

Statistical Analysis of Trends in the Red River  
Over a 45 Year Period

by

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# Executive Summary

Statistical evaluation of trends in water quality over a 45-year period will be useful for assessing the effects of variation in precipitation in the Red River watershed and the impact that landscape change has on runoff water quality. The Red River discharges into Lake Winnipeg and the eutrophication of Lake Winnipeg is a research priority of Environment Canada and Manitoba Water Stewardship. This project is supported by the International Red River Board in response to a presentation made by the Canadian Co-Chair of its Aquatic Ecosystems Subcommittee.

Statistical trend analysis was performed on the following dissolved ion concentrations: Calcium, Sodium, Potassium, Magnesium, Sulphate, Chloride, total dissolved solids, and specific conductance, as available. Hydrometric stations used for analysis consisted of the Emerson water quality monitoring station, the South Floodway at St. Norbert monitoring station where data were comprised of the sum of the flow from the Ste. Agathe station and the Rat River hydrometric station. The flow data used for the Selkirk monitoring station was gathered from a hydrometric station nine km upstream at Lockport, Manitoba. Concentration data were made available from the Manitoba Water Stewardship and Environment Canada. Streamflow data were gathered from Environment Canada's Archived Hydrometric data website. Non-parametric and parametric methods were used on the original data and data weighted for flow volume.

The non-parametric methods used by Nancy Glozier, Environment Canada were run with WQSTAT v.1.56 and consist of defining hydrologic seasons from concentrations, testing for seasonality using the Kruskal-Wallis test and applying either the

Mann-Kendall or Seasonal Mann-Kendall test for a trend. Seasonality is evident in all water quality parameters, where the minimum data size was met, and in turn the Seasonal Mann-Kendall test was used to test for trend. The Seasonal Mann-Kendall test found significant trends for most constituents except dissolved Chloride at the Emerson station and specific conductance at both the South Floodway and Selkirk monitoring stations.

Non-parametric methods do not rely on known probability distributions, in contrast to parametric statistics. There are advantages and drawbacks to both methods as they were used in comparison for trend analysis. Advantages of the Seasonal Mann-Kendall test are: it is easy to compute; has few underlying assumptions and results are not affected by data values lying far beyond the majority of the data (outliers). Disadvantages are: this method assumes a single linear trend; seasons must be defined; flow adjustments must be done separately and they may not be as powerful in detecting trends.

Parametric methods were run using QWTREND, developed by Aldo Vecchia, United States Geological Survey, and was used for constituents with enough data to satisfy the requirements of the program. Parametric methods using QWTREND also come with their own advantages and disadvantages. Advantages are: they can be used to model more than just a single linear trend; trends can be explained by magnitude and direction; also with livestock or farming data; streamflow and concentration can be modeled together and QWTREND uses the full power of statistical theories. The drawbacks to these methods are: they are computation intensive; require care in verifying assumptions and require more data than non-parametric methods.

A difference in methods that should be noted is that the non-parametric methods compute trends on a linear scale while QWTREND computes log-linear slopes. Both methods were used to analyze the water quality constituents and yielded fairly similar conclusions. Trends in dissolved calcium were highly significant using the non-parametric methods however, significance could not be determined using the parametric method. Trends in dissolved sodium and potassium produced a highly

significant positive trend with the non-parametric and parametric methods, total dissolved solids and specific conductance were also highly significant using both methods at the Emerson monitoring station. Dissolved Magnesium produced a significant trend using non-parametrics however, did not meet the all the requirements of the parametric method. There is approximately ten years of missing data from 1965-1975 thus a trend was fitted for the data from 1975 to 2007 and yielded significant results with both the non-parametric and parametric methods. Dissolved sulphate produced a highly significant trend at the Emerson station using non-parametric methods, but significance using parametric methods could not be determined by a single linear trend. Dissolved Chloride showed an insignificant trend using non-parametric methods, while the parametric methods produced a significant trend.

In regards to the South Floodway and Selkirk monitoring stations the only constituent with a complete data set that meet the requirements of QWTREND was specific conductance. This was where the remaining inconsistencies were exhibited between the two statistical methods. Using the non-parametric methods the trends in this constituent were insignificant however, once the parametric methods were applied to these constituents the trends at both stations were highly significant. In such situations it is uncertain whether the non-parametric methods are powerful enough at finding trends.

There are certain recommendations that can be made in order to achieve the most accurate results possible. Due to the scarcity of the data from the provincially monitored stations it should be said that in order to have accurate results and interpretation, a statistically sound sampling scheme should be implemented. If the parametric methods are chosen QWTREND will compute sampling designs in order to combat this problem and will allow almost 80% of trends to be detected when they exist. If a comparison is to be made between the original data and data weighted for flow, the non-parametric approach can deal with this and then compare results between the two. When data is adjusted for flow, one is able to see the magnitude and significance of a trend that is not explained by streamflow.



Using ancillary data, data obtained from agriculture around the basin of study, the significance and magnitude of trends can be better explained. Not all trends can be explained by a simple linear model, the parametric methods allow for fitting more than just a single linear trend. For example, Dissolved Sulphate is one such constituent that would best be modeled with two monotonic trends in this case.

The parametric approach can test a wide variety of trends other than linear and is more powerful at detecting trends. Using QWTREND with a properly devised sampling scheme and the inclusion of ancillary variables will be the best method of explaining the statistical significance of trends in water quality.

# Acknowledgments

There have been many contributions by various individuals that led to the completion of this project. I would like to thank Drs. Brad Johnson (principal investigator), John Brewster (co-investigator) and Liqun Wang (co-investigator) of the Department of Statistics, University of Manitoba; Dr. Gordon Goldsborough (co-investigator), Canadian representative, International Red River Board, Department of Biological Sciences, University of Manitoba; and Dr. Brian Parker, Aquatic Ecosystems Scientist, Environment Canada. Also, a very special and sincere thank-you goes out to Aldo Vecchia of the United States Geological Survey for all his invaluable support and assistance and to Nicole Armstrong of the Manitoba Water Stewardship for all her help with the provincial data. Thank you to Dr. David Donald for serving as the scientific authority of this project and of course a final thank you to the International Joint Commission for funding this project.

# Chapter 1

## Introduction

The Red River of the North is formed by the confluence of the Bois de Sioux and Otter Tail Rivers in the United States. It flows northward through the Red River Valley and forms the border between the states of Minnesota and North Dakota before continuing into Manitoba, Canada, and finally discharging into Lake Winnipeg (Figure 1.1). Along its path, the Red River flows through Greater Grand Forks and Fargo, in the United States, and through Winnipeg in Canada. The Canadian portion of the Red River is about 249 km long, while the US portion is approximately 636 km in length. The river falls 70 m on its trip to Lake Winnipeg where it spreads into the vast deltaic wetland known as Netley Marsh. The entire Red River Basin encompasses 287,500 square kilometers of rich agricultural lands, forests, wetlands, and prairies and contains numerous lakes.

Statistical evaluation of trends in water quality data over the 45-year period of record is useful for assessing effects of the variation in precipitation in the Red River and the impact that landscape runoff has on water quality. Changes in the Red River water quality have a direct bearing on Lake Winnipeg into which it discharges; the eutrophication of Lake Winnipeg is a research priority for Environment Canada and the Manitoba Water Stewardship.

This report, which focuses on three water quality monitoring stations along the Red River, presents results of trend analysis using parametric methods devel-

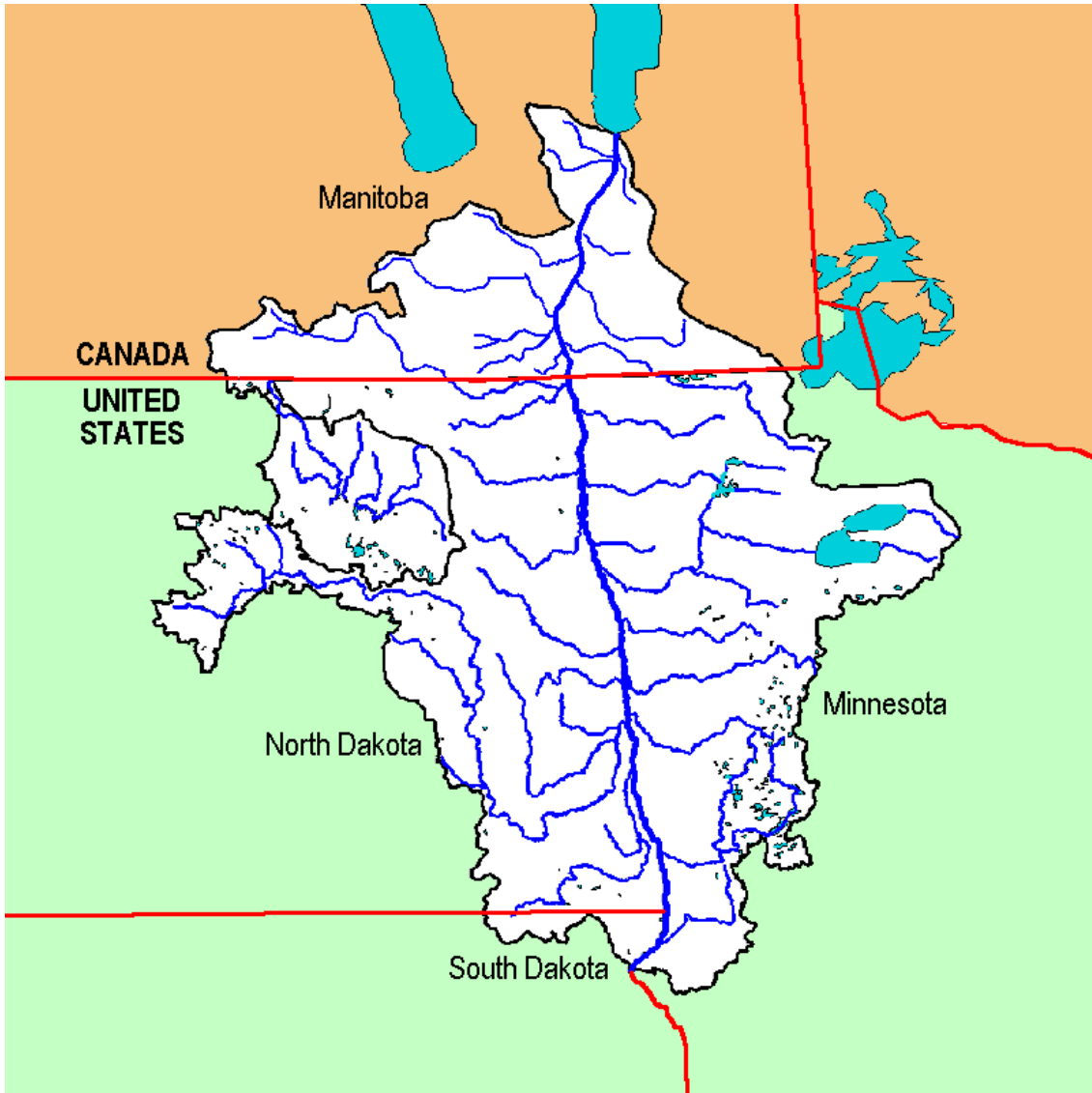


Figure 1.1: The Red River Basin

oped by Aldo Vecchia (United States Geological Survey)(Vecchia 2000, 2003, 2005) and non-parametric methods such as those used by Nancy Glozier (Environment Canada)(Glozier et. al. 2004). Comparisons between methods are made and recommendations are presented. The results presented in this report are based on streamflow data from January 1958 through to December 2007 and on concentration data from January 1963 to December 2007. The constituents for the report include six dissolved major ions (calcium, sodium, potassium, magnesium, sulphate, and chloride), total dissolved solids and specific conductance. The constituents were evaluated for three monitoring stations along the Red River: the Red River at Emerson station; the south gate of the floodway near St. Norbert; and the Selkirk water quality monitoring station. Constituents were evaluated on the basis of availability. The streamflow data were obtained from the Water Survey of Canada-Archived Hydrometric Data website (<http://www.wsc.ec.gc.ca/hydat/H2O>), federal concentration data were obtained through Environment Canada and provincial concentration data were obtained from Manitoba Water Stewardship, Province of Manitoba.

## **1.1 Description of the Red River**

From about 12,500 years ago to 7,500 years ago, pro-glacial Lake Agassiz covered much of what is known today as western Minnesota, eastern North Dakota, southern Manitoba, and southwestern Ontario. As a result of deglaciation Lake Agassiz virtually disappeared, leaving few remnants, one of which is Lake Winnipeg. Lake Agassiz left behind a fertile, flat plain that ultimately drains to the Hudson Bay. The Red River meanders north along this plain to Lake Winnipeg. A difference in elevation occurs along route, at its starting point the elevation is 287 meters above mean sea level while the elevation at Lake Winnipeg is 218 meters. above mean sea level. The Red River, being located in a flat plain, also has a shallow river channel meandering northward 636 km to the Canadian border. Due to the northerly flow of the river, the flatness of the basin, the shallow river channel and the timing of the spring thaw and snowmelt severe flooding can occur. Four major

floods have occurred since Europeans settled in the area, in 1826, 1950, 1997, and 2009 but it is believed there have been many other floods of equal or larger size prior to European settlement. The climate of the Red River of the North basin is continental and ranges from dry sub-humid in the western part of the basin to sub-humid in the eastern part (Stoner, et al., 1993). Mean annual precipitation for the Red River basin ranges from about 43 cm in the extreme western part of the basin to about 66 cm in the extreme eastern part of the basin. Precipitation across the basin generally increases from southwest to northeast(Stoner, et al., 1993). Actual evapotranspiration from the basin also generally increases from southwest to northeast but at a lesser rate than precipitation. Thus, mean annual runoff from the basin also increases in that direction. The Red River of the North receives 75 percent of its annual flow from eastern tributaries. Concentrations of dissolved chemical constituents in surface waters are normally low during spring runoff and after thunderstorms. The Red River of the North generally has a dissolved solids concentration less than 600 mg/l with mean values near 406 milligrams per litre at the Canadian border near Emerson, Manitoba. Calcium and magnesium are the principal cations and bicarbonate is the principal anion along most of the reach of the Red River of the North. Dissolved solids concentrations generally are lower in the eastern tributaries than in the tributaries draining the western part of the basin. As the river flows further downstream, dissolved solids concentration increases, and magnesium and sulphate are predominant ions. Nitrogen and phosphorous in surface runoff from cropland fertilizers, manure and domestic sewage can contribute nutrients to lakes, reservoirs, and streams.

## Chapter 2

# Streamflow Data and Concentration Data Used for Water-Quality Trend Analysis

The three water quality monitoring stations selected for this analysis are depicted in Figure 2.1. Selected station characteristics are given in Table 2.1. Contributing drainage areas for the stations range from 287,000 square kilometers at the Selkirk monitoring station, to 102,000 square kilometers at the Emerson monitoring station. For the Red River at Emerson, Manitoba, monitoring station the data that will be used for analysis was collected by the Government of Canada. At the remaining two stations, South entrance of the floodway near St. Norbert and Selkirk, data was collected by the provincial government. Both the province and federal government employ different sampling collection methods. The constituents used for analysis are given in Table 2.2 and analysis of constituents are based on availability and sample size which are outlined in Table 2.3.

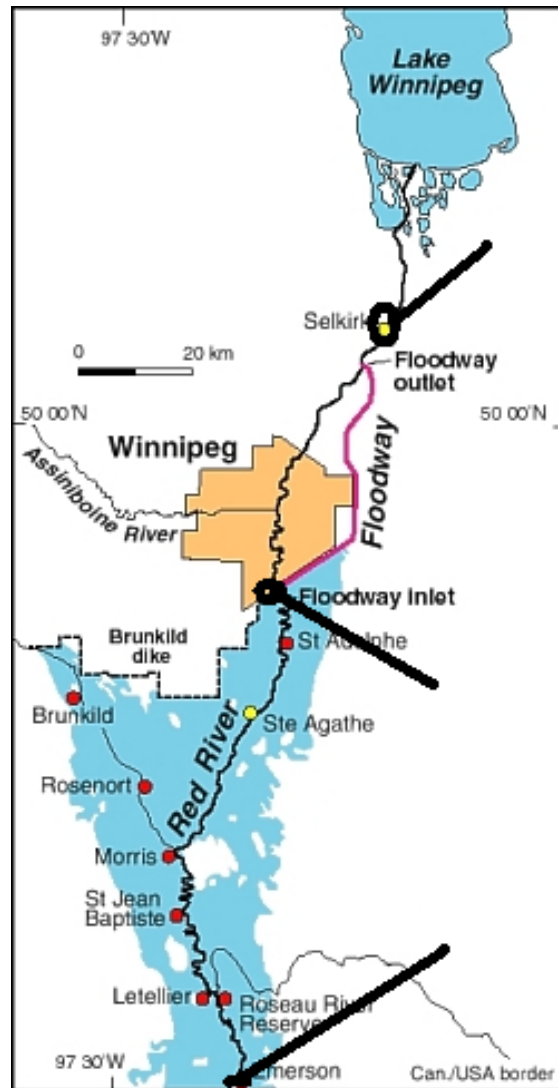


Figure 2.1: Map of the Red River and the central portion of the Red River Valley, Manitoba, depicting the monitoring station locations: (heading upstream) Emerson Station, South Floodway at St. Norbert Stations and Selkirk Station



Table 2.1: Selected characteristics of water quality monitoring stations for trend analysis.

Station #	Name (Station ID)	Drainage Area (sq. km)	Latitude	Longitude
1.	Red River of the North at Emerson, Manitoba (05OC001)	102,000	49° 0' 18" N	97° 12' 54" W
2.	Red River of the North Floodway near St. Norbert (05OC017)	119,450	49° 45' 24" N	97° 7' 36" W
3.	Red River of the North at Selkirk (05OJ005)	287,000	50° 8' 30" N	96° 52' 5" W

Table 2.2: Major ions & dissolved solids used for water quality trend analysis.

Constituent	Unit
Calcium, dissolved	Milligrams per litre (mg/l)
Sodium, dissolved	Milligrams per litre (mg/l)
Potassium, dissolved	Milligrams per litre (mg/l)
Magnesium, dissolved	Milligrams per litre (mg/l)
Sulphate, dissolved	Milligrams per litre (mg/l)
Chloride, dissolved	Milligrams per litre (mg/l)
Total dissolved solids	Milligrams per litre (mg/l)
Specific Conductance	Microsiemens per centimeter <sup>2</sup> (USIE/cm <sup>2</sup> )

## 2.1 Methodologies

Characteristics that complicate the analysis of water quality time series are non-normal distributions, seasonality, flow effects, missing values, values falling below detection levels, and serial correlation (Hirsch, et al., 1982). Three techniques have been used in order to deal with the above complications. The first technique is a non-parametric test for trend known as the Seasonal Mann-Kendall test. It is robust in comparison to the parametric alternatives, however neither of these are considered an exact test in the presence of serial correlation. The second procedure introduces an estimator of trend magnitude known as the Sen slope estimator. The third procedure tests for changes over time in the relationship between constituent concentration and flow, avoiding the problem of identifying the trends in water quality that are due to droughts or floods for example. Much research has been conducted in order to study the trends in water quality. Most of these studies employed various parametric and non-parametric analytical techniques. The Strymon River in Greece was the subject of such a study (Antonopoulus et al., 2001), the objective of this study was to provide a system-wide synopsis of water quality, monitor long-range trends in selected parameters, detect actual or potential water quality problems and to enforce standards. Previous studies proved that water quality data do not usually follow convenient probability distributions and that streamflow data exhibit hydrological persistence and seasonal variation. There are suggestions that, for water quality variables that are highly dependent on streamflow, the confounding effects of discharge variations be removed by analyzing the residuals from the discharge-concentration relationship for trend rather than the raw data. In a technical report about the Red River a lattice model was constructed (Fritz and Zhang, 2006) and correlation was analyzed to determine the strength of interactions between the nearest neighbour nodes. A scaling hypothesis that acts as a modifier to the Mann-Kendall test was introduced by Hamed (2008). The basic hypothesis of scaling is that the data exhibit invariance at any scale greater than annual, so if the results of the Mann-Kendall test show an observed trend is significant, we proceed to check the effect of scaling. Nonparametric methods (Glozier et al., 2004), consist

of testing for seasonality. If it yields a significant result, the Seasonal Mann-Kendall test is applied, otherwise the Mann-Kendall test is conducted. Parametric methods can model both flow and concentration data jointly (Vecchia, 2000) and are good not only for exploratory analysis but explanatory analyses as well.

## 2.2 Analysis Techniques

The Government of Canada and the Province of Manitoba used different sampling protocols. For samples collected at the Emerson stations a 2 litre low density polyethylene bottle is mounted onto a stainless steel sampling iron. This method is used to prevent contamination of the water samples with metals. The bottle is then lowered into the river, partially filled and rinsed two times in order to remove possible contaminants from inside the bottle. On the third drop the sampling iron and bottle are lowered to the bottom of the river and retrieved. This collects an integrated sample of water from the water column. The reason this is done is because water chemistry can vary widely within different levels of the river. Upon retrieval a subsample is removed and sent to the National Laboratory for Environmental Testing (NLET) in Burlington, Ontario for cation and anion analysis. A portion of this sample is then filtered to remove such particulates as algae, bacteria and sediments. Analysis is conducted on the dissolved constituents because extractable ions are not efficient to analyze. Filtering methods differ between the provincial and the federal governments. The Government of Canada filters shortly after collection, while the province filters on return to the lab. This can be approximately 8-10 hours or more after the sample is collected. Filtering of the water sample is important because it removes all of the bacteria and algae from the samples. If the samples are not filtered, then cells can grow, take nutrients out of the water and excrete waste products. This may affect analytical results especially for dissolved nutrients. In order to minimize the growth of cells samples are kept just above freezing.

The provincial water samples collected at the St. Norbert and Selkirk stations are collected using either a 2.0 litre Nalgene bottle with 30 m of rope or a 1.0 litre

opaque laboratory bottle on the end of a 3 m reaching pole. Both the Nalgene and laboratory bottles are rinsed three times prior to filling, and are used to transfer water to the sample bottles. Sample bottles are filled and then submitted to Cantest Laboratories for analysis of nutrients, metals, conductivity, total dissolved solids, pesticides, dissolved oxygen, major ions and pH. Prior to April 2001, all water samples were submitted to EnviroTest Laboratories for analysis of these parameters (Hughes C., 2009). All data analyses were done as per standard methods for the examination of water (Eaton et al., 2005). Currently the provincial water quality section does not assess dissolved calcium, dissolved sodium, dissolved potassium or dissolved magnesium.

Table 2.3: Sample size of stations and constituents used for water quality trend analysis

Station #	1960–2007	1960–1965	1966–1970	1971–1975	1976–1980	1981–1985	1986–1990	1991–1995	1996–2000	2001–2007
Calcium, dissolved (mg/l)										
1.	912	232	146	68	70	51	70	61	72	142
2.	4	0	0	0	0	0	0	0	4	0
3.	9	0	0	0	0	0	0	0	9	0
Sodium, dissolved (mg/l)										
1.	900	232	143	68	71	41	70	61	72	142
2.	4	0	0	0	0	0	0	0	4	0
3.	9	0	0	0	0	0	0	0	9	0
Potassium, dissolved (mg/l)										
1.	900	224	141	68	71	51	70	61	72	142
2.	4	0	0	0	0	0	0	0	4	0
3.	9	0	0	0	0	0	0	0	9	0
Magnesium, dissolved (mg/l)										
1.	727	222	27	12	71	50	70	61	72	142
2.	4	0	0	0	0	0	0	0	4	0
3.	9	0	0	0	0	0	0	0	9	0
Sulphate, dissolved (mg/l)										
1.	899	224	135	67	71	58	70	60	72	142
2.	42	0	0	0	0	0	0	0	15	27
3.	140	0	0	0	0	0	0	0	55	85
Chloride, dissolved (mg/l)										
1.	919	239	146	67	66	57	70	60	72	142
2.	42	0	0	0	0	0	0	1	14	27
3.	140	0	0	0	0	0	0	7	48	85
Total dissolved solids (mg/l)										
1.	376	0	0	0	12	33	71	62	64	134
2.	74	0	0	0	0	2	60	12	0	0
3.	159	0	6	54	24	2	60	13	0	0
Specific Conductance (USIE/cm <sup>2</sup> )										
1.	959	234	146	68	70	54	71	92	80	144
2.	247	0	0	0	33	36	56	62	57	3
3.	270	0	0	0	33	36	56	63	79	3

## Chapter 3

# Non-Parametric Methods used for Water Quality Trend Analysis

A modified form of Kendall's  $\tau$  (Kendall, 1938, 1975) is used as a test for trend (Hirsch, et al., 1982). This modification is called the seasonal Kendall test for trend. It is robust in comparison to the parametric alternatives, since non-parametric methods do not rely on known probability distributions. It may also be less powerful when the assumptions of the parametric methods are met. An estimate of trend magnitude that is closely related to the seasonal Kendall test procedure is known as the seasonal Kendall slope estimator or Sen's slope estimator (Sen, 1968). In cases where concentrations of 'less than detection limit' were reported by the laboratories, values equal to half the detection limit are used for statistical calculation and graphical representation (Gilbert, 1987). Key questions in water quality monitoring are: Does the water chemistry change over time?; Can the observed changes be attributed to natural patterns?; And, could the observed changes in water chemistry impact the biological integrity of the aquatic ecosystem? Seasonal patterns, which occur yearly regardless of longer term trends, are normally examined as an aid to understanding the natural patterns of chemical concentrations. Seasons are defined by reviewing monthly frequency graphs for chemical patterns (Figure 3.1). The time periods of the season may be unequal in length but they represent distinct hy-

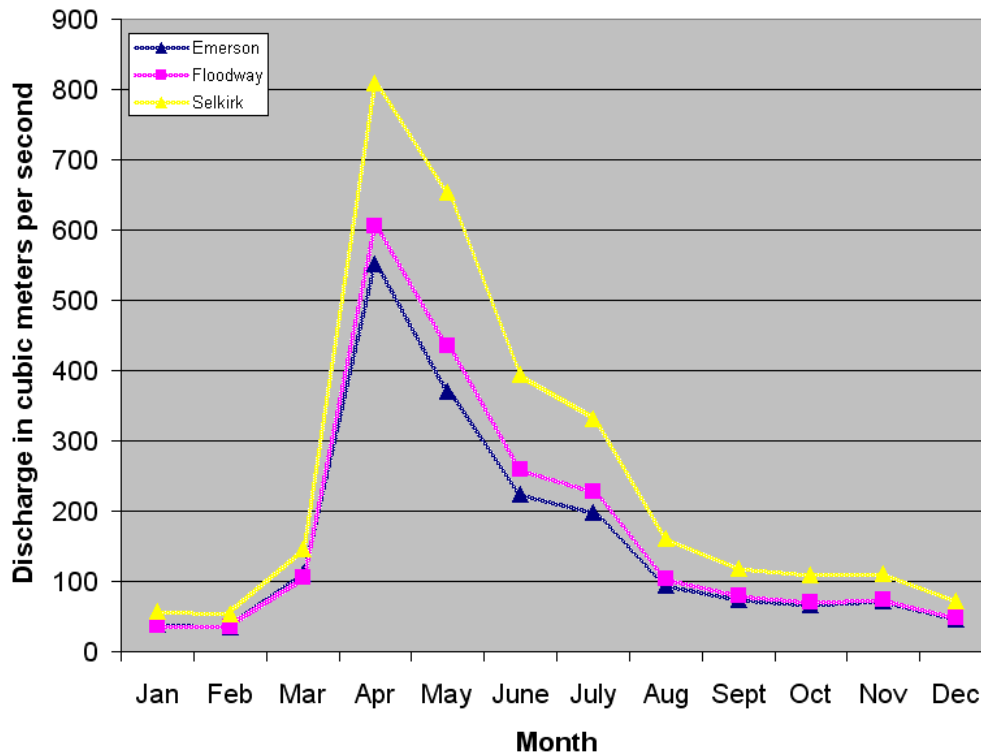


Figure 3.1: Mean monthly streamflow (1960-2007) at each monitoring station in order to define hydrologic seasons

drological periods. Hydrologic seasons generally do not define periods of similarity in conditions, like “summer” or “winter” do for climate, but rather directional tendencies (Glozier, et al., 2004). The yearly streamflow patterns were similar within the three stations with all sites exhibiting peak discharge between March and June. Based on these patterns Table 3.1 represents the seasons defined for the analysis of seasonality. Clearly these time periods are dissimilar in length but represent periods which are distinct hydrologically.

In order to get a graphical representation of the data for each constituent we can examine boxplots of the concentrations. A boxplot is a five-number summary of the data depicting the minimum and maximum values of the data, the first and third quartiles and the median, or middle number of the data.

Table 3.1: Defined Seasons.

Season	Months	Description
Spring	February - March	rising limb of hydrograph
Summer	April - May	peak streamflow
Fall	June - August	falling limb of hydrograph
Winter	September - January	low flow, ice-cover period

Concentrations of dissolved calcium (Figure 3.2) are quite similar between the three stations however data were sparse at the south floodway near St. Norbert and the Selkirk monitoring stations. At the Emerson monitoring station the boxplot is symmetric and takes the appearance of an approximately normal distribution. Concentrations of dissolved sodium (see appendix Figure A.2) appear to be extremely skewed to the right with a few outlying observations with a maximum value at 305.0 mg/l and high values of dissolved sodium occurring from November 1988 through January 1989. The median values of the concentrations of dissolved potassium and magnesium (see appendix Figures A.3 and A.4) are similar between stations and follow an approximately normal distribution at the Emerson station. There is more data for the analysis of the concentrations of dissolved sulphate at the south floodway near St. Norbert and Selkirk monitoring stations (see appendix Figure A.5) than the previous constituents. The Emerson station exhibits the greatest degree of variability amongst the three stations possessing values from 4.0 mg/l to 1050.0 mg./l of dissolved sulphate.

Concentrations of dissolved calcium have median concentrations between 56.3 mg/l and 73.0 mg/l and range from 4.60 mg/l to 130.0 mg/l with few evident outliers. The median and mean concentration of dissolved sodium are similar amongst the stations, however the Emerson station exhibit values ranging from 1.70 mg/l to 305.0 mg/l, this can be indicative of seasonal change and change in flow rate. The medians and means for the concentrations of dissolved sulphate are much higher at the Selkirk monitoring station compared with the Emerson and south floodway near St. Norbert stations. Total dissolved solids which are calculated by summing the



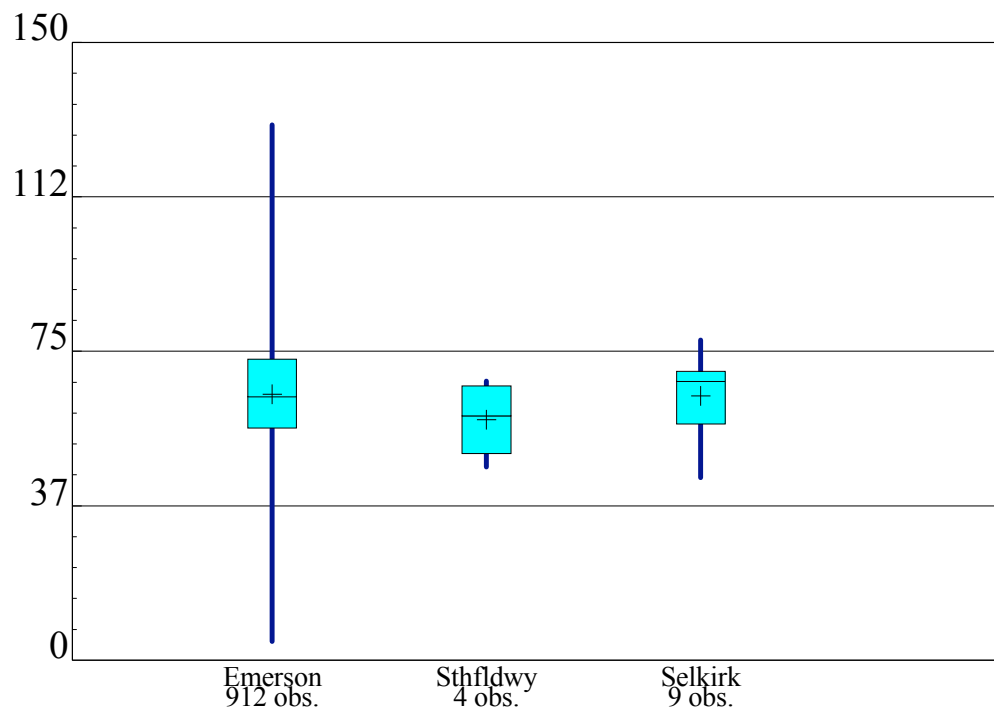


Figure 3.2: Boxplot of dissolved calcium (mg/l) depicting the five number summary of the constituent

Table 3.2: Five Number Summaries for Selected Constituents

Station #	Min.	First Quartile	Median	Third Quartile	Max.	Mean	Std. Dev.
Calcium, dissolved (mg/l)							
1.	4.60	56.30	63.90	72.98	130.00	64.48	13.53
2.	46.90	48.53	59.25	67.13	67.80	58.30	9.84
3.	44.30	57.35	67.70	70.00	77.70	64.09	9.85
Sodium, dissolved (mg/l)							
1.	1.70	25.00	34.00	47.00	305.00	42.43	32.64
2.	20.40	23.78	34.10	34.75	34.90	30.88	7.00
3.	20.10	21.75	45.40	53.25	57.20	39.72	15.04
Potassium, dissolved (mg/l)							
1.	0.38	5.48	6.40	7.54	18.40	6.59	1.82
2.	4.70	4.85	5.55	6.48	6.70	5.63	0.85
3.	6.80	7.15	7.60	8.75	8.90	7.90	0.84
Magnesium, dissolved (mg/l)							
1.	3.30	27.00	31.25	36.68	61.00	31.90	8.56
2.	19.40	21.08	27.50	32.65	33.90	27.08	6.05
3.	18.60	27.95	31.50	35.85	40.40	31.30	6.44
Sulphate, dissolved (mg/l)							
1.	4.00	69.60	92.20	119.00	1050.00	99.04	55.78
2.	40.00	76.13	94.50	118.50	220.00	98.86	37.67
3.	32.00	100.00	128.50	160.00	240.00	127.81	44.71
Chloride, dissolved (mg/l)							
1.	0.10	21.70	31.00	50.00	473.00	46.33	51.09
2.	8.40	16.75	25.10	36.30	160.00	32.99	28.98
3.	6.10	20.00	32.20	42.40	120.00	35.39	22.08
Total Dissolved Solids (mg/l)							
1.	0.00	375.00	447.50	527.40	1289.00	459.46	140.10
2.	210.00	425.00	550.00	670.00	1140.00	564.66	200.74
3.	240.00	450.00	510.00	600.00	1500.00	535.44	152.03
Specific Conductance (USIE/cm <sup>2</sup> )							
1.	278.00	585.00	676.00	806.00	2253.00	716.79	230.49
2.	7.70	592.00	700.00	821.00	1875.00	741.06	261.86
3.	157.00	621.80	756.50	867.00	1497.00	757.30	223.68

concentrations of major anions and cations, have similar means; however, the south floodway at St. Norbert station exhibits a high degree of variability. A comparison of specific conductance shows virtually identical spatial patterns. Specific conductance increases slightly from the Emerson to Selkirk water monitoring stations. Specific conductance measures the amount of dissolved ions in the water, when there is an increase of base flow relative to run off, the specific conductance increases. Specific conductivity is lowest in the spring season when the snow melts and measurements were taken on the field samples as opposed to laboratory samples. The summary statistics for constituents are shown in Table 3.2.

