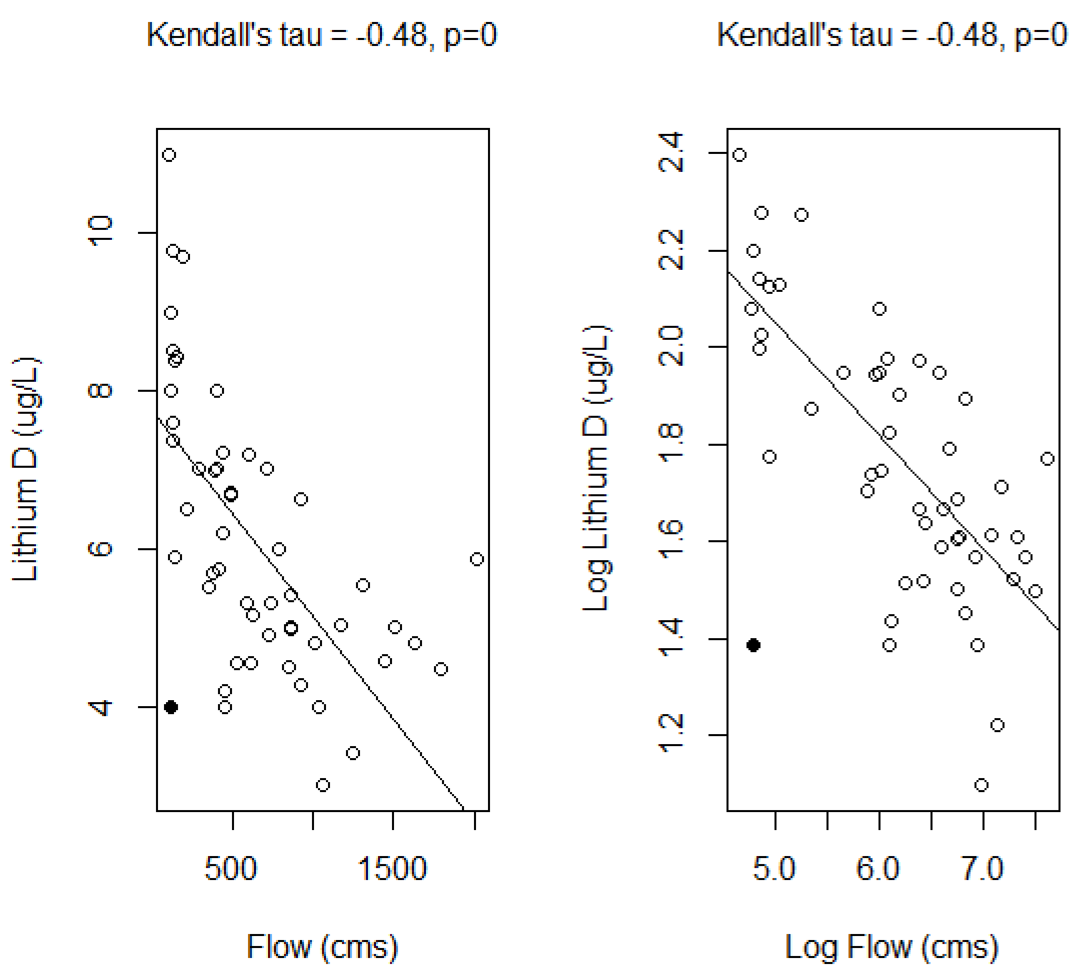
Summary statistics

```
### Calculate summary statistics
# The median was calculated as usual since the level of censoring was less th an 50%. Mean and standard deviation were calculated using cenfit in the NADA package (Kaplan-Meier method).

# Median
median(wq$Value)

## [1] 5.71

# Estimate the empirical cumulative distribution function using the KM method
ecdf <- with(wq,cenfit(Value,ValueCen))
```

```
# Mean
mean(ecdf)

##    mean      se 0.95LCL 0.95UCL
##  6.0673  0.2457  5.5857  6.5489

# Standard Deviation
sd(ecdf)

## [1] 1.772
```

Relationship with flow

```
### Test for a relationship between concentration and flow
# Determine if there is a relationship (possibly between flow and concentrati
on (or their logs).
source("func_plotvflow.r")
plotvflow(wq.in=wq,wq.invar=wqvar)
```

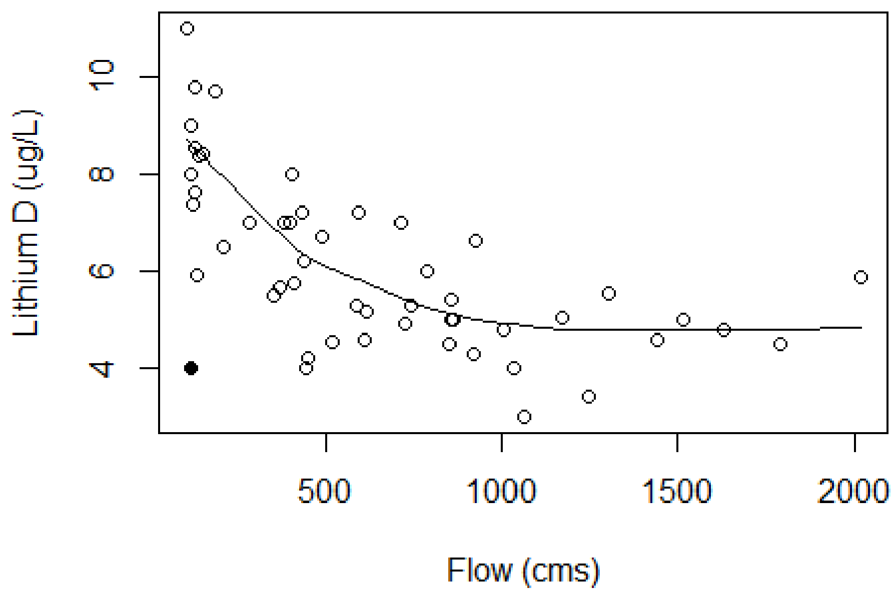


```
# Open circles are uncensored observations and solid circles are censored obs
ervations. The solid line is the ATS slope with Turnbull estimate of intercep
t.
```

