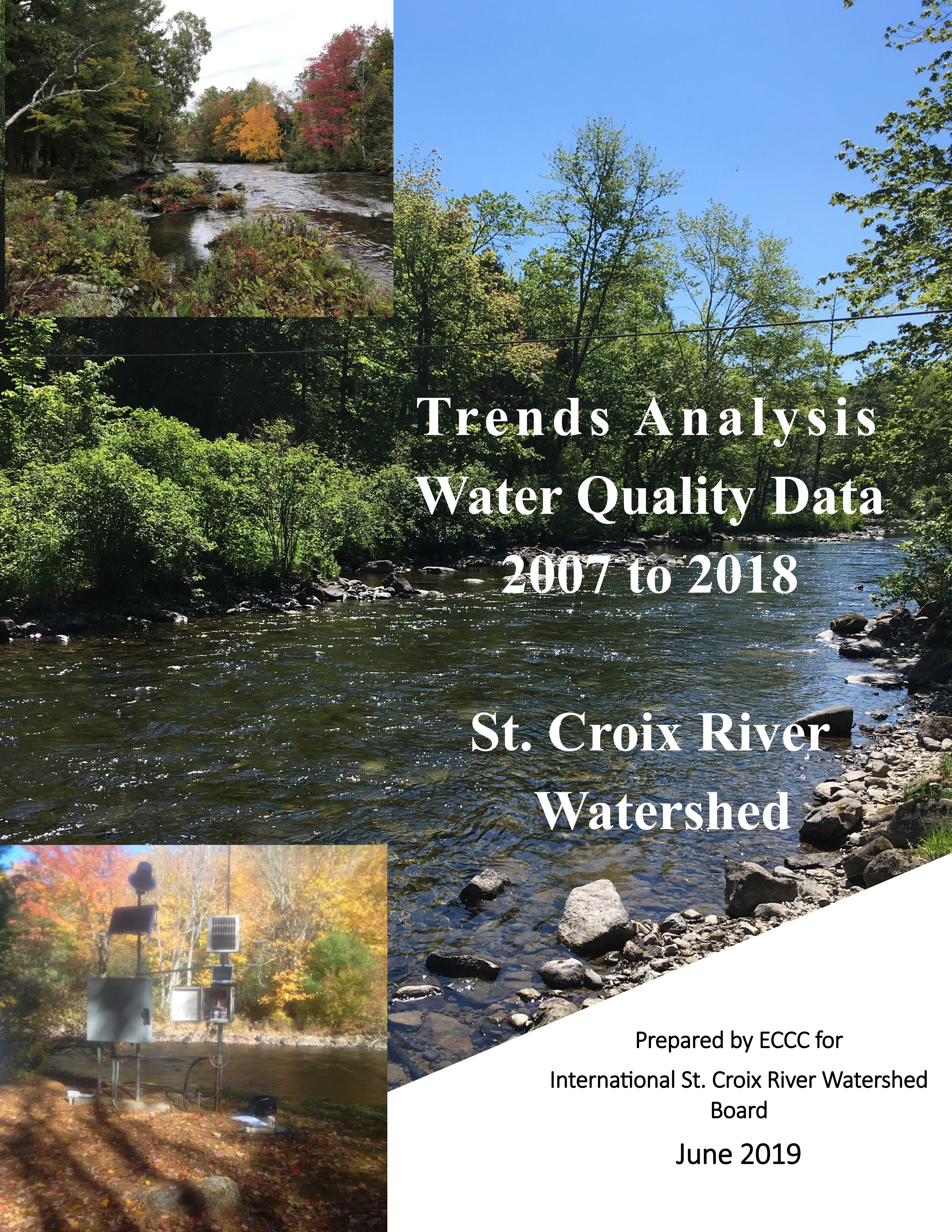

# Trends Analysis Water Quality Data 2007 to 2018

# St. Croix River Watershed

Prepared by ECCC for

International St. Croix River Watershed Board

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# 1 Introduction

As part of its long-term water quality monitoring of the St. Croix River Watershed, Environment and Climate Change Canada (ECCC) collects grab samples at regular intervals from two locations. One is located at the outflow of East Grand Lake at Forest City, Maine, and the other at the Milltown Dam in St. Stephen, New Brunswick. The collection records for these sites go back as far as 1965 and provide a long-term record of the status of water resources in the watershed. However, ECCC's support of its water quality monitoring programs were reduced from approximately 1995 to 2006 and therefore sample collection and analysis during this period was limited.