When testing for seasonality; the existence of seasonal patterns in water chemistry was analyzed using the non-parametric Kruskal-Wallis test (Conover, 1999). The null hypothesis for this test was that the populations for each season have the same median; versus the alternative hypothesis that not all medians are the same. In order to test for trends in water quality parameters, the Mann-Kendall test for trend and Sen's slope (Hirsch, et al.,1982) was implemented to help evaluate the correlation of selected constituent concentrations with time. This test does not depend on the assumption of a particular parametric form for the underlying distribution and hence is a "non-parametric" method. WQSTAT PLUS v.1.56, (NIC Environmental Division developed with assistance from Colorado State University faculty), is the program used for the non-parametric methods and there are certain data requirements for this program:

1. The application of the Kruskal-Wallis test for seasonality requires a minimum sample size of four data points in each "hydrologic season"
2. For the trend analysis statistics, (Sen's Slope and the Mann-Kendall Test)if there are fewer than 41 data points an *exact test procedure* is performed
3. If 41 or more data points are available, the normal approximation test is used by this program (equivalently a Chi-Square test)
4. If the Seasonal Mann-Kendall test is required, that test requires a minimum sample size of four data points in each "hydrologic season"

The Kruskal-Wallis test statistic, H is;

$$H = \left[ \frac{12}{N(N+1)} \sum_{i=1}^n \frac{R_i^2}{N_i} \right] - 3(N+1),$$

where the  $k$  seasons are first ordered and assigned ranks ( $R_i$ ) and

$R_i$  is the sum of the ranks of the  $i$ th station;

$N_i$  is the number of observations in the  $i$ th station;

$N$  is the total number of observations; and

$k$  is the number of seasons;

This test statistic has an approximate Chi-Square distribution on  $k - 1$  degrees of freedom.

Using the seasons defined in Table 3.1, the following table indicates the constituents exhibiting seasonality at the 5% level of significance. A significant result indicates at least one season has a significantly different median concentration than one or more other seasons. The  $p$ -value is approximately the probability of a chi-squared random variable with  $k - 1$  degrees of freedom exceeding the observed value of H. At certain stations, there was insufficient data for some constituents and that is denoted by “n/a”.

Seasonality is evident in all water quality parameters tested (shown in Table 3.3) and most parameters demonstrate similar seasonal patterns across all sites. Two basic seasonality patterns emerged; dissolved calcium, sodium, magnesium, total dissolved solids and specific conductance exhibit peak concentrations in the winter months. This follows an inverse pattern to the hydrograph, where maximum concentrations occur during the low flow winter months. Major ions derived from geological weathering and ground water become more concentrated as flows decrease in winter and ground water comprises a higher proportion of flow (Glozier, et al., 2004). Parameters exhibiting the winter pattern tend to be correlated positively

Table 3.3: Kruskal-Wallis test for seasonality results.

Station	Seasonality	<i>p</i> -value	Seasonality	<i>p</i> -value
	Calcium, Dissolved (mg/l)		Sulphate, Dissolved (mg/l)	
1.	yes	< <u>0.005</u>	yes	< <u>0.005</u>
2.	n/a		n/a	
3.	n/a		yes	< <u>0.005</u>
	Sodium, Dissolved (mg/l)		Chloride, Dissolved (mg/l)	
1.	yes	< <u>0.005</u>	yes	< <u>0.005</u>
2.	n/a		n/a	
3.	n/a		yes	< <u>0.005</u>
	Potassium, Dissolved (mg/l)		Total Dissolved Solids (mg/l)	
1.	yes	< <u>0.005</u>	yes	< <u>0.005</u>
2.	n/a		yes	< <u>0.005</u>
3.	n/a		yes	< <u>0.005</u>
	Magnesium, Dissolved (mg/l)		Specific Conductance (USIE/cm <sup>2</sup> )	
1.	yes	< <u>0.005</u>	yes	< <u>0.005</u>
2.	n/a		yes	< <u>0.005</u>
3.	n/a		yes	< <u>0.005</u>

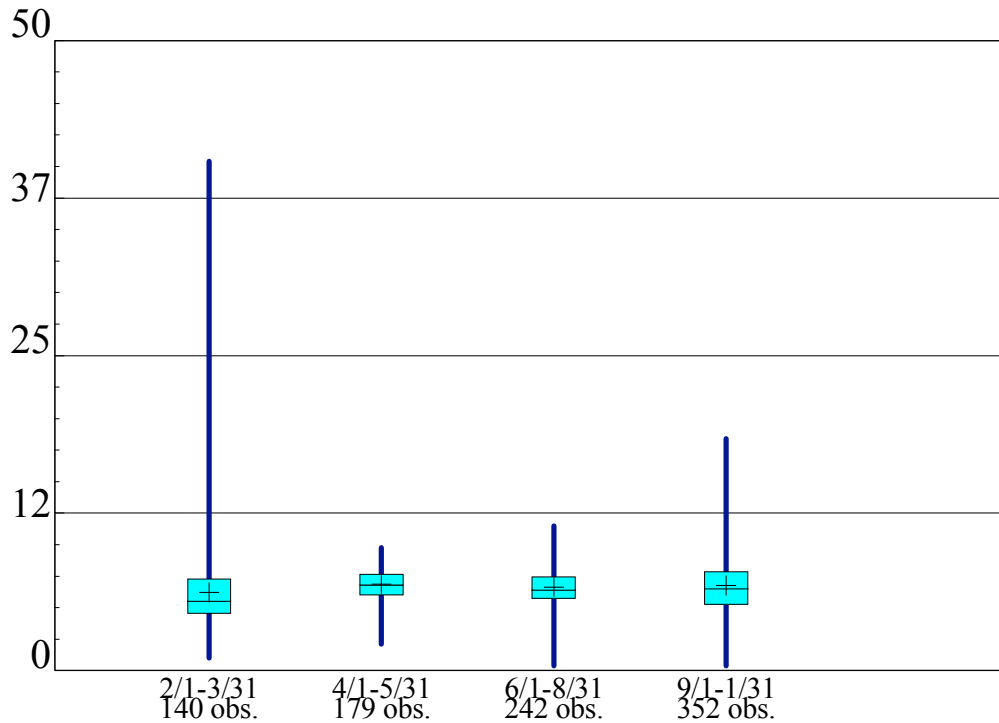


Figure 3.3: Boxplots of Dissolved Potassium (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations

with each other and inversely with discharge. The second typical seasonal pattern observed had maximum concentrations occurring in conjunction with high summer/fall discharge levels. The parameter demonstrating this pattern is dissolved sulphate. Significant seasonality was detected for dissolved potassium, it is low in Feb/Mar but slightly higher in other seasons (Figure 3.3). The seasonality patterns of the remaining constituents can be seen in appendix Figures A.9 to A.16.

In order to test for trend the seasonal Mann-Kendall test and Sen's slope was used for the stations that exhibited seasonality. The null hypothesis for this test is that no temporal trend exists versus the alternate hypothesis that a significant upward (or downward) temporal trend exists. The direction of the alternative hypothesis (upward/downward) is specified and hence this is a one-sided test. Sen's slope estimator procedure is a simple nonparametric procedure developed by Sen (1968) and presented in Gilbert (1987) to estimate true slope.

The  $N'$  individual slope estimates,  $Q$ , are computed for each time period:

$$Q = \frac{x_{i'} - x_i}{i' - i},$$

where

$x_{i'}$  and  $x_i$  are the data values at time  $i'$  and  $i$  (in days), respectively,  $i' > i$  and;

$N'$  is the number of observations in the  $p$ th group

Sen's slope estimator is then calculated by choosing the middle-ranked slope as follows;

$$\begin{cases} Q_{[N'=n(n-1)/2]} & \text{if } N' \text{ is odd} \\ \frac{1}{2} \left( Q_{\frac{N'}{2}} + Q_{\frac{N'+1}{2}} \right) & \text{if } N' \text{ is even;} \end{cases}$$

where  $n$  is the number of time periods; this value is multiplied by 365 to give the yearly slope value.

The seasonal Mann-Kendall test is an extension of the Mann-Kendall test for trend that removes seasonal cycles. To compute the seasonal Mann-Kendall statistic,  $S_i$ , for each season there must be a minimum sample size of four data points in each season.

$$S_i = \sum_{k=1}^{n_i-1} \sum_{l=k+1}^{n_i} \text{sgn}(x_{il} - x_{ik})$$

where  $S_i$  is the statistic for the  $i$ th season and

$$\text{sgn}(x) = \begin{cases} -1, & \text{if } x < 0; \\ 0, & \text{if } x = 0; \\ 1, & \text{if } x > 0. \end{cases}$$

With use of the normal approximation (i.e.: greater than 41 observations) the Mann-Kendall test statistic,  $S$  is calculated. When there are no tied values, the

variance of S is computed;

$$\text{Var}(S) = \frac{n(n-1)(2n+5)}{18}$$

and the test statistic  $Z$ , is as follows;

$$Z = \begin{cases} \frac{S-1}{[\text{Var}(S)]^{1/2}}, & \text{if } S > 0; \\ 0, & \text{if } S = 0; \\ \frac{S+1}{[\text{Var}(S)]^{1/2}}, & \text{if } S < 0. \end{cases}$$

When there are tied values,

$$\text{Var}(S) = \frac{1}{18} \left[ n(n-1)(2n+5) - \sum_{p=1}^g t_p(t_p-1)(2t_p+5) \right],$$

where  $g$  is the number of tied groups and  $t_p$  is the number of observations in the  $p$ th group

Once  $\text{Var}(S_i)$  is computed, we pool across the  $K$  seasons and our test statistic  $Z$  is computed. If the result of the test statistic for a one sided test is greater than 1.645 we reject our null hypothesis that no trend exists at the 5% level of significance.

The seasonal Kendall slope estimator procedure is as follows;

First we compute individual  $N_i$  slope estimates for the  $i$ th season:

$$Q_i = \frac{x_{il} - x_{ik}}{l - k},$$

where  $x_{il}$  the data for the  $i$ 'th season of the  $l$ 'th year and  $x_{ik}$  the data for the  $i$ 'th season of the  $k$ 'th year ( $l > k$ ).

This process is computed for each of the  $K$  seasons. Then rank the  $N'1 + N'2 + \dots + N'K = N'$  individual slope estimates and find their median. This median is the seasonal Kendall slope estimator.



As most parameters consistently exhibited significant seasonality, the Seasonal Mann-Kendall test was used for trend analysis. For certain constituents the requirement that there be a minimum per season sample size of four was not met. The analysis is summarized in Table 3.4, “n/a” implies the size requirements were not met, a positive slope is indicative of an increasing trend. If the  $p$ -value of the statistic is less than our 5% significance level we reject the null hypothesis of there being no trend.

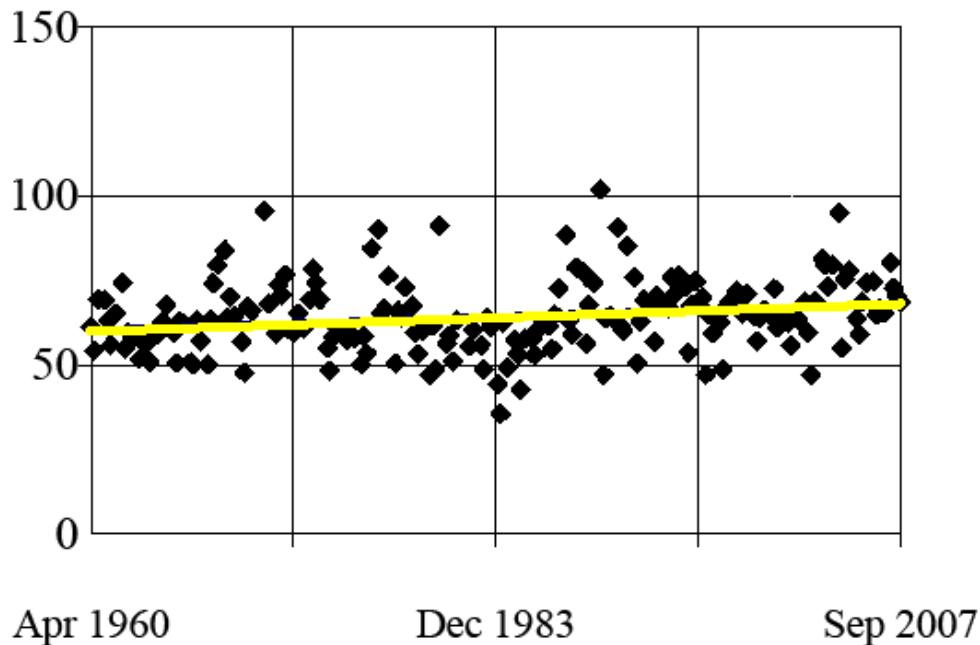


Figure 3.4: Long term temporal trend of Dissolved Calcium (mg/l) at the Emerson monitoring station

Concentrations in dissolved calcium presented an increasing significant trend at the Emerson monitoring station (Figure 3.4). There was insufficient data at the south floodway near St. Norbert monitoring station as well as the Selkirk station (remaining constituents can be seen in the appendix). Dissolved sodium has a significant increasing trend at the Emerson water quality monitoring station with insufficient data again at the other two water quality monitoring station. The dissolved potassium constituent has a significant slightly increasing slope at the Emerson monitoring station with the minimum sample size not being met at the south floodway near St. Norbert station and Selkirk monitoring station. Dissolved sulphate both have increasing significant slopes at the Emerson and Selkirk water quality monitoring stations, and minimum sample size was not met at the south floodway station. The slope of dissolved chloride at the Emerson station has an insignificant slopes at the 5% level of significance, while there was insufficient data at the south floodway station. Total dissolved solids produced significant increasing

Table 3.4: Seasonal Mann-Kendall Test for Trend Results.

Station	Slope		Slope	
	(units/year)	<i>p</i> -value	(units/year)	<i>p</i> -value
	Calcium, dissolved (mg/l)		Sulphate, dissolved (mg/l)	
1.	0.1665	< <u>0.001</u>	1.190	< <u>0.001</u>
2.	n/a	n/a	n/a	n/a
3.	n/a	n/a	4.860	< <u>0.001</u>
	Sodium, dissolved (mg/l)		Chloride, dissolved (mg/l)	
1.	0.1957	< <u>0.001</u>	0.113	0.330
2.	n/a	n/a	n/a	n/a
3.	n/a	n/a	1.246	< <u>0.001</u>
	Potassium, dissolved (mg/l)		Total Dissolved Solids (mg/l)	
1.	0.0428	< <u>0.001</u>	4.356	< <u>0.001</u>
2.	n/a	n/a	29.55	<u>0.005</u>
3.	n/a	n/a	3.479	<u>0.003</u>
	Magnesium, dissolved (mg/l)		Specific Conductance (USIE/cm <sup>2</sup> )	
1.	0.2372	< <u>0.001</u>	2.973	< <u>0.001</u>
2.	n/a	n/a	0.702	0.337
3.	n/a	n/a	0.587	0.424

Table 3.5: Flow Adjusted Seasonal Mann-Kendall Test for Trend Results.

Station	Slope (units/year)	<i>p</i> -value
Calcium, dissolved (mg/l)		
1.	0.1710	< <u>0.001</u>
2.	n/a	n/a
3.	n/a	n/a
Sodium, dissolved (mg/l)		
1.	0.2580	< <u>0.001</u>
2.	n/a	n/a
3.	n/a	n/a
Potassium, dissolved (mg/l)		
1.	0.0460	< <u>0.001</u>
2.	n/a	n/a
3.	n/a	n/a
Magnesium, dissolved (mg/l)		
1.	0.3567	< <u>0.001</u>
2.	n/a	n/a
3.	n/a	n/a

slopes at all three monitoring stations and an extremely large slope at the south floodway monitoring station and specific conductivity produced an increasing significant slope at the Emerson station and insignificant slopes at the south floodway and Selkirk monitoring stations. Certain constituents were also weighted for flow and trends re-examined using this non-parametric method. Flow adjusting data shows how streamflow relates with the constituents and by flow adjusting we can remove flow effects. Slopes from the four constituents selected increased slightly and remained significant. The question is how one would handle such increases; if the slope is only increasing slightly relative to others with large increases the latter should be looked at and evaluated first. Although the slopes are significant, the *p*-values given in Table 3.4 and Table 3.5 are that of Kendall's  $\tau$ .

## Chapter 4

# Parametric Methods used for Water Quality Trend Analysis

In the previous section non-parametric methods of water quality trend analysis was examined, namely the seasonal Mann-Kendall test. The advantages to such methods are that it is easy to compute, requires few assumptions, they are robust to outliers and can handle numerous data from many stations. A weakness of the seasonal Mann-Kendall test is that it assumes monotonic trend and seasons must be defined. Some advantages of parametric methods are: they can be used to model complex trends; and are good for explanatory and not just exploratory analysis. Introducing ancillary data such as livestock or farming data can help better explain certain trends. These methods use the full power and flexibility of maximum likelihood theory, and flow and concentration are modeled jointly (Vecchia, 2004). However disadvantages of parametric methods are: they require specification of a parametric model; usually are computationally intensive; require care in fitting the model and verifying assumptions and may require more data than non-parametric methods do. QWTREND, developed by Aldo Vecchia (USGS), was used to analyze trends in water quality. There are specific data requirements for this program:

1. Record length at least 15 years (not necessarily consecutive)

2. Average of at least 4 samples per year (sampling frequency may vary from year-to-year)
3. At least 10 samples during each 3-month “season” (Jan-Mar, Feb-Apr, Mar-May, . . . , Dec-Feb)
4. Less than 10 percent of values can fall below detection limit (may be more, but extra care required to interpret results)
5. Full record of daily streamflow from 5 years before the first water quality sample through the end of the record

Streamflow variation exists on many time scales (annual, seasonal, daily, etc.), and the variation can affect concentrations in complex and diverse ways (Vecchia, 2004). Seasonal and annual variability in streamflow in the Red River Basin is high. Generally, high flows occur during spring and early summer (primarily from snowmelt or rainfall runoff from spring storms) and low flows occur during late fall and winter (primarily from ground-water or reservoir discharges). Streamflow data were complete for the Emerson station from 1955 to 2007. Flow data for the Red River at St. Norbert was insufficient for the trend analysis program, therefore, flows for the analysis of that station were calculated by summing the flow data from the Red River at Ste. Agathe hydrometric station with those from the Rat River at Otterburne hydrometric station (Jones and Armstrong, 2001). Selkirk station data ranged from 1950 to 1969, so flow data for the trend analysis at the Selkirk station was obtained from the hydrometric station located approximately 9 km upstream at Lockport.

The general time series structure defined by Vecchia (2000) is;

The **streamflow** data is expressed as:

$$\log(Q) = M_Q + ANN_Q + SEAS_Q + HFV_Q,$$

where

$\log$  denotes the base-10 logarithm;

$Q$  is streamflow, in cubic feet per second;

$M_Q$  is the long-term mean of the log-transformed streamflow, as the base-10 logarithm of cubic feet per second;

$ANN_Q$  is the annual streamflow anomaly (dimensionless);

$SEAS_Q$  is the season streamflow anomaly (dimensionless); and

$HFV_Q$  is the high-frequency variability of the streamflow.

The **concentrations** data is expressed as:

$$\log(C) = M_C + ANN_C + SEAS_C + TREND_C + HFV_C,$$

where

$C$  is the concentration, in milligrams or micrograms per litre;

$M_C$  is the long-term mean of the log-transformed concentration, as the base-10 logarithm of milligrams or micro-milligrams per litre;

$ANN_C$  is the annual concentration anomaly (dimensionless);

$SEAS_C$  is the seasonal concentration anomaly (dimensionless);

$TREND_C$  is the concentration trend; and

$HFV_C$  is the high-frequency variability of the concentration (dimensionless).

The different scales of variation of streamflow are expressed as:

$$\log(Q) - M_Q = ANN_Q + SEAS_Q + HFV_Q,$$

where

$ANN_Q$  represents inter-annual (year to year) variation;

$SEAS_Q$  represents seasonal variation within the year;

$HFV_Q$  represents high-frequency (short-term) variation.

For a particular time ( $t$ , in decimal years);

$ANN_Q = A5YR + A1YR$  “annual streamflow anomaly”

$A5YR$  is the average of  $\log Q - M_Q$  for five years up to and including time  $t$  (“5 year streamflow anomaly”).

$A1YR$  is the average of  $\log Q - M_Q - A5YR$  for one year up to and including time  $t$  (“1 year streamflow anomaly”).

$SEAS_Q = A3M + APER$

$A3M$  is the average of  $\log Q - M_Q - ANN_Q$  for 3 months up to and including time  $t$  (“3 month streamflow anomaly”).

$APER =$  Periodic function of  $t$  with period 1-year.

The top graph in Figure 4.1 depicts the daily streamflow at the Emerson monitoring station while the bottom one depicts the streamflow by month. The two plots of dissolved calcium (Figure 4.2) show that sampling started in 1960 and ended in 2007. This range of data is most complete, there are 47 years with at least 1 sample and an average of 16 samples per year, thereby making enough data for time series analysis. Further plots for the remaining constituents are in the appendix.

The program employs a periodic auto-regressive moving average model (PARMA model) to remove the “non-random” structure in the high-frequency variability of the streamflow. The result is a trend in the concentration data that reflects what the trend in the data would be if the variation due to the flow is minimized. By examining the residuals of the flow adjusted concentrations possible monotonic trends can be seen. There are two complementary approaches for fitting trends (Vecchia, 2004). Exploratory trend analysis will provide the best statistical fit to the data using generalized likelihood ratio tests. The second approach is an explanatory trend analysis which will use ancillary time-series data such as livestock data, to explain the trends in concentration.



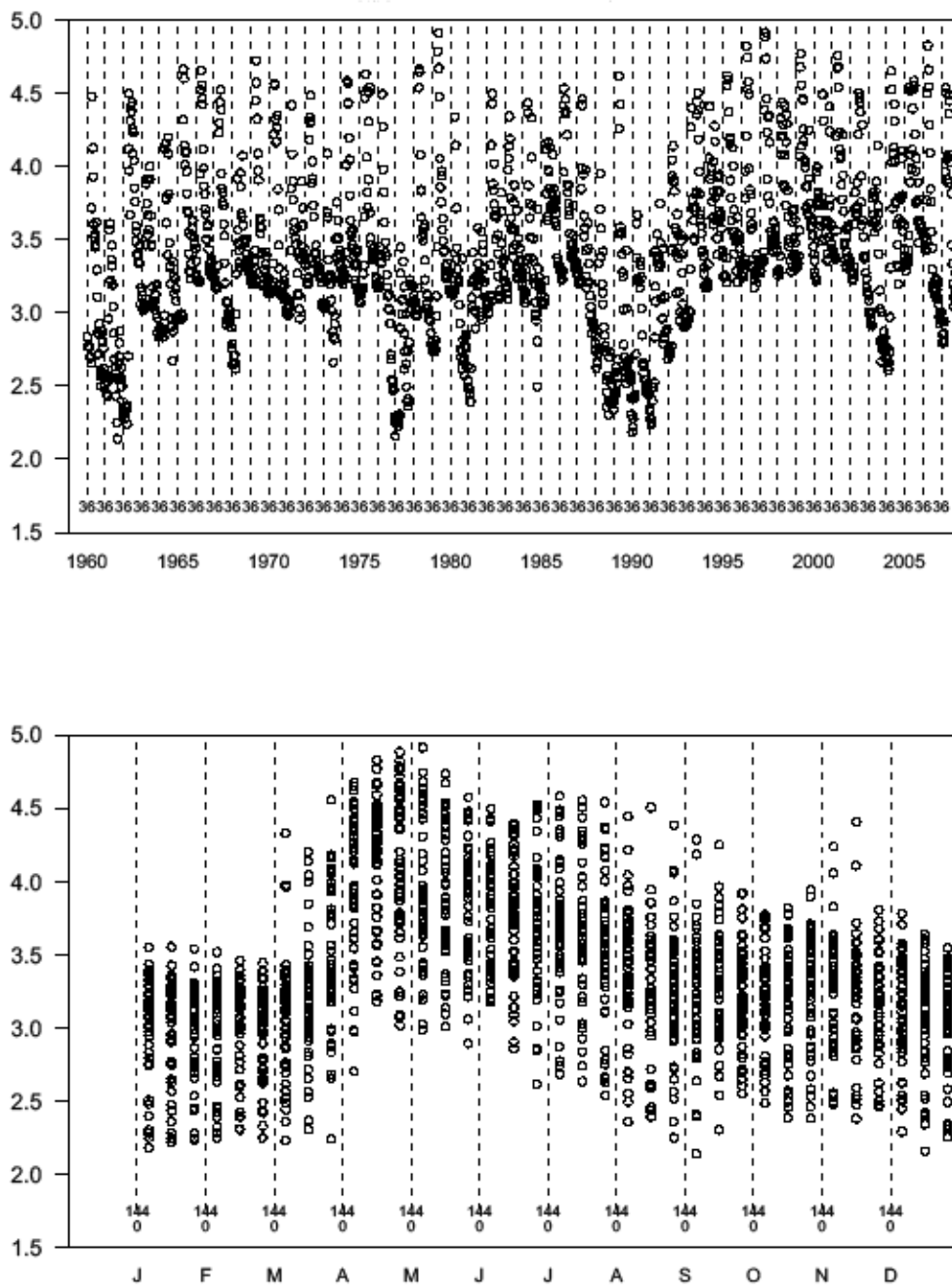


Figure 4.1: Daily Streamflow at Emerson ( $\log_{10} \text{ m}^3/\text{s}$ )

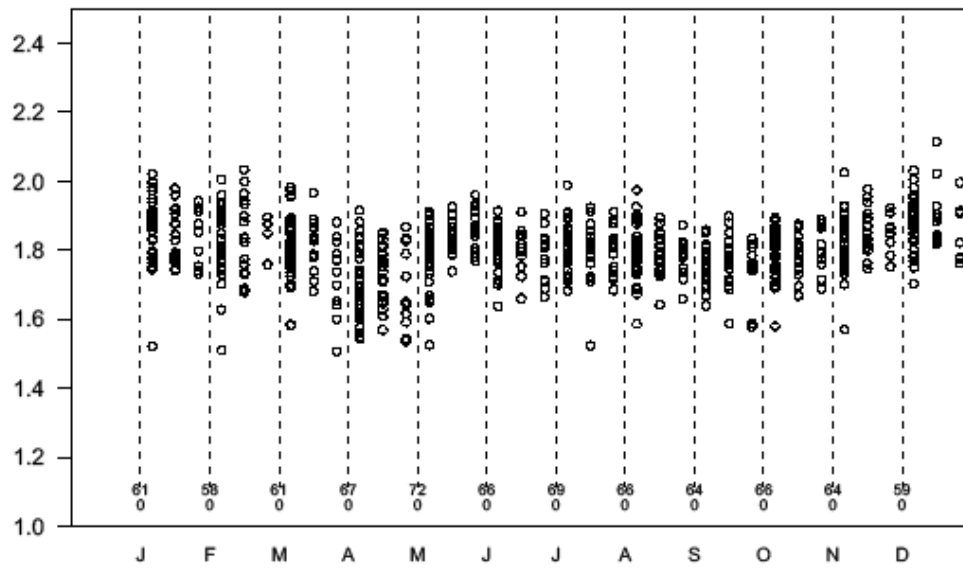
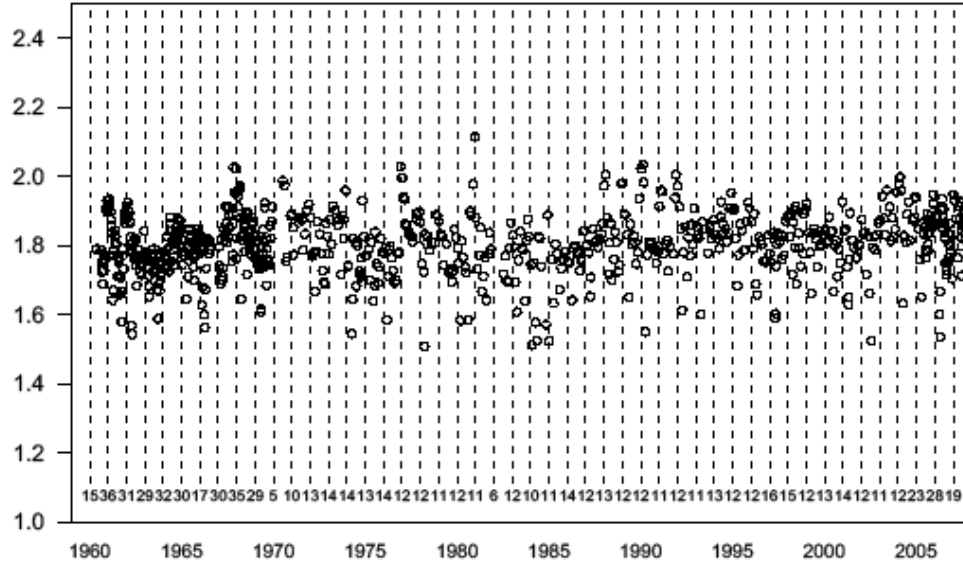


Figure 4.2: Dissolved Calcium at Emerson ( $\log_{10}$  mg/l)

Figures 4.3–4.8 depict the recorded data of dissolved Calcium and the Emerson monitoring station, seasonally adjusted and de-trended data, the seasonally adjusted and flow-adjusted data and the PARMA model residuals and a line showing the lowess smooth. The plots of the remaining constituents for the rest of the constituents and stations can be seen in the appendix.

## 4.1 Generalized Likelihood Ratio

To compute the overall significance of the fitted trend model we are testing the null hypothesis that there is no trend versus the alternate hypothesis that at least one trend coefficient is non-zero. The  $p$ -value of the test follows a chi-square distribution with  $k$  degrees of freedom, where  $k$  is the number of trend functions. The no trend model was initially fitted for the Emerson station constituents, a single linear trend was then fitted for all constituents and upon closer examination of the residuals it can be seen that dissolved sodium and dissolved sulphate exhibit two monotonic trends, dissolved chloride and specific conductance exhibit a single monotonic trend while the remaining constituents show three monotonic trends. Also given is the percent change in the median of the flow-adjusted concentration trend line over the period of reporting. The reason we use the percent change in the median rather than the mean is due to the fact that the fitted trend is derived from the  $\log_{10}$  transformed data.