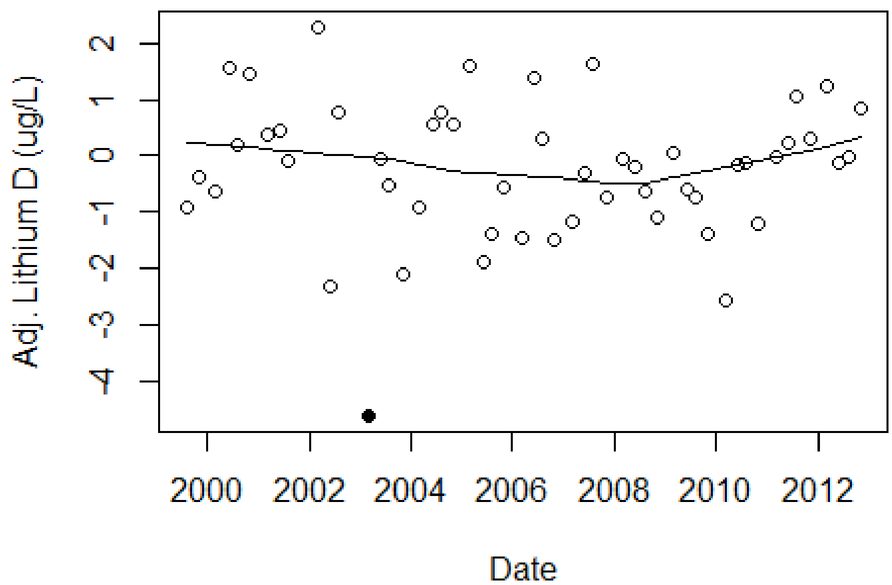
- Kendall's tau is significant and the ATS line fits well on the log-log scale.

Relationship with flow - lowess smooth

```
### Relationship with flow - lowess smooth
plotvflow_smooth(wq.in=wq,wq.invar=wqvar)
```

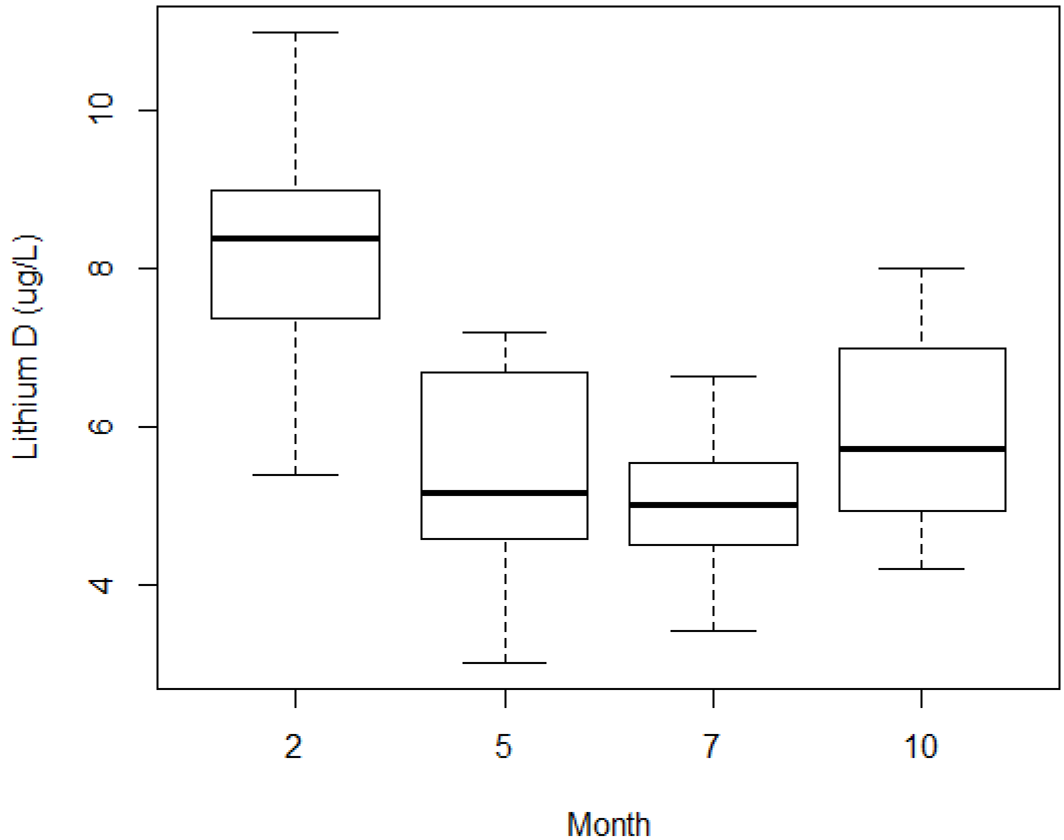



```
# Open circles are uncensored observations and solid circles are censored obs
ervations. The solid line is the lowess smooth.

### Plot of water quality data and flow vs Date
source("func_timeseriesplot.r")
timeseriesplot_adj(wq.in=wq,wq.invar=wqvar)
```