Each year, ECCC provides the International St. Croix River Watershed Board with monthly summaries and annual charts of automated water quality data and grab sample results for the previous calendar year. Measurements are compared to their relevant Canadian Council of Ministers for the Environment (CCME) and New Brunswick provincial guidelines for the protection of aquatic life. Parameters exceeding guidelines in any given year are highlighted.

In this report, ECCC provides the results of trend analyses for water chemistry data obtained at both the Forest City and Milltown stations. Mann-Kendall trend tests (or the Seasonal variant of the test) were conducted for each water quality parameter, to identify monotonic changes in concentrations for a suite of parameters over a long time period. Trends were assessed for most parameters over a 12 year period from 2007 – 2018, and for selected metal parameters (antimony, arsenic, beryllium, chromium, cobalt, copper, lead, nickel, molybdenum, selenium, titanium, vanadium, and zinc) over an eight year period from 2011 – 2018. The shorter time period for metals was due to changes in laboratory methodology in 2010, which improved sensitivity and lowered detection limits. These new trend analyses are the first step in investigating long-term changes within the St. Croix watershed.

The recent (2007 – 2018) data used for these analyses are available from the ECCC Saint John River/St. Croix River OpenData portal, while historical data came from ECCC's internal database.

# 2 St. Croix River Watershed and Site Descriptions

The St. Croix River Watershed covers an area of approximately 4271 $km^2$ that straddles the international border between Maine and New Brunswick. The overall population in the watershed was approximately 24,300 as of 2006 (ISCRWB, 2008). Population densities throughout the St. Croix River Watershed are generally low and much of the watershed consists of forested land. The majority of the population and four of the five population centers (population > 1000) are situated within the lower stretch of the watershed, along with most of the industrial activity in the region (ISCRWB, 2008).

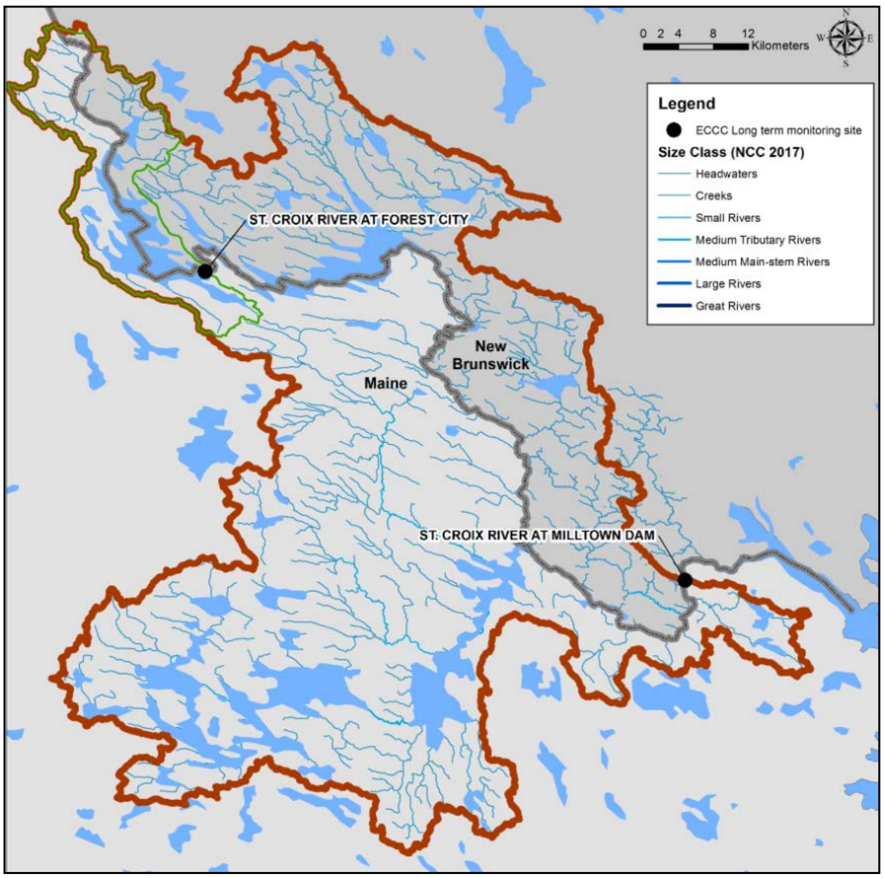


**Figure 1**. Map of the St. Croix River Watershed. The red outline denotes the extent of the watershed, while the grey line shows the international border. The two active ECCC long-term monitoring sites have been visited on a regular basis since 2006.