Table 4.1 shows the results of fitting a single linear trend model to the data from the Emerson monitoring station. For each of the eight constituents considered, the percent change is calculated as  $(10^x - 1) * 100$ , where  $x$  is the estimated coefficient. For the Emerson station there was a 4.7% increase in the median concentration of dissolved calcium between 1960 and 2007 however, the value of the log likelihood is slightly greater than that of the no-trend model so the significance of this trend can not be computed. For dissolved sodium and dissolved potassium constituents there was a 47.9% and a 32.7% respective significant increase from 1960-2007. Dissolved magnesium did not meet the all the requirements of QWTREND, there is a period

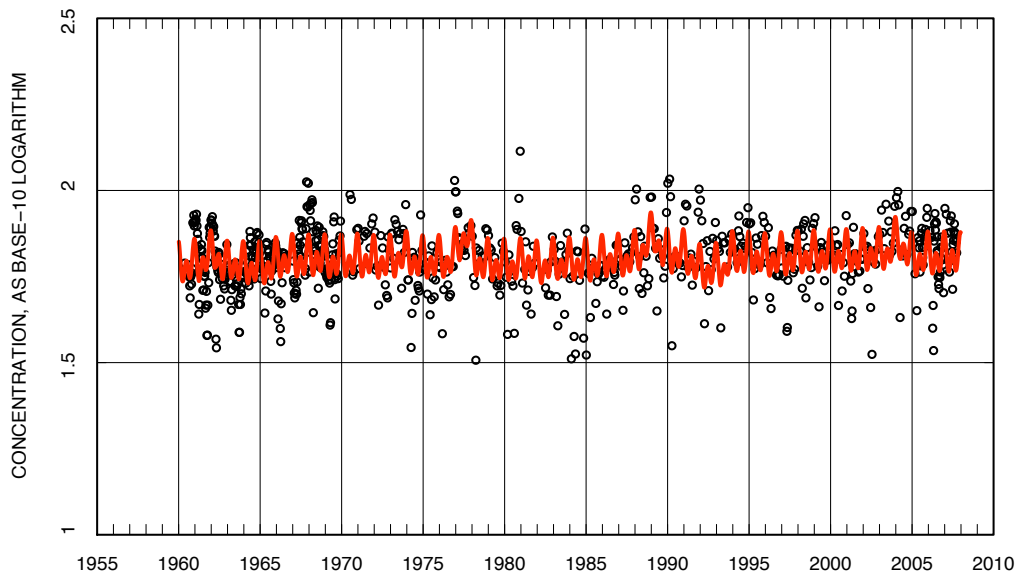


Figure 4.3: Emerson: Dissolved Calcium concentrations (points) and streamflow related anomaly + trend (line)

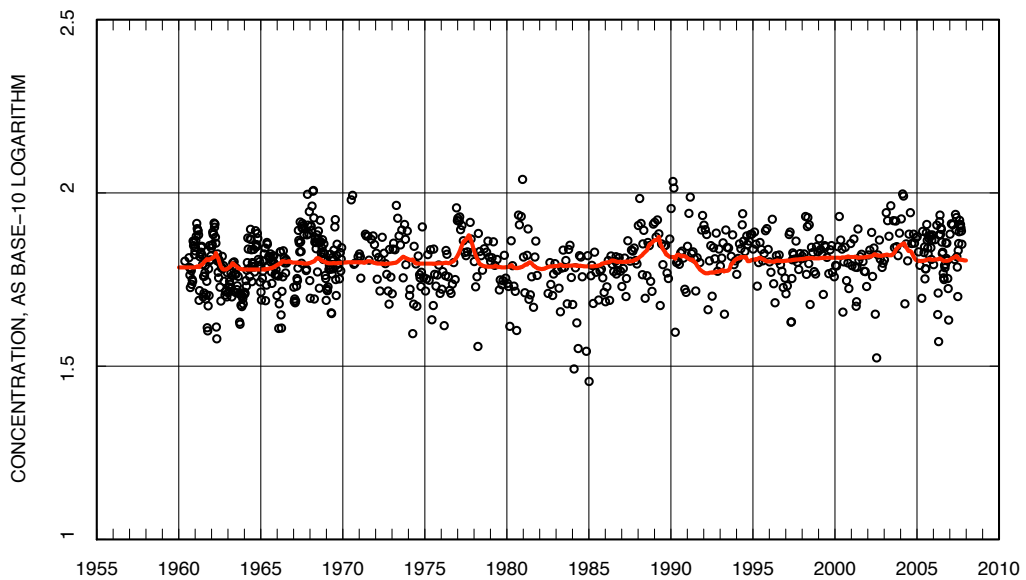


Figure 4.4: Emerson: Dissolved Calcium Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

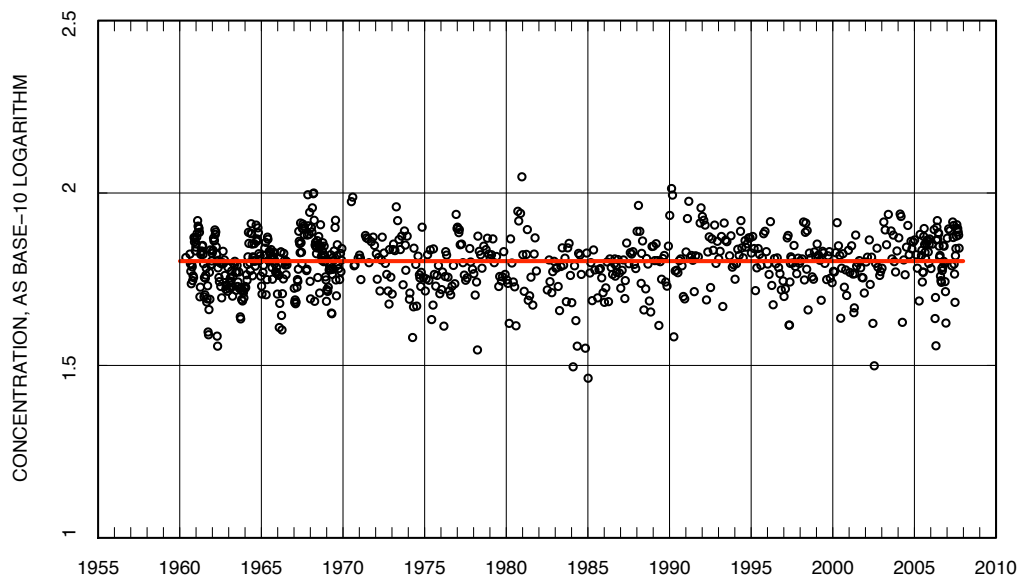


Figure 4.5: Emerson: Dissolved Calcium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

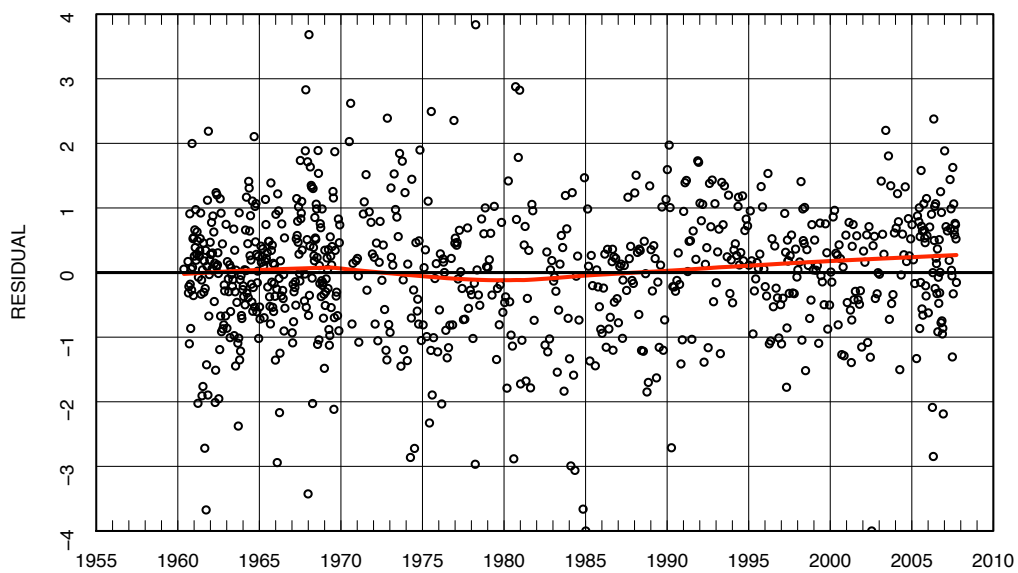


Figure 4.6: Emerson: Dissolved Calcium Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

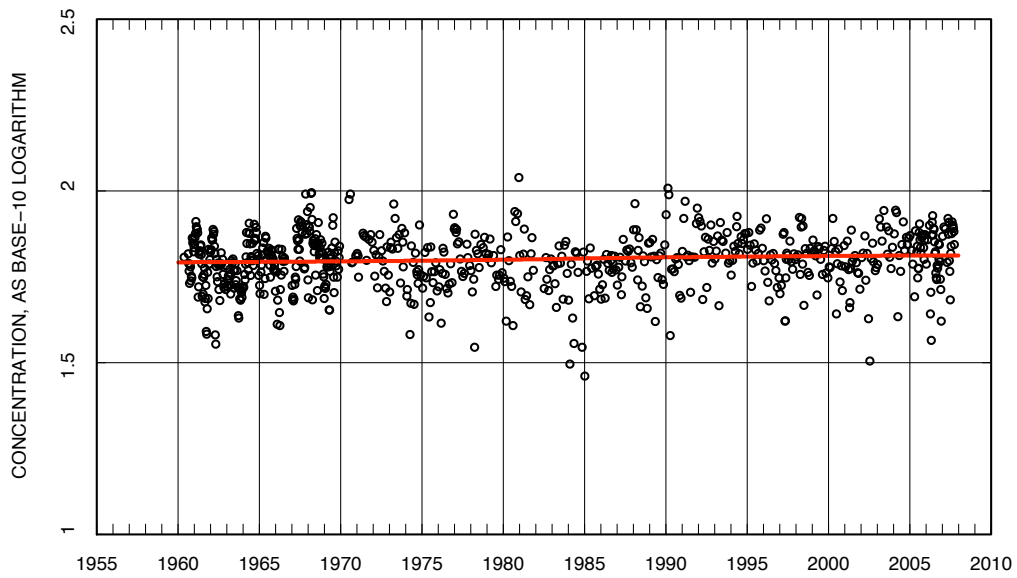


Figure 4.7: Emerson: Dissolved Calcium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

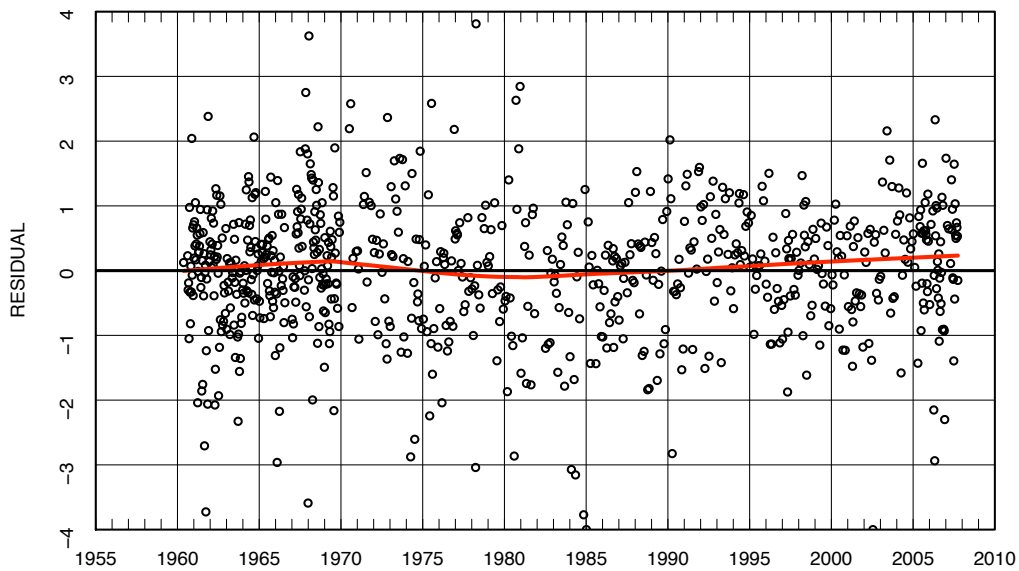


Figure 4.8: Emerson: Dissolved Calcium Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

Table 4.1: Fitted Single Linear Trends at the Emerson Station

Constituent	% change	est. coef.	std. error	<i>p</i> -value	time period
Dissolved Calcium	4.7	0.020	1.632	can't determine	1960-2007
Dissolved Sodium	47.9	0.170	6.401	< <u>0.001</u>	1960-2007
Dissolved Potassium	32.7	0.123	7.279	< <u>0.001</u>	1960-2007
Dissolved Magnesium	21.1	0.083	4.190	< <u>0.001</u>	1975-2007
Dissolved Sulphate	52.5	0.183	6.363	can't determine	1960-2007
Dissolved Chloride	39.0	0.143	3.439	0.001	1960-2007
Total Dissolved Solids	43.2	0.183	6.363	< <u>0.001</u>	1985-2007
Specific Conductance	28.8	0.110	6.974	0.001	1960-2007

of time where no data was collected as seen in the top graph of Figure A.33 thus the trend was fitted on the data from 1975 to 2007 which yielded a significant 21.1% increase in median concentration. Total dissolved solids significantly increased 43.2% from 1985-2007. Dissolved chloride and specific conductance both had significant increasing trends from 1960-2007 at 39.0% and 28.8% respectively with *p*-values of 0.001. Dissolved sulphate also had a 52.4% increase in median concentration from 1960-2007, however, a single linear trend is not an appropriate measure for this constituent.

After closer examination of the residual plots it can be seen for dissolved calcium and dissolved potassium seem to exhibit three monotonic trends; a slight increase from 1960-1970 a slight decline until 1983 and then increase again to 2007. The trend for was examined from 1975 and shows a decrease until 1983 and then proceeds to increase through to 2007. Total dissolved solids also show three different monotonic trends, an increase from 1982-1992 then a slight decrease until 1999 and then increase again until 2007. Similarly for dissolved sodium and dissolved sulphate, after examining the residual plots of those constituents, there seem to be two monotonic trends. It can be seen that there is a decrease from 1960 until 1977 and then increases until 2007. The purpose of this report is to compare the results

with those of the non-parametric method and since the non-parametric method tests for a single linear trend we will examine the single linear trends of the parametric methods.

For the constituents at the South Floodway monitoring station, a no trend model was fitted for three constituents, dissolved sulphate, dissolved chloride and specific conductance. However, since QWTREND has quite specific requirements as stated earlier, for the South Floodway at St. Norbert and Selkirk monitoring stations the only constituent with enough data for trend analysis is specific conductance. There was found to be a 34.9% significant increase in specific conductance from 1976-2007 with a  $p$ -value  $< 0.001$  and for the Selkirk monitoring station there was a 30.9% significant increase in concentration from 1976-2007 with a  $p$ -value  $< 0.001$  as well. Both of these results contradicted the insignificant results obtained by using the non-parametric methods.



## Chapter 5

# Comparison of Non-Parametric and Parametric Results and Future Recommendations

### 5.1 Comparisons

The non-parametric method is more simple to employ and can be done with less data as opposed to the specific requirements of QWTREND. Small sample size and short period of record coupled with the high variability in data make the detection of statistically significant trends using the parametric approach quite difficult. However, QWTREND allows one to fit trends using an exploratory approach that indicate the approximate times and directions of changes in concentrations. In order to explain the change this program will also allow the introduction of ancillary data to see if the changes are a result of human causes (ie, changes in land use, agricultural practices, sewage treatment, etc.) (Vecchia, 2004).

Both methods exhibited similarities with significant trend results amongst dissolved Sodium, dissolved Potassium and dissolved Magnesium. The significance of the trend for dissolved Calcium can not be computed however from looking at

Table 5.1: Comparison Results with respective p-values

Station #	Constituent	Non-Parametric	Parametric
1.	dissolved calcium	< <u>0.001</u>	n/a
1.	dissolved sodium	< <u>0.001</u>	< <u>0.001</u>
1.	dissolved potassium	< <u>0.001</u>	< <u>0.001</u>
1.	dissolved magnesium	< <u>0.001</u>	< <u>0.001</u>
1.	dissolved sulphate	< <u>0.001</u>	n/a
3.	dissolved sulphate	< <u>0.001</u>	n/a
1.	dissolved chloride	0.330	0.001
3.	dissolved chloride	< <u>0.001</u>	n/a
1.	total dissolved solids	< <u>0.001</u>	< <u>0.001</u>
2.	total dissolved solids	0.005	n/a
3.	total dissolved solids	0.003	n/a
1.	specific conductance	< <u>0.001</u>	0.001
2.	specific conductance	0.337	< <u>0.001</u>
3.	specific conductance	0.424	< <u>0.001</u>

Figure 4.7 there seems to be no visible trend. Another commonality between the methods, is that there was only enough data from the Emerson station to be used for those constituents. Total dissolved solids was significant at the Emerson station using both methods, however the data from the South Floodway and Selkirk stations were too sparse to employ the parametric method. There are also some obvious differences. For example, using non-parametric techniques dissolved chloride concentrations at the Emerson monitoring station did not exhibit a significant trend. Preliminary results suggest that this also is true for specific conductance at the South Floodway and Selkirk monitoring stations. Using parametric techniques specific conductance at both stations had significant increases which proves to be an interesting contradiction. Table 5.1 summarizes the comparisons of each method with their respective p-values.

## 5.2 Future Recommendations

First and foremost there should be a **sampling design** employed for monitoring concentration trends in order to make a complete data set for future water quality monitoring projects. If all stations are continually monitored then this design should be uniform throughout. QWTREND computes effective sampling designs for monitoring trends in order for parametric trend results to be as accurate as possible. Designs can be variable or fixed to be the same year after year. Variable sampling frequencies should be considered only if you can specify the starting time and duration of the trend, since this is quite difficult a fixed sampling design is a more efficient method. Fixed sampling designs can be compared by two characteristics, their sensitivity and efficiency. An efficient design is one that maximizes the likelihood of detecting a trend for a fixed cost. After fitting the time series model for analyzing historical trends, the model can be used to compute the characteristic trend for any specified design using QWTREND. The characteristic trend is the increase (or decrease) in concentration, in percent, that has an 80% chance of being detected after 5 years of sampling. Trends larger than this characteristic trend will have more than an 80% chance of being detected, while trends smaller will have less than an 80% chance of being detected. For future studies this would be useful to establish.

If a comparison is to be made between concentration data and concentration data weighted for flow, then that should be done using the non-parametric method as well. WQSTAT allows for a **flow-adjusting** procedure to be computed on the raw data in order to relate streamflow to various constituents and to remove flow effects prior to further statistical analysis. By flow adjusting before trend analysis, one can determine the magnitude and statistical significance of trends, which are not explained by flow. If this non-parametric method is to be used, there must be enough data in order for the trend results to be correctly interpreted (Helsel and Hirsch, 1992).

**Ancillary data** could also be used in order to better explain the trends in concentrations and whether or not they are ecologically significant. Cropland and

livestock data for the Red River are reported by the National Agricultural Statistics Service, this available data can be incorporated into QWTREND and allows one to have more of an explanation as to why certain fitted trends make sense. For example, if there has been an increase in the amount of cattle in an area surrounding the Red River, does that explain a certain percent increase in phosphorus concentration?

Parametric time series analysis should be considered when complex trends appear in flow-adjusted concentrations and if sampling is highly variable from year to year. There are advantages and disadvantages to both methods for trend detection, they are summarized below:

**Advantages of Non-Parametric Methods** using WQSTAT:

- Easy to compute
- Requires few assumptions
- Robust to outliers
- Simple to use

**Disadvantages of Non-Parametric Methods** using WQSTAT:

- Not as powerful in detecting trends
- “Hydrologic” seasons must be clearly defined
- Assumes monotonic trend
- No flexibility for defining trend lengths

**Advantages of Parametric Methods** using QWTREND:

- Can model complex trends
- Good for explanatory and exploratory analysis

- Uses full power of the maximum likelihood theory
- Flow and concentration are modeled jointly
- Fitted trends indicate approximate times and direction of the changes in concentrations

**Disadvantages of Parametric Methods** using QWTREND:

- Requires specification of a parametric model
- Certain data requirements must be met
- Requires care in fitting the model and verifying assumptions
- Computationally intensive

# Chapter 6

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# Appendix A

## Figures

### A.1 Boxplots of Constituents

The following figures are the boxplots of the selected constituents at all three monitoring stations: Emerson, South Floodway and Selkirk. These boxplots show the five-number summaries of the data. The tails extend to the maximum and minimum value of our data, while the box encompasses the middle 50% of our data.

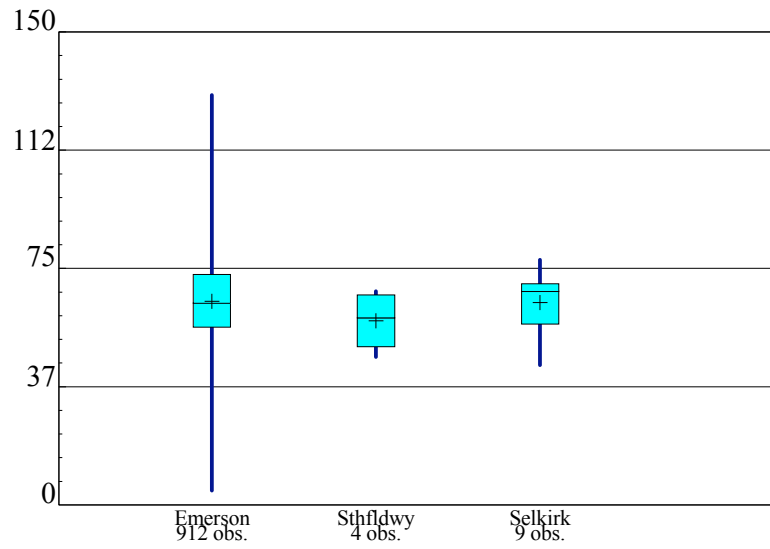


Figure A.1: Boxplot of dissolved Calcium (mg/l) depicting the five number summary of the constituent

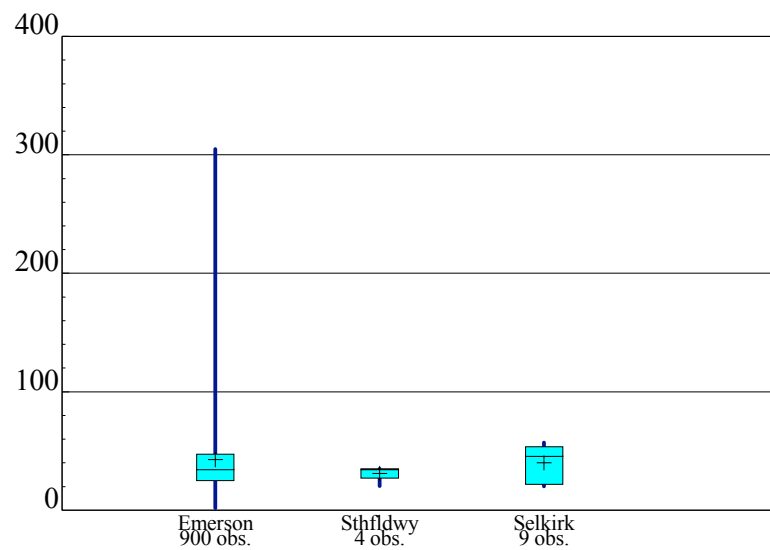


Figure A.2: Boxplot of Dissolved Sodium (mg/l) depicting the five number summary of the constituent

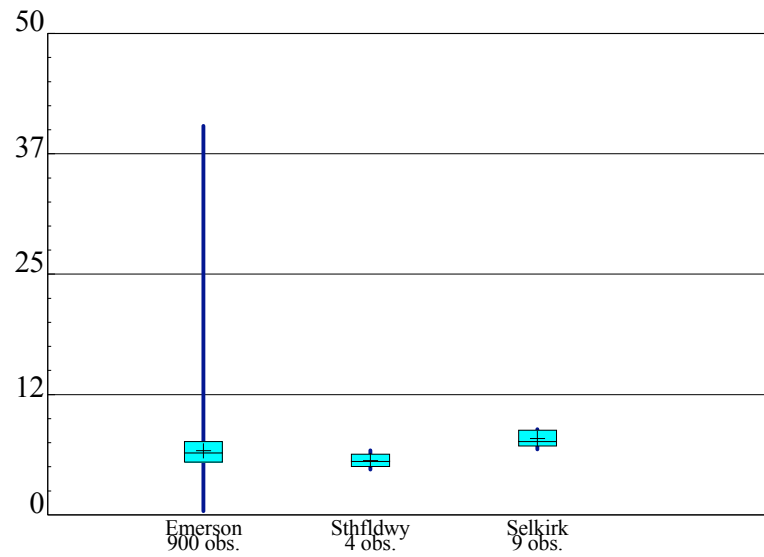


Figure A.3: Boxplot of Dissolved Potassium (mg/l) depicting the five number summary of the constituent

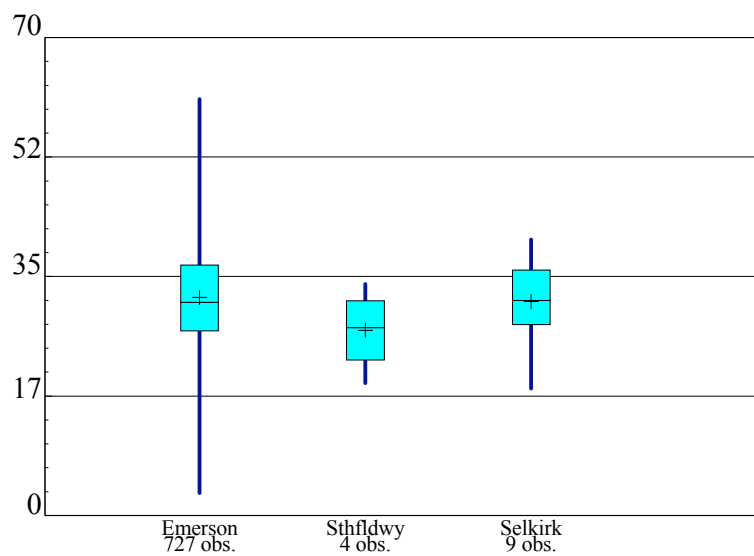


Figure A.4: Boxplot of Dissolved Magnesium (mg/l) depicting the five number summary of the constituent

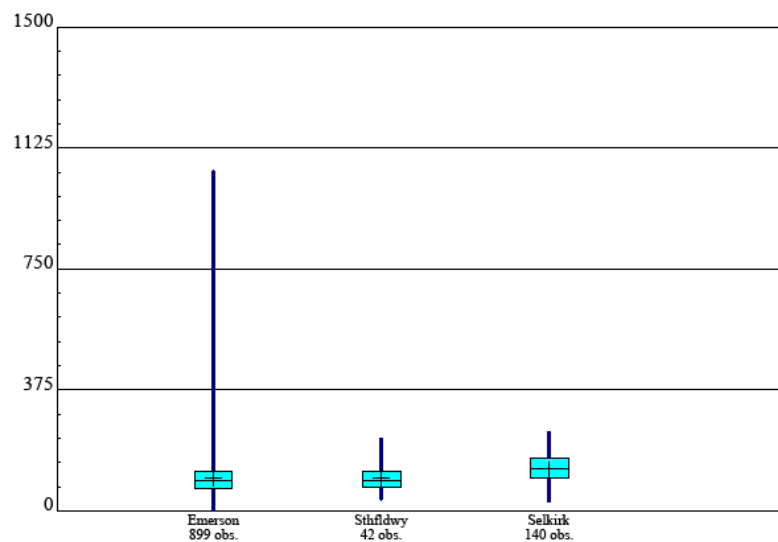


Figure A.5: Boxplot of Dissolved Sulphate (mg/l) depicting the five number summary of the constituent

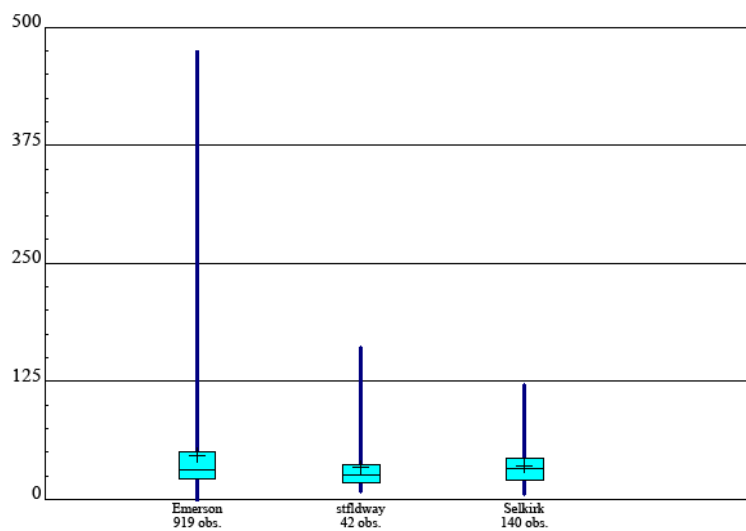


Figure A.6: Boxplot of Dissolved Chloride (mg/l) depicting the five number summary of the constituent

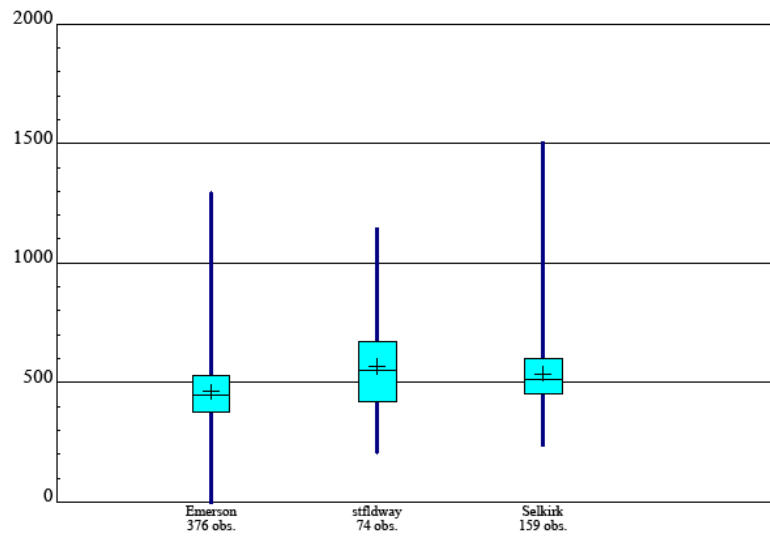


Figure A.7: Boxplot of Total Dissolved Solids (mg/l) depicting the five number summary of the constituent

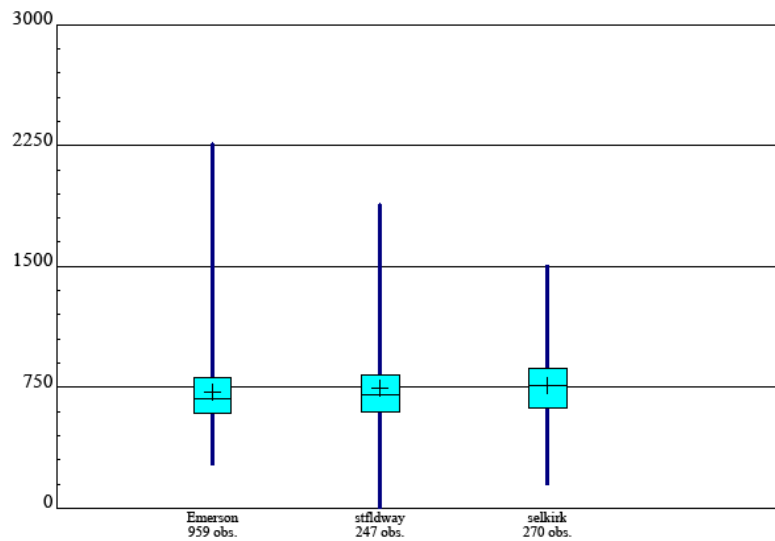


Figure A.8: Boxplot of Specific Conductance (USIE/cm<sup>2</sup>) depicting the five number summary of the constituent

## A.2 Seasonal Boxplots

The following figures are the seasonal boxplots of the selected constituents at all three monitoring stations: Emerson, South Floodway and Selkirk. These boxplots show the seasonal patterns of the constituents defined by their “hydrologic seasons.”

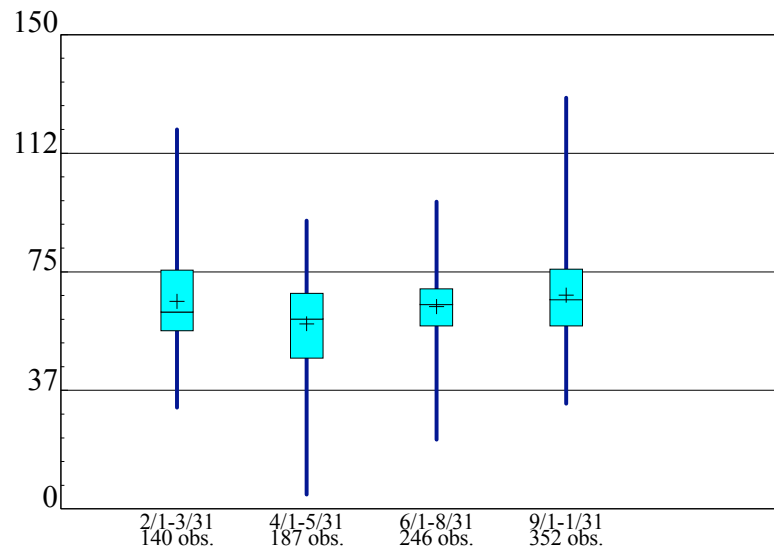


Figure A.9: Seasonality pattern of Dissolved Calcium (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations

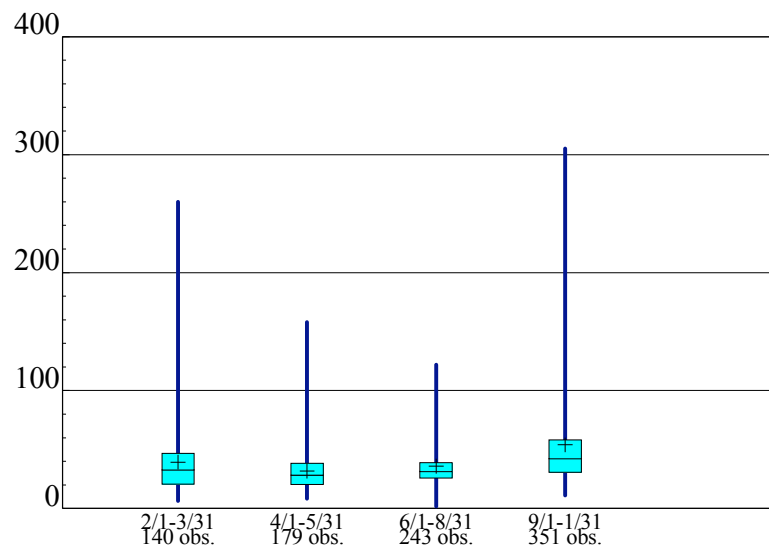


Figure A.10: Seasonality pattern of Dissolved Sodium (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations

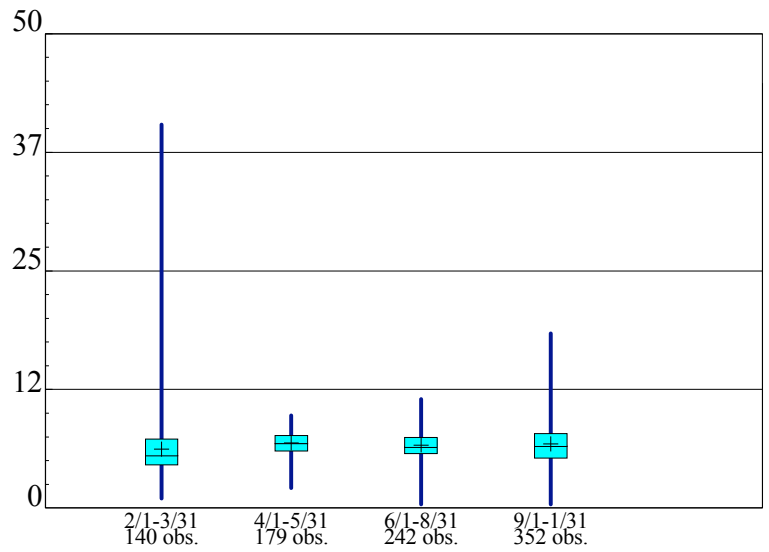


Figure A.11: Boxplots of Dissolved Potassium (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations

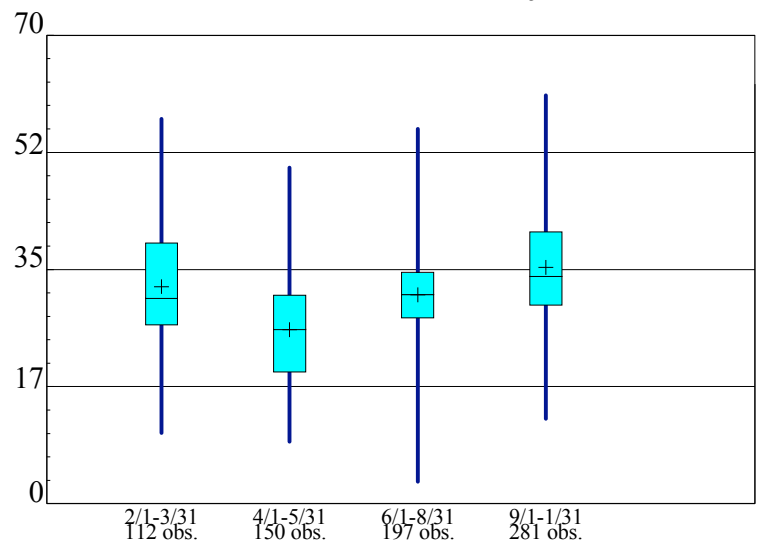


Figure A.12: Seasonality pattern of Dissolved Magnesium (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations



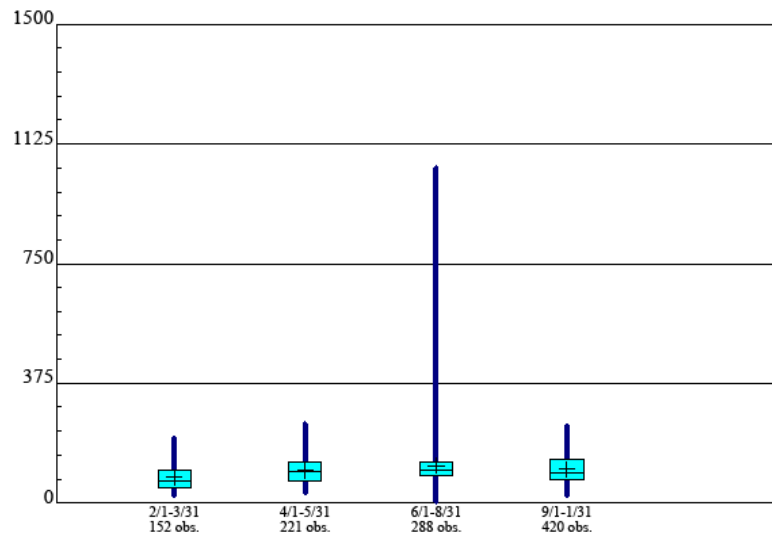


Figure A.13: Seasonality pattern of Dissolved Sulphate (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations

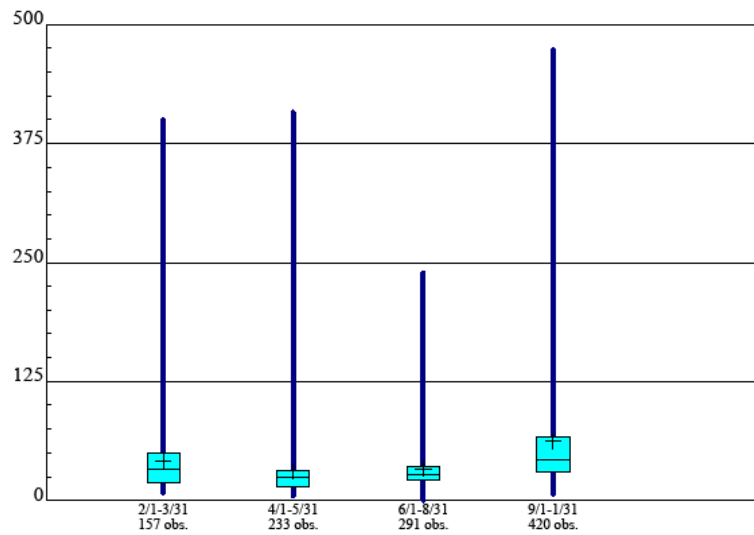


Figure A.14: Seasonality pattern of Dissolved Chloride (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations

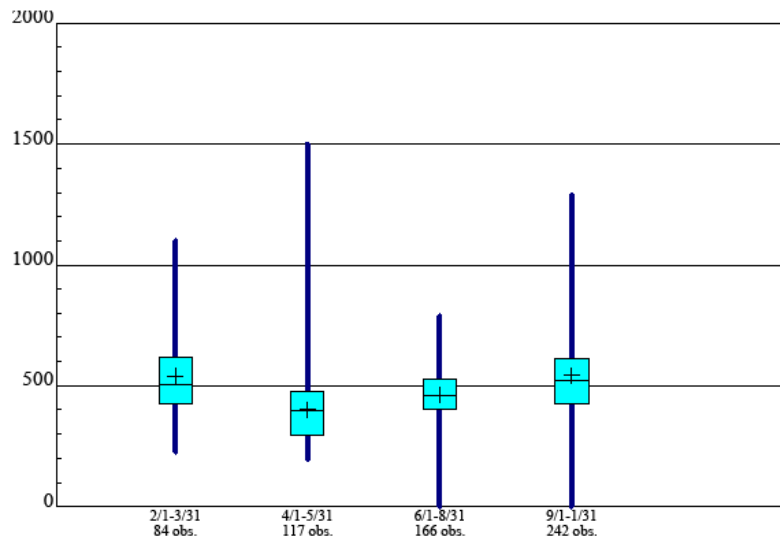


Figure A.15: Seasonality pattern of Total Dissolved Solids (mg/l) depicting the seasonal pattern of the constituent amongst all three monitoring stations

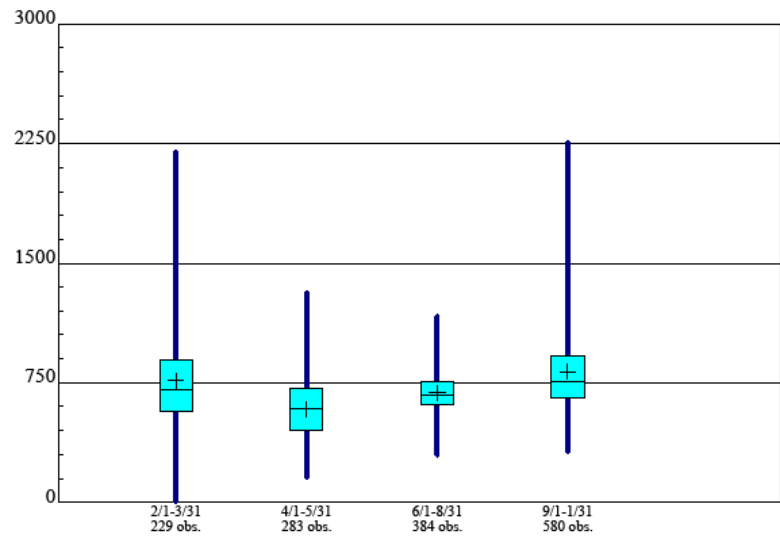


Figure A.16: Seasonality pattern of Specific Conductance (USIE/cm<sup>2</sup>) depicting the seasonal pattern of the constituent amongst all three monitoring stations

### **A.3 Non-Parametric Trend Results**

The following figures depict the long term temporal trend of each constituent at each monitoring station. These were calculated using the Mann-Kendall Test and Sen's slope.

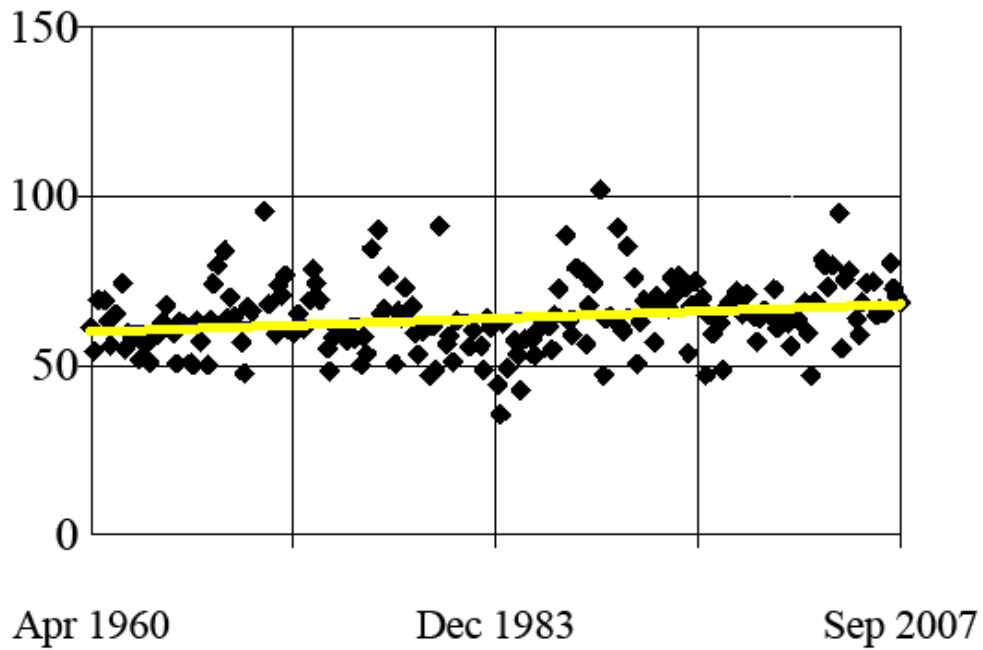


Figure A.17: Long term temporal trend of dissolved calcium (mg/l) at the Emerson monitoring station

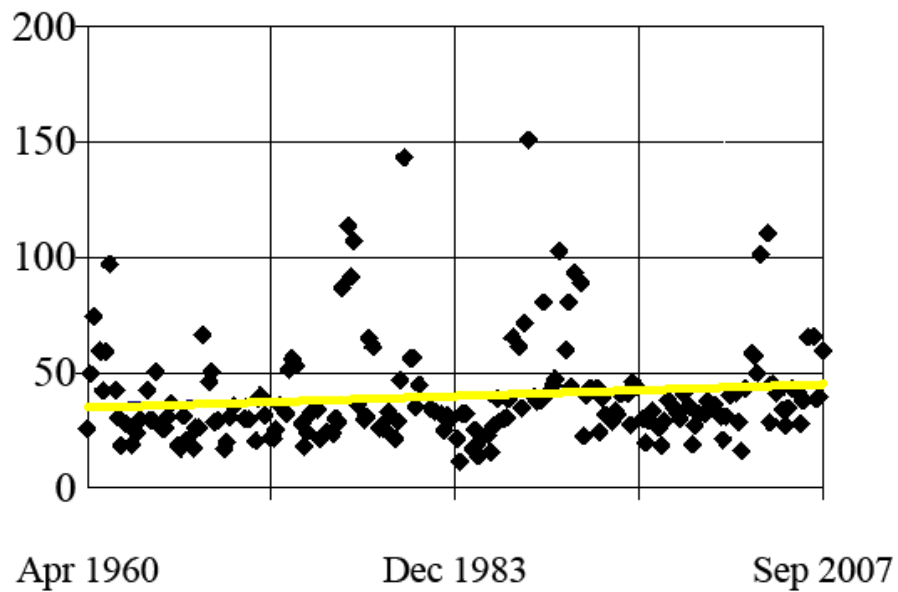


Figure A.18: Long term temporal trend of dissolved sodium (mg/l) at Emerson

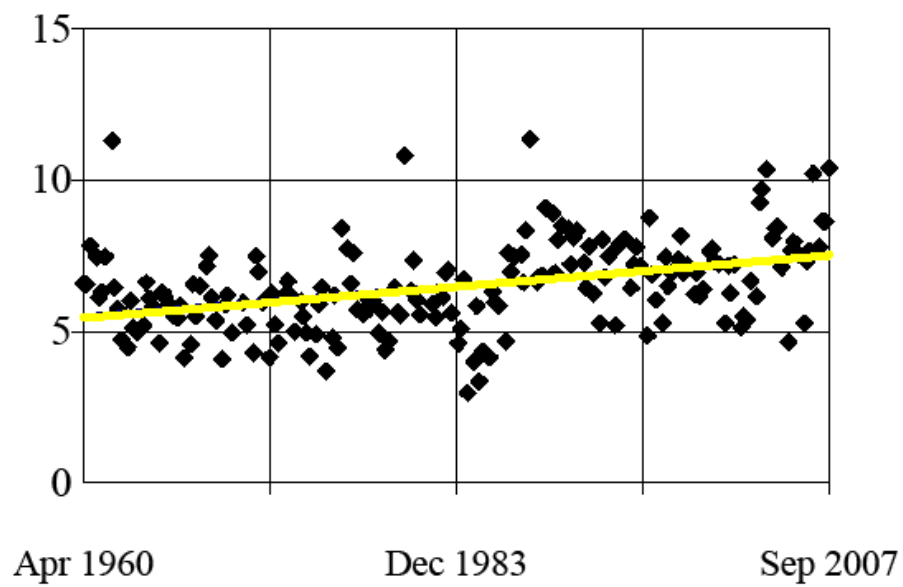


Figure A.19: Long term temporal trend of dissolved potassium (mg/l) at Emerson

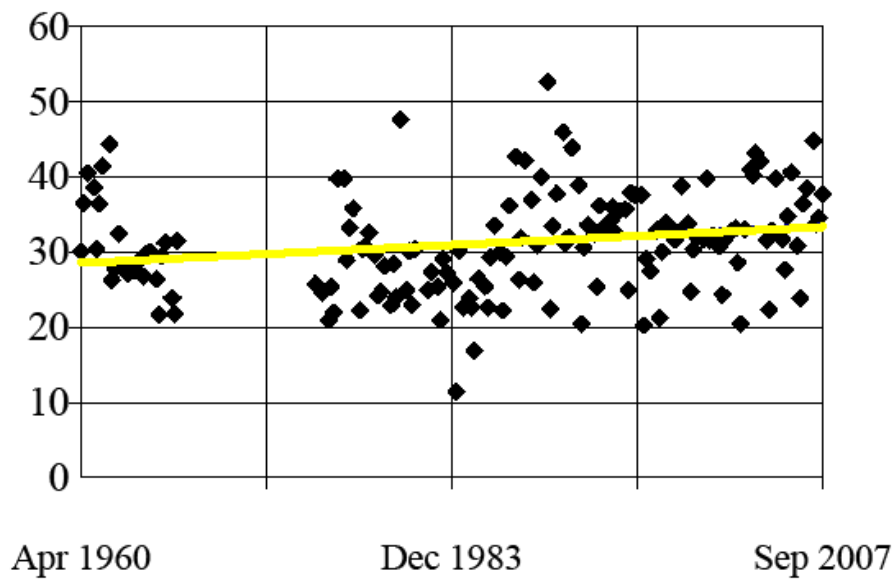


Figure A.20: Long term temporal trend of dissolved magnesium (mg/l) at Emerson

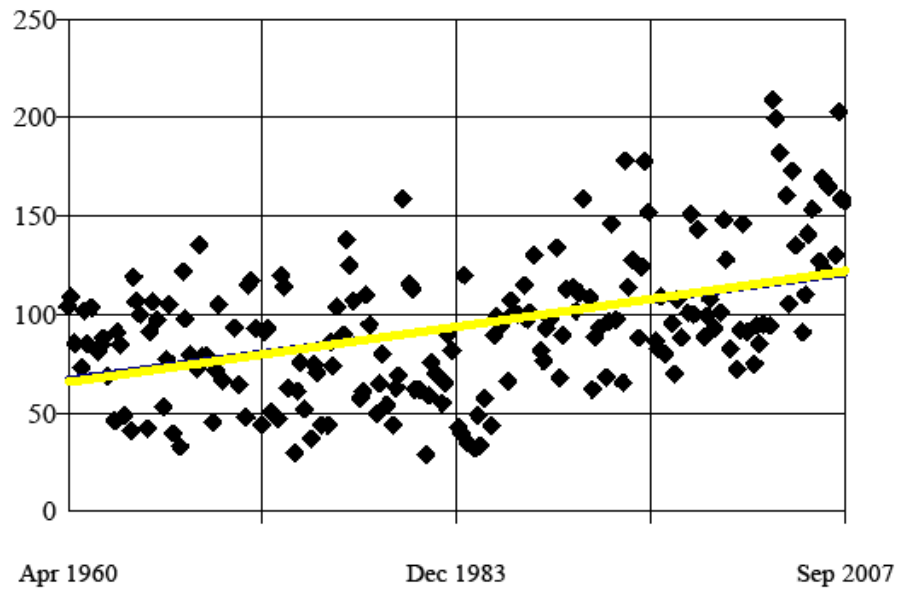


Figure A.21: Long term temporal trend of dissolved sulphate (mg/l) at Emerson

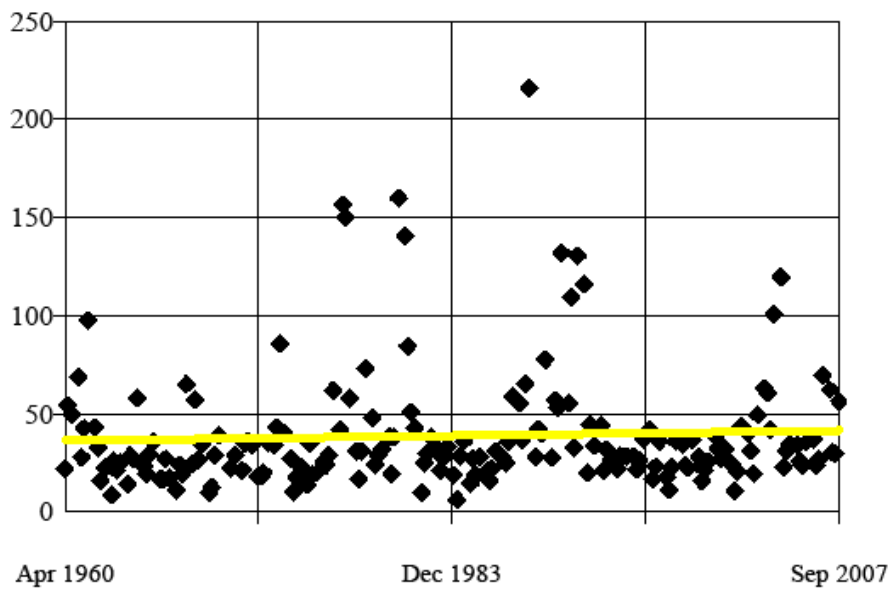


Figure A.22: Long term temporal trend of dissolved chloride (mg/l) at Emerson

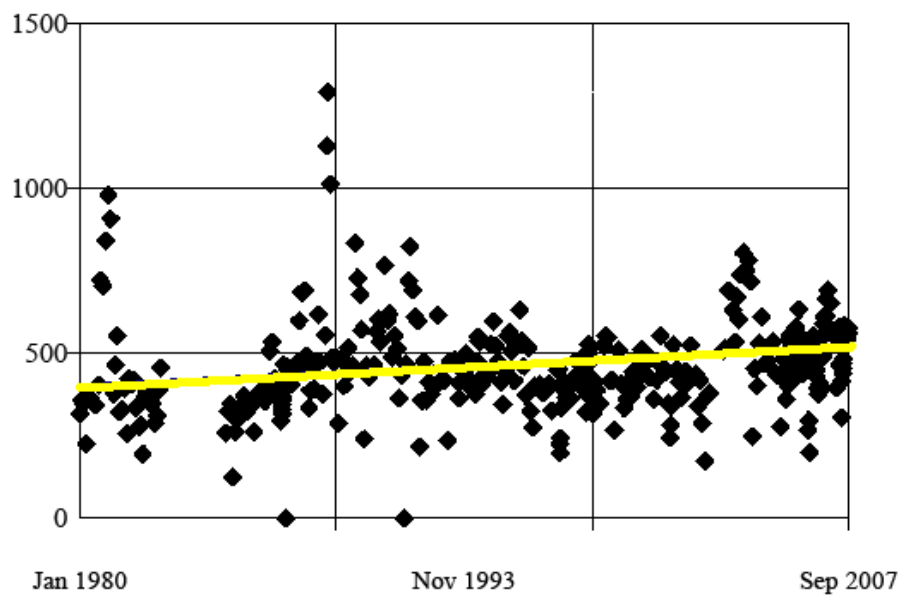


Figure A.23: Long term temporal trend of total dissolved solids (mg/l) at Emerson

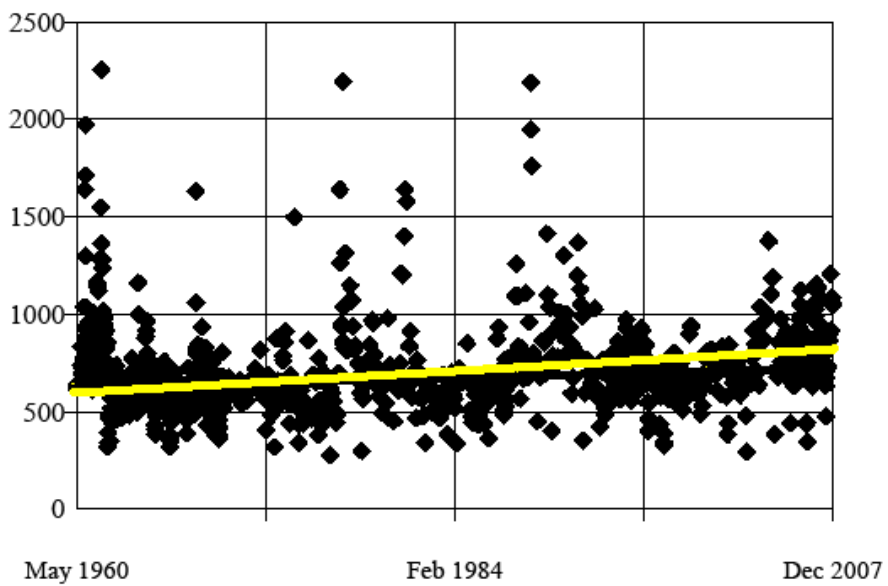


Figure A.24: Long term temporal trend of specific conductance (USIE/cm<sup>2</sup>) at Emerson

### A.3.1 South Floodway at St. Norbert Monitoring Station



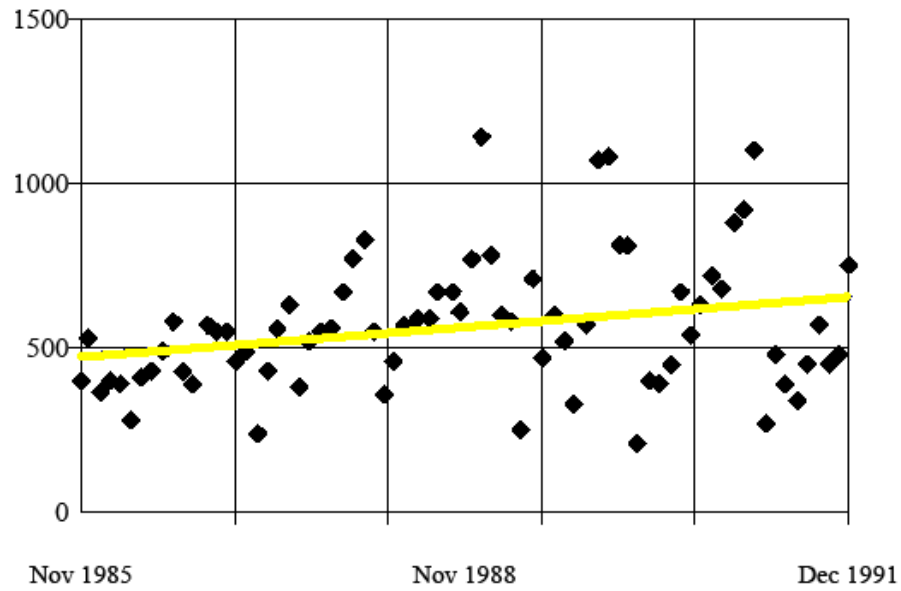


Figure A.25: Long term temporal trend of total dissolved solids (mg/l) at South Floodway

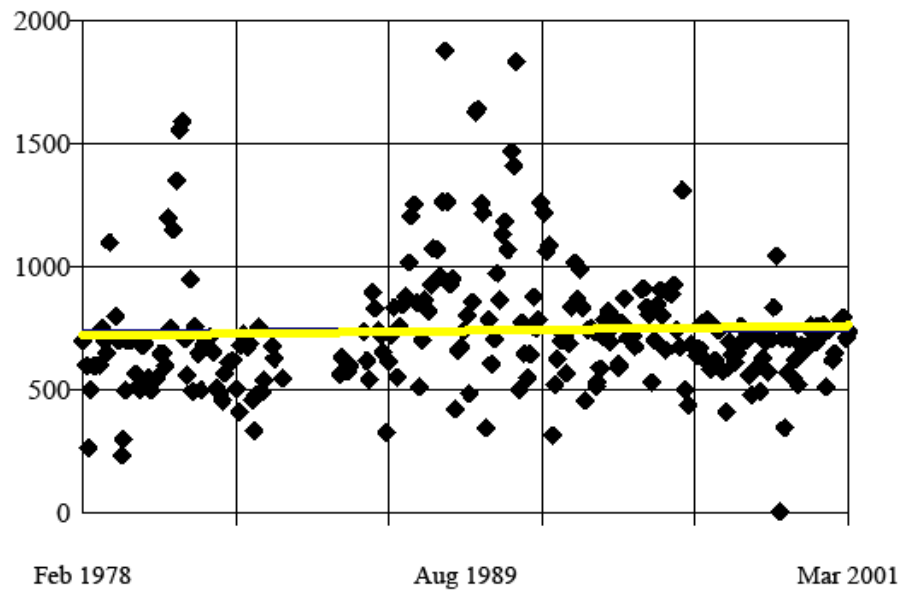


Figure A.26: Long term temporal trend of specific conductance (USIE/cm<sup>2</sup>) at South Floodway

### A.3.2 Selkirk Monitoring Station

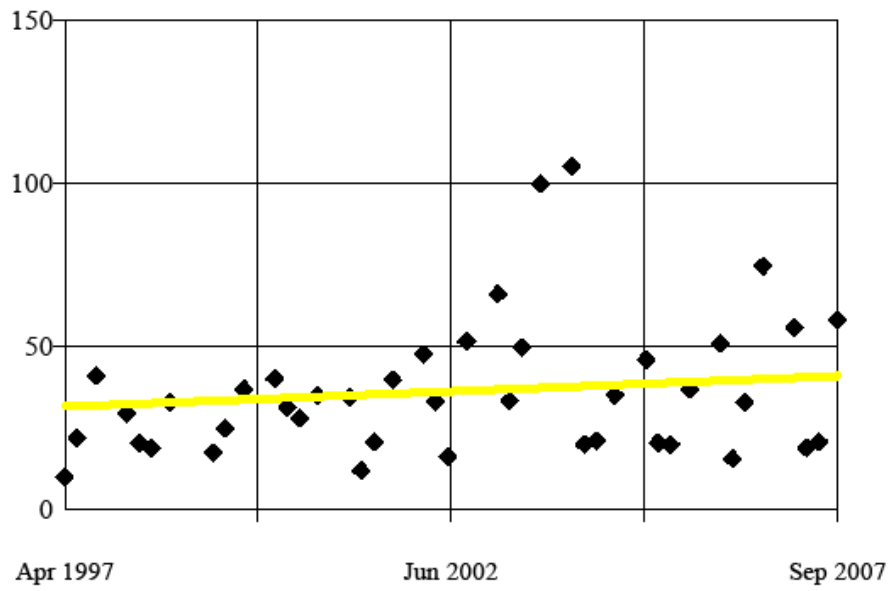


Figure A.27: Long term temporal trend of dissolved chloride (mg/l) at Selkirk

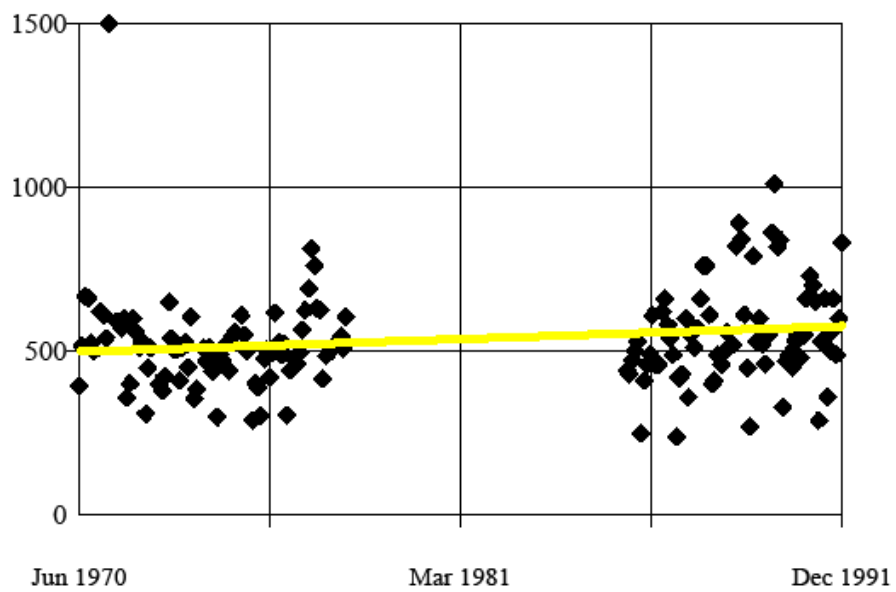


Figure A.28: Long term temporal trend of total dissolved solids (mg/l) at Selkirk

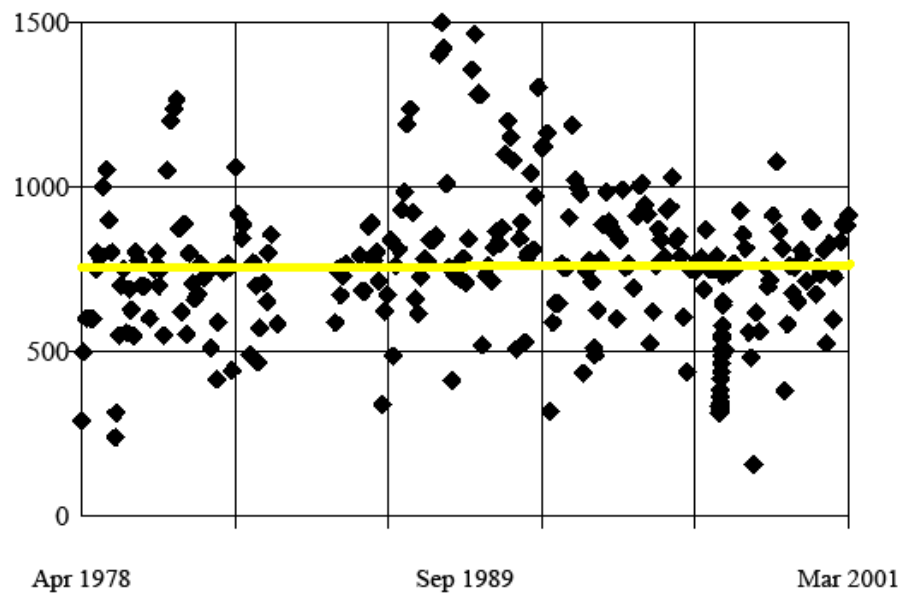


Figure A.29: Long term temporal trend of specific conductance (USIE/cm<sup>2</sup>) at Selkirk

## A.4 Parametric Trend Results

The following figures depict the raw data of the constituents being used with QWTREND. The figures below pertain only to the Emerson Monitoring Station. The upper plots are the data points while the lower plots depict the number of data points by month.

