

# PRAIRIE PROVINCES WATER BOARD

Report #176

Long-Term Trends in Water Quality Parameters at Twelve Transboundary River Reaches

> Prepared for the Prairie Provinces Water Board By the Committee on Water Quality

> > December 2016



Prepared for the Prairie Provinces Water Board By the Committee on Water Quality

# **Executive Summary**

Long-term water quality monitoring has been conducted on major transboundary rivers crossing the Alberta/Saskatchewan and the Saskatchewan/Manitoba boundaries since the late 1960s. In 1992 eleven of these transboundary water quality monitoring stations were included in the Master Agreement on Apportionment's (MAA) Schedule E that relates to water quality. For each monitoring station interprovincial water quality objectives were established and also included in Schedule E of the MAA. In 1994, a twelfth monitoring site on Cold River was added to the interprovincial water quality monitoring network. Water quality samples have been collected on a regular monthly basis from these transboundary sites, with the exception of three locations (Cold, Churchill and Red Deer [at Erwood] rivers), which have been sampled regularly, but on a less frequent basis ranging from quarterly to six times a year. Water quality data have been collected for a range of water quality parameters including nutrients, major ions, physicals and metals.

The Prairie Provinces Water Board (PPWB) is the body responsible for the administration and reporting on the commitments of the MAA. Schedule E defines the mandate of the Board in interprovincial water quality management and the duties of the Board. The PPWB has established an active water quality program to assess and monitor interprovincial water quality. As part of the water quality program, trend assessments have been recognized as an important component to assess whether there have been significant changes in water quality over time to help maintain the quality of these transboundary rivers.

The purpose of this report is to summarize analyses conducted examining monotonic trends in water quality variables at the twelve transboundary rivers for the water quality sampling period of record. Trend assessments can be reported as increasing (statistically significant positive slope), decreasing (statistically significant negative slope) or as showing no statistically significant change over time. The trend assessment work was conducted to help support a review of the interprovincial water quality objectives at the twelve transboundary sites, and to provide a basis for future evaluations, investigations and work prioritization at the transboundary sites by the PPWB or the participating jurisdictions.

Long-term monotonic trend assessment was completed for the 12 transboundary river sites for nutrients, major ions, physicals and metals using the non-parametric seasonal Mann-Kendall/Mann-Kendall (Sen Slope estimator). As water chemistry can be affected by river discharge, trend assessments were adjusted for the influence of flow.

Flow-weighted long-term trend assessment at the 12 transboundary sites found a number of increasing and decreasing trends at each of the sites. Overall a total of 338 trend assessments were performed on the long-term water quality monitoring data from the 12 transboundary rivers. Of the total number of trend assessments performed 20% showed statistically significant increasing trends in the flow adjusted data. Major ions showed the greatest number of statistically significant positive (increasing) trends followed by physicals, nutrients and metals. Of the total number of trend assessments completed 31% showed statistically significant

negative (decreasing) trends, with nutrients and metals showing the greatest number of decreasing trends for all 12 transboundary rivers.

On the Alberta/Saskatchewan boundary six transboundary rivers were assessed for long-term water quality trends. Of these the Battle River and the South Saskatchewan River showed the most statistically significant monotonic increasing trends. For each of these two transboundary rivers, major ions, pH and sodium adsorption ratio (SAR) had increasing trends (positive slope) over time. Total phosphorus and lithium (dissolved) had statistically significant increasing trends in the Battle River, while the South Saskatchewan River had increasing trends in total nitrogen. For the six rivers on the Alberta/Saskatchewan boundary, the North Saskatchewan River had the least number of statistically significant increasing trends. The North Saskatchewan water quality monitoring station was moved in 1988, so trends conducted at this site were over the shortest period of all sites.

Conversely, on the Alberta/Saskatchewan Boundary, the South Saskatchewan River and the Beaver River had the most significant number of decreasing (negative) trends. For the South Saskatchewan River total phosphorus, total dissolved phosphorus and total ammonia-nitrogen had significant decreasing trends, as well as 11 of the metals trended. The Beaver River showed decreasing trends in all parameter groups including: ammonia-nitrogen, nitrate-nitrate nitrogen, total dissolved phosphorus, fluoride, sodium, sulphate, SAR, chromium total, cobalt total and dissolved, copper total, manganese dissolved, and molybdenum total and dissolved.

Trend assessments were also performed on six transboundary rivers on the Saskatchewan/Manitoba boundary. On this border, the Red Deer River near Erwood and the Assiniboine River showed the most number of statistically significant increasing trends. Red Deer River trend assessment demonstrated increasing trends for total and dissolved phosphorus, chloride, sodium, total dissolved solids (TDS), SAR, copper (dissolved), lithium (dissolved), and molybdenum (total and dissolved). The Assiniboine River had statistically significant increasing monotonic trends in all major ions, SAR, total suspended solids (TSS) and lithium (dissolved). The Qu'Appelle River was the only transboundary river that did not have statistically significant increasing trends over the period of record.

On the Saskatchewan/Manitoba boundary the Saskatchewan River and the Qu'Appelle River has the most number of statistically significant decreasing monotonic trends. For the Saskatchewan River decreasing trends were reported for nutrients (ammonia-nitrogen, nitrate-nitrate nitrogen and phosphorus (total and dissolved) and 9 metals, while for the Qu'Appelle River decreasing trends were found for total phosphorus, total dissolved phosphorus, sodium, dissolved oxygen and metals (aluminum total, cadmium total, chromium total, cobalt dissolved, iron total, lithium total, zinc total and dissolved).

Results of the long-term monotonic trend assessment do not describe variations, notably non-monotonic patterns in the trends over time including for the recent past. The identification of causes for the identified trends was beyond the scope of this report.

# **Table of Contents**

E	кес	utive	Summary	I
Ta	able	e of (	Contents	iii
Li	st c	of Fig	rures	iv
1.	•	Intro	oduction	. 1
	1.3	1	Objectives and Scope of this Report	. 1
2.		Mor	nitoring Stations	. 5
3.		Met	hods	. 6
	3.1	1	Trend Analysis	. 6
		3.1.	1. Seasonality	. 6
		3.1.2	2. Time period	. 7
		3.1.3	3. Censored data	. 7
		3.1.4	4 Step in Data	. 8
		3.1.	5. Serial Correlation (autocorrelation)	. 8
		3.1.6	5 Flow Adjusted	. 8
	3.2	2	Descriptive Statistics	. 9
	3.3	3	Trend Significance	. 9
4.		Resu	ults and Discussion	. 9
	4.1	1	Nutrients	. 9
	4.2	2	Major lons	١3
	4.3	3	Physicals	16
	4.4	4	Metals	18
5.		Con	clusions1	19
6.		Ackr	nowledgements2	23
7.		Com	mittee on Water Quality Members2	23
g		Rofe	prences	) 2

# **List of Figures**

Figure 1	PPWB Water Quality Monitoring Locations on the Alberta/Saskatchewan Boundary	3
Figure 2	PPWB Water Quality Monitoring Locations on the Saskatchewan/Manitoba Boundary	y4
Figure 3	Trend in Total Dissolved Phosphorus Concentration for the North Saskatchewan Rive	r (1988
	to 2008)	11
Figure 4	Trend in Total Nitrogen Concentration for the North Saskatchewan River (1988 to 20	08)12
Figure 5	Trend in Chloride (dissolved) for the South Saskatchewan River (1968 to 2008)	14
List of 7	Γables	
Table 1	PPWB Water Quality Monitoring	5
Table 2	Seasons for Water Quality Parameters at the Saskatchewan/Manitoba Boundary site	s 7
Table 3	Flow-Weighted Trend Summary for Nutrients - Alberta/Saskatchewan Boundary	11
Table 4	Flow-Weighted Trend Summary for Nutrients - Saskatchewan/Manitoba Boundary	13
Table 5	Flow-Weighted Trend Summary for Major Ions - Alberta/Saskatchewan Boundary	15
Table 6	Flow-Weighted Trend Summary for Major Ions - Saskatchewan/Manitoba Boundary .	
Table 7	Flow-Weighted Trend Summary for Physical and Other Parameters- Alberta/Saskatch	
	Boundary	17
Table 8	Flow-Weighted Trend Summary for Physical and Other Parameters -	
	Saskatchewan/Manitoba Boundary	
Table 9	Flow-Weighted Trend Summary for Metals - Alberta/Saskatchewan Boundary	
Table 10	Flow-Weighted Trend Summary for Metals - Saskatchewan/Manitoba Boundary	20
List of A	Appendices	
Appendix A	A: Basic Statistics of Trended Water Quality Parameters	27
Appendix I	B: Nutrients Trending Graphs	41
Appendix (	C: Major Ions Trending Graphs	133
	D: Physicals Trending Graphs	
	E: Metals Trending Graphs	
	F: Trending Summary Tables	
Appendix (	G: Magnitude of Trend Tables	605

## Trends in Water Quality Parameters at Twelve Transboundary River Reaches

## 1. Introduction

Long-term water quality monitoring has been undertaken on transboundary prairie rivers by Environment Canada since the late 1960s. This long-term water quality monitoring program is conducted to fulfill the monitoring requirements under the Master Agreement on Apportionment (MAA). The MAA is a multi-jurisdictional agreement that was signed in 1969 by the governments of Alberta, Saskatchewan, Manitoba and Canada. The agreement provides for equitable sharing of surface water in eastward flowing rivers across interprovincial boundaries. The Prairie Provinces Water Board (PPWB) is accountable for the administration of the agreement and reporting of findings and results to governments.