Industrial activities related to natural resource development, including logging, pulp milling, and textiles production, have historically negatively influenced the water quality of the St. Croix Watershed (ISCRWB, 2008). For example, the Baileyville pulp mill (currently Woodland Pulp LLC) is a major operation that has been active since 1904 (Environment Canada, 1987).

The two long-term water quality monitoring sites represent two distinct parts of the watershed. The Forest City site (N45.6641, W67.7336) at the outflow of East Grand Lake is located within the northern portion of the watershed, an area of very low population density. This site experiences minimal industrial or land-use activity and thus represents a less disturbed site. Meanwhile, the Milltown site, situated just above the Milltown dam (N45.1753, W67.2930), is found within the more densely populated, southern part of the watershed. This site is downstream from the municipality of Baileyville and the Baileyville pulp mill, two major producers of effluent. Both sites have been sampled between 4 and 12 times per year since 2006 for physical parameters, major ions, metals, and nutrients.

A single water quality objective has been set for the St. Croix River by the International St. Croix River Watershed Board, which requires dissolved oxygen concentrations to be maintained above 5 mg/L for the protection of fish populations. This objective has been met consistently at both sites since 1998 (ISCRWB, 2008).

# 3 Comparison of Past and Present Water Quality at Milltown

Of the two long-term monitoring sites, Milltown has a longer and more consistent record of water quality measurements where ECCC has collected grab samples since 1965. This enables broad comparisons of present and past water quality. Two ECCC sites have existed at Milltown - the first sampling site, operated from 1965 to 1996, was located at the International Bridge in Milltown (N45.1697, W67.2972), approximately one kilometer upstream of the present site at the Milltown dam. Following a pause in sampling visits, regular sampling resumed in 2005 at the present Milltown dam site (N45.1753, W67.2930).

Water quality parameters at the Milltown site are heavily influenced by upstream pollution sources, including the Baileyville wastewater treatment plant and the pulp mill (ISCRWB, 2016). In particular, mill effluent in the past has raised major ion concentrations and contributed to the decline of dissolved oxygen (Environment Canada, 1987). Operations at the pulp mill have changed over time and improvements in both mill processes and effluent treatment have reduced concentrations of major ions, reduced biological oxygen demand, and regulated discharge rates (Environment Canada, 1987). Production capacity at the plant was expanded in 2016 with the addition of tissue paper production, although the volume of surface water releases have remained fairly constant since 2009 (EPA, 2019a). In this report, concentrations of select parameters from the historical (1978-1987) and present (2007-2018) periods are compared. Differences between the two periods generally reflect changes to mill operations and upwind emissions.

When a Mann-Whitney Rank Sum test was applied, statistically significant differences ($p < 0.05$) were detected between the historical and present concentrations of total organic carbon, dissolved chloride, and dissolved sodium (**Figure 2**). Improvements in water quality, observed as lower major ion concentrations in the more recent period, can be attributed to improvements in effluent treatment at the pulp plant that have reduced releases (Environment Canada, 1987).