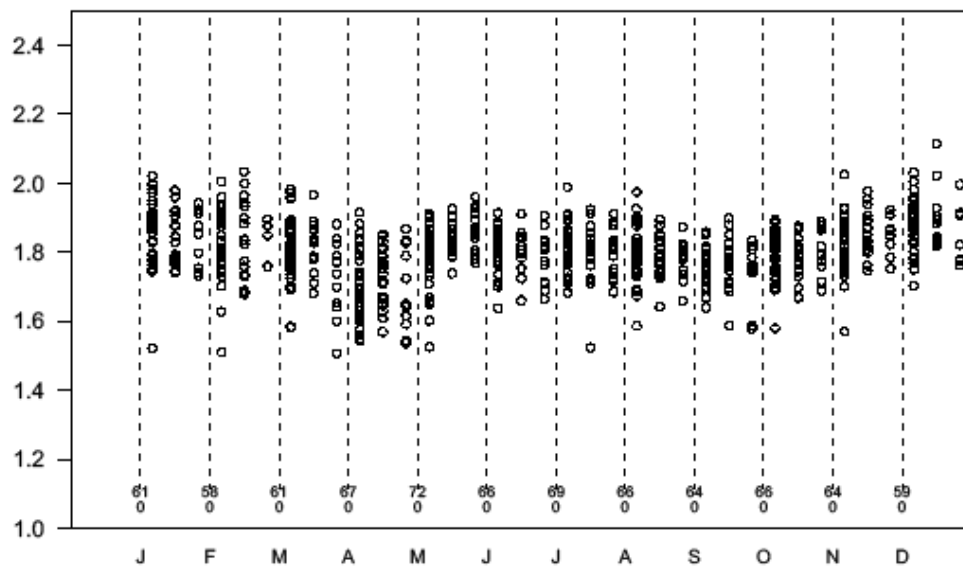
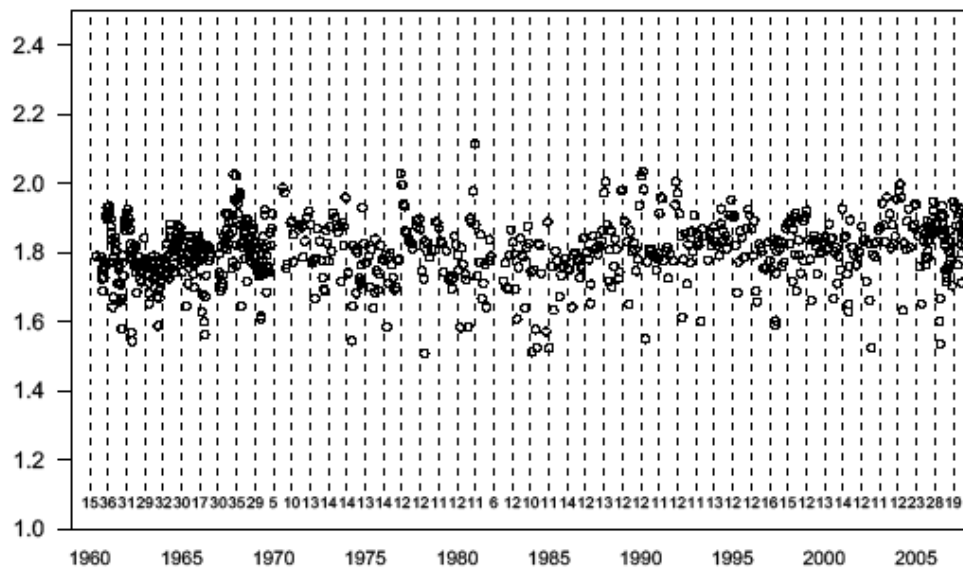


Figure A.30: Dissolved Calcium at Emerson ( $\log_{10}$  mg/l)

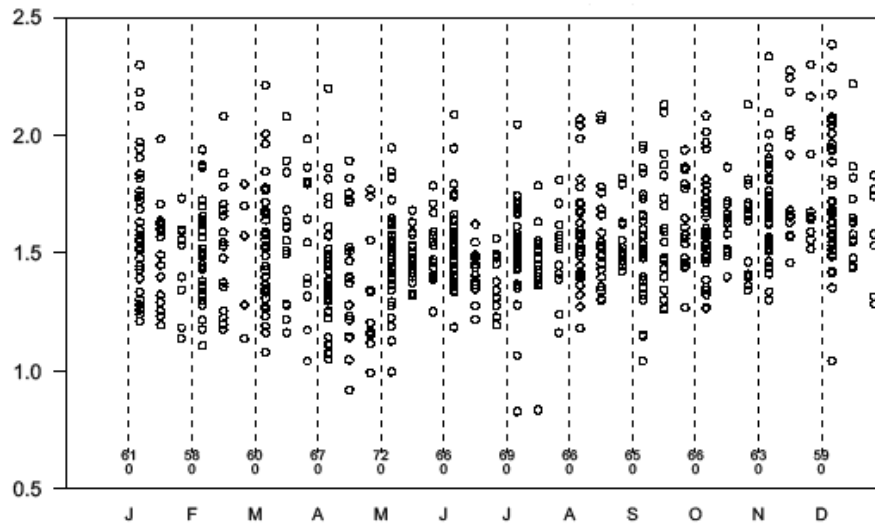
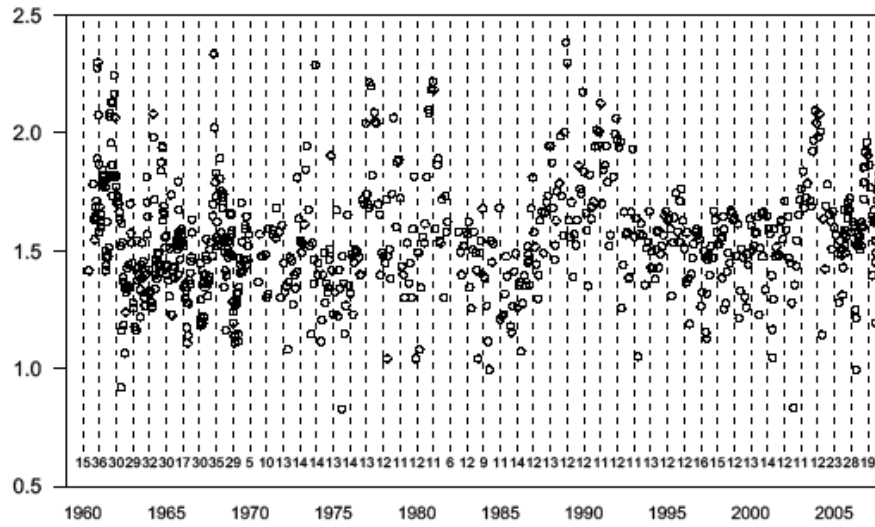


Figure A.31: Dissolved Sodium at Emerson (log<sub>10</sub> mg/l)

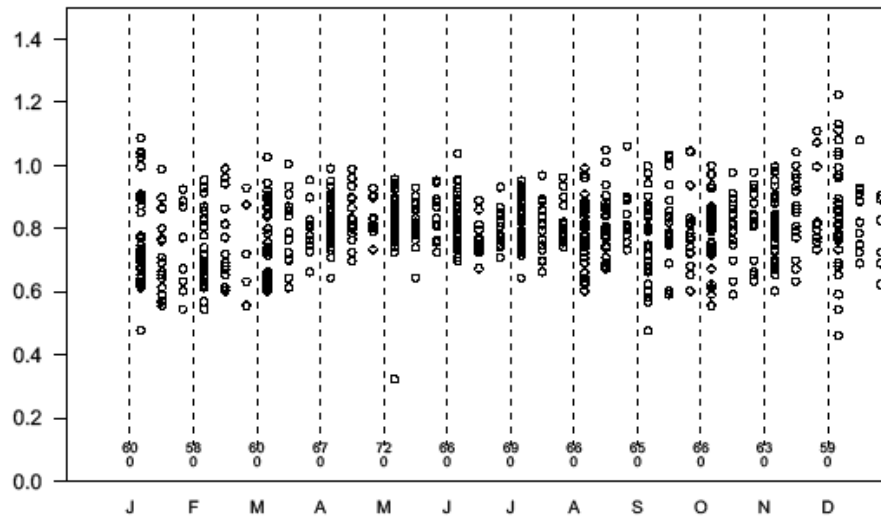
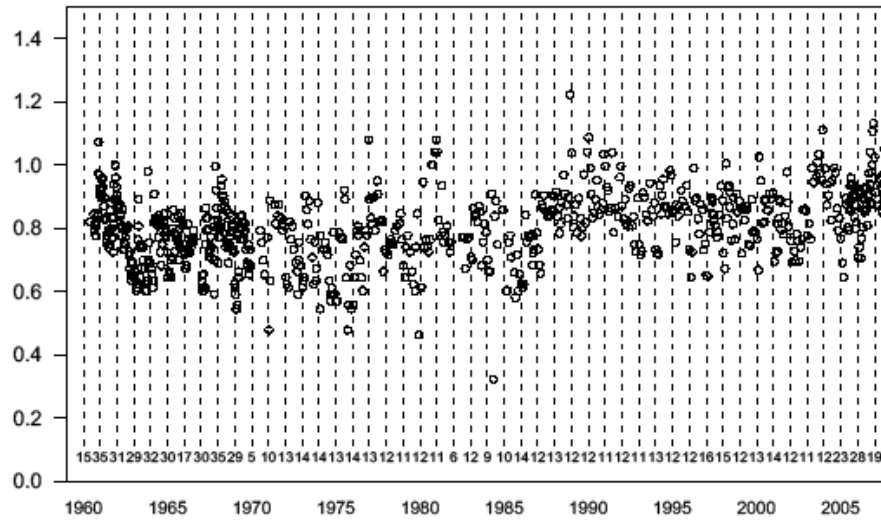


Figure A.32: Dissolved Potassium at Emerson (log<sub>10</sub> mg/l)



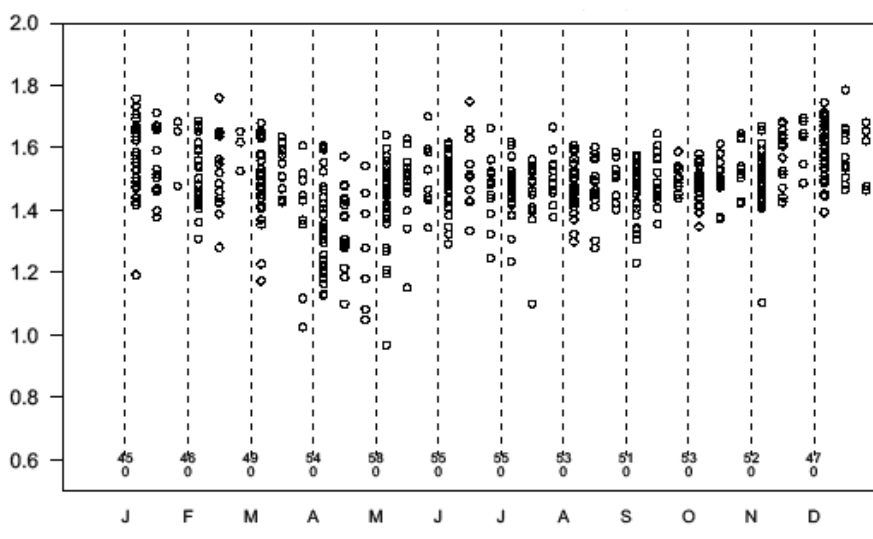
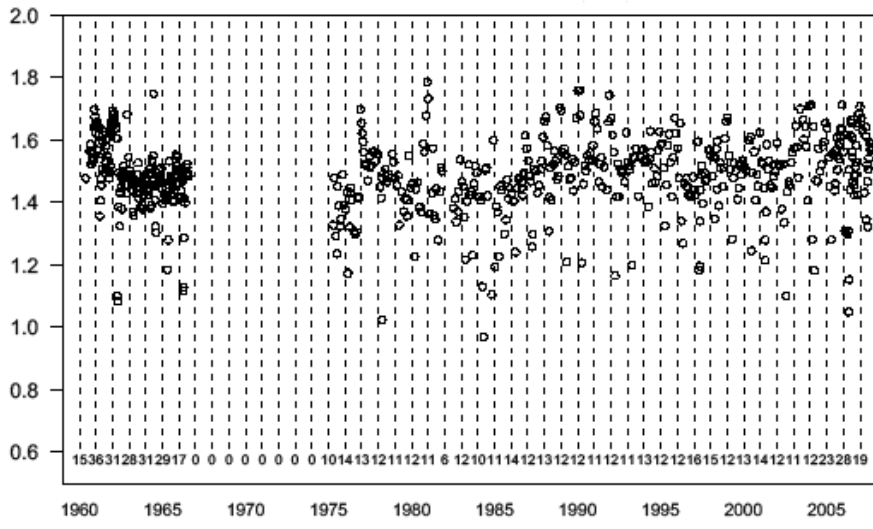


Figure A.33: Dissolved Magnesium at Emerson (log<sub>10</sub> mg/l)

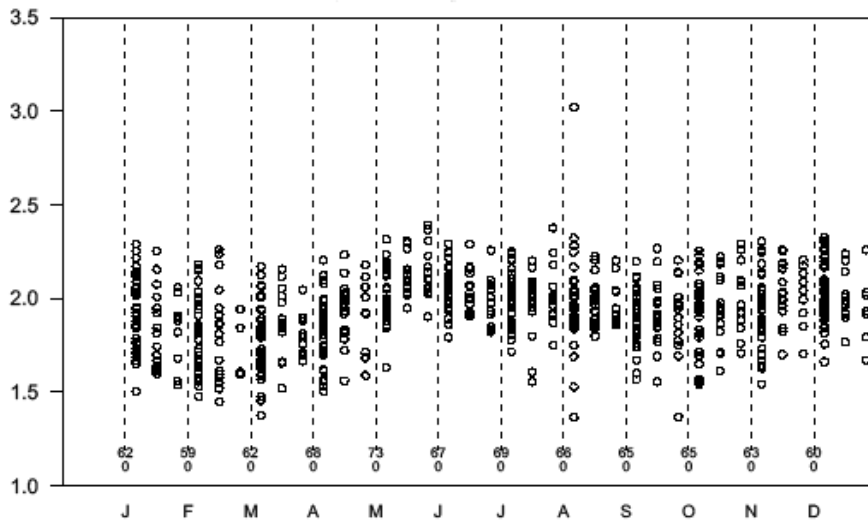
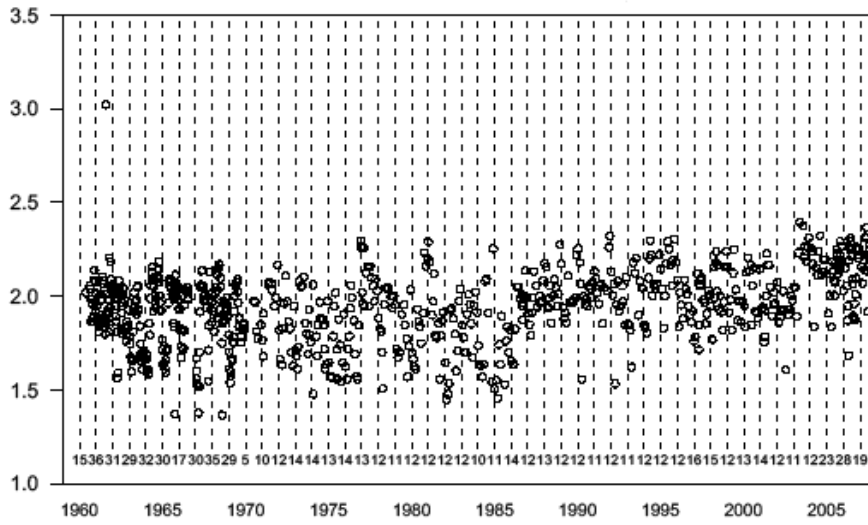


Figure A.34: Dissolved Sulphate at Emerson (log<sub>10</sub> mg/l)

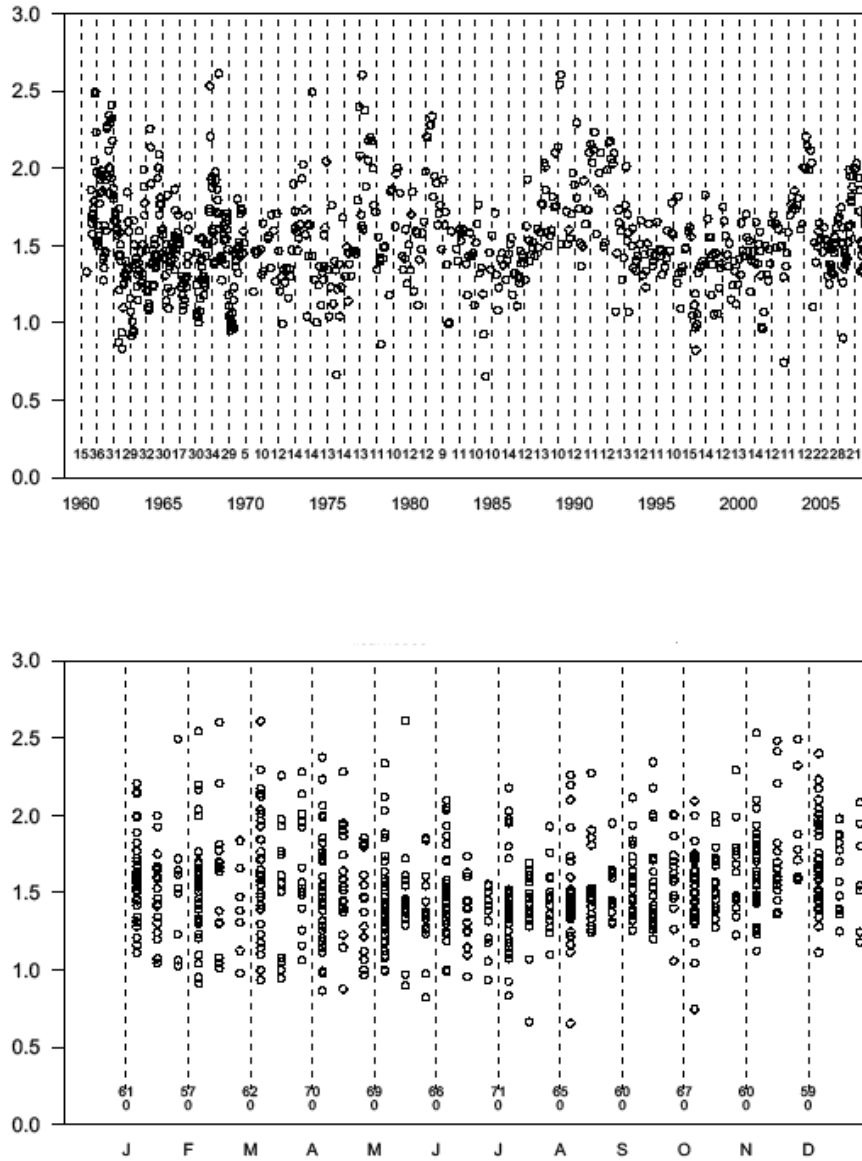


Figure A.35: Dissolved Chloride at Emerson ( $\log_{10}$  mg/l)

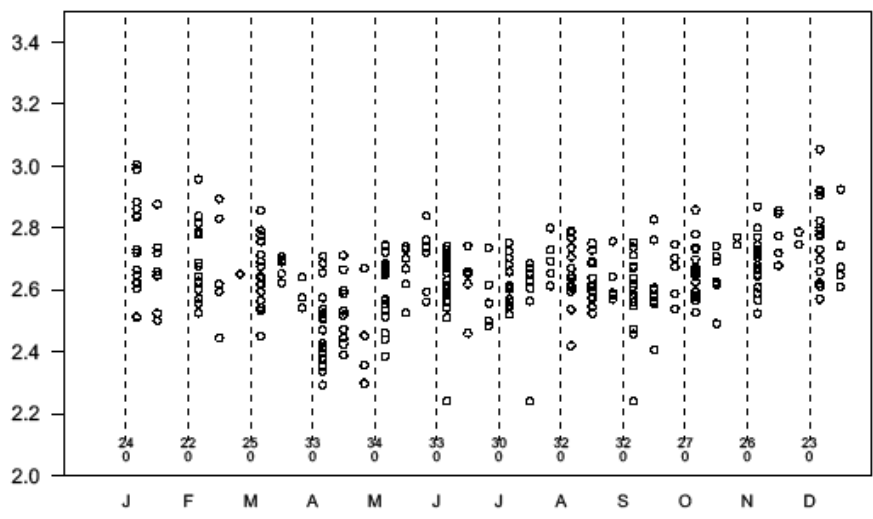
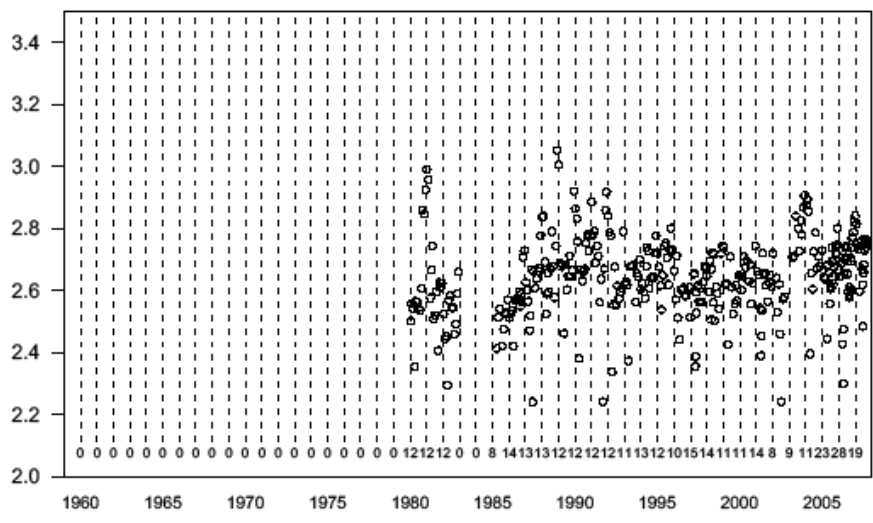


Figure A.36: Total Dissolved Solids at Emerson ( $\log_{10}$  mg/l)

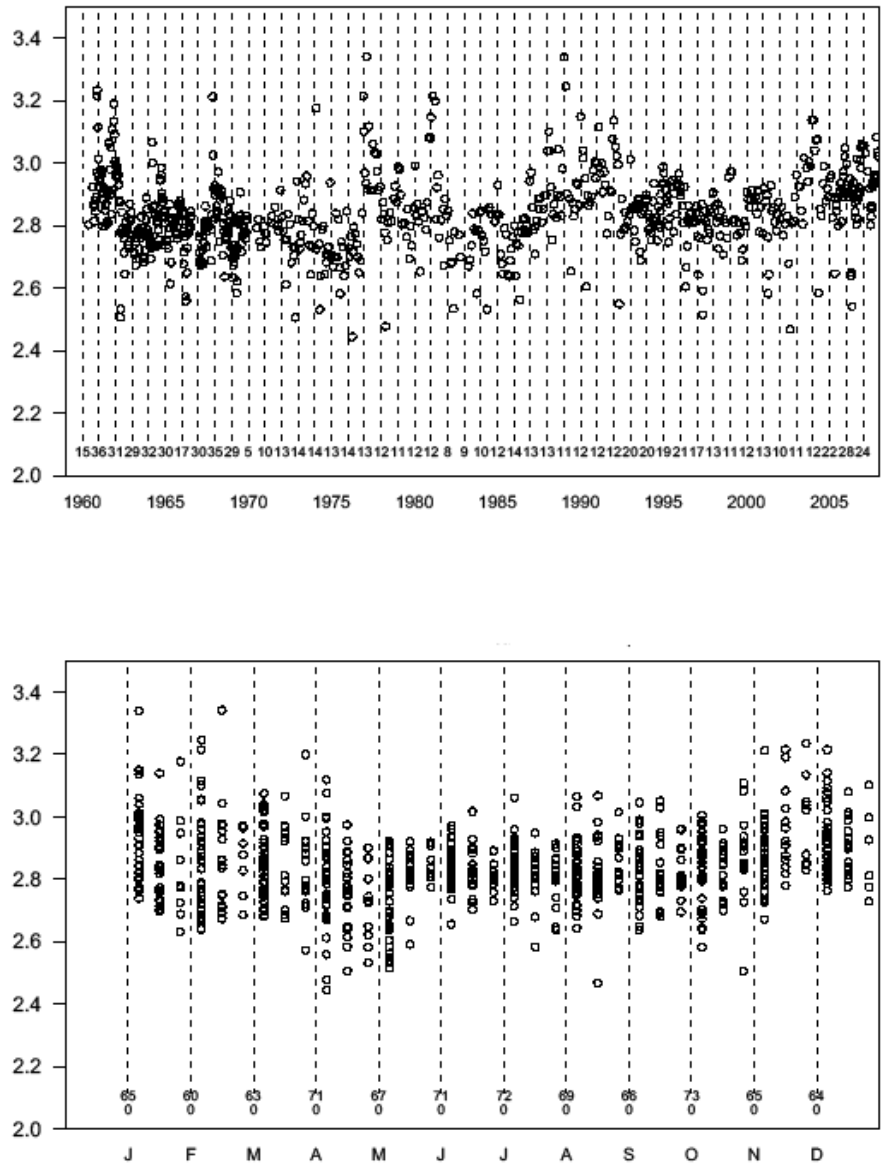


Figure A.37: Specific Conductance at Emerson ( $\log_{10}$  USIE/cm<sup>2</sup>)

## **A.5 Flow Adjustment Plots**

The following sequence of plots (Figures [A.38](#)–[A.83](#)) show the streamflow related anomaly (plus trend); the seasonally adjusted and de-trended data and annual streamflow anomalies; the seasonally adjusted and flow adjusted data (with flat trend line); and the residual plots for the following constituents: dissolved calcium, dissolved sodium, dissolved potassium, dissolved magnesium, dissolved sulphate, dissolved chloride, total dissolved solids and specific conductance. These provide a baseline for further examinations of trends as discussed in the text.

### **A.5.1 Emerson Monitoring Station**

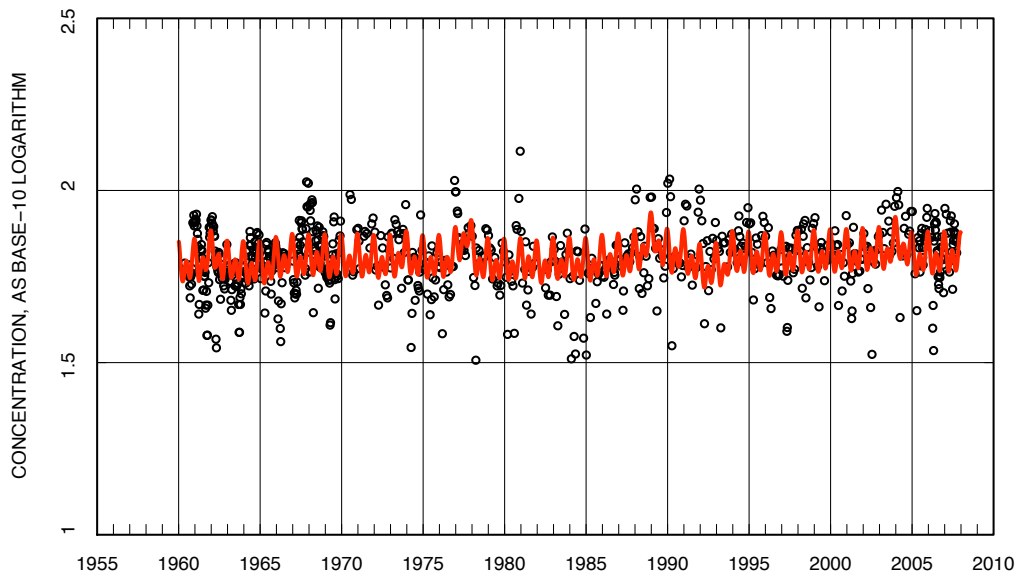


Figure A.38: Dissolved Calcium concentrations (points) and streamflow related anomaly + trend (line)

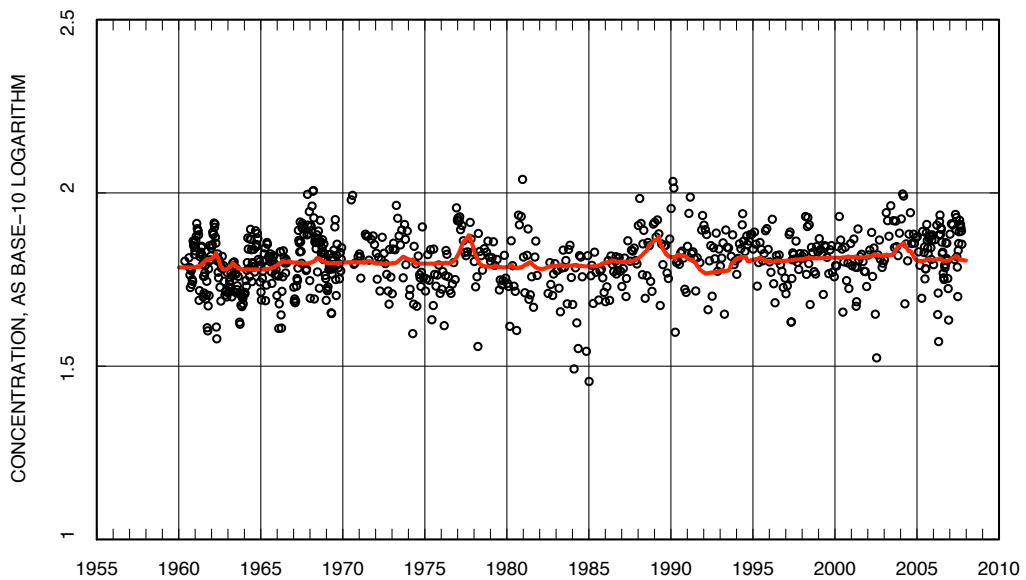


Figure A.39: Dissolved Calcium Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

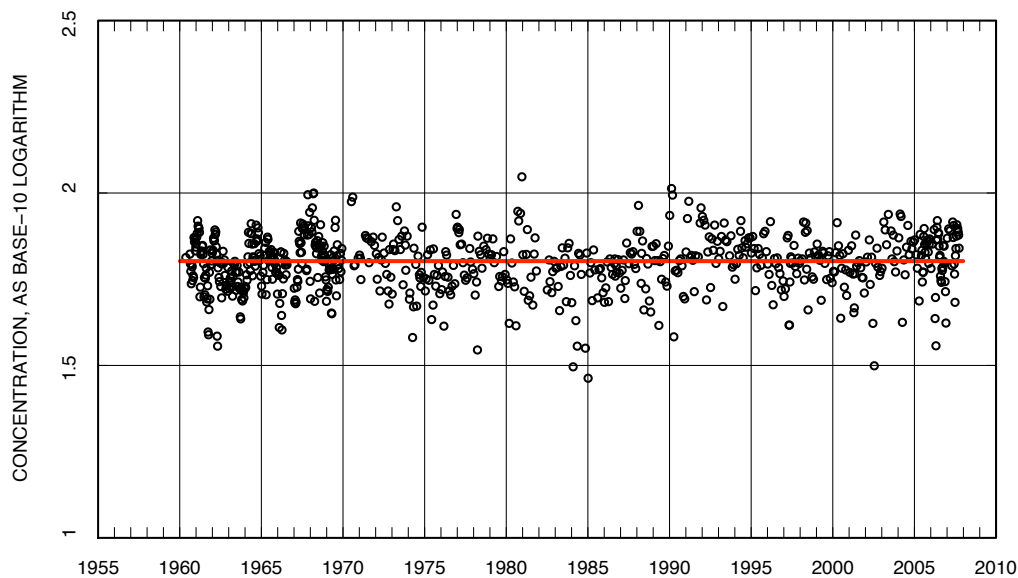


Figure A.40: Dissolved Calcium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

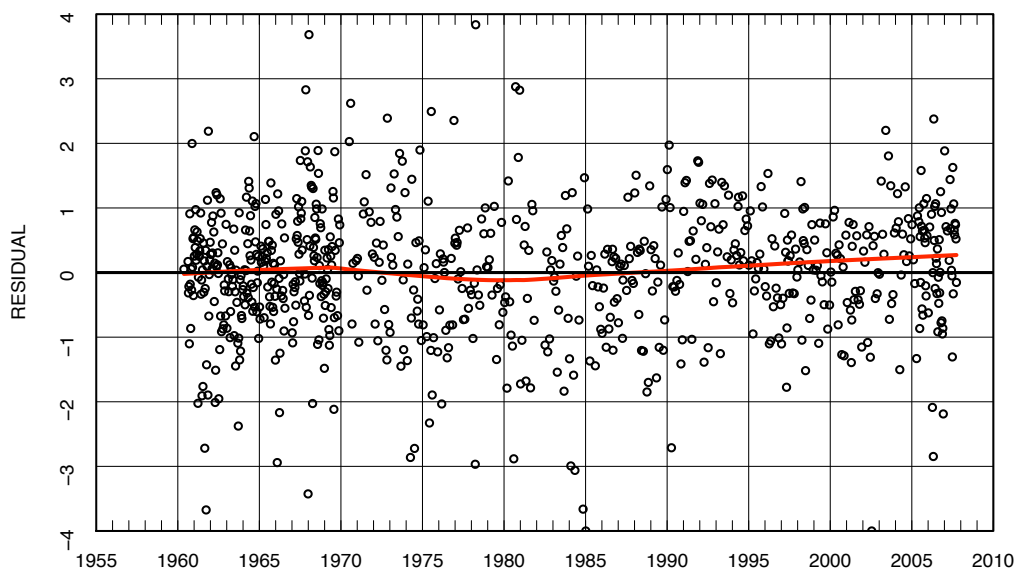


Figure A.41: Dissolved Calcium Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .



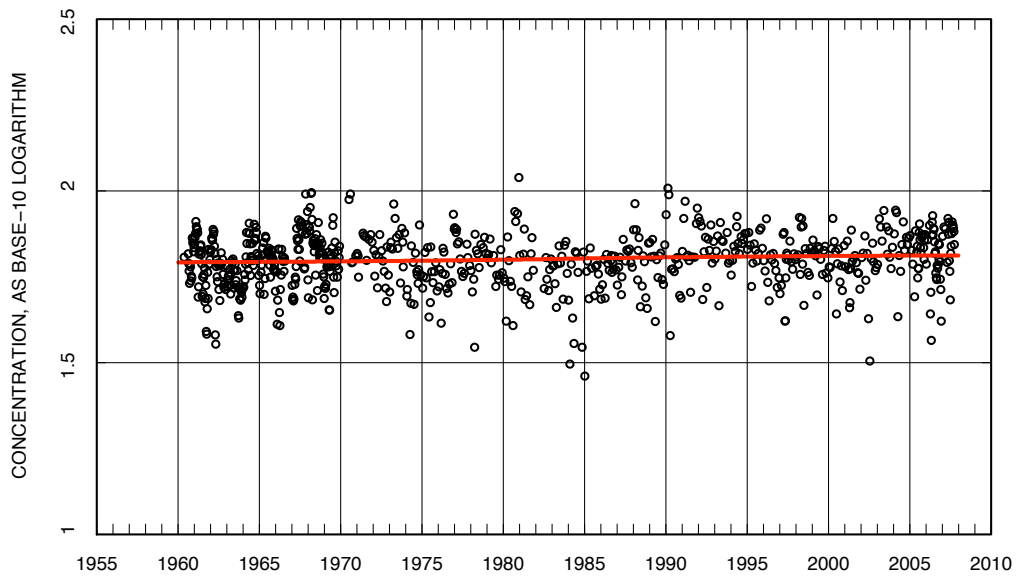


Figure A.42: Dissolved Calcium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

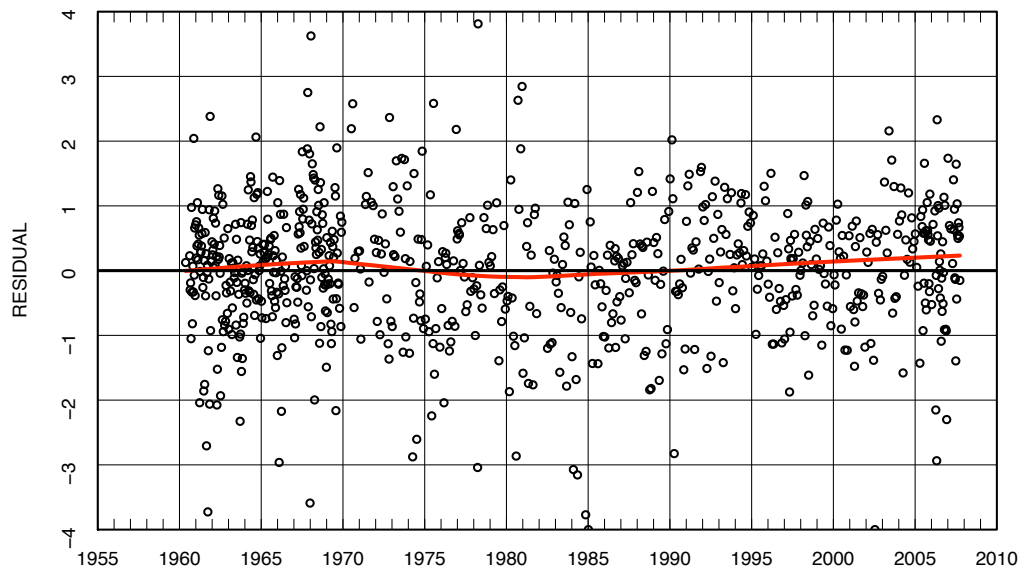


Figure A.43: Dissolved Calcium Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

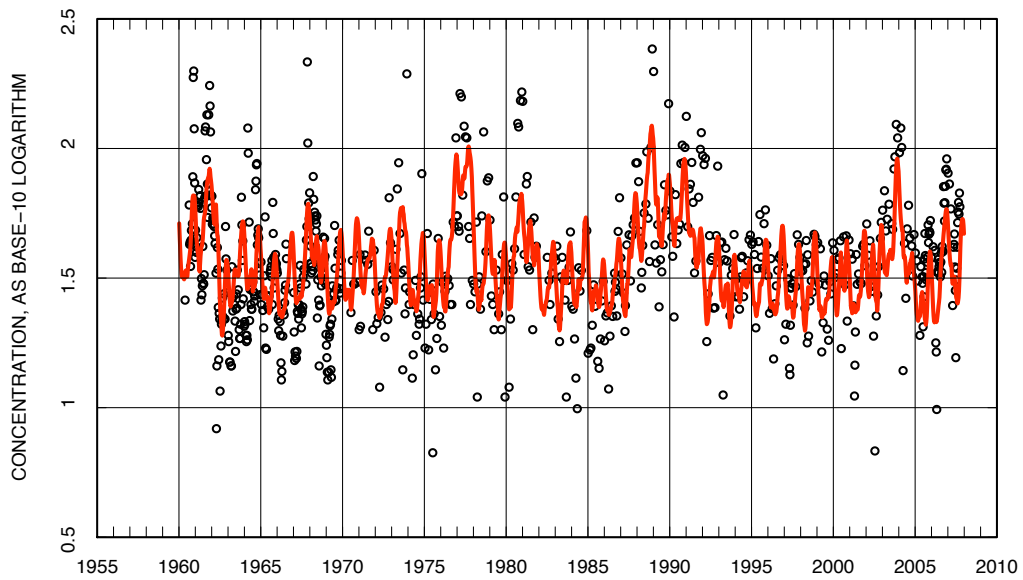


Figure A.44: Dissolved Sodium concentrations (points) and streamflow related anomaly + trend (line)

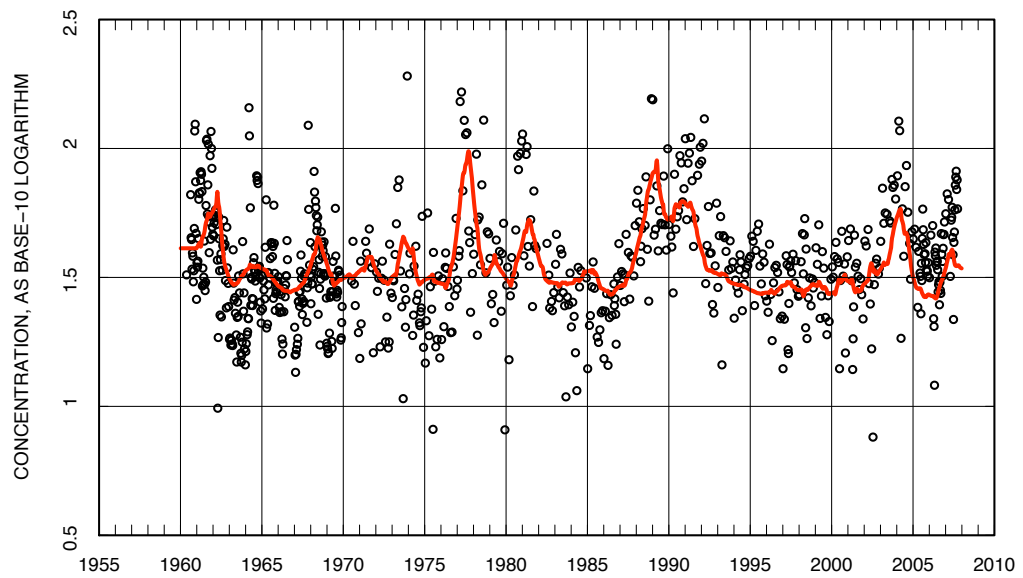


Figure A.45: Dissolved Sodium Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

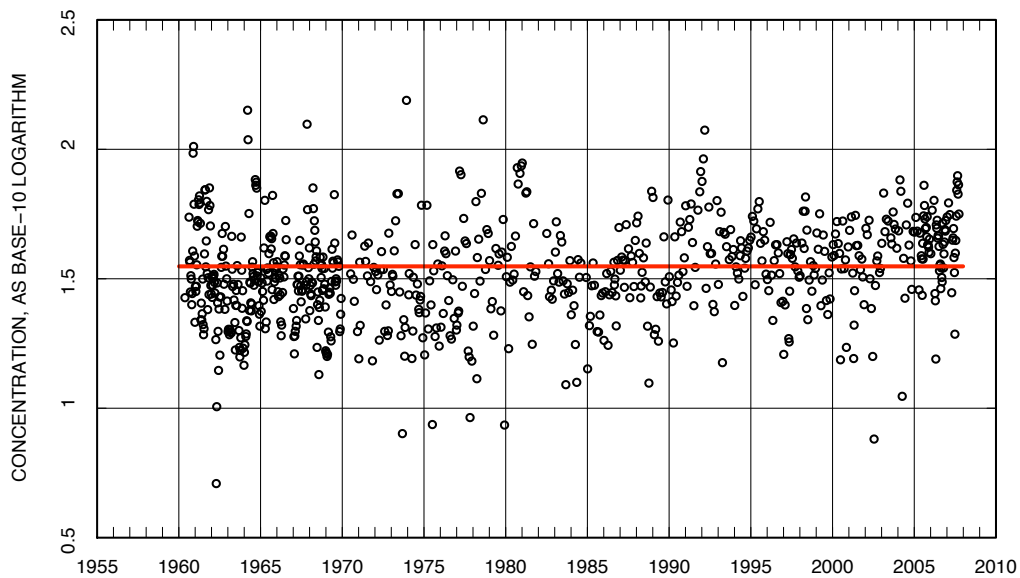


Figure A.46: Dissolved Sodium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

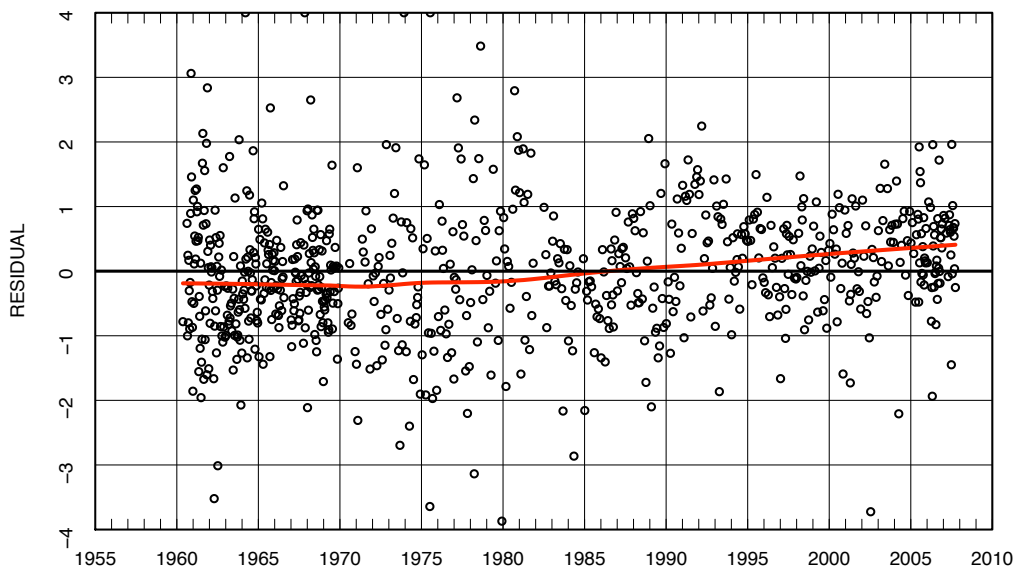


Figure A.47: Dissolved Sodium Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

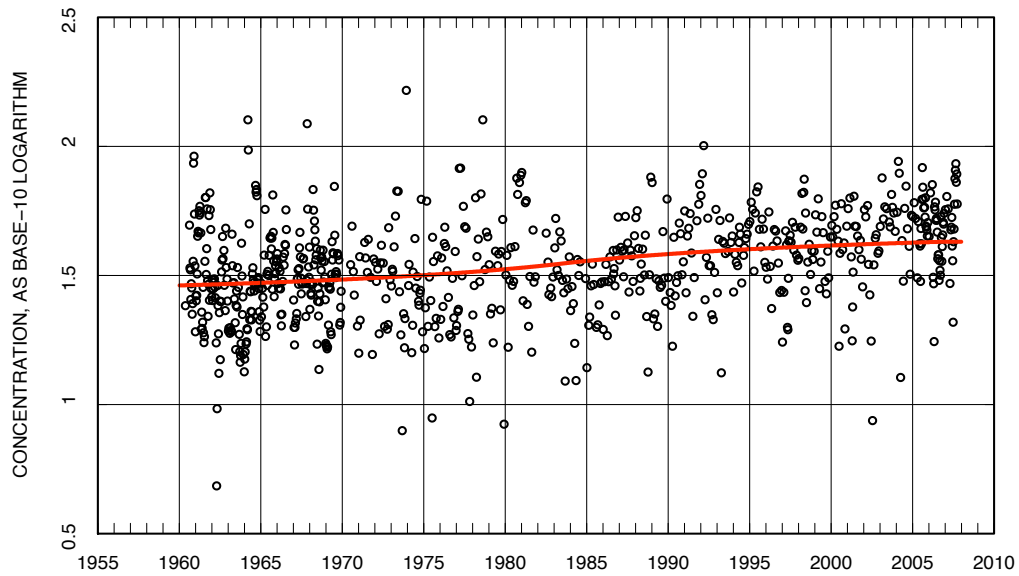


Figure A.48: Dissolved Sodium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

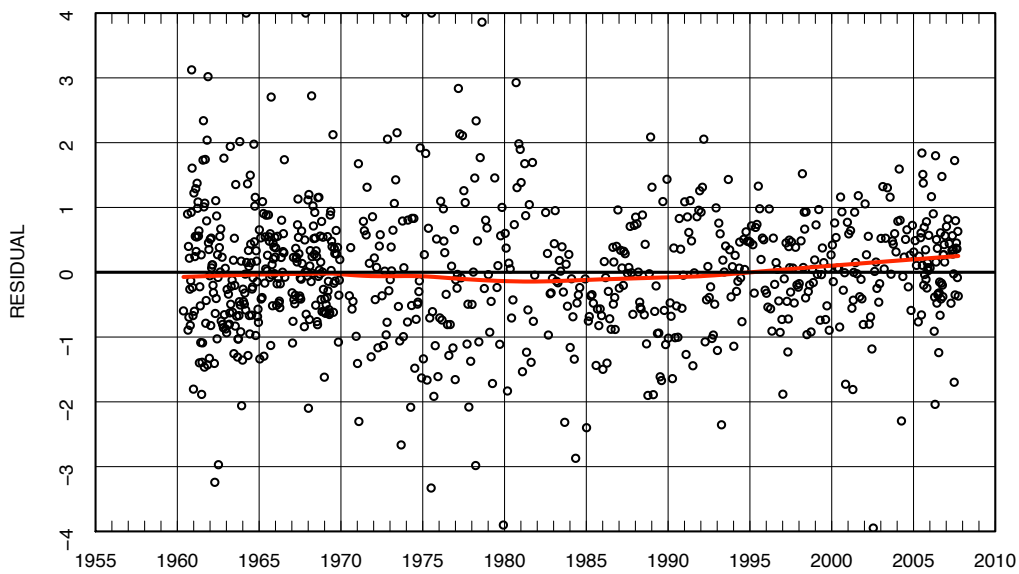


Figure A.49: Dissolved Sodium Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

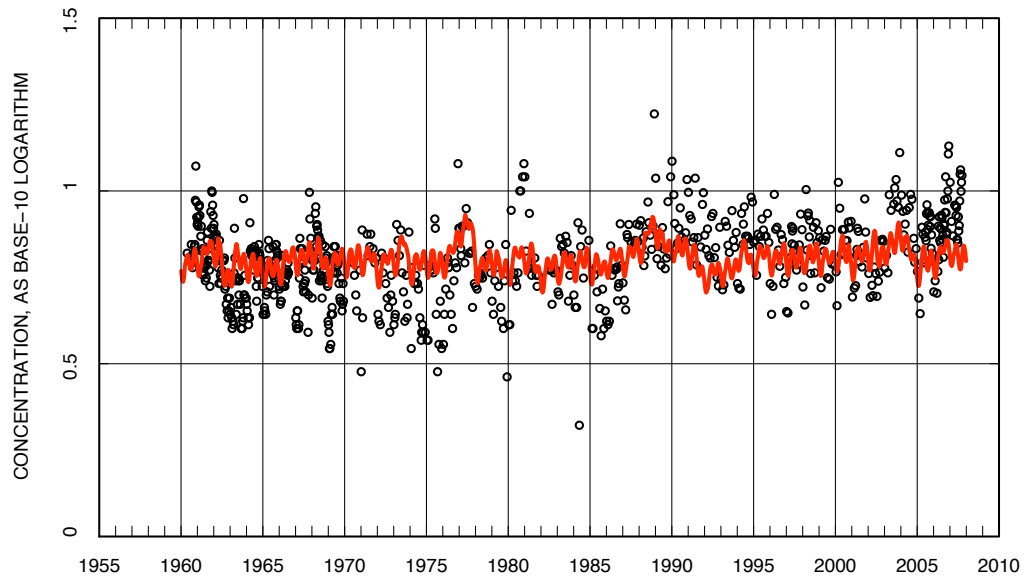


Figure A.50: Dissolved Potassium concentrations (points) and streamflow related anomaly + trend (line)

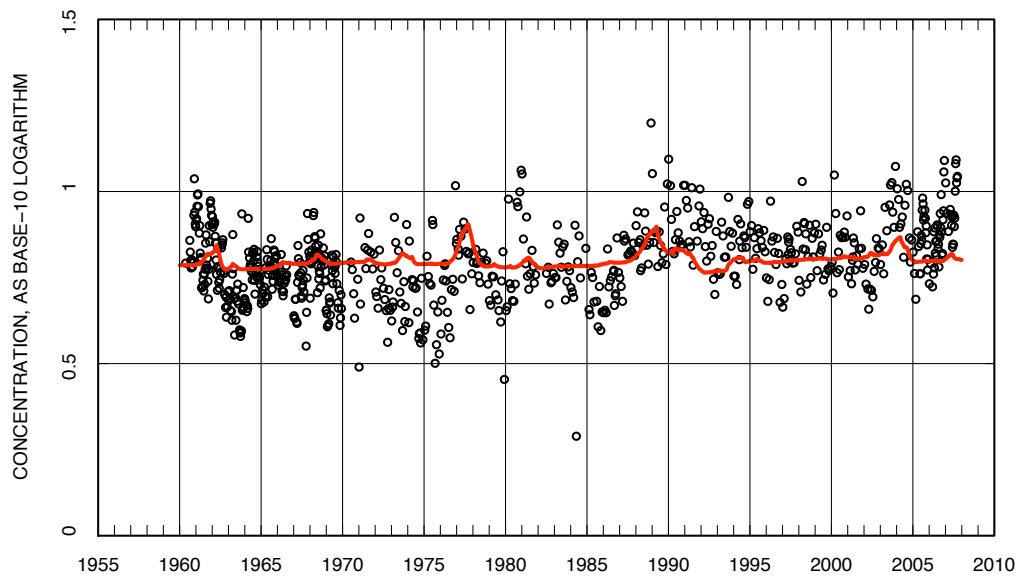


Figure A.51: Dissolved Potassium Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

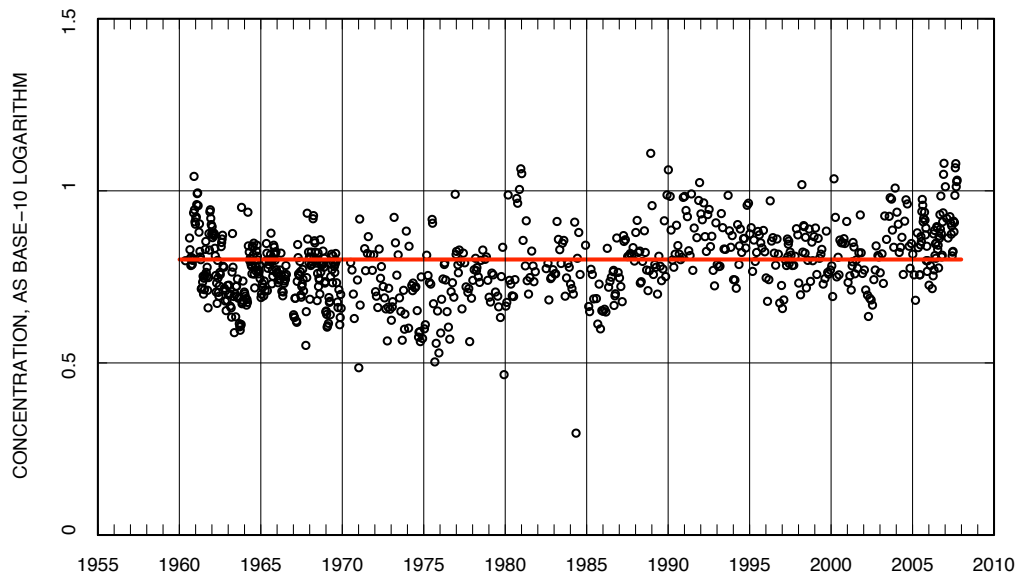


Figure A.52: Dissolved Potassium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

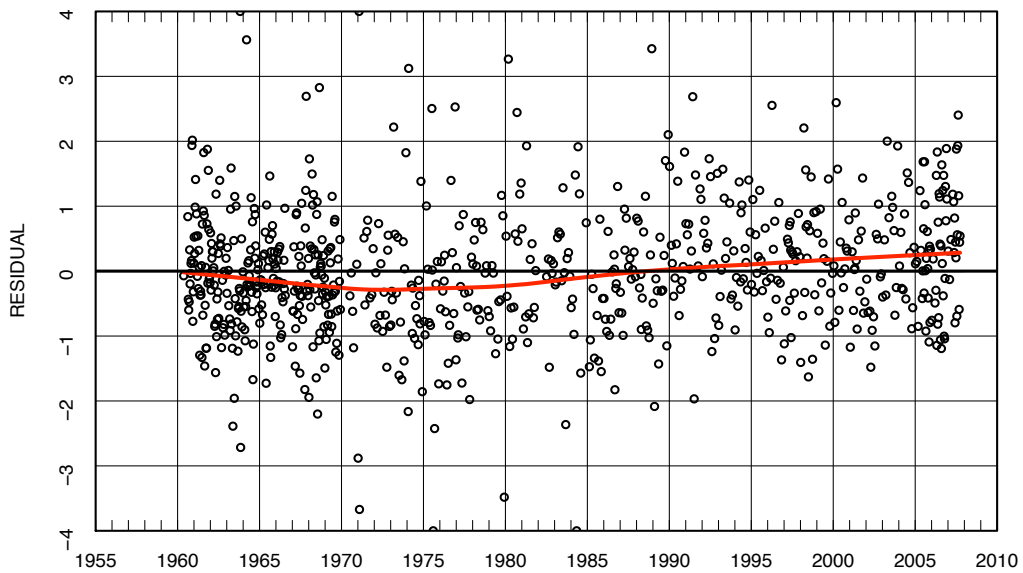


Figure A.53: Dissolved Potassium Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

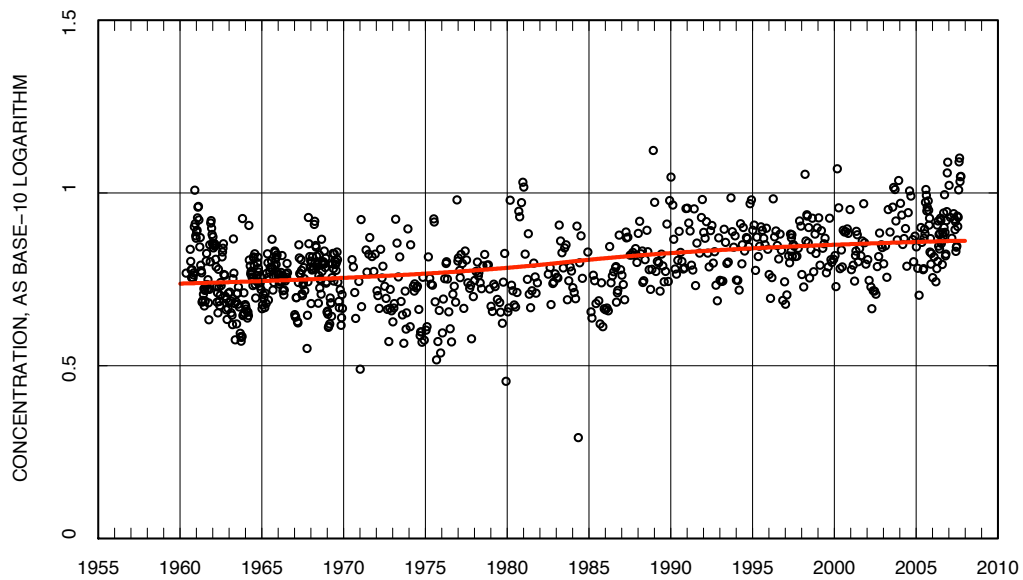


Figure A.54: Dissolved Potassium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

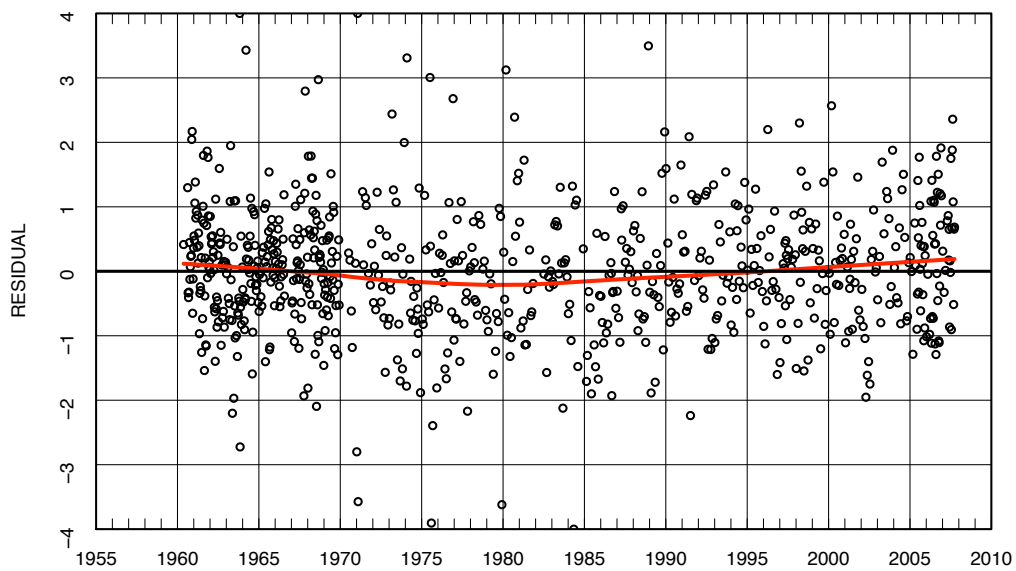


Figure A.55: Dissolved Potassium Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

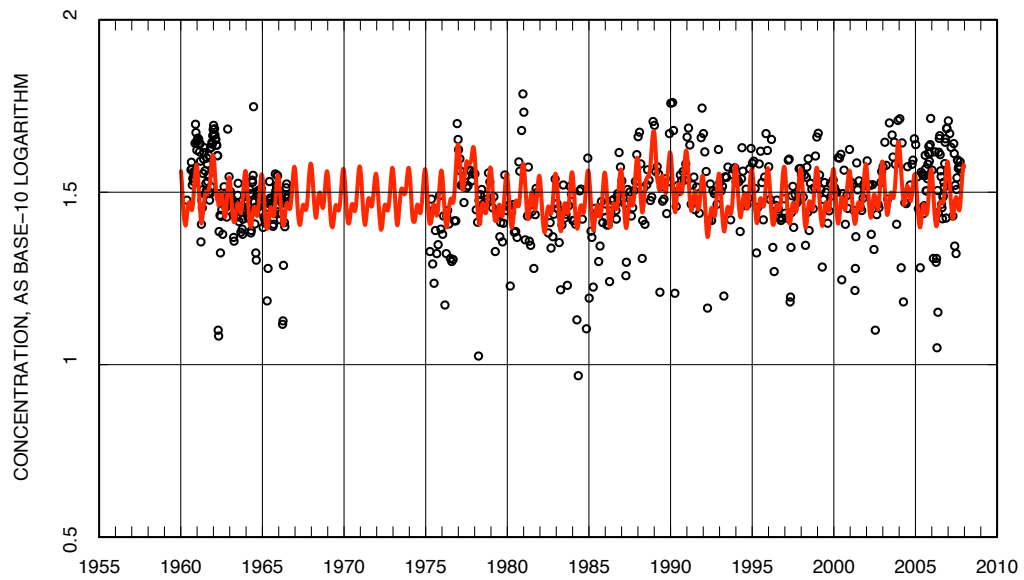


Figure A.56: Dissolved Magnesium concentrations (points) and streamflow related anomaly + trend (line)

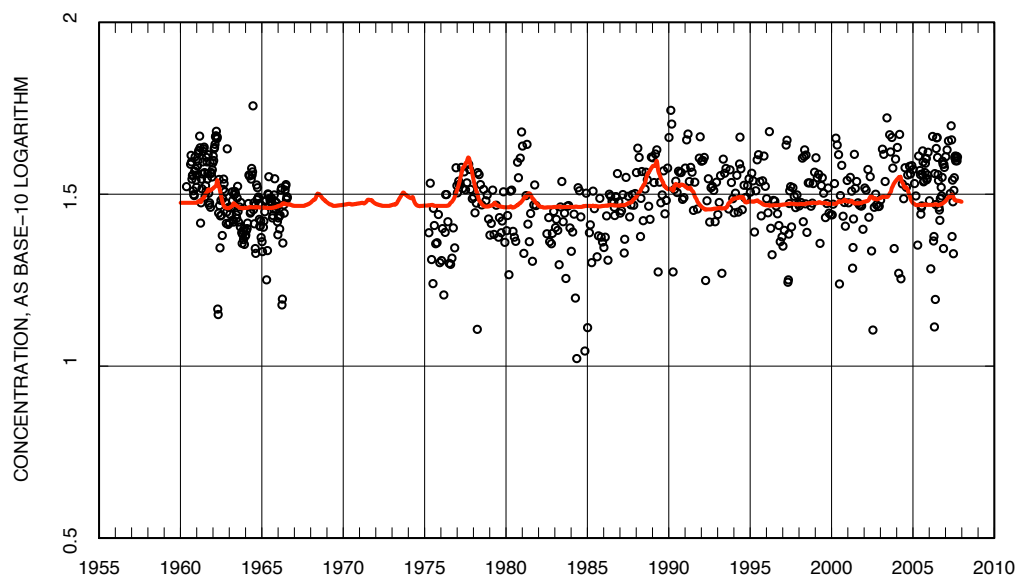


Figure A.57: Dissolved Magnesium Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).



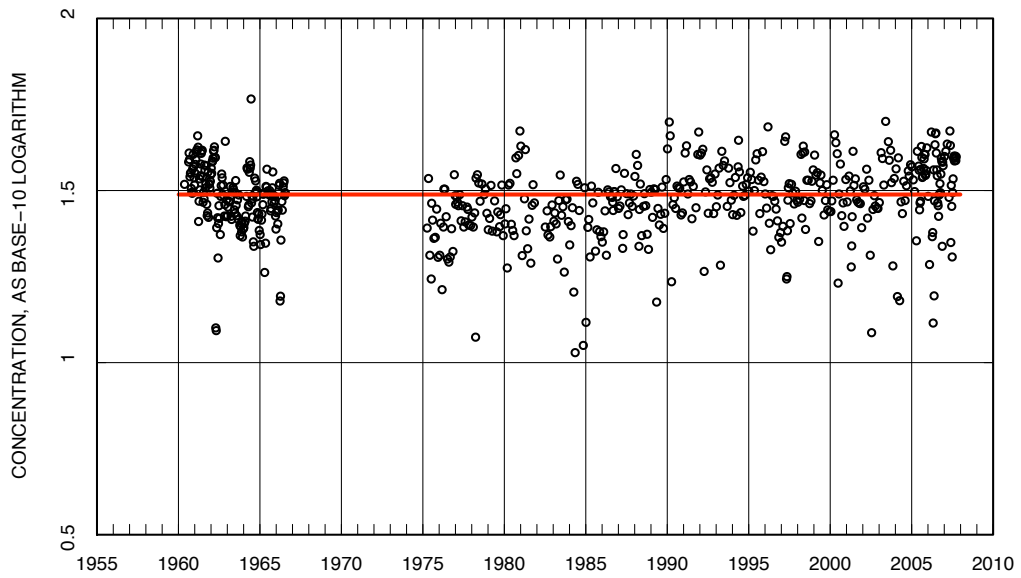


Figure A.58: Dissolved Magnesium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

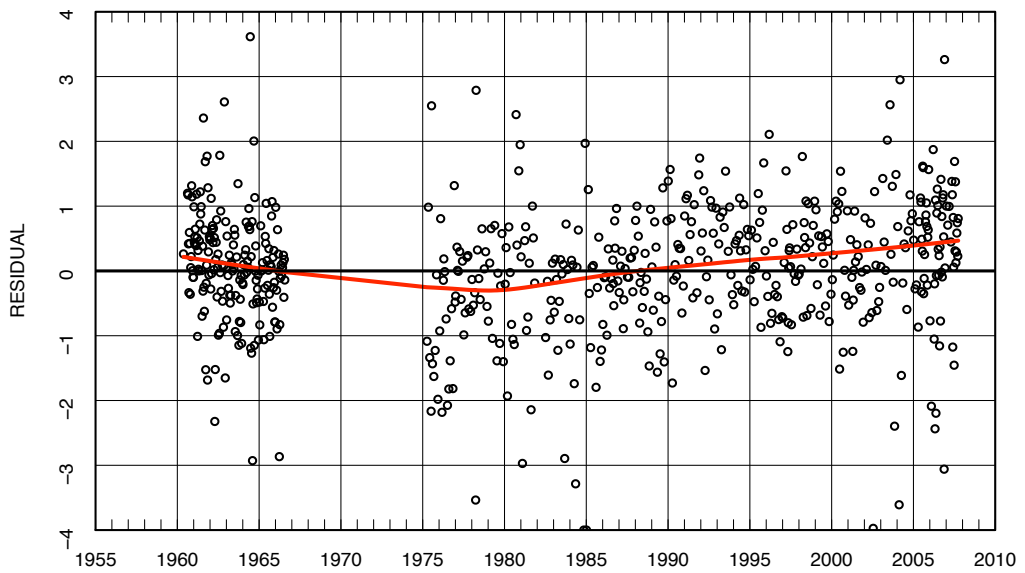


Figure A.59: Dissolved Magnesium Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

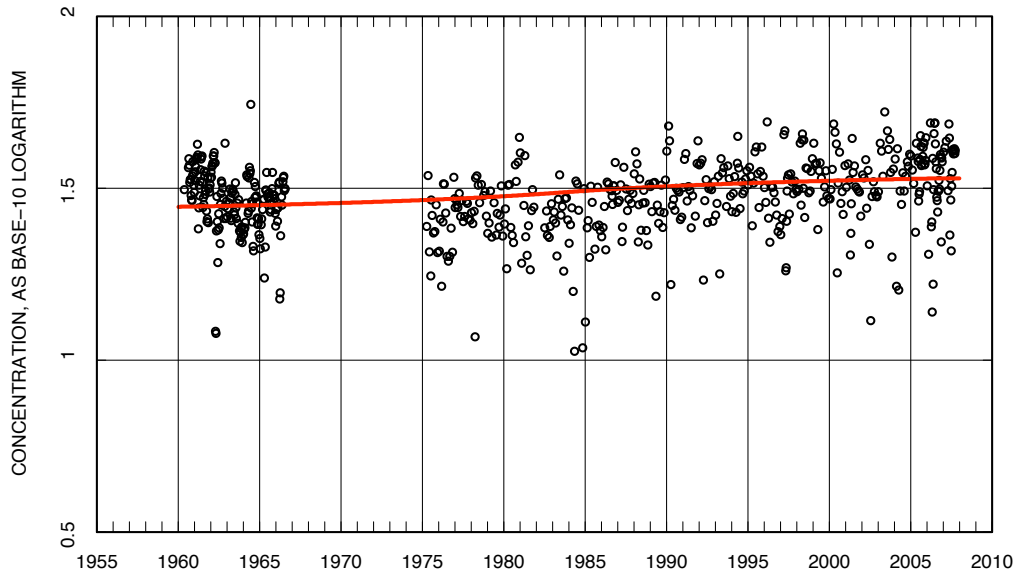


Figure A.60: Dissolved Magnesium Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

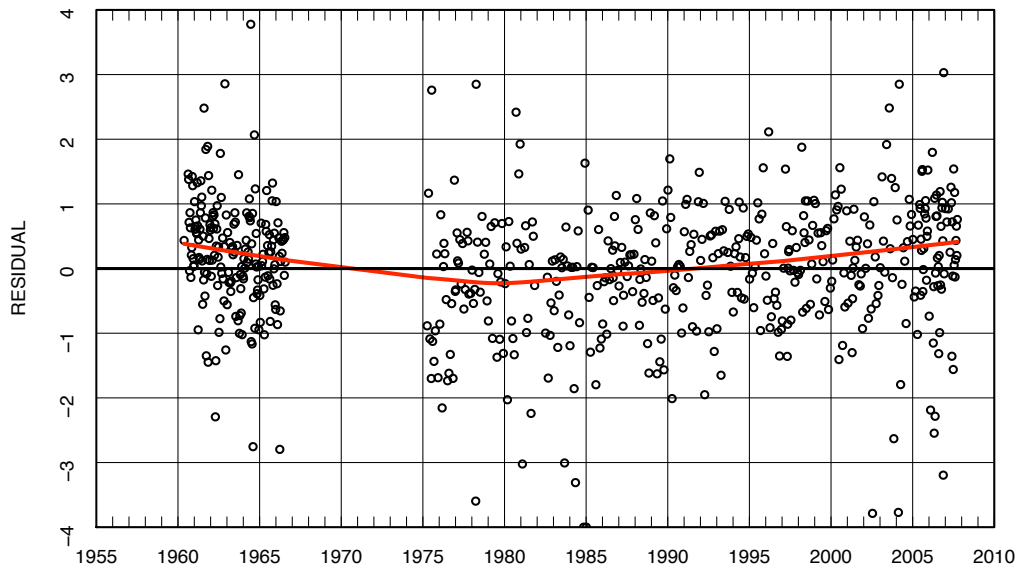


Figure A.61: Dissolved Magnesium Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

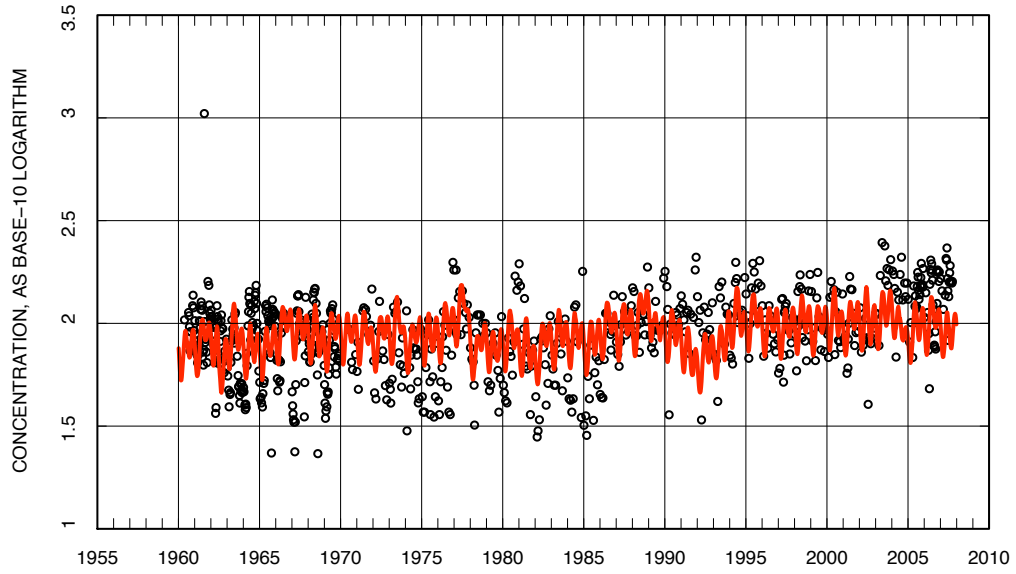


Figure A.62: Dissolved Sulphate concentrations (points) and streamflow related anomaly + trend (line)