Schedule E to the MAA defines the water quality mandate of the PPWB which is "to foster and facilitate interprovincial water quality management among the parties that encourages the protection and restoration of the aquatic environment". As part of Schedule E water quality monitoring occurs at 12 transboundary river reaches. Of these 12 water quality monitoring sites, six are located on the Alberta/Saskatchewan boundary (Battle River, Beaver River, Cold River, North Saskatchewan River, Red Deer River near Bindloss and the South Saskatchewan River) (Figure 1). The other six sites are located on the Saskatchewan/Manitoba boundary (Assiniboine River, Carrot River, Churchill River, Red Deer River near Erwood, Qu'Appelle River and the Saskatchewan River) (Figure 2).

For 11 of the 12 sites, the monitoring results are compared to water quality objectives and include chemical, physical and biological parameters; prior to 2015 no objectives were established for the Cold River. Water quality objectives were established to protect various water quality uses. Signatories to the agreement have agreed to take all reasonable and practical measures to meet these objectives within the transboundary river reaches. Signatories also recognized in Schedule E that any changes in water quality should be assessed and that long-term trend analysis would be an important component of the PPWB water quality program. Schedule E states that "where the water quality is better than the agreed upon water quality objectives, and if trend analysis indicates that water quality has been or may be significantly altered, the parties shall agree as to the reasonable and practical measures that will be taken to maintain the water quality in the river reaches".

The identification of changes in water quality can be difficult due to natural variations in water quality and anthropogenic influences. Therefore, the PPWB conducts long-term monotonic trend analysis to determine if specific water quality variables are statistically increasing, decreasing or remaining the same over time as part of its inter-jurisdictional water quality management program. Identifying long-term increasing trends or deteriorating water quality will assist the Board in its interprovincial water quality management responsibilities and in its assessment of potential areas of concern before water quality objectives are exceeded or the downstream jurisdictions are impacted.

# 1.1 Objectives and Scope of this Report

The purpose of this report is to provide an analysis of long-term water quality data that has been collected from the PPWB transboundary sites since the beginning of the long-term monitoring program. Monitoring data for these transboundary sites can include up to 40 years of data depending on the parameter and the site. In this analysis, the period of record is defined as the earliest available sample dates up to and including the end of 2008. The long-term trend assessment work was conducted to:

- 1. Assess the PPWB long-term data set for changes in water quality over time,
- 2. Assist the PPWB in identifying potential transboundary water quality concerns,
- 3. Assist the PPWB in a review of the interprovincial water quality objectives.

While the purpose of this report was to identify long-term trends in water quality at the boundary sites, the intention of this report was not to investigate the potential causes of trends identified. However, the information provided will form the basis for further investigative work by the PPWB or its member agencies. The report describes the trend assessment methods used by the PPWB, the parameters assessed, and the results of the trend assessment for the 12 transboundary river reaches. Trends were assessed for a variety of parameters including nutrients, major ions, physical parameters and metals.

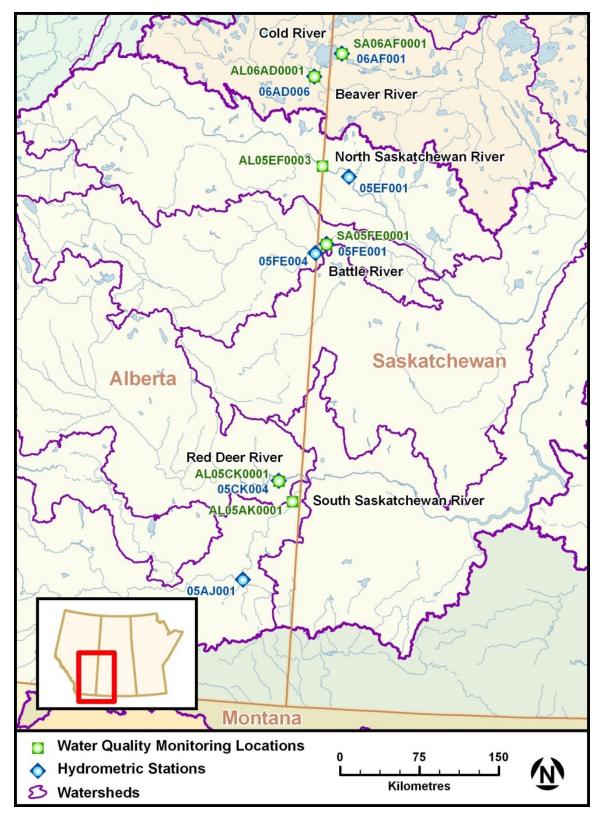


Figure 1 PPWB Water Quality Monitoring Locations on the Alberta/Saskatchewan Boundary

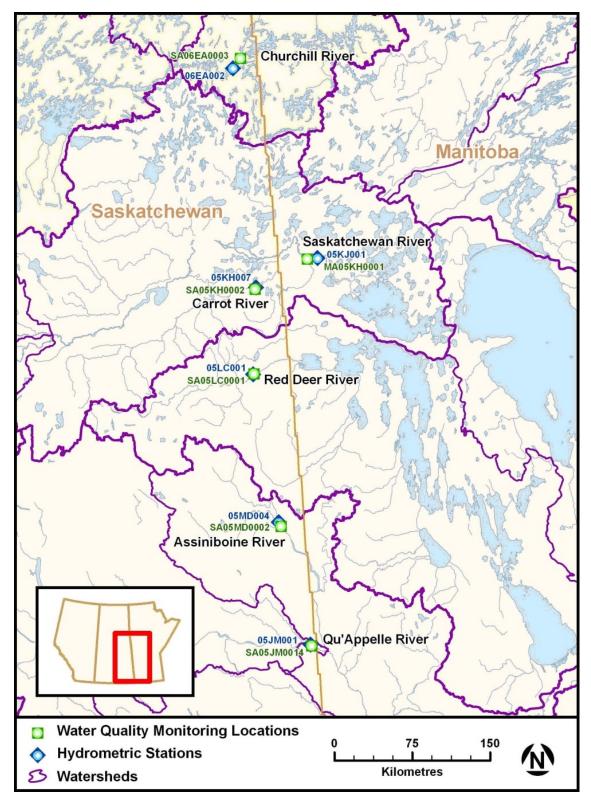


Figure 2 PPWB Water Quality Monitoring Locations on the Saskatchewan/Manitoba Boundary

# 2. Monitoring Stations

Long-term water quantity and quality monitoring has been conducted on major transboundary rivers crossing the Alberta/Saskatchewan and Saskatchewan/Manitoba boundaries as part of the administration of the MAA. Environment Canada currently monitors water quantity and quality for the transboundary river reaches including a network of hydrometric stations and 12 water quality monitoring stations (Table 1).

One of the criteria for the long-term trend analysis was that water quality sampling had to be conducted at the same location, using comparable sample collection techniques and samples analyzed in a consistent manner over the time period. With the exception of the Cold River and the North Saskatchewan River, water quality has been monitored at the same transboundary river locations since the late 1960s or early 1970s. Monitoring on the Cold River was initiated in 1993 at the outlet from Cold Lake. Given the location of this sampling site the water quality of the Cold River is more indicative of the water quality in Cold Lake, rather than a river catchment watershed like the other monitoring sites in this program. The monitoring station on the North Saskatchewan River has been moved three times over the period of record. The most recent site move for the North Saskatchewan River was in 1988. With the exception of the North Saskatchewan River, trend assessment at each site included data from the beginning of the period of record until the end of 2008. For the North Saskatchewan River trends were assessed from 1988 onwards.

The frequency of monitoring at the transboundary river sites has varied since the start of the program but in general has been conducted monthly. However, for parts of the period of record, the Cold River and the Churchill River were monitored quarterly and the Red Deer River at Erwood was monitored six times per year. Water quality parameters incorporated in the long-term monitoring program and included in the trend assessment were nutrients, major ions, metals, and physical parameters such as dissolved oxygen, pH, TSS and SAR.

Table 1 PPWB Water Quality Monitoring

Water Quality Station Name	Water Quality Station Number	Year Water Quality Monitoring Started	Hydrometric Station Number
Battle River near Unwin, Saskatchewan	SA05FE0001	1966	05FE004
Beaver River at Beaver Crossing	AL06AD0001	1966	06AD006
Cold River at Outlet of Cold Lake	SA06AF0001	1993	06AF001
North Saskatchewan River at Highway #17 Bridge	AL05EF0003	1988	05EF001
Red Deer River near Bindloss, Alberta	AL05CK0001	1967	05CK004
South Saskatchewan River at Hwy 41	AL05AK0001	1970	05AJ001*
Assiniboine River at Hwy 8 Bridge	SA05MD0002	1968	05MD004
Carrot River near Turnberry	SA05KH0002	1974	05KH007
Churchill River Below Wasawakasik	SA06EA0003	1974	06EA002
Qu'Appelle River	SA05JM0014	1975	05JM001
Red Deer River at Erwood	SA05LC0001	1967	05LC001
Saskatchewan River above Carrot River	MA05KH0001	1974	05KJ001**

<sup>\*</sup>Estimated flow at the South Saskatchewan River is based on recorded flow at the Medicine Hat, plus the recorded flow at Seven Persons Creek (05AH005) and Ross Creek (05AH052) with a two day lag.

<sup>\*\*</sup> Estimated flow at the Saskatchewan River is Saskatchewan River at the Pas minus the adjusted flow of the Carrot River near Turnberry.