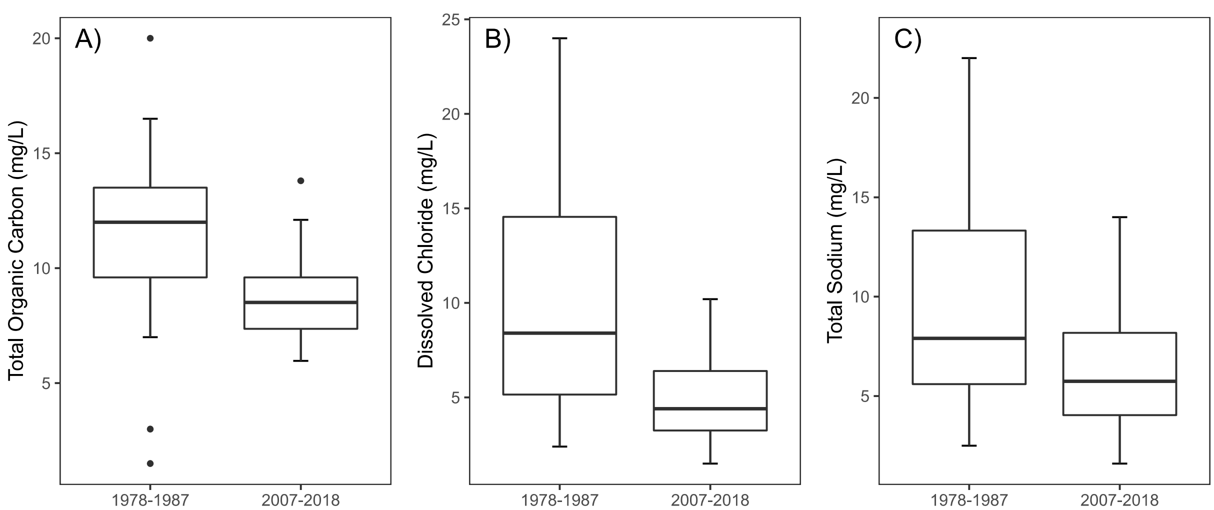


**Figure 2**. Box plots of (A) total organic carbon, (B) dissolved chloride, and (C) dissolved sodium concentrations between the two periods of water quality data records at the Milltown site. In each box plot, the center line represents the median of the data, the lower and upper edges represent the 25$^{th}$ and 75$^{th}$ percentiles, and the whiskers represent data up to 1.5 times the interquartile range (25$^{th}$ to 75$^{th}$ percentile) above and below the box. Dots show values that lie outside the range of the whiskers.

Meanwhile, lower sulphate concentrations and higher pH in the present period (**Figure 3**) are likely due to overall reductions in the emission of air pollutants, such as sulfur dioxide, from industrial activities upwind of the watershed (Aas et al., 2019). These changes are representative of a return to pre-acidification conditions at this site. Although the pulp mill has used a sulphite process with no effluent treatment in the past, this practice ended in 1966 and would not have contributed to elevated sulphate concentrations noted in our historical period (Environment Canada, 1987).

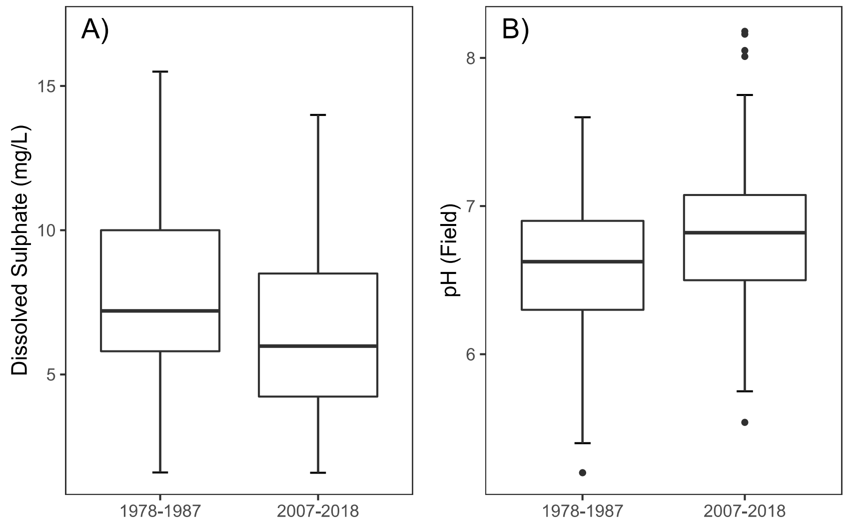


**Figure 3**. Box plots of (A) dissolved sulphate concentrations and (B) field pH measurements at Milltown between the two periods of water quality data records.

When assessing aquatic nutrient concentrations, only total nitrogen was found to differ significantly between the two periods (**Figure 4A**). The increase in total nitrogen in recent years matches a broader trend of increasing nitrogen throughout Atlantic Canada, despite general decreases in nitrogen deposition from atmospheric sources in the region (Zbeiranowski and Aherne, 2011; Hember, 2018). The population within the watershed has increased by approximately 12% from 1980 to 2006, and at the same time there has been an increase in rural land use for residences (ISCRWB, 2008). These demographic shifts within the watershed as well as widespread changes in precipitation patterns driven by climate change could explain the difference in TN levels between the two periods (Sinha et al., 2017). Recent phosphorus records appear to have a lower frequency of guideline value exceedances (**Figure 4B**), though there was no statistically significant difference in values between the two periods.