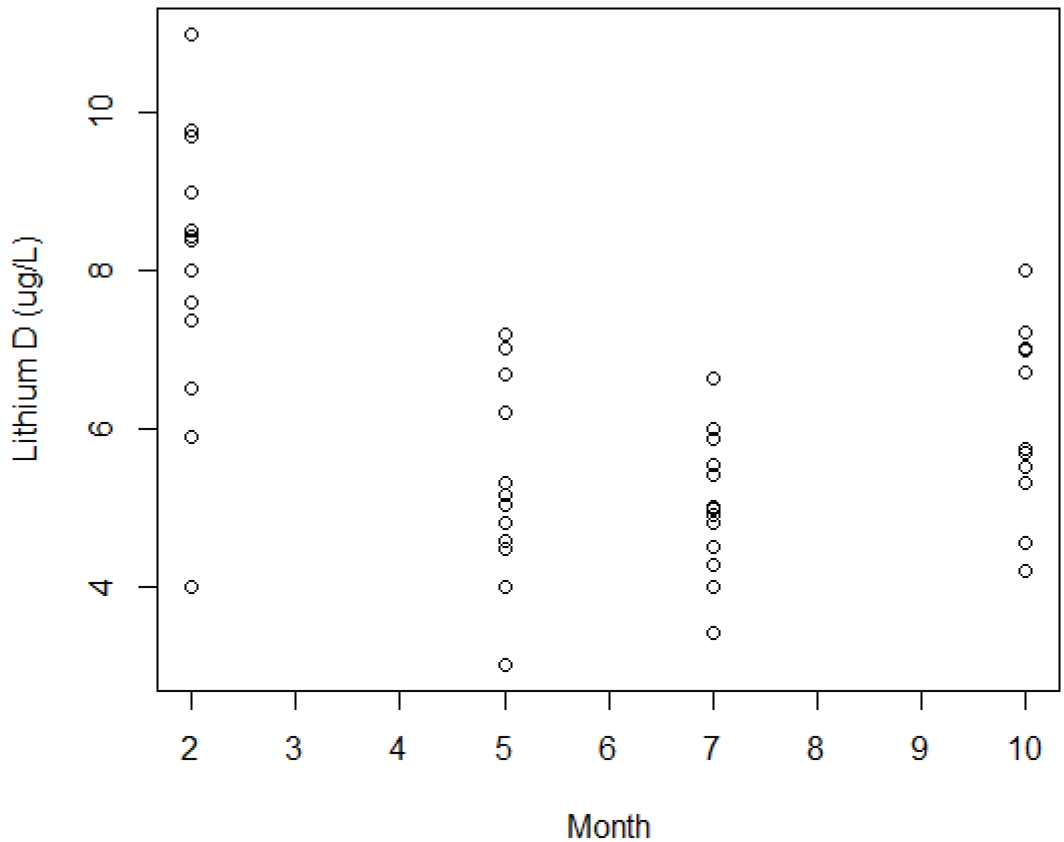


Seasonality in concentration

```
### Test for seasonality - concentration

# Number of observations per season (month)
table(wq$Month)

##
##  2  5  7 10
## 13 13 14 12

# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
bp <- cenboxplot(obs=wq$Value,cen=wq$ValueCen,group=wq$Month,log=FALSE,xlab="
Month",ylab=paste(wqvar," (",wq$Units[1],")",sep=""))
```




```
# Points
with(wq,plot(Value~Month,xlab="Month",ylab=paste(wqvar," (",wq$Units[1],")",sep=""),xaxp=c(1,12,11)))
# add nondetects
points(x=wq[wq$ValueCen==TRUE,"Month"],y=wq[wq$ValueCen==TRUE,"Value"],pch=16)
```



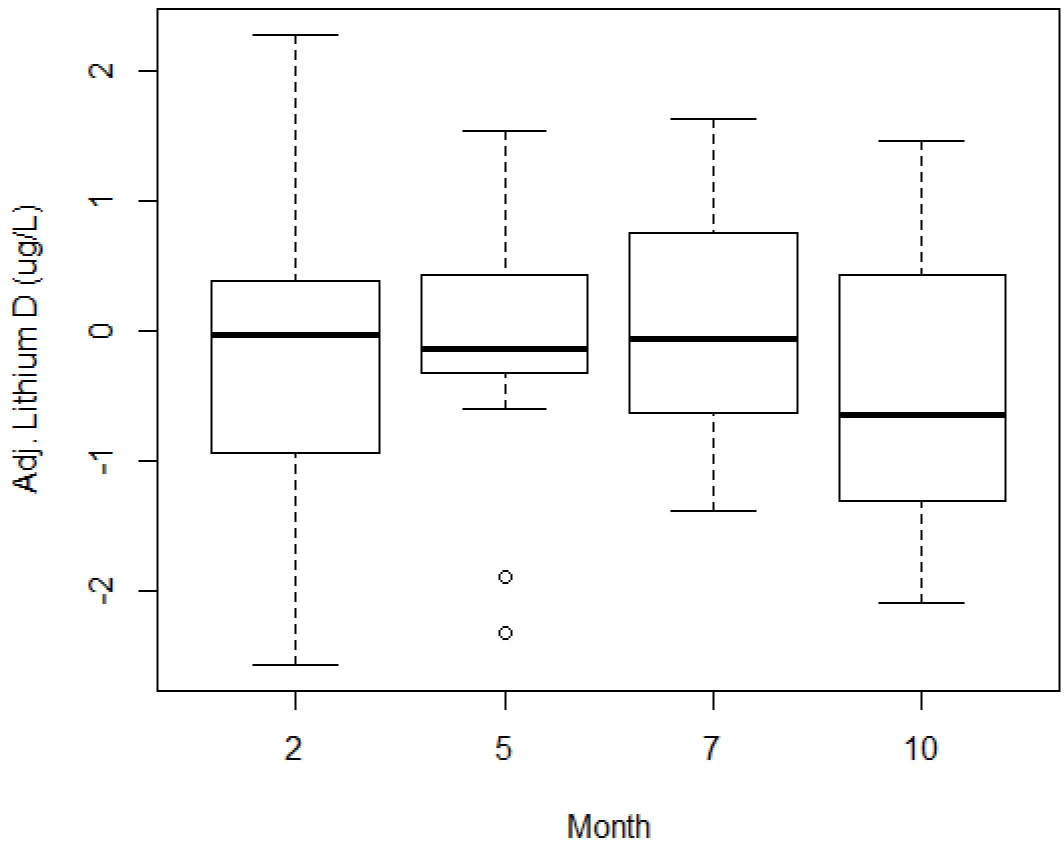

```
# Test Censored ECDF differences
with(wq,cendiff(Cen(Value,ValueCen)~Month))

##             N Observed Expected (O-E)^2/E (O-E)^2/V
## Month=2  13    10.27     2.92  1.85e+01  28.80850
## Month=5  13     5.47     7.92  7.59e-01   1.64554
## Month=7  14     4.69     9.66  2.56e+00   6.22258
## Month=10 12     6.19     6.12  9.68e-04   0.00183
##
##  Chisq= 30.7  on 3 degrees of freedom, p= 9.7e-07
```

- The plots suggest that there is some seasonal differences, and the test for differences in censored ecdfs between months is significant.