#### 3. Methods

Monotonic trend analysis was used to determine statistically significant changes in water quality (*i.e.* increasing, decreasing or no change) over time. Several factors can influence the detection of trends including seasonality, serial correlation (or auto correlation), missing data, outliers, and censored data. Depending on the statistical technique used for trend assessment assumptions about the data set must be considered, including data distribution and independence. Except where noted, all statistical analyses were conducted with WQStat Plus v.9 © 2009 Sanitas Technologies.

## 3.1 Trend Analysis

Trend assessment was undertaken with the non-parametric Mann-Kendall/Seasonal Mann Kendall method. A non-parametric method was selected because most water quality data do not follow standard normal distribution curves. The assumption for parametric trend methods is that the data distribution is normal. In addition, non-parametric methods tend to be more robust when there are missing data, outliers and censored data. In addition, the Mann Kendall/Seasonal Mann Kendall non-parametric method is used by several jurisdictions involved in the PPWB. It was also established as part of the background evaluations of this study that parametric methods used elsewhere (WQTrend from Vecchia 2003) compared well with the Mann Kendall/Seasonal Mann-Kendall method. The comparison criteria included similarity of slopes and determination of significance when using the same time series data from a PPWB station.

Prior to trend analysis, water quality data were reviewed for censored data, missing data, outliers, anomalies in the individual data points and seasonality. Erroneous data or anomalies were typically related to database, laboratory or field analysis issues and were removed prior to trend analysis.

#### 3.1.1. Seasonality

Water quality parameters frequently exhibit seasonal patterns. Changes in water chemistry often follow changes in hydrologic patterns, temperature, and biological activity. For the trend assessments in this report two seasons were used for each transboundary river. Seasons were defined to be five to seven months long depending on the river. The two seasons were determined visually based on a review of the entire PPWB data set. Approximately thirty five years of water quality monitoring data was summarized graphically to show the annual distribution of the water quality parameter of interest and the data were divided into two seasons. In selecting the seasons the Committee also considered major ecological periods such as: ice cover *versus* open water; more stable *versus* highly variable flows; and low/stable water temperatures in fall/winter *versus* higher and more variable temperatures and biological growth during the open-water period. Where possible, the two seasons were defined for the transboundary river rather than for individual parameters. Where possible, seasons were also selected to be consistent with those selected previously by jurisdictions based on their review of these data sets.

As a result, the seasons selected for the Alberta/Saskatchewan boundary rivers were April to October for the open water season and November to March for the ice covered season for all parameters. For the Saskatchewan/Manitoba boundary, the open water season began in either April or May depending on the transboundary river and/or water quality parameter (Table 2).

Table 2 Seasons for Water Quality Parameters at the Saskatchewan/Manitoba Boundary Sites

Station Name	Doromotor	Se	Season			
Station Name	Parameter	Summer	Winter			
Churchill River below	TP, TDP, TN, TDS, TSS,					
Wasawakasik	metals and major ions	May to Oct	Nov to Apr			
Saskatchewan River	TP, TDP, TN, TDS, TSS,					
above Carrot River	metals and major ions	Apr to Oct	Nov to Mar			
Carrot River near	TP, TDP, TN, TDS, major ions	May to Oct	Nov to Apr			
Turnberry	TSS, metals	Apr to Oct	Nov to Mar			
Red Deer River at	TP, TDP, TN, TDS, TSS,					
Erwood	metals and major ions	May to Oct	Nov to Apr			
Assiniboine River at Hwy	TP, TDP, TN, TDS, TSS,					
8 Bridge	metals and major ions	Apr to Oct	Nov to Mar			
Qu'Appelle River	TP, TDP, TN, TDS, major ions	May to Oct	Nov to Apr			
	TSS, metals	Apr to Oct	Nov to Mar			

Seasonality was tested with the non-parametric Kruskal-Wallis test. Data were considered seasonal if the Kruskal-Wallis test was significant at a 95% significant level ( $\alpha \le 0.05$ ). If the dataset showed seasonality then the Seasonal Mann-Kendall was used for the trend analysis. If the dataset was not seasonal then the Mann-Kendall/Sen Slope Estimator test was used for the trend assessment. The seasonal Mann-Kendall considers seasonal variability, in this case the two defined seasons, whereas the Mann Kendal/Sen slope estimator does not consider season.

#### 3.1.2. Time period

Trend assessment was completed for nutrients, major ions, physical and other parameters and metals. Trend analysis included all of the PPWB monitoring data since the monitoring site inception until the end of 2008. Seasons for trend analysis were those previously defined in section 3.1.1. For all parameters consecutive data for a minimum of ten years was required to conduct the trend assessment.

#### 3.1.3. Censored data

For parameters with observations below the analytical detection limit (censored data) the less than value was replaced with a constant value. The approach used for censored data was to substitute the less than value with half the detection limit value (Gilbert 1987). These constant values were then used in all statistical analyses. While different approaches to generating censored data exist (Helsel 2005) the approach in this application is valid because the Mann-Kendall/Seasonal Mann-Kendall uses relative magnitude of adjacent data rather than the actual value. The method is based on ranks *versus* actual values. However, since changes in the detection limit can influence the trend assessment a parameter was only considered for trend analysis if the censored data made up less than 20% of the entire period. This criterion mainly affected the trending of metals. There have been numerous analytical method changes for metals over the period of record. As the methods have changed detection limits have improved and in the later years there was significantly less censored data.

#### 3.1.4 Step in Data

Changes in analytical methods can result in substantial changes in method detection limits (MDLs) and/or result in steps in the dataset. This was true for a number of the metals where there have been a number of method changes over the period of record for the PPWB. To determine whether there was a significant step within the metal datasets the non-parametric Wilcox Rank Sum (Mann-Whitney) statistical methods were used and compared data pre and post analytical method changes. For the metal datasets values analyzed prior to 1994 were determined not to be comparable to later methods used, and therefore data prior to 1994 was not included in the trend assessment. In 1994 the laboratory switched to an inductively coupled plasma-optical emission spectrometry (ICP-OES) scan for all metal analysis. In 2003 the laboratory changed the detector to a sector field mass spectrometry (ICP-SFMS) which resulted in subsequent improvements in the resolution of the methodology and improved detection limits. Dates for the changes in analytical methods for metals were provided by the Environment Canada NLET Laboratory in Burlington. A step was statistically significant if  $\alpha \leq 0.05$ . For those parameters that exhibited a statistically significant step in the dataset only data post analytical method change were used in the monotonic trend assessment.

The switch to ICP-SFMS in 2003 substantially improved the analytical detection limit of metals and in some cases, while no statistical significant step in the data was found, the improved detection limit visually appears to be potentially influencing the magnitude of the trend result, particularly for decreasing trends in the dissolved metal fraction (cadmium, cobalt, copper, and molybdenum). Conducting trend analysis of the metals data with subsequent years of data (i.e. since 2008) will provide further insight into the trend of the metals that may have been influenced by this method change.

In addition to metals, for dissolved nitrogen (DN) and total nitrogen (TN), a change in the laboratory analytical method in October 1993 resulted in a step in concentration of these data between the pre and post method change (Glozier *et al*, 2004). The pre and post 1993 data are not directly comparable.

#### 3.1.5. Serial Correlation (autocorrelation)

One key assumption of the Mann-Kendall/Season Mann-Kendall test is that the data are independent (Mann, 1945; Kendall 1975; Hirsch *et al.* 1982; Hirsch and Slack, 1984). Most water quality data that are collected monthly are not independent. The closer water samples are collected together usually the greater the serial correlation. The presence of serial correlation can increase the chance of a type I error. A type 1 error occurs when the null hypothesis is rejected and a trend is reported when there is none. While there are techniques that can be used to correct for serial correlation thereby reducing type I errors, this can lead to an increase in type II errors. Type II errors occur when it is incorrectly concluded that there is no significant trend when there is a trend. In this trend assessment work, water quality data were not corrected for serial correlation.

#### 3.1.6 Flow Adjusted

Water chemistry can be affected by river discharge, with the result that a constituent could be higher or lower under different flow conditions. For example, some constituents may increase with river discharge resulting from greater influx and surface runoff, while other constituents may decrease as a result of dilution. Point sources and groundwater influences are often diluted with increased river discharges while other parameters influenced by overland inputs may be higher under higher flow conditions.

Flow adjustment techniques are often used in trend assessments to remove its influence on the concentration of a parameter. In this study prior to completing the trend assessments the concentration of a variable was adjusted for flow. All data were flow adjusted with a regression equation based on the flow *versus* concentration relationship:

Log [Concentration] = Log [flow] b+a

Where:

Concentration = Concentration of parameter Flow = Flow of the River b = slope a = intercept

Trends on flow adjusted time series data were reported at the 95% significance level ( $\alpha \le 0.05$ ).

## 3.2 Descriptive Statistics

Descriptive statistics including mean, standard deviation, median, minimum value, maximum value, number of samples and the  $90^{th}$  and  $10^{th}$  percentile were produced using Sigma Plot v.  $11.2 \odot 2008$  Systat Softwate Inc. The  $90^{th}$  and  $10^{th}$  percentiles were calculated using the Cleveland method.

# 3.3 Trend Significance

The goal for undertaking the trend analyses was to assess whether there were significant trends among different parameters at different sites. The null hypothesis was therefore that there would be no trends with the alternate hypothesis being that there were trends for some parameters at some sites (increasing or decreasing trends). Given that multiple tests were conducted (338) within this hypothesis, there is an expectation that a proportion of the identified significant trends, based on an unadjusted significance level, would be of a type I error where the null hypothesis is incorrectly rejected. At an alpha of ≤0.05 it would be expected that 1 in 20, or 17 of the 338 tests, would present as being significant by random chance when in fact they are not significant. The significant trend results summarized in this report are based on an alpha ≤0.05. The alpha was not adjusted for the multiple trend assessments conducted, in part because this analysis is designed to identify potential trends and in part because of the lack of consistent approaches for correcting alpha in studies such as this. Regardless, the results provide a means to prioritize further assessment based on the level of significance and magnitude of slope.