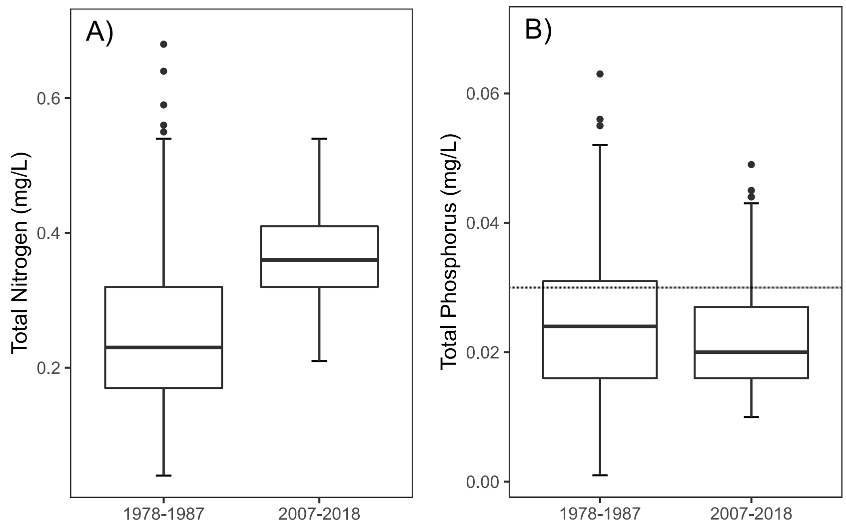


**Figure 4**. Box plots of (A) total nitrogen and (B) total phosphorus concentrations at Milltown between the two periods of water quality data records. The dashed line in the phosphorus plot indicates the Ontario Ministry of the Environment phosphorus guideline of 0.03 mg/L (OMOE,1994).

Aluminum, iron, and zinc all showed no significant difference in concentration between the two periods (**Figure 5A,B,C**). Concentrations of these parameters are likely to be largely driven by bedrock and soil weathering in the watershed. Detection limits were higher for all metals in the historical data but that was only apparent for zinc and copper. In particular, copper values were much higher in the historical period and were above the detection limit in approximately half the samples (**Figure 5D**). Because of the large number of non-detects, it was not possible to conduct a Mann-Whitney Rank Sum test for copper. Differences in copper concentrations identified visually may be due to improvements in effluent treatments.