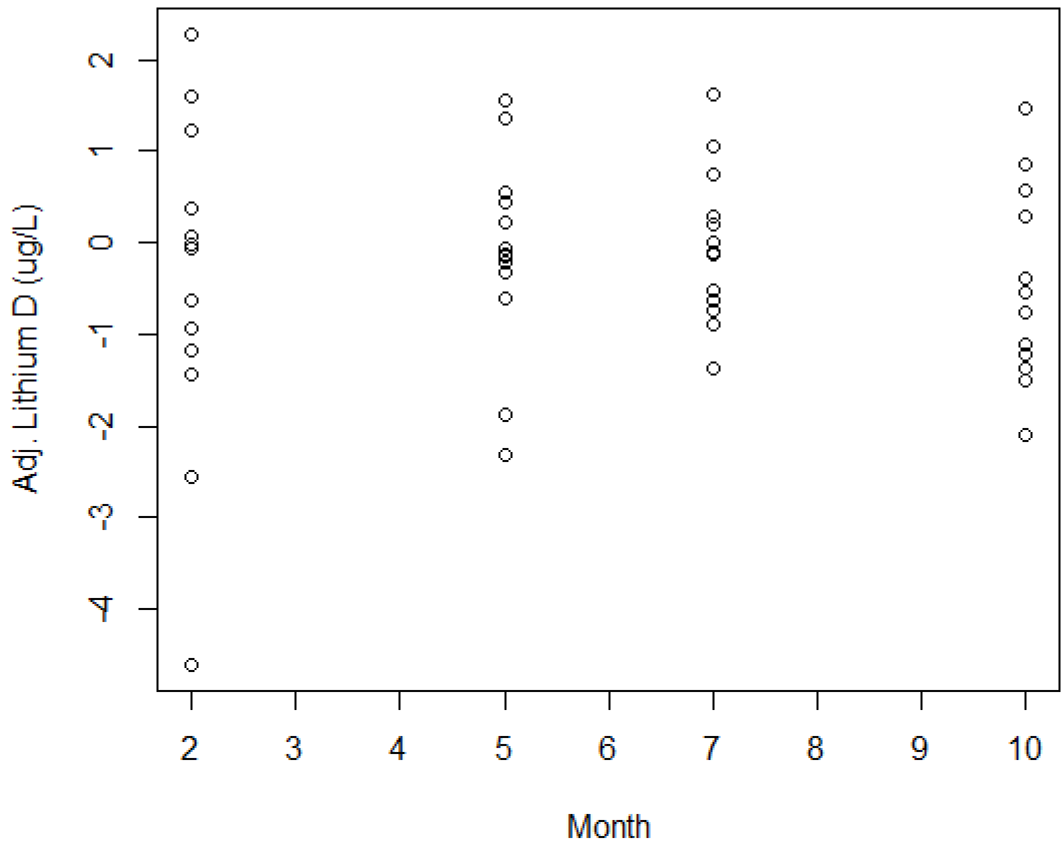
Seasonality in concentration after flow adjustment

```
### Test for seasonality - flow-adjusted concentration

# Number of observations per season (month)
table(wq$Month)

##
##  2  5  7 10
## 13 13 14 12
```

```
# Plot of observations by season
# Boxplot (not many obs per month, beware interpretation)
bp <- cenboxplot(obs=wq$Value.Adj,cen=wq$ValueCen,group=wq$Month,log=FALSE,xl
ab="Month",ylab=paste("Ad. ",wqvar," (",wq$Units[1],")",sep=""))
```




```
# Points
with(wq,plot(Value.Adj~Month,xlab="Month",ylab=paste("Adj. ",wqvar," (",wq$Un
its[1],")",sep=""),xaxp=c(1,12,11)))
# add nondetects
points(x=wq[wq$ValueCen==TRUE,"Month"],y=wq[wq$ValueCen==TRUE,"Value.Adj"],pc
h=16)
```




```
# Test Censored ECDF differences
with(wq,cendiff(Cen(Value.Adj,ValueCen)~Month))
```

```
##            N Observed Expected (O-E)^2/E (O-E)^2/V
## Month=2  13     6.33     6.88    0.0452    0.0941
## Month=5  13     7.02     6.23    0.0998    0.1900
## Month=7  14     7.98     6.29    0.4554    0.8531
## Month=10 12     5.15     7.08    0.5226    1.1006
##
##  Chisq= 1.7  on 3 degrees of freedom, p= 0.641
```

- The plots show no seasonal differences between months.
- The test for differences in censored ecdfs between months is not significant.
- We can conclude that the seasonality in dissolved lithium is due to seasonal variations in flow, as seasonal differences are no longer apparent once dissolved lithium concentration was adjusted for flow.