### 4. Results and Discussion

Descriptive statistics for each water quality parameter are included in Appendix A. Time series, seasonality and flow-weighted trending graphs for the various parameters analyzed are presented in Appendices B to E. Trend summaries including slopes of the trend are presented in Appendix F and magnitude of the change (%) are shown in Appendix G.

#### 4.1 Nutrients

Nutrients are an important part of the aquatic ecosystem although increases in nutrient concentrations can lead to eutrophication of river systems and their receiving waterbodies. While prairie river systems and lakes are known to be naturally high in nutrients, human activities that contribute non-point nutrients such as agriculture, forestry or other land disturbance activities and point source nutrients such as wastewater and industrial effluent

discharges can increase nutrients within river systems (Rock and Mayer 2006; Leavitt et al. 2006; Carlson et al. 2013; Yates et al. 2013).

Five nutrients were included in the long-term trend assessment at the 12 transboundary river monitoring locations. Nutrients included total ammonia nitrogen (NH<sub>4</sub>-N), nitrate-nitrite nitrogen (NO<sub>3</sub>-NO<sub>2</sub>), total nitrogen (TN), total phosphorus (TP) and total dissolved phosphorus (TDP). The PPWB recently established water quality objectives for all five of these nutrients and excursions to the objectives will be reported on an annual basis starting with data collected in 2015. Two of the objectives (NH<sub>4</sub>-N and NO<sub>3</sub>-NO<sub>2</sub>) are toxicological objectives for the protection of aquatic life and the remaining nutrients (TP, TDP and TN) were set as background objectives with the aim of maintaining and managing water quality within these prairie inter-jurisdictional rivers.

## Alberta/Saskatchewan Boundary

Of the 30 flow-weighted trend assessments that were conducted on the six Alberta/Saskatchewan transboundary rivers over half of the analyses were statistically significantly negative (decreasing) (Table 3). Three of the rivers, the North Saskatchewan, the South Saskatchewan and the Red Deer, are larger river systems that originate on the eastern slopes of the Rocky Mountains and flow eastward through Alberta into Saskatchewan. All three of these larger rivers had decreasing trends in both TP and TDP (Figure 3) concentrations over time. The Red Deer River also showed decreasing trends in NH<sub>4</sub>-N and NO<sub>3</sub>-NO<sub>2</sub> with no statistically significant change in TN. In the North Saskatchewan River, TN (Figure 4) and NO<sub>3</sub>-NO<sub>2</sub> showed decreasing trends, with no change in ammonia-nitrogen over the period of record. For the North Saskatchewan and Red Deer rivers the trend results would suggest improvement in the nutrient river water quality. For the North Saskatchewan River, this improvement in nitrogen concentrations is believed to be in direct response to improvements to the Gold Bar wastewater treatment plant in Edmonton in 2001 (Anderson 2012). The Battle and Beaver rivers, which tend to be lower flow rivers, also showed statistically significant decreasing trends in the toxicological parameters NH<sub>4</sub>-N and NO<sub>3</sub>-NO<sub>2</sub> and no change over the period of record for TN.

However, not all the flow-weighted trend results had decreasing slopes and four increasing trends in nutrients were identified on three of the Alberta/Saskatchewan transboundary rivers (Table 3). Total phosphorus was shown to have an increasing trend on the Battle River. For the Battle River, there were a total of 420 TP samples collected over the period of record with a concentration range of 0.01 to 0.75 mg/L, with a mean concentration value of 0.108 mg/L and median of 0.061 mg/L. While the South Saskatchewan River had decreasing trend for phosphorus, it did have an increasing trend for TN.

The Cold River monitoring site is located just downstream of Cold Lake, and hence water quality is reflective of the water quality in the lake. Residence time in the lake is approximately 33 years and hence changes in water quality could be due to in-lake changes. While the different forms of phosphorus did not have statistically significant monotonic trends, TN and NH<sub>4</sub>-N were statistically increasing trends. As the monitoring has been more limited on the Cold River (monitoring was initiated in 1993, and sampling was quarterly) there have been fewer samples collected. For TN the concentration has ranged from 0.33 to 0.956 mg/L, with a median concentration of 0.407 mg/L. Similarly, for NH<sub>4</sub>-N the concentration has ranged from 0.0025 to 0.078 mg/L with a median concentration value of 0.01 mg/L.

Table 3 Flow-Weighted Trend Summary for Nutrients - Alberta/Saskatchewan Boundary

Parameter	Battle	Beaver	Cold	North Saskatchewan	Red Deer (AB)	South Saskatchewan
Nutrients						
Ammonia Nitrogen Total	Ţ	Ţ	<b>↑</b>	$\leftrightarrow$	$\downarrow$	<u> </u>
Nitrate-nitrate as N	i i	J	$\leftrightarrow$	↓	$\downarrow$	$\leftrightarrow$
Nitrogen Total	$\leftrightarrow$	$\leftrightarrow$	<b>↑</b>	. ↓	$\leftrightarrow$	<b>↑</b>
Phosphorus Total	<b>↑</b>	$\leftrightarrow$	$\leftrightarrow$	<b>1</b>	$\downarrow$	<b>\</b>
Phosphorus Total Dissolved	$\leftrightarrow$	$\downarrow$	$\leftrightarrow$	,	$\downarrow$	,

No Seasonality in Data, Trend Analysis Completed with Sen Slope Estimator

↑ statistically significant increasing trend; ↓ statistically significant decreasing trend; ↔ no significant trend

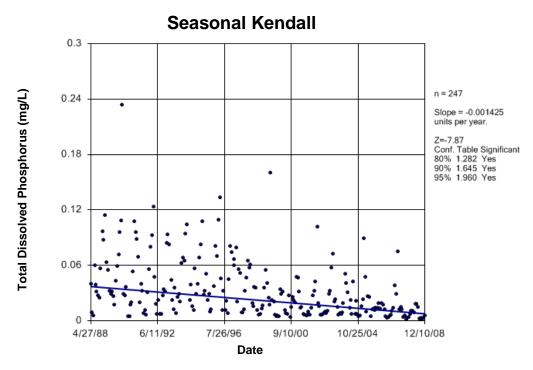


Figure 3 Trend in Total Dissolved Phosphorus Concentration for the North Saskatchewan River (1988 to 2008).

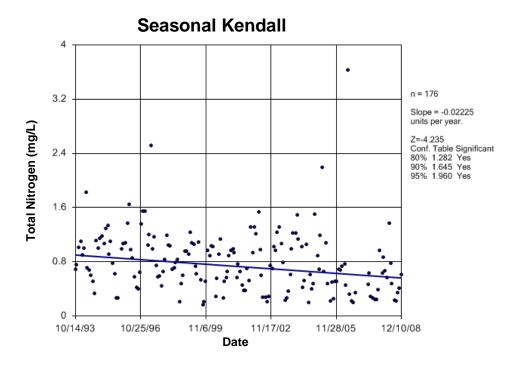


Figure 4 Trend in Total Nitrogen Concentration for the North Saskatchewan River (1993 to 2008).

## Saskatchewan/Manitoba Boundary

For the six transboundary rivers on the Saskatchewan/Manitoba boundary, long-term trend assessments for the five nutrients showed overall there was statistically little change in nutrient concentrations over time. Of the 30 trend assessments close to half (14/30) showed no statistically significant flow-weighted monotonic trend over the period of record. Statistically significant decreasing trends were also observed in a number of the transboundary rivers for both nitrogen and phosphorus (Table 4). Of note, however was the Carrot River which showed statistically increasing trends in TP, TDP, and TN. The Red Deer River also showed statistically increasing trends in both TP and TDP. The Carrot River flows northeast, with agricultural activities dominating in the upper watershed and forests and wetlands making up most of the eastern portion of the watershed. Similarly, for the Red Deer River, the western portion of the basin is dominated by agricultural lands, while the eastern portion is largely forested. Although the causes for the increases in nutrient concentrations, particularly in TP, are not clear and further investigation is warranted, drainage of wetland areas in other watersheds has been found to increase runoff and subsequent nutrient loads (Yates *et al.*, 2014 Brunet & Westbrook, 2012).

Table 4 Flow-Weighted Trend Summary for Nutrients - Saskatchewan/Manitoba Boundary

Parameter	Assiniboine	Carrot	Churchill	Qu'Appelle	Red Deer (MB)	Saskatchewan
Nutrients						
Ammonia Nitrogen Total	$\leftrightarrow$	$\leftrightarrow$	<b>1</b>	$\leftrightarrow$	$\downarrow$	$\downarrow$
Nitrate-Nitrate as N	<u> </u>	Ţ	$\leftrightarrow$	$\leftrightarrow$	j	j
Nitrogen Total	$\leftrightarrow$	<u> </u>	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$
Phosphorous Total	$\leftrightarrow$	1	$\leftrightarrow$	$\downarrow$	1	<b>↓</b>
Phosphorous Total Dissolved	$\leftrightarrow$	1	$\leftrightarrow$	$\downarrow$	<b>↑</b>	$\downarrow$

No Seasonality in Data, Trend Analysis Completed with Sen Slope Estimator

↑ statistically significant increasing trend; ↓ statistically significant decreasing trend; ↔ no significant trend

## 4.2 Major Ions

Major ions are present in all natural waters and concentrations and composition of major ions are determined by the type of rock and soil that the water comes into contact with throughout the watershed. Major ions can be affected by anthropogenic activities including wastewater discharges and land use activities. Major ions can also be affected by other factors, including changes in effective drainage area with return period and groundwater. Sodium (Na) and chloride (Cl) are often associated with road salt and municipal waste discharges (Environment Canada 2001; Turnbull and Ryan 2012; Corsi *et al.*, 2015). Fluoride does occur naturally in surface waters but anthropogenic sources include wastewater discharges from municipalities using fluorinated drinking water and a number of industries that use fluoride including herbicides, insecticides, phosphate fertilizers, aluminum smelting and chemical manufacturing.