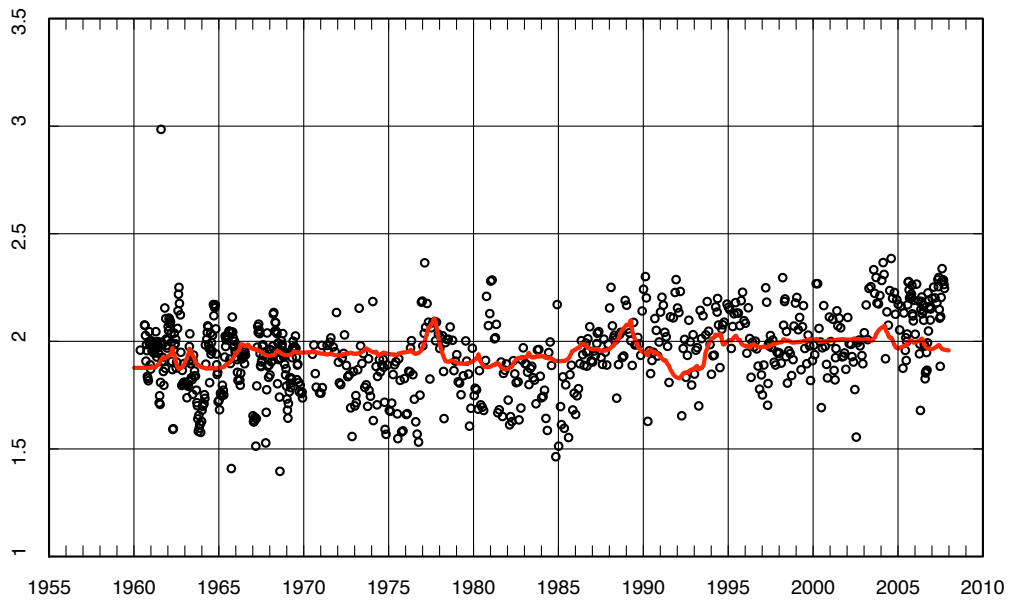


Figure A.63: Dissolved Sulphate Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

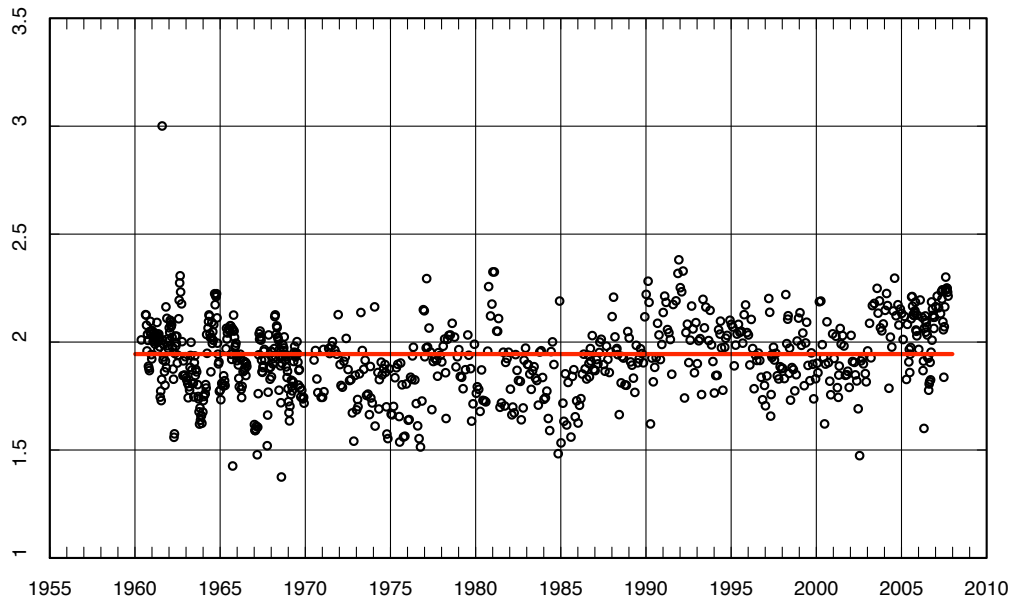


Figure A.64: Dissolved Sulphate Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

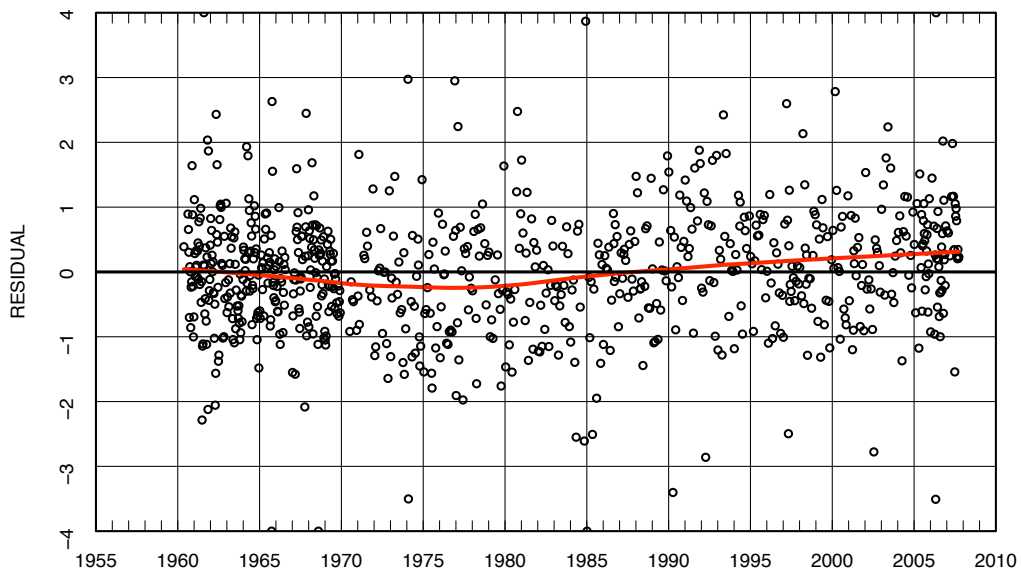


Figure A.65: Dissolved Sulphate Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

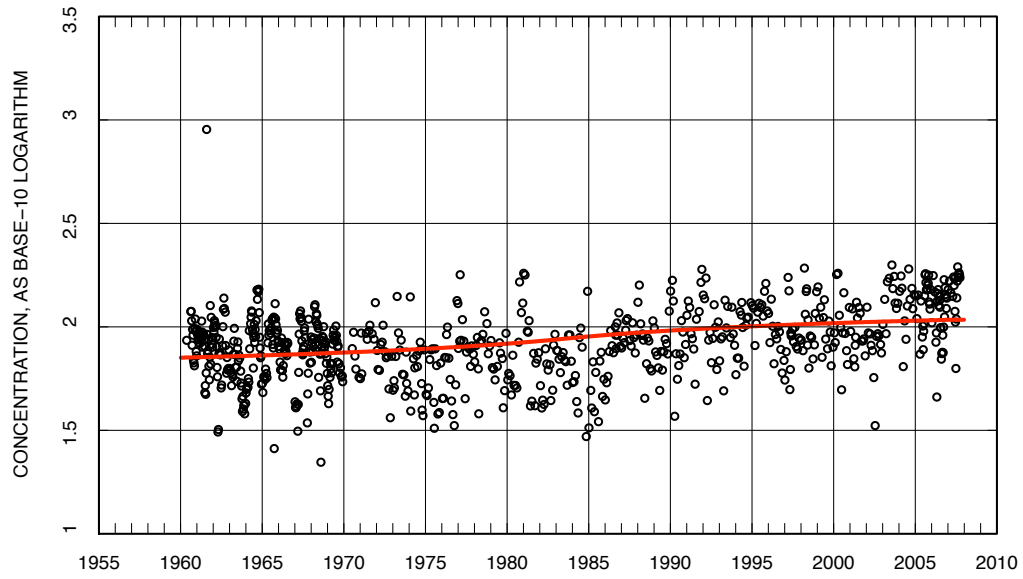


Figure A.66: Dissolved Sulphate Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

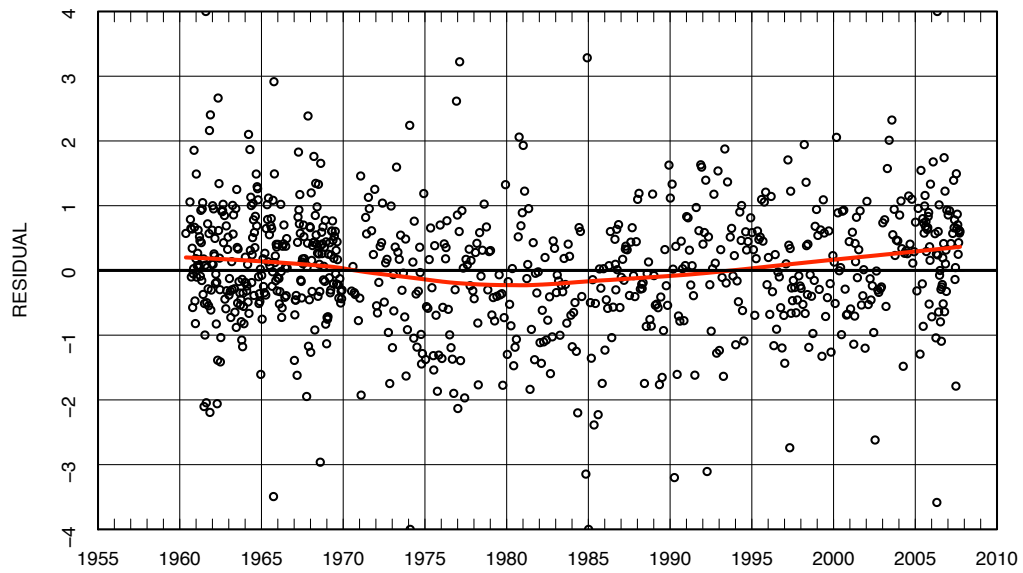


Figure A.67: Dissolved Sulphate Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

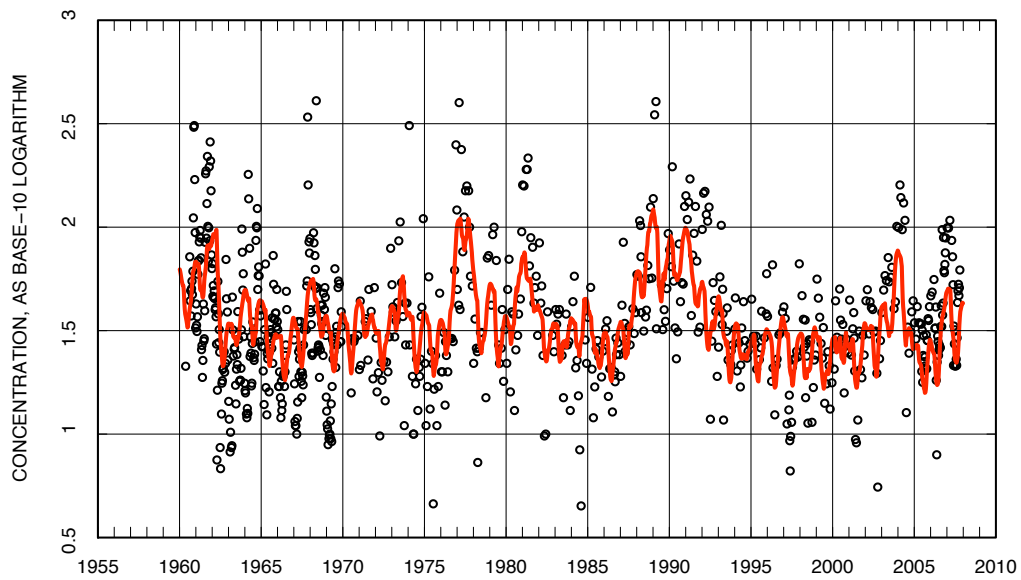


Figure A.68: Dissolved Chloride concentrations (points) and streamflow related anomaly + trend (line)

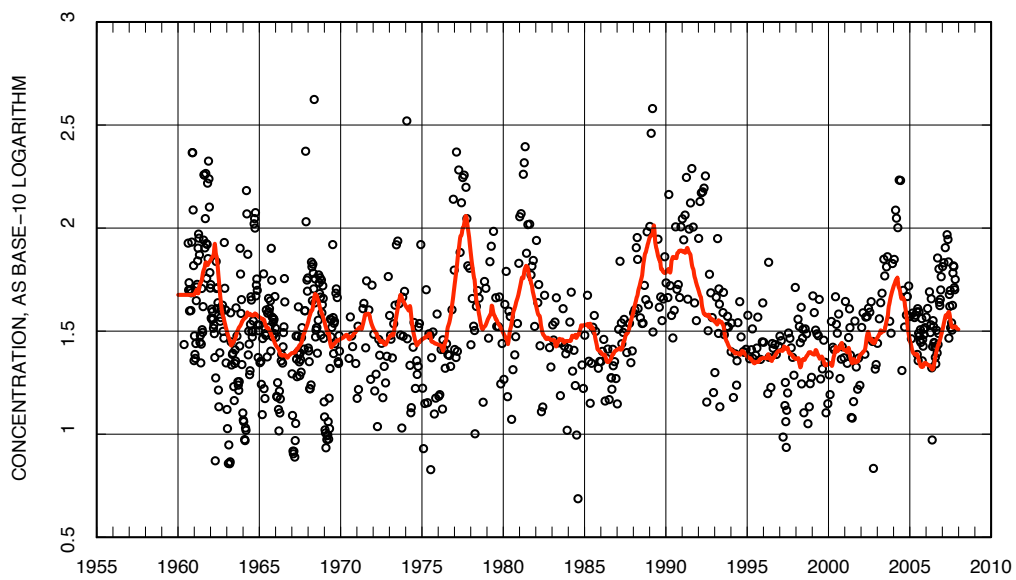


Figure A.69: Dissolved Chloride Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

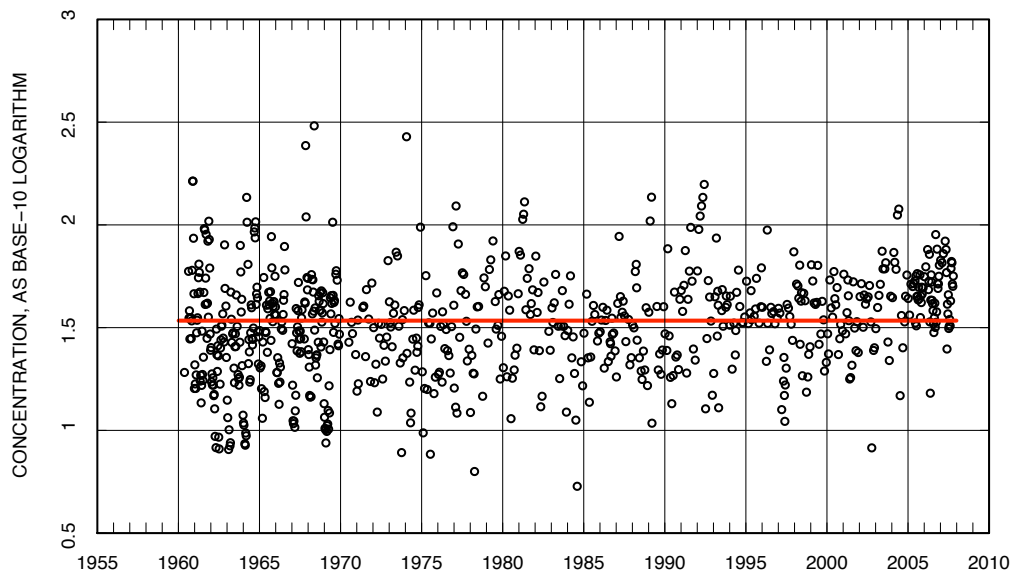


Figure A.70: Dissolved Chloride Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

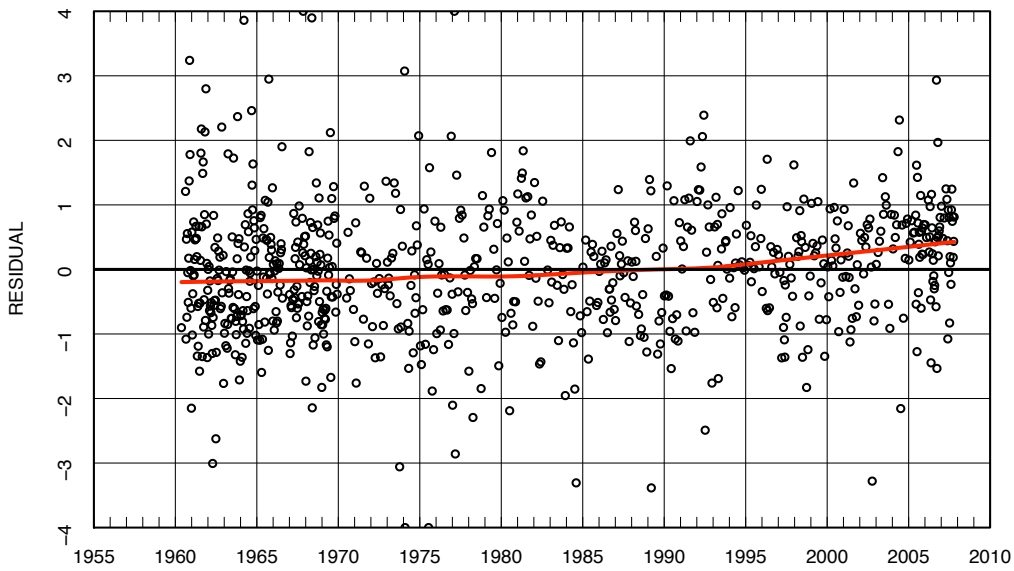


Figure A.71: Dissolved Chloride Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

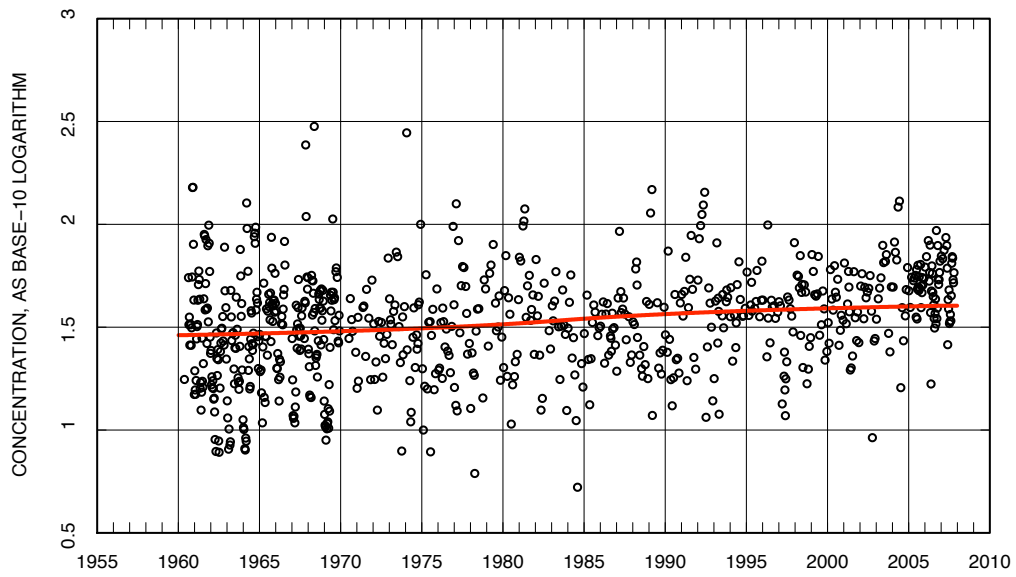


Figure A.72: Dissolved Chloride Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

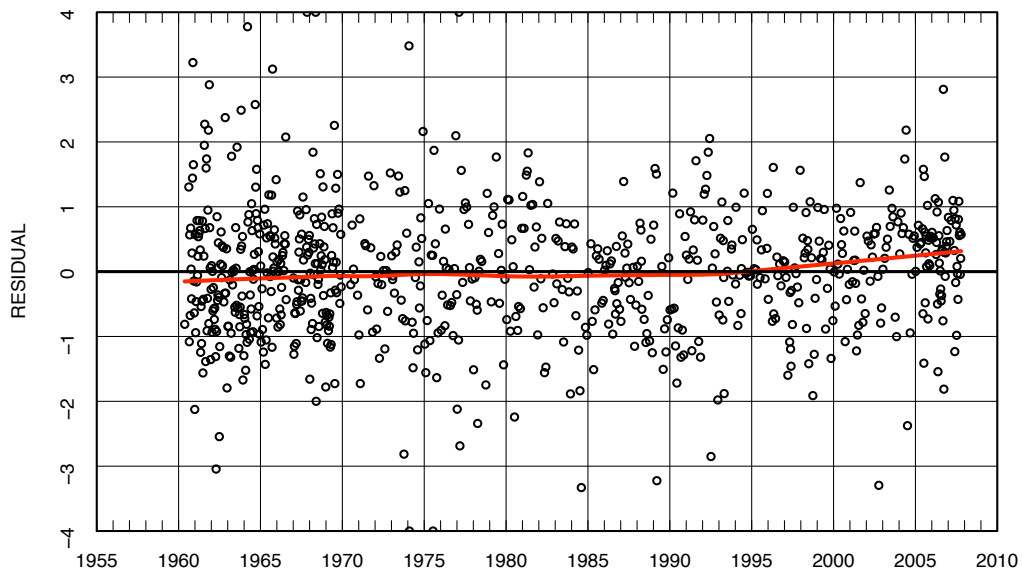


Figure A.73: Dissolved Chloride Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .



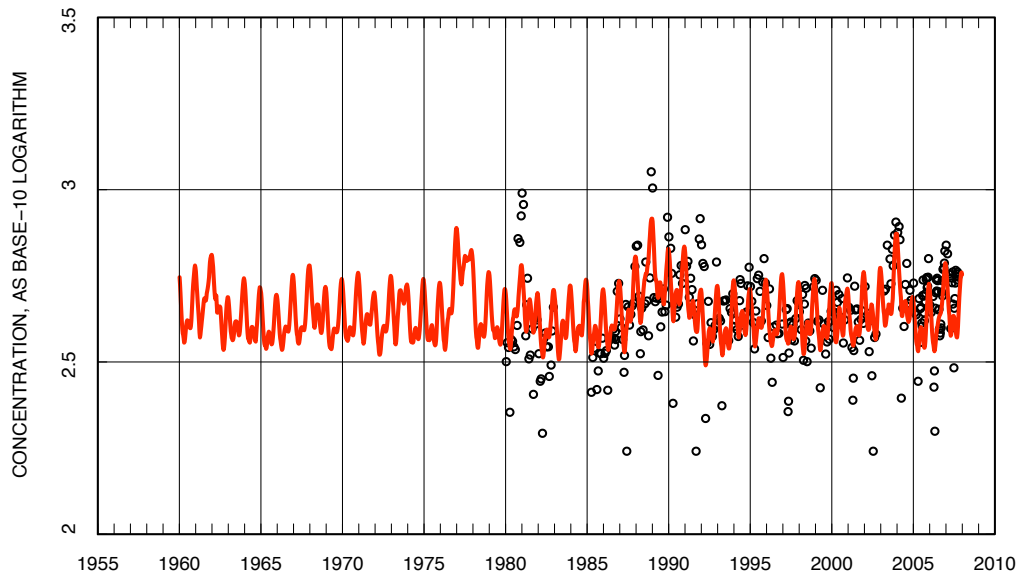


Figure A.74: Total Dissolved Solids concentrations (points) and streamflow related anomaly + trend (line)

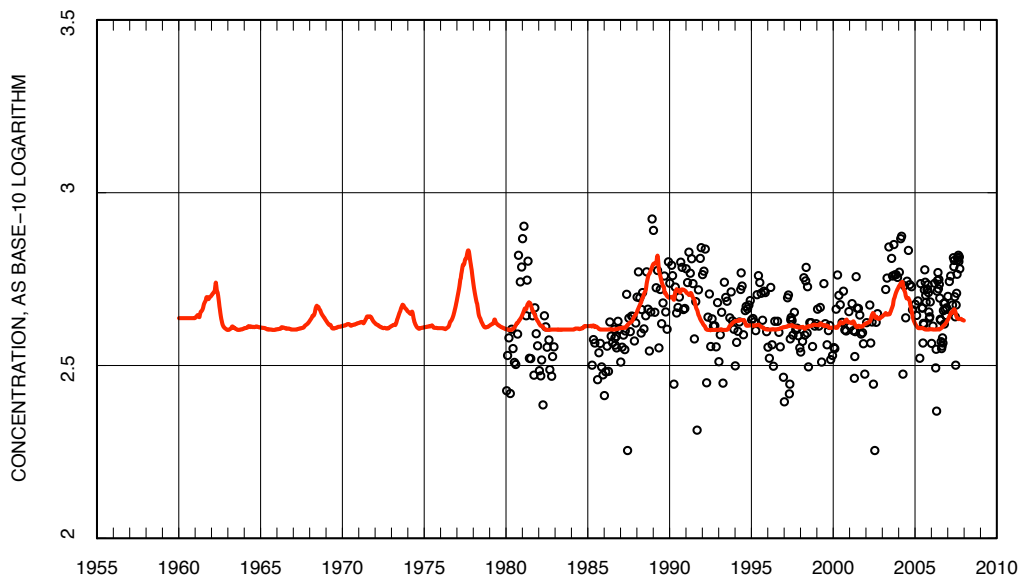


Figure A.75: Total Dissolved Solids Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

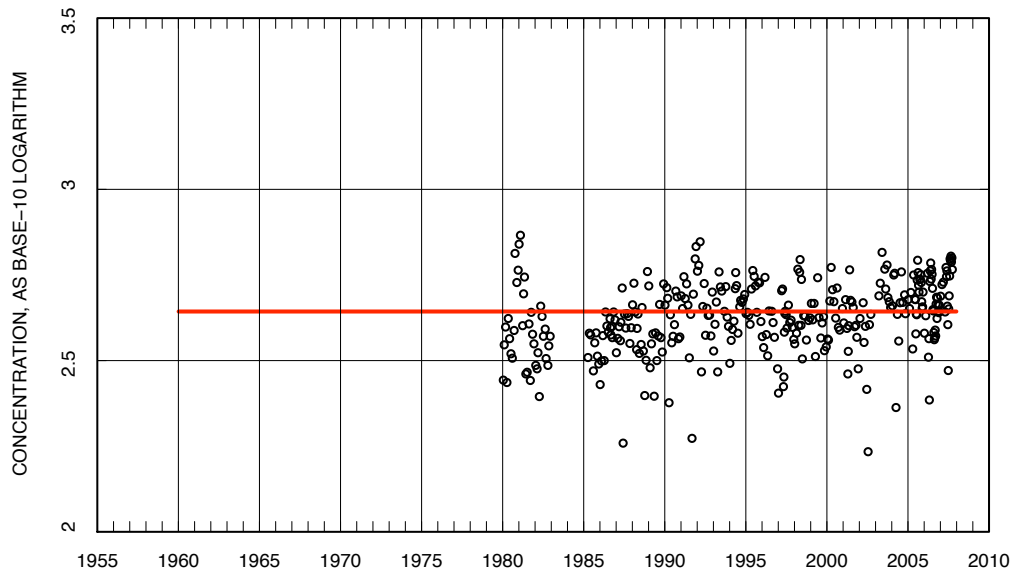


Figure A.76: Total Dissolved Solids Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

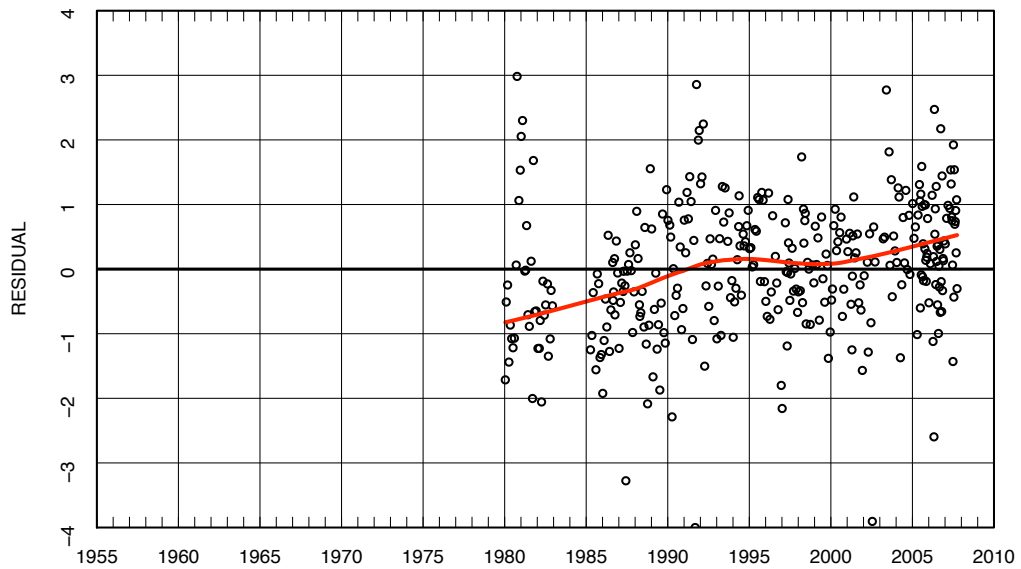


Figure A.77: Total Dissolved Solids Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

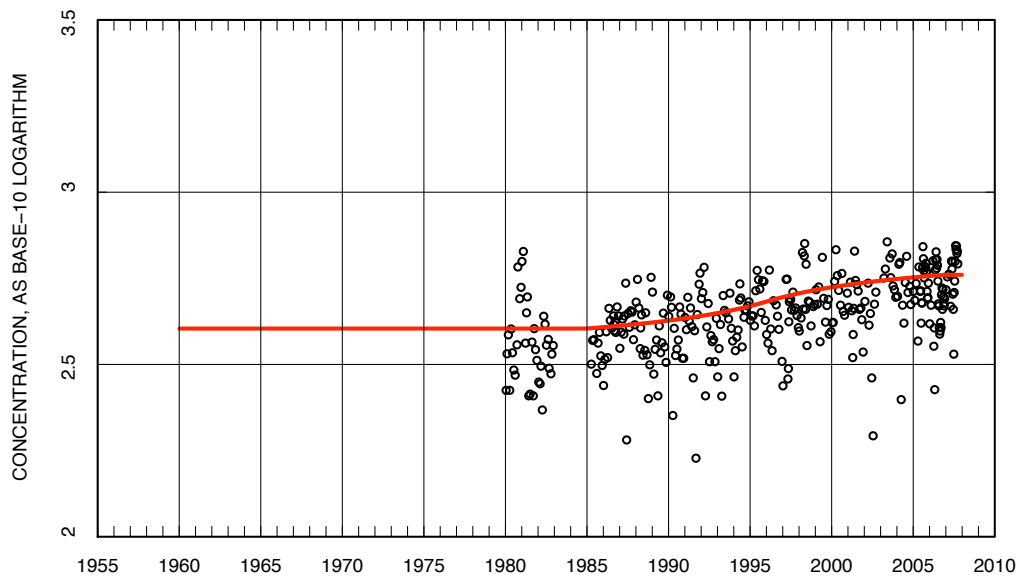


Figure A.78: Total Dissolved Solids Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

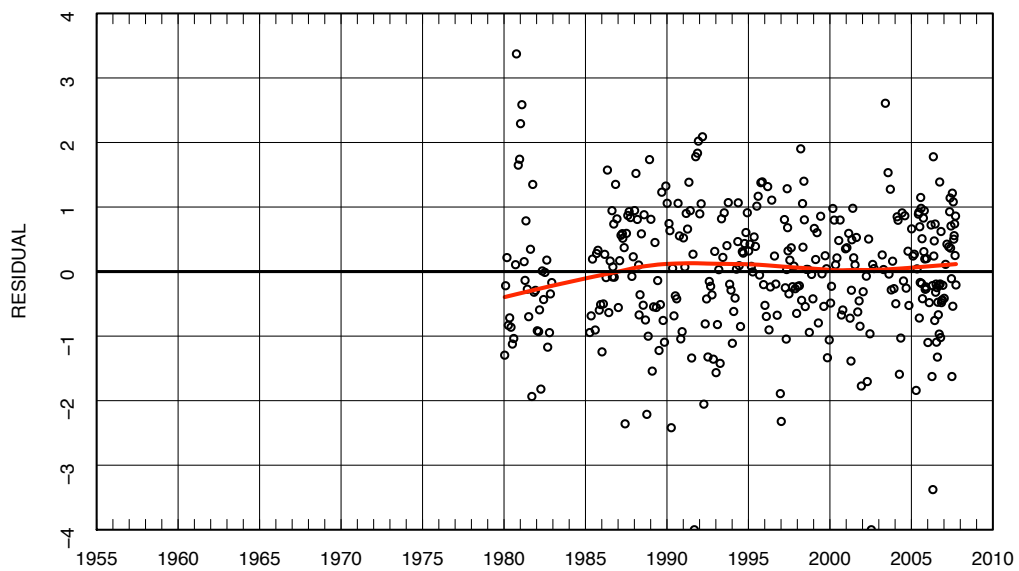


Figure A.79: Total Dissolved Solids Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