Trend tests – Seasonal Mann-Kendall on concentration

```
### Kendall seasonal trend test (EnvStats) on concentration
Value.trend <- kendallSeasonalTrendTest(Value~as.character(Month)+Year,data=w
q,alternative="two.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.trend
```

```
##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 4 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       = -0.01652
##                                  slope     = -0.00100
##                                  intercept = -8.37604
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = Value
##                                  season = as.character(Month)
##                                  year   = Year
##
## Data Source:                     wq
##
## Sample Sizes:                    7     = 14
##                                  10    = 12
##                                  2     = 13
##                                  5     = 13
##                                  Total = 52
##
## Test Statistics:                 Chi-Square (Het) =  0.7520
##                                  z (Trend)        = -0.1216
##
## Test Statistic Parameter:        df = 3
##
## P-values:                        Chi-Square (Het) = 0.8609
##                                  z (Trend)        = 0.9032
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
```

```
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.09831
##                                  UCL =  0.08919

## Recall that the estimates of slope and intercept are incorrect. The releva
nt result here is Kendall's tau and the associated p-value, as well as the va
n Bell test for heterogeneity.
```

- There is no significant trend over time in dissolved lithium; there is no heterogeneity in seasonal trends.

Trend tests – Mann-Kendall on concentration after flow adjustment

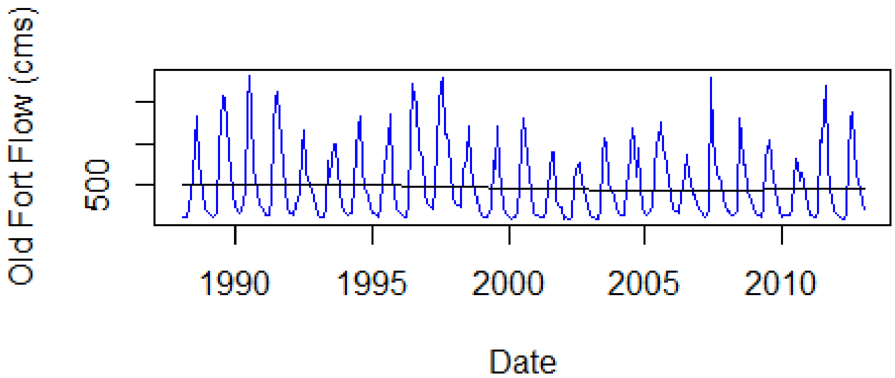
```
### Kendall trend test (EnvStats) on flow adjusted concentration
Value.Adj.trend <- kendallTrendTest(Value.Adj~DateDec,data=wq,alternative="tw
o.sided",ci.slope=TRUE,independent.obs=TRUE)
Value.Adj.trend

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 tau = 0
##
## Alternative Hypothesis:          True tau is not equal to 0
##
## Test Name:                       Kendall's Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =   0.021116
##                                  slope     =   0.008651
##                                  intercept = -17.486774
##
## Estimation Method:               slope:      Theil/Sen Estimator
##                                  intercept:  Conover's Estimator
##
## Data:                            y = Value.Adj
##                                  x = DateDec
##
## Data Source:                     wq
##
## Sample Size:                     52
##
## Test Statistic:                  z = 0.2131
##
## P-value:                         0.8313
```

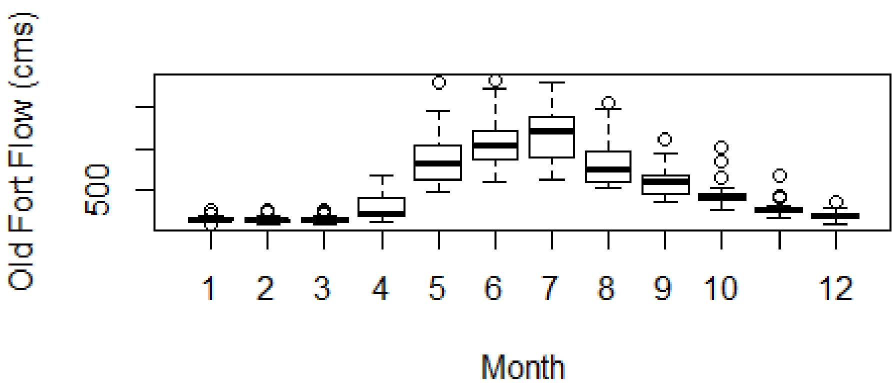
```
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification
##                                  of Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = -0.07997
##                                  UCL =  0.09542

## Recall that the estimates of slope and intercept are incorrect. The releva
nt result here is Kendall's tau and the associated p-value.
```

- There is no significant trend over time in dissolved lithium after flow adjustment

A.7 - Flow at Old Fort Station

Flow - 1988-2012






```
# Kruskal-Wallis test
kruskal.test(oldft.median~month,data=flow_mo[flow_mo$year>1987,])

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            oldft.median by month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 254.3503
##
## Test Statistic Parameter:        df = 11
##
## P-value:                         3.427653e-48

### Trend test
```