Total dissolved solids (TDS) concentration is a measure of inland salinity (Williams and Sherwood 1994). Four major ions were included in the long-term trend assessment for the 12 transboundary prairie rivers: chloride, fluoride, sodium, sulphate. Additionally TDS was included to assess the overall change in salinity. The PPWB has established water quality objectives for these five parameters, which protect a range of water uses including the protection of aquatic life, agricultural uses and water treatability for drinking water.

## Alberta/Saskatchewan Boundary

On the Alberta/Saskatchewan boundary of the 30 flow-weighted monotonic trend assessments that were run just over half of the major ions (53%) had statistically significant increasing trends (Table 5). For two of the Alberta/Saskatchewan transboundary rivers, the Battle and South Saskatchewan rivers, all the major ions showed increasing trends over time. Decreasing trends were observed over the period of record for 20% of the major ions that were assessed on the six rivers, with 27% of the major ions showing no change in concentration over time. Three rivers on the Alberta/Saskatchewan boundary had at least one decreasing trend for major ions. The Beaver River had the most number of decreasing trends including fluoride, sodium and sulphate. The Cold River also had two decreasing trends for chloride and sulphate and the North Saskatchewan River had a decreasing trend for fluoride.

Total dissolved solids (TDS) showed statistically significant increasing trends on four of the six transboundary rivers. This included the four rivers contributing to the Saskatchewan River system: North Saskatchewan, South Saskatchewan, Red Deer and Battle rivers. Over the period of record the North Saskatchewan River had a TDS concentration ranging from 105 to 317 mg/L with a median value of 203 mg/L. The South Saskatchewan River had a TDS

concentration ranging from 98 to 374 mg/L with a median value of 229 mg/L, while the Red Deer River had a TDS concentration ranging from 212 to 589 mg/L with a median of 278 mg/L over the period of record. At these concentration ranges TDS is unlikely to restrict the use of the water in these rivers, however, the potential cause of the significant changes in TDS should be further investigated. The Battle River, a smaller tributary of the Saskatchewan River system, had overall higher TDS values with a range of 218 to 1729 mg/L with a median value of 602 mg/L.

Two key constituents of TDS, sulphate and chloride also showed statistically significant increasing trends in 50% of the Alberta/Saskatchewan transboundary rivers. Sulphate showed increasing trends in the North Saskatchewan and South Saskatchewan rivers and the Battle River. Sulphate concentrations over the period of record ranged from 2.4 to 75 mg/L with a median value of 47.4 mg/L for the North Saskatchewan River; from 20.8 to 102 mg/L with a median of 59.6 mg/L for the South Saskatchewan River, and from 14 to 389 mg/L with a median value of 139.2 mg/L for the Battle River. The current Canadian drinking water quality guideline for sulphate is 500 mg/L (Health Canada, 2010).

Since the late 1960s/early 1970s chloride has shown statistically significant increasing trends in the Battle River, Red Deer River and the South Saskatchewan River (Figure 5). Chloride is a conservative solute that remains unaffected by biological river processes and is often used as a tracer for treated wastewater. Increases in chloride in river systems have been attributed to sources such as municipal waste water and road salt (Turnbull 2012; Environment Canada 2001). Chloride levels in the Battle River ranged from 0.4 to 175 mg/L, with a median value of 21 mg/L. For the Red Deer River chloride ranged from 0.05 to 45 mg/L with a median value of 4.71 mg/L. While chloride in the South Saskatchewan River has a statistically significant increasing trend over the period of record, concentrations range from 0.05 to 17.8 mg/L with a median of 6 mg/L.

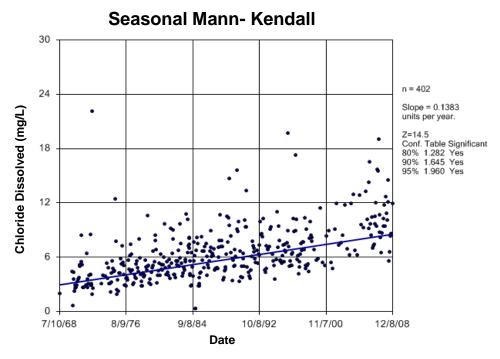


Figure 5 Trend in Chloride (dissolved) for the South Saskatchewan River (1968 to 2008)

Fluoride showed statistically significant increasing trends in four of the six rivers on the Alberta/Saskatchewan boundary (Battle, Cold, Red Deer and South Saskatchewan rivers). While fluoride does occur naturally in water, it can also enter water from a number of anthropogenic sources. Wastewater from municipalities using fluoridated drinking water can discharge significant amounts of fluoride into the environment. Health Canada (2010) reported that for the three prairie provinces of Alberta, Saskatchewan and Manitoba the population using fluorinated drinking water was 75, 37 and 70% respectively. For the rivers with statistically significant increasing trends in fluoride, concentrations ranged from 0.02 to 0.79 mg/L. Median concentrations were 0.23, 0.11, 0.16 and 0.15 mg/L for the Battle, Cold, Red Deer, and South Saskatchewan rivers respectively.

Table 5 Flow-Weighted Trend Summary for Major Ions - Alberta/Saskatchewan Boundary

Parameter	Battle	Beaver	Cold	North Saskatchewan	Red Deer (AB)	South Saskatchewan
Major Ions						
Chloride Dissolved	1	$\leftrightarrow$	Ţ	$\leftrightarrow$	<b>↑</b>	<b>↑</b>
Fluoride Dissolved	<b>†</b>	Ţ	<u>†</u>	Ţ	<b>↑</b>	<b>↑</b>
Sodium Dissolved/Filtered	<b>†</b>	j	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	<b>↑</b>
Sulphate Dissolved	<b>†</b>	J	$\downarrow$	<b>↑</b>	$\leftrightarrow$	<b>↑</b>
Total Dissolved Solids (TDS)	<b>†</b>	$\leftrightarrow$	$\leftrightarrow$	<b>†</b>	<b>↑</b>	1

No Seasonality in Data, Trend Analysis completed with Sen Slope Estimator

↑ statistically significant increasing trend; ↓ statistically significant decreasing trend; ↔ no significant trend

## Saskatchewan/Manitoba Boundary

Long-term trend assessment of five major ions on the Saskatchewan/Manitoba boundary found 50% of the trends increased significantly (Table 6). Over the period of record the Assiniboine River showed increasing trends in all five major ions. The Red Deer River had increasing trends in all the major ions with the exception of sulphate and the Saskatchewan River had increasing trends in all of the major ions with the exception of sodium. Of the 30 trend assessments completed for the five major ions on the six Saskatchewan/Manitoba transboundary rivers, 40% showed no change over the period of record. Ten percent of the trend assessments for the Saskatchewan/Manitoba transboundary rivers showed statistically significant decreasing trends.

The Churchill River showed no changes in major ions over the period of record except for fluoride which showed an increasing trend. Similarly, the Qu'Appelle River showed no significant changes in major ions except for sodium which had a decreasing trend. The Carrot River was the only river on the Saskatchewan/Manitoba boundary to have both increasing and decreasing trends in major ion constituents. For this river fluoride has a statistically significant increasing trend, while chloride and sodium had statistically significant decreasing monotonic trends. Sulphate and TDS each showed no statistically significant change over time in the Carrot River.

Fluoride showed increasing trends in all the rivers with the exception of the Qu'Appelle River. Total dissolved solids and chloride were also increasing in 50% of the transboundary rivers. Total dissolved solids and chloride had statistically significant positive trends on the Assiniboine, Red Deer at Erwood and the Saskatchewan rivers. Total dissolved solids median

concentrations for the three rivers were 645, 277 and 218 mg/L respectively; while for chloride the median concentrations for these three rivers were 19, 4.4 and 7.2 mg/L respectively.

Table 6 Flow-Weighted Trend Summary for Major Ions - Saskatchewan/Manitoba Boundary

Parameter	Assiniboine	Carrot	Churchill	Qu'Appelle	Red Deer (MB)	Saskatchewan
Major Ions						
Chloride Dissolved	<b>↑</b>	Ţ	$\leftrightarrow$	$\leftrightarrow$	1	<b>↑</b>
Fluoride Dissolved	<b>†</b>	<u> </u>	1	$\leftrightarrow$	<b>↑</b>	<b>†</b>
Sodium Dissolved/Filtered	1	Ţ	$\leftrightarrow$	Ţ	1	$\leftrightarrow$
Sulphate Dissolved	<b>†</b>	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	<b>†</b>
Total Dissolved Solids (TDS)	1	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	<b>↑</b>	1

No Seasonality in Data, Trend Analysis completed with Sen Slope Estimator

↑ statistically significant increasing trend; ↓ statistically significant decreasing trend; ↔ no significant trend

## 4.3 Physicals

Water Quality objectives have been established by the PPWB for four physicals including dissolved oxygen (DO), pH, sodium adsorption ratio (SAR) and total suspended solids (TSS). Dissolved oxygen, pH and TSS objectives were established for the protection of aquatic life, while a SAR objective was established for irrigation.