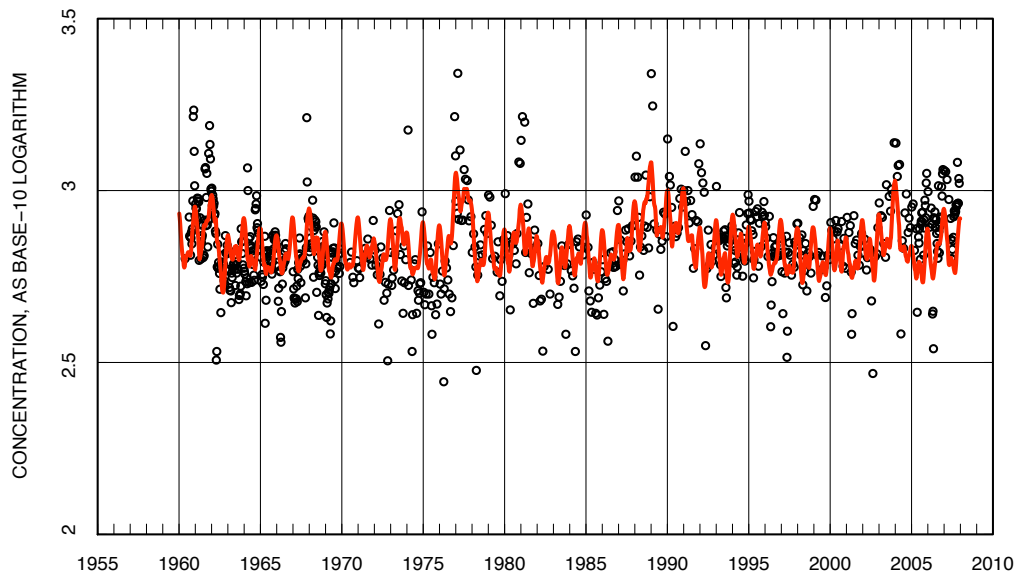


Figure A.80: Specific Conductance concentrations (points) and streamflow related anomaly + trend (line)

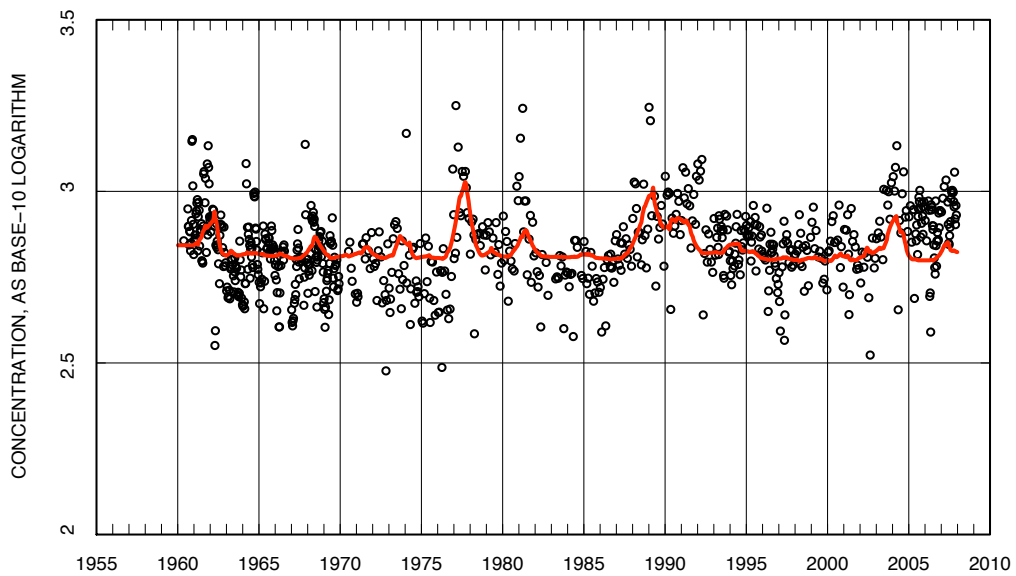


Figure A.81: Specific Conductance Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

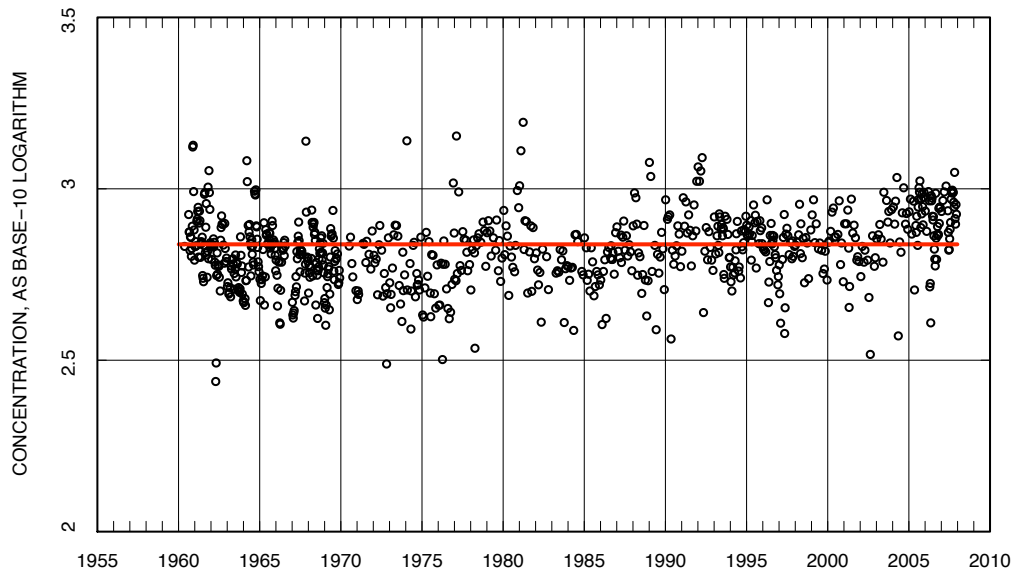


Figure A.82: Specific Conductance Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and no-trend (line).

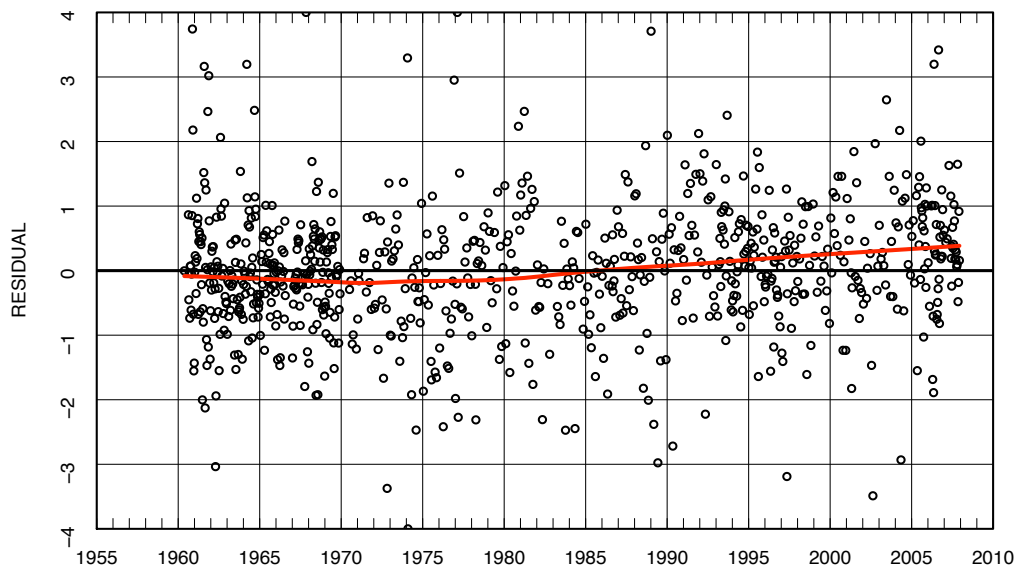


Figure A.83: Specific Conductance Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

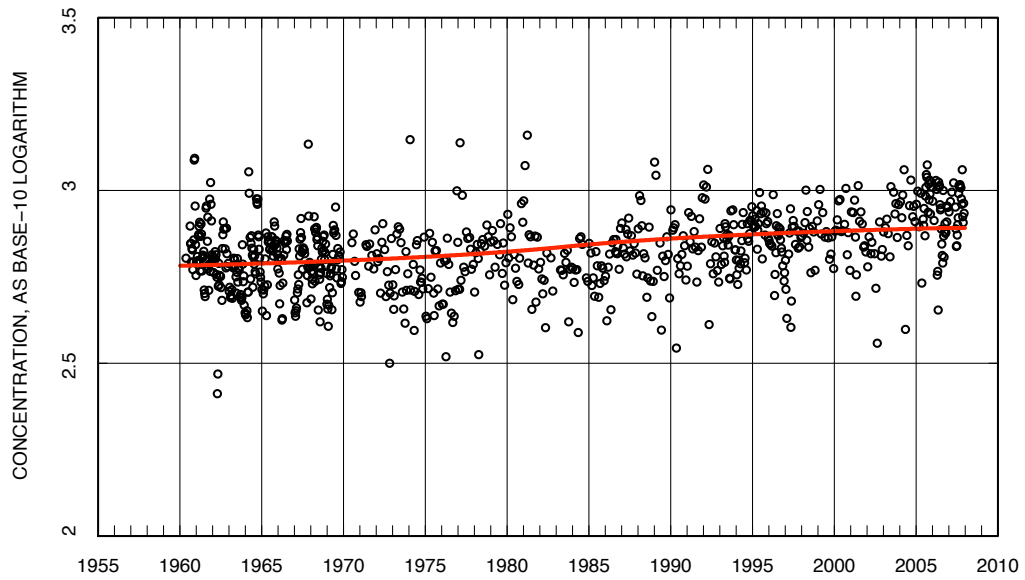


Figure A.84: Specific Conductance Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

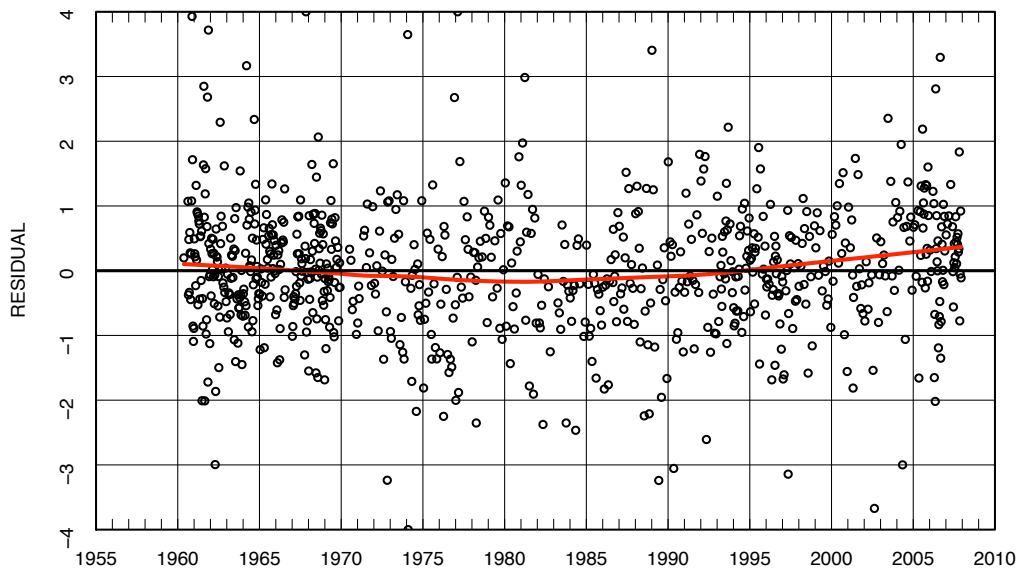


Figure A.85: Specific Conductance Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

## A.5.2 South Floodway at St. Norbert Monitoring Station

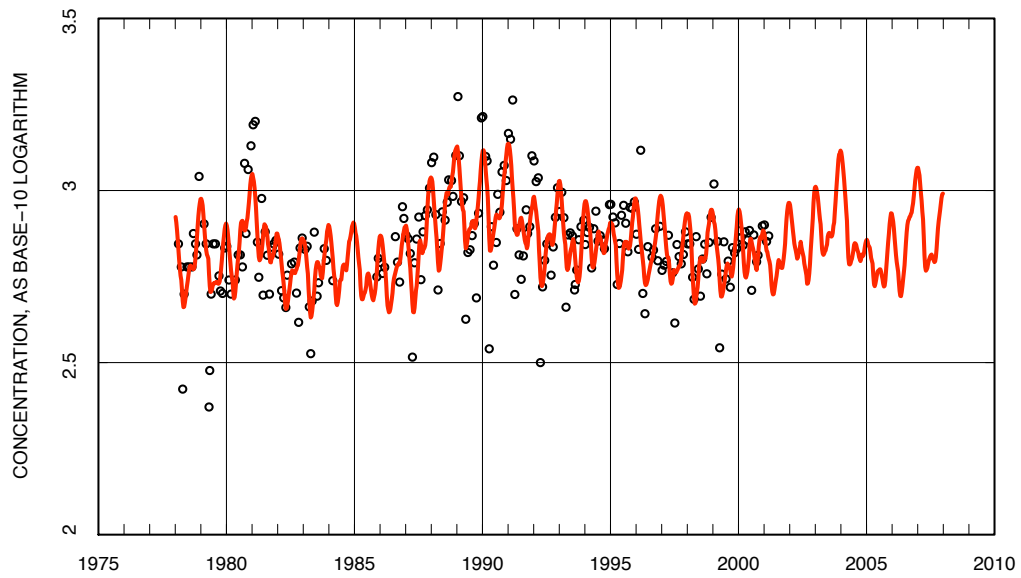


Figure A.86: Specific Conductance concentrations (points) and streamflow related anomaly + trend (line)

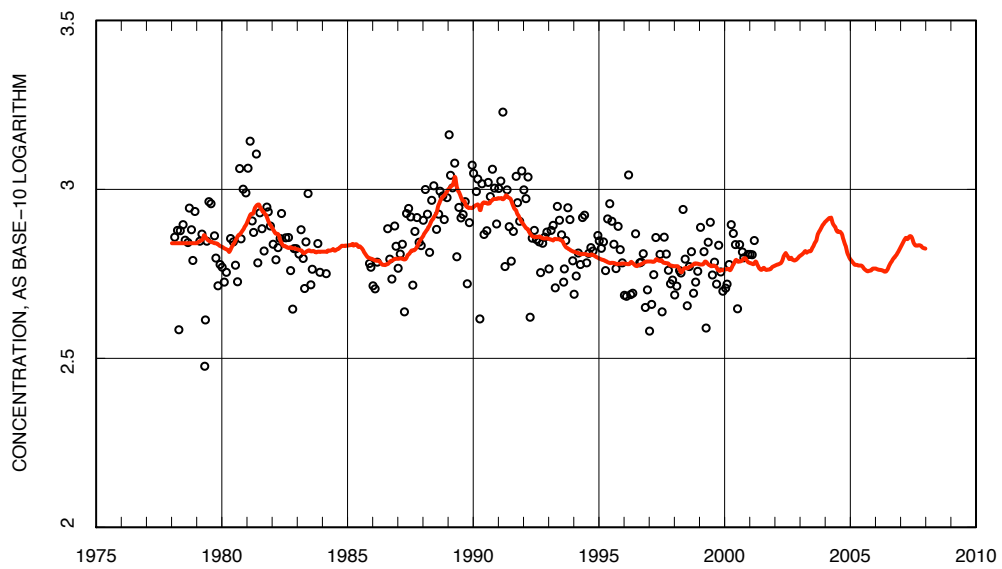


Figure A.87: Specific Conductance Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).



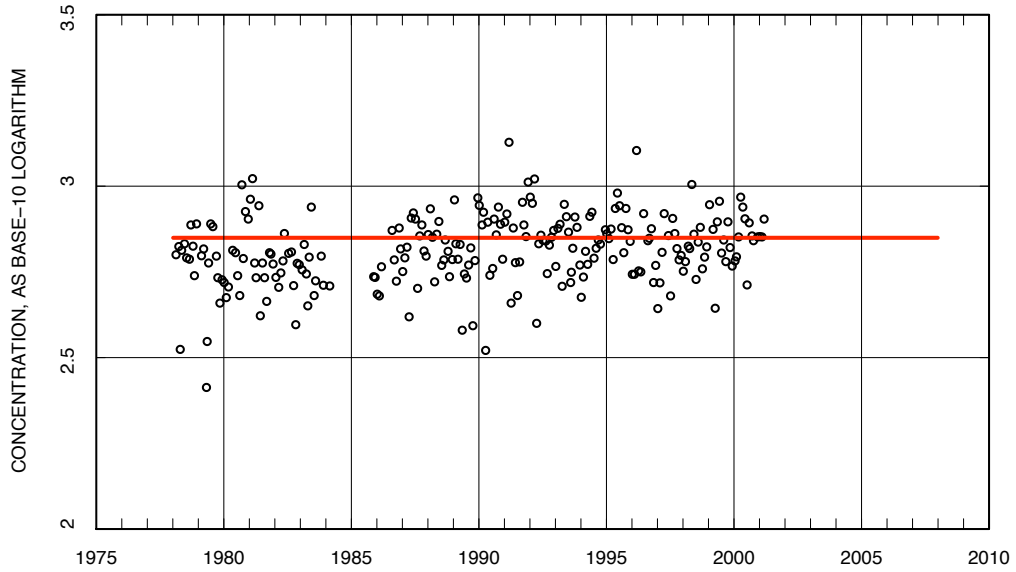


Figure A.88: Specific Conductance Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and trend (line).

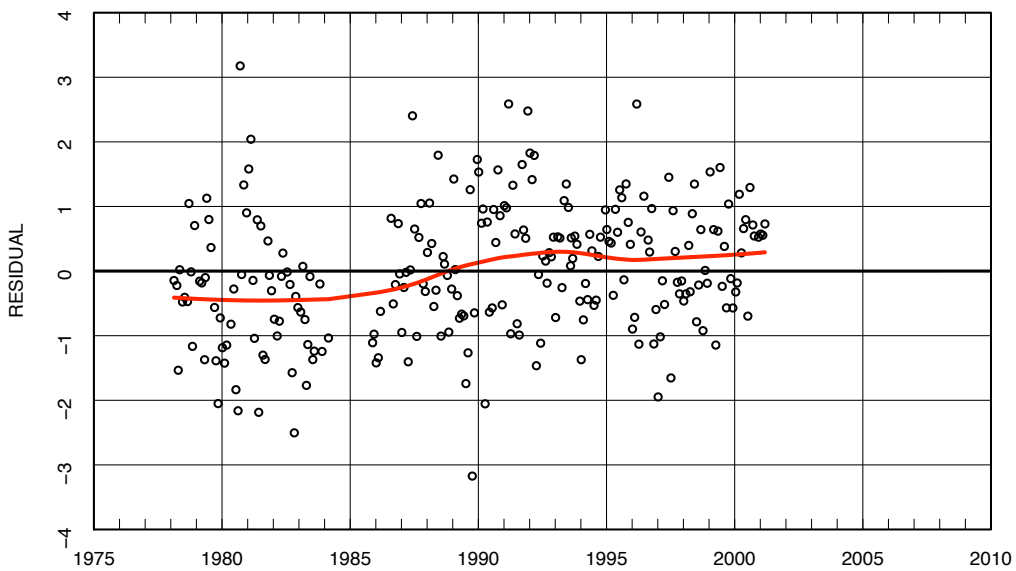


Figure A.89: Specific Conductance Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

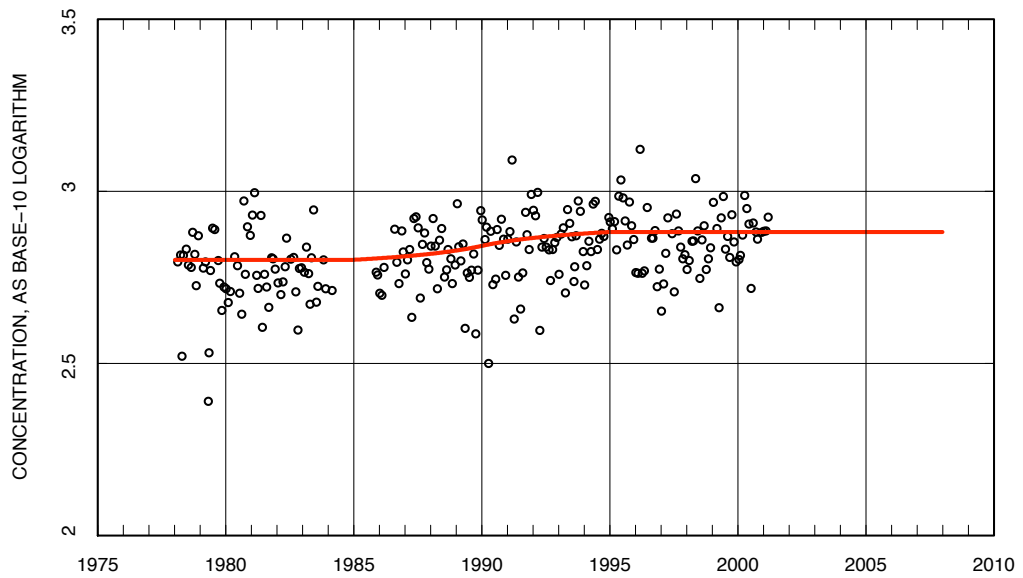


Figure A.90: Specific Conductance Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

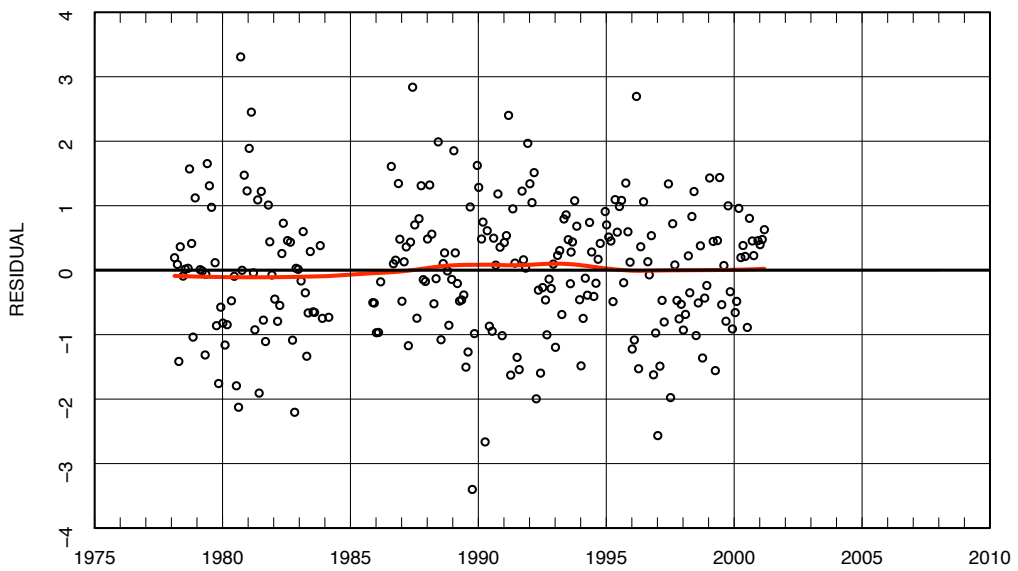


Figure A.91: Specific Conductance Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

### A.5.3 Selkirk Monitoring Station

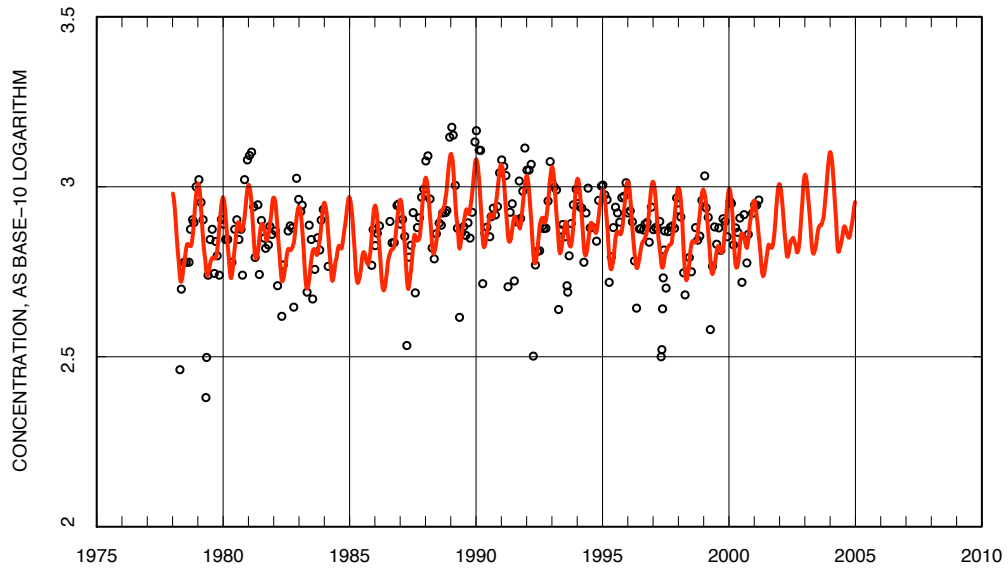


Figure A.92: Specific Conductance concentrations (points) and streamflow related anomaly + trend (line)

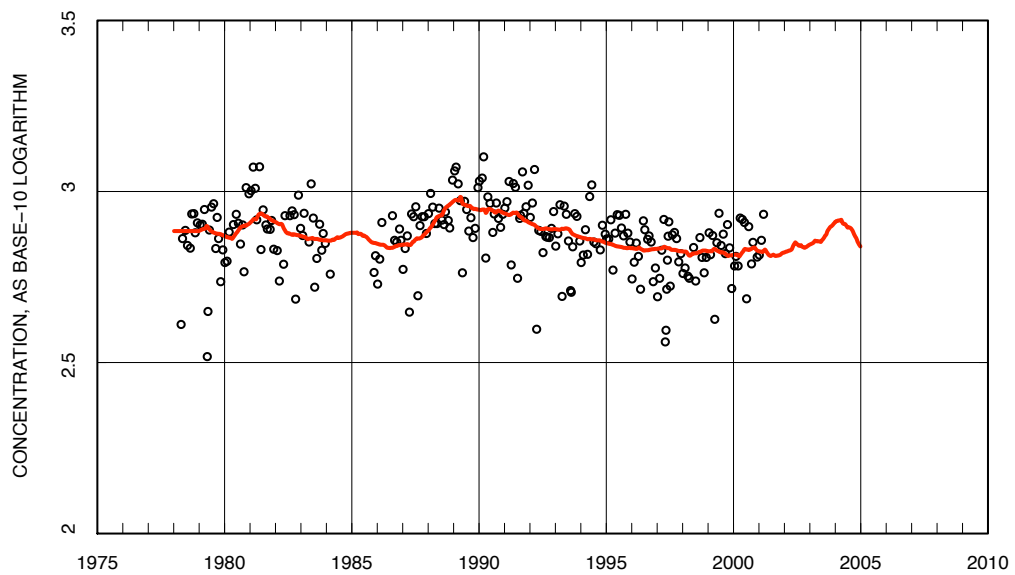


Figure A.93: Specific Conductance Flow Adjustments — Seasonally adjusted and de-trended data (points) and annual streamflow-related anomaly (line).

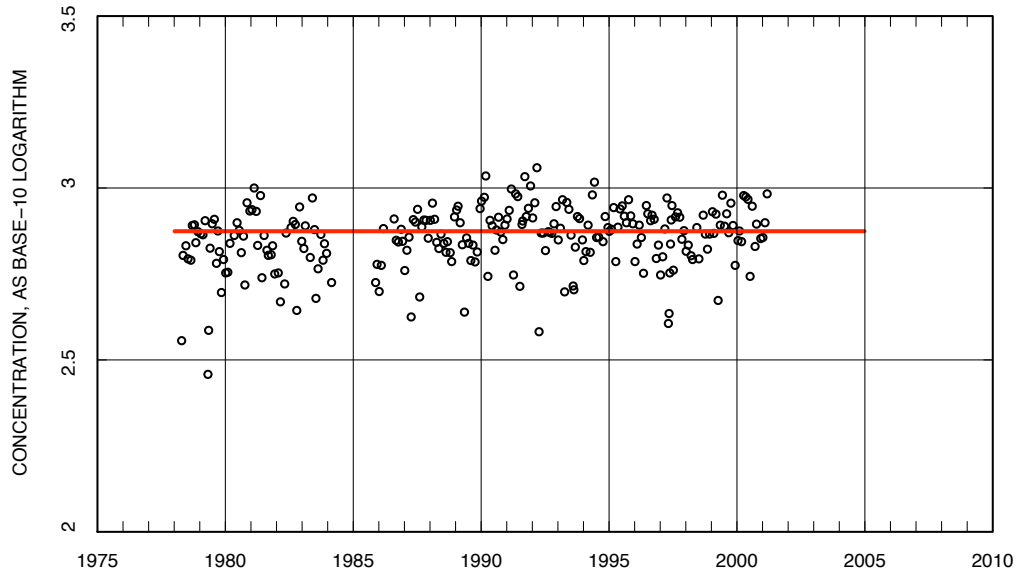


Figure A.94: Specific Conductance Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and trend (line).

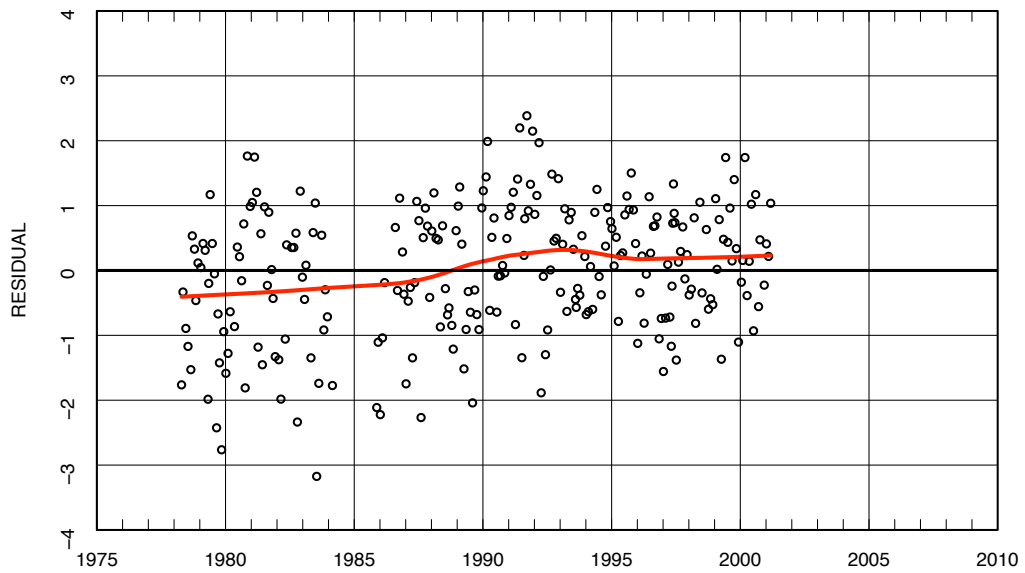


Figure A.95: Specific Conductance Flow Adjustments — Parametric no-trend model residuals (points) and lowess smooth line with  $F = 0.5$ .

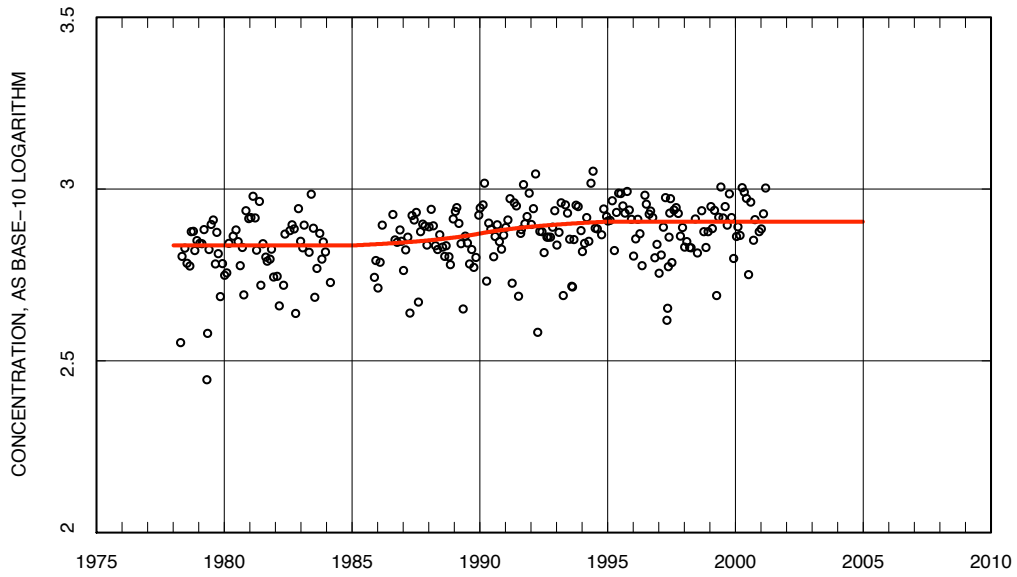


Figure A.96: Specific Conductance Flow Adjustments — Seasonally adjusted and flow adjusted data (points) and single trend (line).

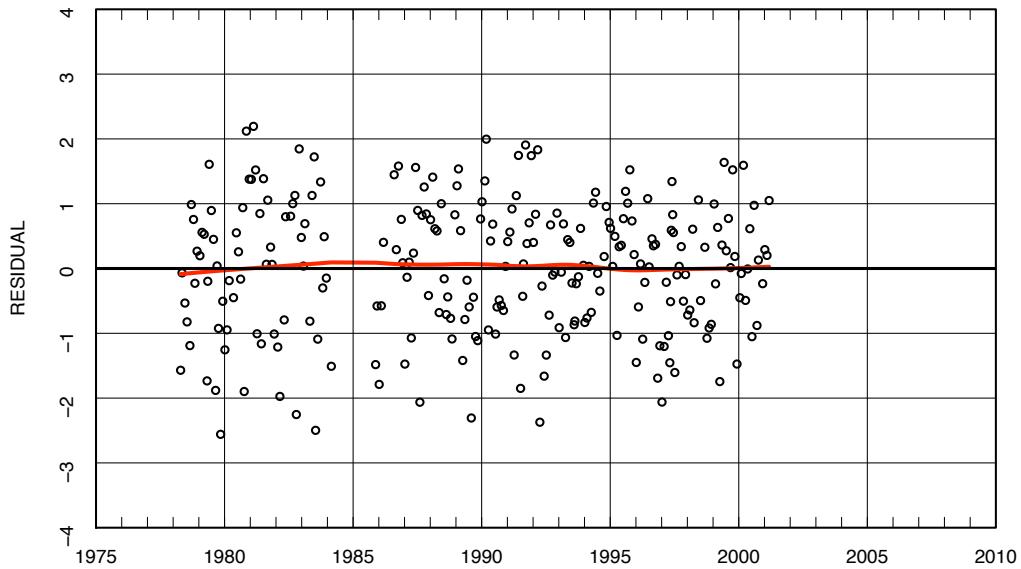


Figure A.97: Specific Conductance Flow Adjustments — Parametric single trend model residuals (points) and lowess smooth line with  $F = 0.5$ .