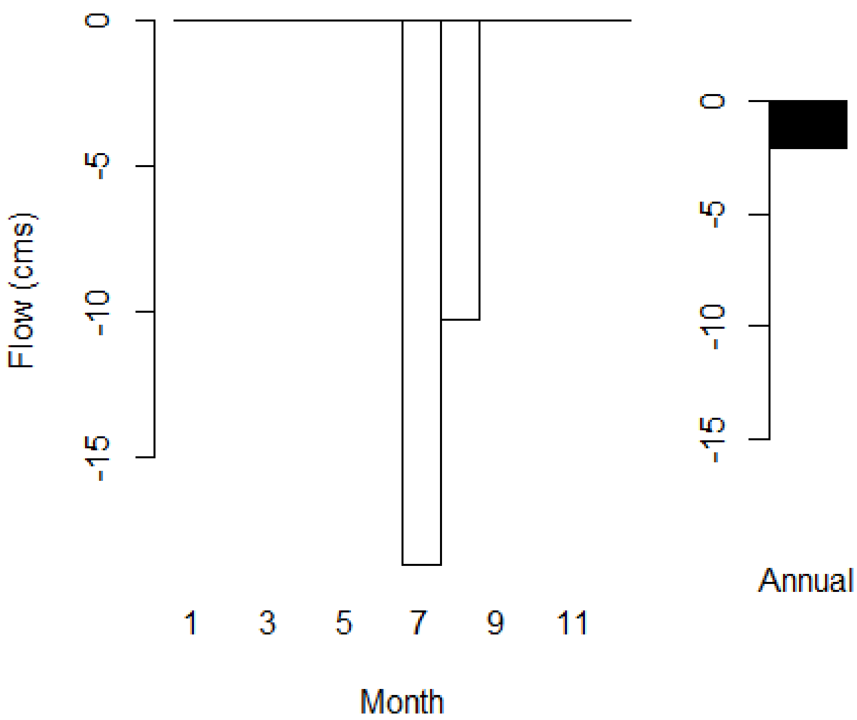
```
flow.trend.1988 <- kendallSeasonalTrendTest(oldft.median~month+year,data=flow
_mo[flow_mo$year>1987,],alternative="two.sided",ci.slope=TRUE,independant.obs
=FALSE)
flow.trend.1988

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =   -0.1494444
##                                  slope     =   -2.0574359
##                                  intercept = 7131.3541667
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = oldft.median
##                                  season = month
##                                  year   = year
##
## Data Source:                     flow_mo[flow_mo$year > 1987, ]
##
## Sample Sizes:                    1     =  25
##                                  2     =  25
##                                  3     =  25
##                                  4     =  25
##                                  5     =  25
##                                  6     =  25
##                                  7     =  25
##                                  8     =  25
##                                  9     =  25
##                                  10    =  25
##                                  11    =  25
```

```
##                                   12    =  25
##                                   Total = 300
##
## Test Statistics:                  Chi-Square (Het) =  3.927995
##                                   z (Trend)        = -3.620618
##
## Test Statistic Parameter:         df = 11
##
## P-values:                         Chi-Square (Het) = 0.9719761401
##                                   z (Trend)        = 0.0002939004
##
## Confidence Interval for:          slope
##
## Confidence Interval Method:       Gilbert's Modification of
##                                   Theil/Sen Method
##
## Confidence Interval Type:         two-sided
##
## Confidence Level:                 95%
##
## Confidence Interval:              LCL = -3.4492857
##                                   UCL = -0.9375639
```

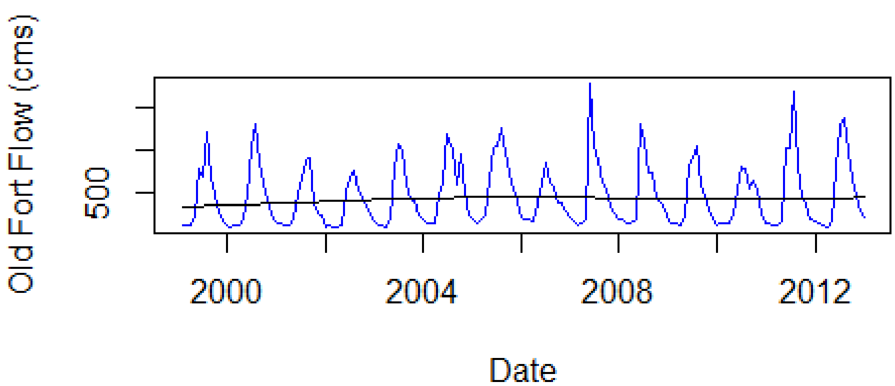
```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
flow.trend.1988 <- seastrends(flow.trend.1988,alternative="two.sided")
flow.trend.1988$seasonal.estimates
```

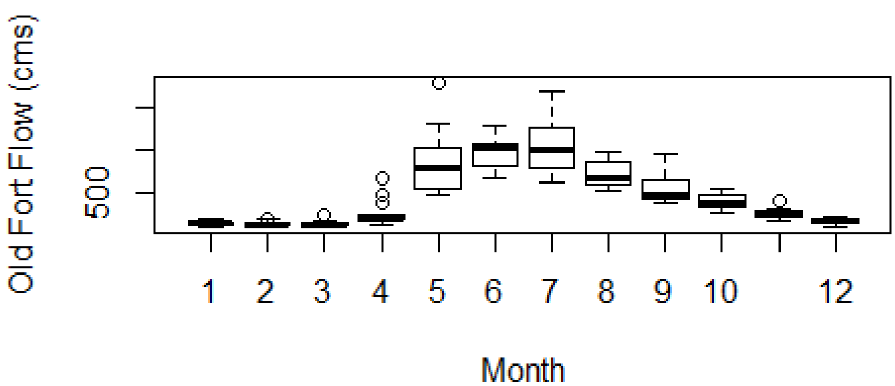
```
##            tau       slope  intercept           z          p
## 1  -0.01000000  -0.1090909   368.4818 -0.04672268 0.96273425
## 2  -0.07333333  -0.5890977  1315.0455 -0.49045433 0.62381244
## 3  -0.22666667  -1.3166667  2772.4333 -1.56478288 0.11763383
## 4  -0.20000000  -3.3119792  6855.9083 -1.37794313 0.16822085
## 5  -0.05333333  -5.1682353 11157.1706 -0.35032452 0.72609516
## 6  -0.14666667  -9.3043706 19653.3413 -1.00426364 0.31525156
## 7  -0.24666667 -18.6524671 38509.9342 -1.70491269 0.08821071
## 8  -0.25333333 -10.2866667 21317.6333 -1.75162262 0.07983872
## 9  -0.20000000  -7.7648496 16133.2492 -1.37794313 0.16822085
## 10 -0.22000000  -3.4925000  7406.8000 -1.51807294 0.12899601
## 11 -0.08666667  -0.6131250  1488.0500 -0.58387421 0.55930495
## 12 -0.07666667  -0.9419255  2071.4509 -0.51394949 0.60728730
```

```
# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas_flow(test.trend=flow.trend.1988)
```