## Alberta/Saskatchewan Boundary

On the Alberta-Saskatchewan boundary 24 monotonic trend assessments were completed for the four physical parameters on the six transboundary rivers (Table 7). Overall, this group of parameters appeared to either show no change in concentrations over time or statistically significant increasing trends. Only one decreasing trend was observed which was for SAR on the Beaver River. Overall 50% of the trend assessments showed no change in the water quality, 46% showed an increasing trend over time.

Of note was that pH showed an increasing trend in all Alberta/Saskatchewan transboundary rivers. Dissolved oxygen showed no significant trends across all the Alberta-Saskatchewan transboundary rivers with the exception of the Cold River. In this case an increasing monotonic trend in dissolved oxygen was observed. For TSS, there was no change over time for the larger flow rivers including the North Saskatchewan, South Saskatchewan and the Red Deer River. There was also no trend in TSS for the Cold River, which is not unexpected given that the Cold River monitoring site is located at the outlet to the lake. As a result, TSS will have been deposited and retained within the lake. However, statistically significant increasing trends for TSS were observed for the two smaller, low flow rivers, the Battle and Beaver rivers on the Alberta/Saskatchewan boundary. The TSS concentration range for the Battle River ranged from 0.5 to 1146 mg/L with a median value of 13 mg/L. For the Beaver River the TSS ranged from 0.5 to 202 mg/L with a median value of 6.3 mg/L.

Sodium adsorption ratio is a specific water use index and is important for assessing suitability of irrigation. Sodium adsorption ratio trends varied among the transboundary river sites. Increasing trends in SAR were observed for the Battle River and the South Saskatchewan River, which is consistent with the increasing trend of sodium for these two rivers. The Beaver River showed a decreasing trend in SAR which is also consistent with the decreasing trend observed for sodium. No significant trends in SAR were observed over the last 15 years for the

Cold River, the last 20 years for the North Saskatchewan or 40 years for the Red Deer rivers. Again this is consistent with no significant increase of sodium in these rivers.

Table 7 Flow-Weighted Trend Summary for Physical and Other Parameters-Alberta/Saskatchewan Boundary

Parameter	Battle	Beaver	Cold	North Saskatchewan	Red Deer (AB)	South Saskatchewan
Physicals						
Oxygen Dissolved	$\leftrightarrow$	$\leftrightarrow$	1	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$
pH – Field	<b>↑</b>	1	<b>†</b>	1	1	1
Sodium Adsorption Ratio (SAR)	<b>†</b>	$\downarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	1
Total Suspended Solids (TSS)	<b>↑</b>	<b>↑</b>	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$

No Seasonality in Data, Trend Analysis completed with Sen Slope Estimator

## Saskatchewan/Manitoba Boundary

Of the 24 monotonic trend assessments completed on the Saskatchewan/Manitoba boundary for physical and other parameters, 50% showed no change in these measured parameters over the period of record for the six PPWB transboundary rivers. Eight parameters showed statistically significant increasing trends and four showed statistically significant decreasing trends (Table 8).

Dissolved oxygen showed a decreasing trend in three rivers on the Saskatchewan/Manitoba boundary (Assiniboine, Qu'Appelle and Saskatchewan rivers), and no significant trend in the other three rivers on this boundary (Carrot, Churchill and Red Deer rivers). For dissolved oxygen, a decreasing trend implies less oxygen within the river systems. pH in the Saskatchewan/Manitoba rivers had significantly significant increasing trends in three of the rivers (Carrot, Churchill and Saskatchewan). In the Assiniboine, Red Deer and Saskatchewan rivers no significant change in pH over time was observed.

The Assiniboine River and the Carrot River both showed increasing trends in TSS. Increasing trends in SAR over the period of record were also observed in the Assiniboine and Red Deer rivers. Similar, to the Alberta/Saskatchewan boundary rivers, this increase in SAR corresponds to increases in sodium on these rivers. The Churchill River also showed an increasing trend in SAR over the period of record, although for this river this was not consistent with sodium which showed no change over the period of record.

The Qu'Appelle River and the Saskatchewan River did not show any change in TSS. This lack of change might be attributed to the number of lakes/reservoirs that the rivers pass through prior to reaching the Saskatchewan/Manitoba boundary. These reservoirs have been found to sequester a large proportion of nutrients (Donald et al. 2015); this retention capacity also affects total suspended solid concentrations.

<sup>↑</sup> statistically significant increasing trend; ↓ statistically significant decreasing trend; ↔ no significant trend

Table 8 Flow-Weighted Trend Summary for Physical and Other Parameters - Saskatchewan/Manitoba Boundary

Parameter	Assiniboine	Carrot	Churchill	Qu'Appelle	Red Deer (MB)	Saskatchewan
Physicals						
Oxygen Dissolved	<b>\</b>	$\leftrightarrow$	$\leftrightarrow$	<b>↓</b>	$\leftrightarrow$	$\downarrow$
pH – Field	$\leftrightarrow$	1	<b>↑</b>	$\leftrightarrow$	$\leftrightarrow$	1
Sodium Adsorption Ratio (SAR)	<b>1</b>	<b>↓</b>	<b>1</b>	$\leftrightarrow$	<b>↑</b>	$\leftrightarrow$
Total Suspended Solids (TSS)	1	<u> </u>	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$

No Seasonality in Data, Trend Analysis completed with Sen Slope Estimator

↑ statistically significant increasing trend; ↓ statistically significant decreasing trend; ↔ no significant trend

### 4.4 Metals

Trend assessments were completed for a number of metals for the 12 transboundary rivers. However, due to numerous analytical method changes over the period of record resulting in steps in the data, censored data or limited years of data not all trace metals could be trended. Trace metals can be important given their potential to cause toxic responses in aquatic life and the impacts on other water uses such as irrigation, livestock watering and municipal uses. Water quality objectives are established at the transboundary river sites for the protection of water uses including protection of aquatic life, agricultural uses (irrigation and livestock watering) and treatability of the water as a drinking water source. Metals can enter river water through natural processes such as erosion and weathering of soils, minerals and ores. Anthropogenic sources include industrial waste waters, mining and sewage effluents.

## Alberta/Saskatchewan Boundary

In total 86 trend assessments were performed for the six Alberta/Saskatchewan transboundary rivers incorporating 14 different metals (Table 9). Overall most metals (57%) exhibited no significant change in concentration over time. Statistically significant decreasing trends were observed in 42% of the assessments. Only one statistically significant increasing trend was observed, for dissolved lithium in the Battle River. The lithium (dissolved) concentration for the Battle River ranged from 6 to 210  $\mu$ g/L, with a median concentration of 77  $\mu$ g/L. While there is no PPWB objective for dissolved lithium there is an objective for total lithium.

Metals showing statistically significant decreasing trends, for at least four of the transboundary rivers, included aluminum (total), cobalt (dissolved), copper (total), and molybdenum (dissolved). Metals showing decreasing trends in three of the six transboundary rivers included chromium (total), cobalt (total) and copper (dissolved). Few metals could be trended for the Cold River given the large amount of censored data for metals at this site.

Table 9 Flow-Weighted Trend Summary for Metals - Alberta/Saskatchewan Boundary

Parameter	Battle	Beaver	Cold	North Saskatchewan	Red Deer (AB)	South Saskatchewan
Aluminum Total	$\downarrow$	$\leftrightarrow$	<b>\</b>	<b>\</b>	$\leftrightarrow$	<b>1</b>
Boron Dissolved	Step	$\leftrightarrow$	Step	Step	Step	Step
Cadmium Total	>20%	>20%	>20%	>20%	>20%	>20%
Chromium Total	$\leftrightarrow$	<b></b>	>20%	<b></b>	$\leftrightarrow$	<b></b>
Cobalt Dissolved	J	j	>20%	j	1	j
Cobalt Total	$\leftrightarrow$	j	>20%	j	$\leftrightarrow$	j
Copper Dissolved	1	>20%	>20%	Step	Ţ	j
Copper Total	j	Ţ	>20%	1	$\leftrightarrow$	j
Iron Dissolved	$\leftrightarrow$	$\leftrightarrow$	>20%	$\leftrightarrow$	Ţ	$\leftrightarrow$
Iron Total	$\leftrightarrow$	Step	$\leftrightarrow$	$\leftrightarrow$	j	J
Lead Total	>20%	>20%	>20%	>20%	$\leftrightarrow$	>20%
Lithium Dissolved	1	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$
Lithium Total	<b>1</b>	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	↓
Manganese Dissolved	$\leftrightarrow$	1	>20%	Step	$\leftrightarrow$	$\leftrightarrow$
Manganese Total	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	<u> </u>
Molybdenum Dissolved	J	1	>20%	<u> </u>	1	j
Molybdenum Total	$\leftrightarrow$	j	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	Step
Nickel Total	$\leftrightarrow$	Step	>20%	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$
Vanadium Total	$\leftrightarrow$	Step	Step	$\leftrightarrow$	$\leftrightarrow$	J
Zinc Dissolved	>20%	>20%	>20%	>20%	>20%	>20%
Zinc Total	$\leftrightarrow$	$\leftrightarrow$	>20%	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$

Step	Step in Data
>20%	> 20% Censored Data

<sup>↑</sup> statistically significant increasing trend; ↓ statistically significant decreasing trend; ↔ no significant trend

## Saskatchewan/Manitoba Boundary

A total of 84 trend assessments were completed for the metals on the Saskatchewan/Manitoba transboundary sites. Of the metals that were trended most (58%) did not have statistically significant changes (Table 10). Of the trends that were observed most were negative (decreasing) (one third of total analyses). Three rivers, the Assiniboine, Red Deer and Saskatchewan rivers, did have at least one statistically significant increasing trend in metal concentration. All three of these rivers had statistically significant positive monotonic trends in lithium (dissolved). The Red Deer and the Saskatchewan rivers also showed increasing trends for molybdenum (total). The Red Deer River also showed a statistically significant increasing trend in molybdenum (dissolved) and copper (dissolved).