Flow - 1999-2012





```
# Kruskal-Wallis test
kruskal.test(oldft.median~month,data=flow_mo[flow_mo$year>1998,])
```

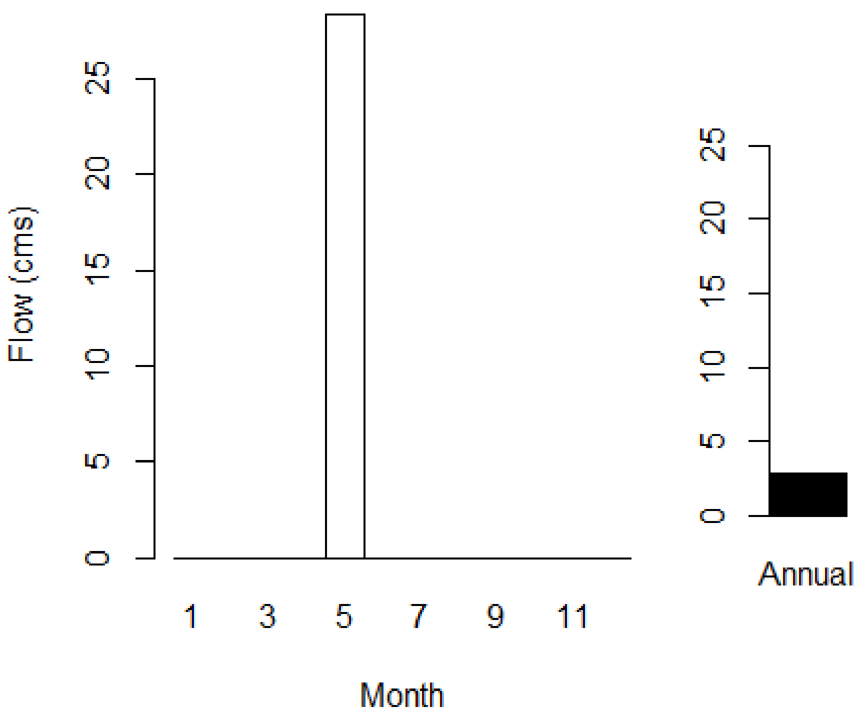
```
##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                       Kruskal-Wallis rank sum test
##
## Data:                            oldft.median by month
##
## Test Statistic:                  Kruskal-Wallis chi-squared = 146.9578
##
## Test Statistic Parameter:        df = 11
##
## P-value:                         6.229404e-26
```

```
### Trend tests

flow.trend.1999 <- kendallSeasonalTrendTest(oldft.median~month+year,data=flow
_mo[flow_mo$year>1998,],alternative="two.sided",ci.slope=TRUE,independant.obs
=FALSE)
flow.trend.1999
```

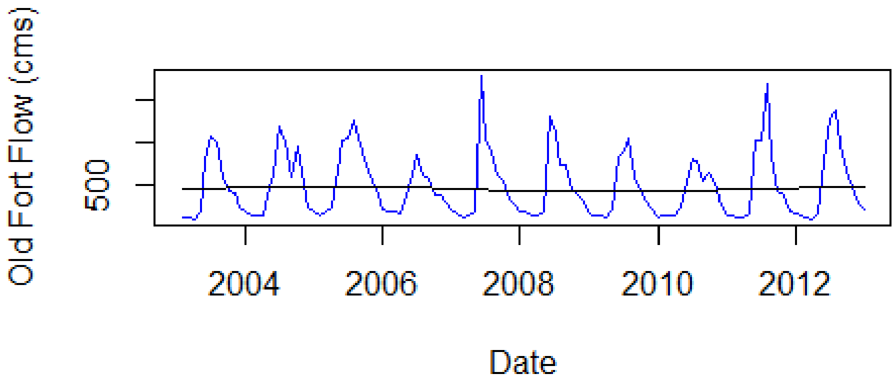
```
##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =     0.1630037
##                                  slope     =     2.8733333
##                                  intercept = -7492.2011364
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
```

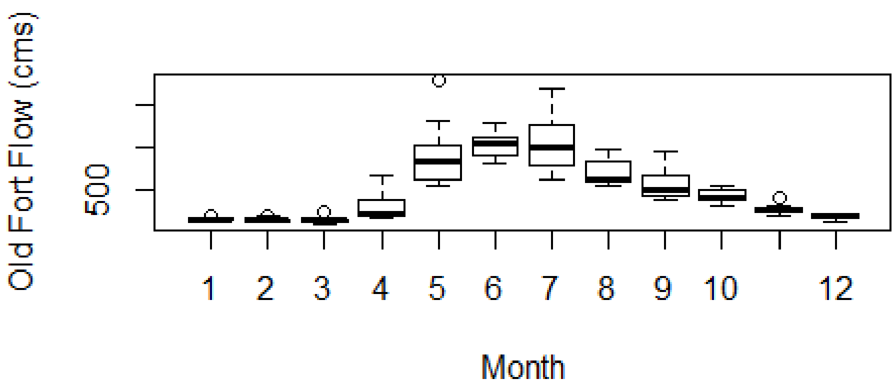
```
##                                  Thiel/Sen Estimator
##                       intercept:  Median of
##                                  Seasonal Estimates
##
## Data:                            y      = oldft.median
##                                  season = month
##                                  year   = year
##
## Data Source:                     flow_mo[flow_mo$year > 1998, ]
##
## Sample Sizes:                    1     =  14
##                                  2     =  14
##                                  3     =  14
##                                  4     =  14
##                                  5     =  14
##                                  6     =  14
##                                  7     =  14
##                                  8     =  14
##                                  9     =  14
##                                  10    =  14
##                                  11    =  14
##                                  12    =  14
##                                  Total = 168
##
## Test Statistics:                 Chi-Square (Het) = 5.357642
##                                  z (Trend)        = 2.797217
##
## Test Statistic Parameter:        df = 11
##
## P-values:                        Chi-Square (Het) = 0.912617361
##                                  z (Trend)        = 0.005154483
##
## Confidence Interval for:         slope
##
## Confidence Interval Method:      Gilbert's Modification of
##                                  Theil/Sen Method
##
## Confidence Interval Type:        two-sided
##
## Confidence Level:                95%
##
## Confidence Interval:             LCL = 1.266623
##                                  UCL = 5.325320

# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
flow.trend.1999 <- seastrends(flow.trend.1999,alternative="two.sided")
flow.trend.1999$seasonal.estimates
```

```
##            tau      slope   intercept          z          p
## 1   0.34065934  2.537500  -4941.1062  1.6423467 0.10051817
## 2   0.20879121  1.516667  -2908.1750  0.9854080 0.32442369
## 3   0.01098901  0.175000   -220.1125  0.0000000 1.00000000
## 4  -0.05494505 -1.490000   3189.2200 -0.2189796 0.82666597
## 5   0.36263736 28.380000 -56120.9400  1.7518365 0.07980193
## 6   0.25274725 20.635000 -40359.3925  1.2043876 0.22843981
## 7   0.03296703  5.716667 -10458.8750  0.1094898 0.91281403
## 8   0.03296703  5.355556 -10078.4167  0.1094898 0.91281403
## 9   0.07692308  3.504167  -6555.0062  0.3284693 0.74255682
## 10  0.16483516  7.412500 -14475.0687  0.7664285 0.44342140
## 11  0.23076923  3.986364  -7738.2523  1.0948978 0.27356141
## 12  0.29670330  3.700000  -7246.1500  1.4233671 0.15462975

# plot trend by season
source("func_plottrendbyseas.r")
plottrend_byseas_flow(test.trend=flow.trend.1999)
```