#### 5. Conclusions

Long-term flow-weighted monotonic trend assessments were completed for nutrients, major ions, physicals and metals at the 12 transboundary rivers that are monitored by the PPWB as part of the MAA. While the PPWB has water quality objectives established at the 12 transboundary sites, trend assessment allows the PPWB to assess changes in water quality over time. Trend assessments are valuable as they can allow more subtle changes in water quality to be highlighted. This process is therefore complementary to annual excursion reporting of water quality objectives. The Board recognized early on during the development of interprovincial water quality objectives as summarized in Schedule E to the MAA, that trend analysis would be an important component of the PPWB water quality program.

Table 10 Flow-Weighted Trend Summary for Metals - Saskatchewan/Manitoba Boundary

Parameter	Assiniboine	Carrot	Churchill	Qu'Appelle	Red Deer (MB)	Saskatchewan
Aluminum Total	$\downarrow$	$\leftrightarrow$	Step	<b>↓</b>	Step	$\downarrow$
Boron Dissolved	Step	$\leftrightarrow$	Step	Step	$\leftrightarrow$	Step
Cadmium Total	>20%	$\downarrow$	>20%	<b>↓</b>	>20%	<b>\</b>
Chromium Total	$\leftrightarrow$	$\leftrightarrow$	>20%	<u> </u>	>20%	$\leftrightarrow$
Cobalt Dissolved	↓ ↓	$\downarrow$	>20%	<u> </u>	>20%	>20%
Cobalt Total	$\leftrightarrow$	$\leftrightarrow$	>20%	$\leftrightarrow$	$\leftrightarrow$	<b>1</b>
Copper Dissolved	$\leftrightarrow$	$\leftrightarrow$	>20%	$\leftrightarrow$	<b>1</b>	$\leftrightarrow$
Copper Total	$\leftrightarrow$	$\downarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	<b>\</b>
Iron Dissolved	$\leftrightarrow$	Step	Step	$\leftrightarrow$	Step	Step
Iron Total	$\leftrightarrow$	$\leftrightarrow$	Step	$\downarrow$	Step	<b>\</b>
Lead Total	>20%	$\leftrightarrow$	>20%	>20%	>20%	$\downarrow$
Lithium Dissolved	<b>↑</b>	$\leftrightarrow$	Step	$\leftrightarrow$	<b>1</b>	1
Lithium Total	$\leftrightarrow$	$\leftrightarrow$	Step	$\downarrow$	$\leftrightarrow$	$\leftrightarrow$
Manganese Dissolved	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$
Manganese Total	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	Step	<b>↓</b>
Molybdenum Dissolved	↓ ↓	$\leftrightarrow$	>20%	$\leftrightarrow$	<b>1</b>	$\leftrightarrow$
Molybdenum Total	$\leftrightarrow$	$\leftrightarrow$	$\leftrightarrow$	Step	1	<b>1</b>
Nickel Total	Step	Step	Step	Step	Step	$\leftrightarrow$
Vanadium Total	$\leftrightarrow$	$\leftrightarrow$	Step	$\leftrightarrow$	Step	<b>↓</b>
Zinc Dissolved	>20%	$\leftrightarrow$	>20%	$\downarrow$	>20%	>20%
Zinc Total	<b>\</b>	$\leftrightarrow$	$\downarrow$	<u> </u>	$\leftrightarrow$	<u> </u>

Step	Step in Data
>20%	> 20% Censored Data

 $\uparrow$  statistically significant increasing trend;  $\downarrow$  statistically significant decreasing trend;  $\leftrightarrow$  no significant trend

Flow-weighted monotonic trend assessment did highlight a number of statistically significant increasing trends over the period of record. Follow up should identify priority parameters where significant trends have been identified and undertake more detailed assessment to describe the nature of the trend, including incorporation of more recent data. It may also be appropriate to further examine some of the decreasing trends to assess the response of rivers to management activities. While the intent and scope of this report did not include investigation of potential causes of trends, further investigative work may be warranted by the PPWB or the participating jurisdictions to assess causes for priority parameters. This trend analysis report will also be complimentary to the excursion reporting process.

Trend assessment of nitrogen and phosphorus in the 12 transboundary prairie rivers showed a number of statistically significant decreasing trends for nutrients. Transboundary rivers where one or more forms of nutrient concentrations decreased were the North Saskatchewan, Red Deer, Battle, South Saskatchewan, and Beaver rivers on the Alberta/Saskatchewan boundary and all the rivers the Saskatchewan/Manitoba boundary.

With the exception of the Battle River, all the other Alberta/Saskatchewan transboundary rivers had a decreasing or had no significant trend for TP. Nitrogen showed a number of statistically significant increasing trends, including TN on the South Saskatchewan River and TN and NH<sub>4</sub>-N on the Cold River. Significantly decreasing concentrations in one or more forms of nitrogen (NH<sub>4</sub>-N, NO<sub>3</sub>-NO<sub>2</sub>, or TN) were found on the Battle, Beaver, North Saskatchewan, Red Deer, and South Saskatchewan rivers.

On the Saskatchewan/Manitoba boundary, two rivers showed long-term increasing trends in nutrients: the Carrot River and the Red Deer River. The Carrot and Red Deer rivers showed strong statistically significant increasing trends over the period of record for TP and TDP.

Of all the parameter groups where long-term flow-weighted monotonic trend assessments were performed, major ions showed the greatest proportion of statistically significant increasing trends. All four major ions (chloride, fluoride, sodium, sulphate) and TDS showed statistically significant increasing trends for the Battle and South Saskatchewan rivers on the Alberta/Saskatchewan boundary, and the Assiniboine River on the Saskatchewan/Manitoba boundary. Across all sites, fluoride, chloride and TDS were shown to be statistically increasing in 50% or more of the rivers. On the Alberta/Saskatchewan boundary sulphate was also found to be significantly increasing in half of the transboundary rivers.

Of the physicals, field pH had increasing trends in all of the rivers on the Alberta/Saskatchewan boundary and in three of the six rivers on the Saskatchewan/Manitoba boundary. As pH impacts many biological and chemical processes this could have implications to the quality of these rivers if the trend continues. While field and laboratory values are typically similar, field pH is traditionally used as it should more closely reflect the conditions in the river, for example changes in pH associated with photosynthesis and respiration. Comparison of the field and laboratory pH monotonic trends showed similar results for all rivers with the exception of three rivers on the Saskatchewan/Manitoba boundary (the Assiniboine, Churchill and Red Deer rivers). For the Assiniboine and Red Deer rivers the laboratory pH values showed a slight increasing trend over time while the field pH showed no significant trend. For the Churchill River the opposite was reported where the field pH had a slight increasing monotonic trend, but the laboratory pH values did not show a significant trend. However, for the majority of the rivers the trend results would suggest that the pH has increased over time.

For other physical parameters, increasing trends in total suspended solid concentrations were found for the Battle and Beaver rivers on the Alberta/Saskatchewan boundary and the Assiniboine and Carrot rivers on the Saskatchewan/Manitoba boundary. Total suspended solids are a measure of the sediment that is transported downstream; this includes in-stream erosion and bedload suspension and inputs from the landscape. Sediment transports nutrients and metals in these riverine systems, depositing them during periods of lower flows or in locations with lower flow, such as receiving lakes and reservoirs.

While dissolved oxygen did not appear to be declining in the Alberta/Saskatchewan rivers, decreasing trends in dissolved oxygen were observed over time for the Assiniboine, Qu'Appelle and Saskatchewan rivers.

Trend assessments were completed on both dissolved and total metals for the 12 transboundary rivers where sufficient data were available. Of all parameters assessed in this study, metals showed the least number of increasing trends over time. For the transboundary rivers, a large number of metals showed no statistically significant change in concentration over time. Statistically significant flow-weighted negative (decreasing) trends were observed on both interprovincial boundaries. For the Alberta/Saskatchewan boundary this included 42% of the metals trended and for the Saskatchewan/Manitoba boundary this included 33.3% of the metals trended. Increasing trends were observed in four metals for the 12 transboundary rivers. This included lithium (dissolved), molybdenum (total and dissolved) and copper (dissolved).

Overall a total of 338 trend assessments were performed on the 12 transboundary rivers incorporating five nutrients, four major ions and TDS, four physical parameters and 14 different metals (in some cases this included both the total and dissolved components of the same

metal). Of the 338 trend assessments performed (excluding dissolved oxygen) 20% showed statistically significant increasing trends on flow adjusted data. Major ions and TDS was the group of parameters that showed the greatest number of statistically significant increasing trends (52%), followed by physical and other (50%), nutrients (15%) and metals (4.7%).

Thirty one percent of the total trend assessments performed (again excluding dissolved oxygen) showed a statistically significant decreasing trend. Within each of the parameter groupings nutrients exhibited the greatest number of decreasing trends (45%), followed by metals (38%), major ions (15%) and physical and others (4%).

The objective for dissolved oxygen, like the lower objective for pH, is met when measured values are greater than the objective, i.e. a lower threshold. This is different than other parameters where the objective represents an upper threshold. Thus, for situations where the objective is met, decreasing trends in oxygen mean that median oxygen values become closer to the objective over time. As a result, dissolved oxygen was not included in the overall or parameter group increasing or decreasing percentages. In the case of dissolved oxygen, one river (Cold River) of the 12 transboundary rivers assessed had an increasing trend, while three rivers (Assiniboine, Qu'Appelle and Saskatchewan rivers) had decreasing monotonic trends.

Of the six transboundary rivers on the Alberta/Saskatchewan boundary the Battle River and the South Saskatchewan River showed the most statistically significant monotonic increasing trends. Of the trend assessments completed on the Battle River a third had increasing trends; this included all the major ions and TDS, TP, pH, SAR, TSS and lithium (dissolved). For the South Saskatchewan River 28% of the trend assessments showed statistically significant increasing monotonic trends. Similar to the Battle River, this included all the major ions and TDS, TN, pH and SAR. The river with the least number of increasing trends on the Alberta/Saskatchewan boundary was the North Saskatchewan River. On this river 10% of the parameters trended showed statistically significant increasing trends. The North Saskatchewan River also had the shortest period of record (1988 – 2008).

For the Saskatchewan/Manitoba boundary the Red Deer River had the most statistically significant increasing trends at 48% of the trend assessments completed for this river (excluding dissolved oxygen). Increasing trends were observed for total and dissolved phosphorus, chloride, fluoride, TDS, SAR, copper (dissolved), lithium (dissolved), and molybdenum (total and dissolved). The Assiniboine River also had statistically significant flow-weighted increasing monotonic trends in over a quarter of the parameters trended including all the major ions, SAR, TSS and lithium (dissolved). The Qu'Appelle River on the Saskatchewan/Manitoba boundary was the only river that did not have any statistically significant increasing trends over the period of record (33 years); however as noted it did have a decreasing trend in dissolved oxygen.

The goal of this analysis was to summarize sites with monotonic trends. The approach taken in this trend assessment exercise was conservative and maintained consistent methods for the analysis. Overall, a high proportion, approximately half, of the analyses conducted had statistically significant trends. No attempt was made to explain the trends and the findings from this report can be used to prioritize more detailed assessment of specific parameters in specific river reaches. This prioritization may include specific parameters, parameters with consistent trends among sites, and/or the significance level and slope magnitude for specific trend results.

As part of the on-going mandate of the PPWB, trend assessments will be re-run on these transboundary river sites at regular intervals, approximately every five years. In the next trend assessment there may be sufficient data available to complete a more comprehensive

assessment of metals given the updates in analytical methodology providing more than 10 years of comparable data.

# 6. Acknowledgements

This report on water quality trend assessments in the 12 transboundary rivers was prepared by Dr. Joanne Sketchell of the PPWB Secretariat, with reviews and comments provided by the COWQ. Water quality data used in the objectives review were provided by Environment Canada, Water Quality Monitoring and Surveillance and water flow data were provided by Environment Canada, Water Survey of Canada through the MAA. Many thanks are also extended to the numerous students who worked with the PPWB Secretariat under the supervision of Dr. Joanne Sketchell on the trend analysis including Destiny Dewalt, Brent Giesbrecht, Ryan Husband, Jacklyn Kraiser, James Leach, Kaitlyn Malowany, Echo Polivka, Conor Renouf, Tyler Smith, Sean Tulloch and Kelly Weibe.

# 7. Committee on Water Quality Members

Mike Renouf, PPWB Executive Director (Chair)
Joanne Sketchell, Environment Canada (PPWB Secretariat)
David Donald/Paul Klawunn, Environment Canada
Bill Schutzman/Sharon Reedyk, Agriculture and Agri-Food Canada
Richard Casey/Gongchen Li Alberta Environment and Parks
John-Mark Davies, Saskatchewan Water Security Agency
Nicole Armstrong, Manitoba Conservation and Water Stewardship

## 8. References

- Anderson, A-M. (2012). Investigations of Trends in Select Water Quality Variables at Long-Term Monitoring Sites on the North Saskatchewan River. December 2012, 26 pp.
- Brunet, N. N. and Westbrook, C.J. (2012) Wetland drainage in the Canadian Prairies: Nutrient, Salt and Bacteria Characteristics. *Agriculture Ecosystems and Environment* 146 p.1-12
- Carlson, J.C., Anderson, J.C., Low, J.E., Cardinal, P., MacKenzie, S.D., Beattie, S.A., Hanson, M.L. (2013). Presence and Hazards of Nutrients and Emerging Organic Micropolutants from Sewage Lagoon Discharges into Dead Horse Creek, Manitoba, Canada. *Science of the Total Environment*, 445, p. 64-68. doi:10.1016/j.scitotenv.2012.11.100
- Corsi, S.R. De Cicco, L.A. Lutz, M.A. and Hirsch, R.M. (2015) River chloride trends in snow affected urban watersheds: increasing concentrations outpace urban growth rate are common among all seasons. *Science of the Total Environment* 508 p. 488-497
- Donald, D.B., Parker, B.R., Davies, J.M. and Leavitt, R.R.. (2015). Nutrient sequestration in the Lake Winnipeg watershed. *Journal of Great Lakes Research*, 41, p. 630–642.

- Environment Canada (2001). Priority Substances List Assessment Report: Road Salts.

  Prepared under the Canadian Environmental Protection Act 1999. Environment Canada Hull, Quebec. hppt://www.ec.gc.ca/substances/ese/eng/psap/final/roadsalts.cfn.
- Gilbert, R. O. (1987). Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold 320.p
- Glozier N.E.; R.W. Crosley, L.A. Mottle and Donald D.B. (2004) Water Quality Characteristics and Trends for Banff and Jasper National Parks: 1973 to 2002. Environment Canada.
- Health Canada. (1996). Guidelines for Canadian Drinking Water Quality. 6th edition. Prepared by the Federal-Provincial-Territorial Committee on Drinking Water. Ottawa: Health Canada. ISBN 0-660-16295-4.

  Updated guidelines on the Internet at <a href="http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/2010-sum\_guide-res\_recom/index-eng.php">http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/2010-sum\_guide-res\_recom/index-eng.php</a>
- Health Canada. (2010). Guidelines for Canadian Recreational Water Quality. 3rd edition. Prepared by the Federal-Provincial-Territorial Committee on Drinking Water. Ottawa: Health Canada.

  Updated guidelines on the Internet at <a href="http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/guide\_water-2012-guide\_eau/index-eng.php">http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/guide\_water-2012-guide\_eau/index-eng.php</a>
- Helsel, D.R. (2005). Nondetects and Data Analysis: Statistics for Censored Environmental Data. Wiley-Interscience, Hoboken, N.J. 250 pp.
- Hirsch, R.M., Slack, J.R., (1984). Non Parametric Trend Test for Seasonal Data with Serial Dependence. *Water Resources Research*, 20 (6), p. 727-732.
- Hirsch, R.M., Slack, J.R., Smith, R.A., (1982). Techniques of Trend Analysis for Monthly Water Quality Data. *Water Resources Research* 18(1), p. 107-121.
- Leavitt, P.R., Brock, C.S., Ebel, C., and Patoine, A. (2006). Landscape-Scale Effects of Urban Nitrogen on a Chain of Freshwater Lakes in Central North America. *Limnology and Oceanography, 51*(5), p. 2262-2277.

  Retrieved from http://www.jstor.org/stable/3841064
- Prairie Provinces Water Board. (1992). Schedule E to the Master Agreement on Apportionment. Regina: PPWB. Internet URL <a href="http://www.ppwb.ca/uploads/files/general/37//ppwb-water-quality-objectives.pdf">http://www.ppwb.ca/uploads/files/general/37//ppwb-water-quality-objectives.pdf</a>
- Rock, L., and Mayer, B. (2006). Nitrogen Budget for the Oldman River Basin, Southern Alberta, Canada. *Nutr Cycl Agroecosyst*, 75, p. 147-162. Doi:10.1007/s10705-006-9018-x
- Sanitas Technologies. (2009). Sanitas and WQStat Plus™ Statistical Analysis Procedures Version 9.
- Turnbull B. and Ryan M.C. (2012). Decadal and Seasonal Water Quality Trends Downstream of Urban and Rural Areas in Southern Alberta Rivers. *Water Quality Research Journal of Canada* 47, (3-4) p. 407-420.
- Vecchia, A.V., (2003). Water-Quality Trend Analysis and Sampling Design for

- Streams in North Dakota, 1971-2000, U.S. Geological Survey Water Resources Investigations Report 2003-4094.
- Williams, W.D. and Sherwood, J.E. (1994). Definition and Measurement of Salinity in Salt Lakes. *International Journal of Salt Lake Research*, 3, p. 53-63.
- Yates, A.G., Culp, J.M., and Chambers, P.A. (2012). Estimating Production from Human Activities in Subcatchments of the Red River, Manitoba. *Journal of Great Lakes Research*, *38*, p. 106-114. doi:10.1016/j.jglr.2011.04.009
- Yates, A.G., Brua, R.B., Culp, J.M., and Chambers, P.A. (2013). Multi-Scaled Drivers of a Prairie Stream Metabolism along Human Activity Gradients. *Freshwater Biology, 58*, p. 675-689. doi:10.1111/fwb.12072
- Yates, A.G., Brua, R.B., Corriveau, J., Culp, J.M., and Chambers, P.A. (2014). Seasonally Driven Variation in Spatial relationships Between Agricultural land Use and In-Stream Nutrient Concentrations. *River Research and Applications* 30 p. 476-493