Flow - 2003-2012






```
# Kruskal-Wallis test
kruskal.test(oldft.median~month,data=flow_mo[flow_mo$year>2002,])

##
## Results of Hypothesis Test
## --------------------------
##
## Alternative Hypothesis:
##
## Test Name:                      Kruskal-Wallis rank sum test
##
## Data:                           oldft.median by month
##
## Test Statistic:                 Kruskal-Wallis chi-squared = 106.0759
##
## Test Statistic Parameter:       df = 11
##
## P-value:                        1.11019e-17
```

```
### Trend test

flow.trend.2003 <- kendallSeasonalTrendTest(oldft.median~month+year,data=flow
_mo[flow_mo$year>2002,],alternative="two.sided",ci.slope=TRUE,independant.obs
```

```
=FALSE)
flow.trend.2003

##
## Results of Hypothesis Test
## --------------------------
##
## Null Hypothesis:                 All 12 values of tau = 0
##
## Alternative Hypothesis:          The seasonal taus are not all equal
##                                  (Chi-Square Heterogeneity Test)
##                                  At least one seasonal tau != 0
##                                  and all non-zero tau's have the
##                                  same sign (z Trend Test)
##
## Test Name:                       Seasonal Kendall Test for Trend
##                                  (with continuity correction)
##
## Estimated Parameter(s):          tau       =   -0.1148148
##                                  slope     =   -2.6555556
##                                  intercept = 5671.8515625
##
## Estimation Method:               tau:        Weighted Average of
##                                              Seasonal Estimates
##                                  slope:      Hirsch et al.'s
##                                              Modification of
##                                              Thiel/Sen Estimator
##                                  intercept:  Median of
##                                              Seasonal Estimates
##
## Data:                            y      = oldft.median
##                                  season = month
##                                  year   = year
##
## Data Source:                     flow_mo[flow_mo$year > 2002, ]
##
## Sample Sizes:                    1     =  10
##                                  2     =  10
##                                  3     =  10
##                                  4     =  10
##                                  5     =  10
##                                  6     =  10
##                                  7     =  10
##                                  8     =  10
##                                  9     =  10
##                                  10    =  10
##                                  11    =  10
##                                  12    =  10
##                                  Total = 120
##
```

```
## Test Statistics:                  Chi-Square (Het) =  6.173333
##                                   z (Trend)        = -1.575013
##
## Test Statistic Parameter:         df = 11
##
## P-values:                         Chi-Square (Het) = 0.8615521
##                                   z (Trend)        = 0.1152534
##
## Confidence Interval for:          slope
##
## Confidence Interval Method:       Gilbert's Modification of
##                                   Theil/Sen Method
##
## Confidence Interval Type:         two-sided
##
## Confidence Level:                 95%
##
## Confidence Interval:              LCL = -6.1045441
##                                   UCL =  0.6454539
```

```
# Look at trend by season
# calculate p-value of trend by season
source("func_seastrends.r")
flow.trend.2003 <- seastrends(flow.trend.2003,alternative="two.sided")
flow.trend.2003$seasonal.estimates
```

```
##            tau      slope    intercept          z         p
## 1  -0.11111111  -0.360000    872.65000 -0.3577709 0.7205148
## 2  -0.20000000  -3.043750   6248.70313 -0.7155418 0.4742744
## 3  -0.37777778  -4.925000  10030.98750 -1.4310835 0.1524063
## 4  -0.42222222 -25.600000  51604.40000 -1.6099689 0.1074046
## 5  -0.02222222  -1.700000   4240.70000  0.0000000 1.0000000
## 6  -0.15555556  -6.337500  13769.45625 -0.5366563 0.5915050
## 7   0.20000000  38.625000 -76533.78750  0.7155418 0.4742744
## 8   0.15555556  14.300000 -28090.60000  0.5366563 0.5915050
## 9   0.02222222   0.287500    -70.70625  0.0000000 1.0000000
## 10 -0.20000000  -2.340000   5095.00000 -0.7155418 0.4742744
## 11 -0.15555556  -5.721429  11754.06786 -0.5366563 0.5915050
## 12 -0.11111111  -4.050000   8323.32500 -0.3577709 0.7205148
```