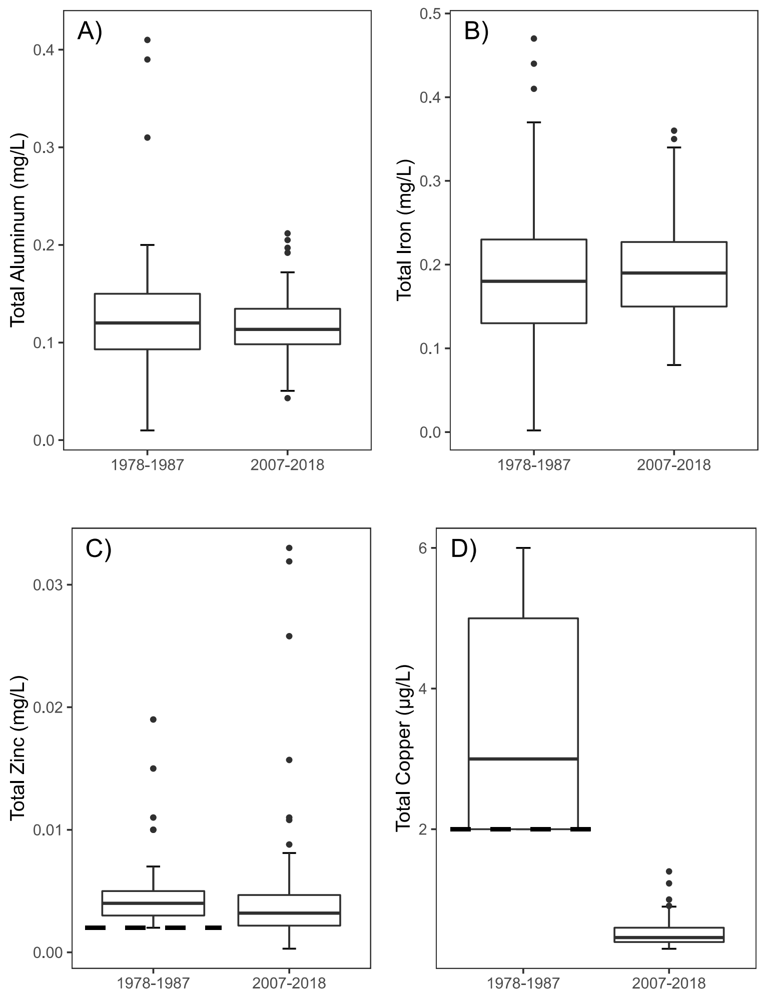


**Figure 5**. Box plots of (A) total aluminum, (B) total iron, (C) total zinc, and (D) total copper concentrations at Milltown between the two periods of water quality data records. The dashed lines in (C) and (D) show the method detection limits for the historical data.

# 4 Recent Trends in Water Quality

## 4.1 Statistical Methods

Analyses were completed in the statistical language R v3.5.1 (R Core Team, 2018) using the packages *stats* and *rkt*. Data were first processed to remove parameters that were highly censored or sampled with low frequency. A summary statistics table was produced for each site, listing the number of measurements, minimum and maximum values, the median and range of the values, and the number and proportion of censored values for each parameter (**Appendices 1 and 2**). Parameters with more than 50% of their measurements below the detection limit were deemed highly censored variables and were excluded. Parameters that were measured in fewer than 25% of site visits were also excluded to ensure that there was sufficient record length.

Given that water quality data is generally not normally distributed, non-parametric statistical tests were used. A Kruskal-Wallis test (K-W test) was used to assess the seasonality of each parameter, testing for difference between values in four seasons per year (Jan – Mar, Apr – Jun, Jul – Sep, Oct – Dec). Seasons were grouped based on site and regional hydrograph trends. Sampling frequency at the two sites varied between 6 and 11 visits per year (with the exception of 1-3 measurements in 2011) and were collapsed to four values per year for the remainder of the analysis. One measurement was selected per season, with a preference given for measurements in Feb, Apr, Aug, and Oct as these corresponded to peak spring and fall flows and typical winter and summer conditions. If there were multiple visits in a given season, the one that was closest to the midpoint of the preferred month was selected.

Mann-Kendall trend tests were performed for each parameter that met the censored data criteria at each site. Two variants of the test were used: the unmodified Mann-Kendall test was used if the K-W test did not indicate seasonality ($p > 0.05$), and the Seasonal Mann-Kendall test was performed if the K-W test indicated seasonality ($p < 0.05$). The Seasonal variant of the Mann-Kendall test is used to account for seasonal effects in the data (Hirsch et al., 1982). A monotonic trend was identified if the Mann-Kendall test result was significant ($p < 0.05$), while the direction of the trend was determined by the sign of tau (positive tau = upward, negative tau = downward).

Finally, visual inspection of the scatterplot for each parameter was used to identify “blocky” parameters. These are generally characterized by values consistently near the detection limit, leading to little variability in the measurements (**Appendix 3**). These parameters produce unreliable trend results and were excluded from the final summary.

## 4.2 Accounting for Discharge

Water quality parameters are often related to discharge rates at a site, which can fluctuate throughout the year. In order to determine whether discharge weighting was required for our sites, the relationships between concentrations of water quality parameters and discharge rates were analyzed. The natural log of discharge was regressed against the natural log of concentrations for each parameter to investigate whether discharge weighting would be necessary. If many parameters showed upward or downward slopes and significant relationships with discharge, weighting of parameter values would be required.

Daily discharge data from the Water Survey of Canada was only available for Forest City as it is not recorded at Milltown due to the impact of dam operations. Of the 32 parameters tested, only two (manganese and zinc) revealed significant relationships between discharge and parameter values, and both parameters had shallow slopes. A Seasonal Mann-Kendall trend test was also conducted on the discharge data, which showed no significant trend over the past 12 years. It was decided not to attempt flow-correction for the Forest City site as it would not provide additional benefits for our analyses. Instead, the trend figure for discharge is included below (**Figure 6**).

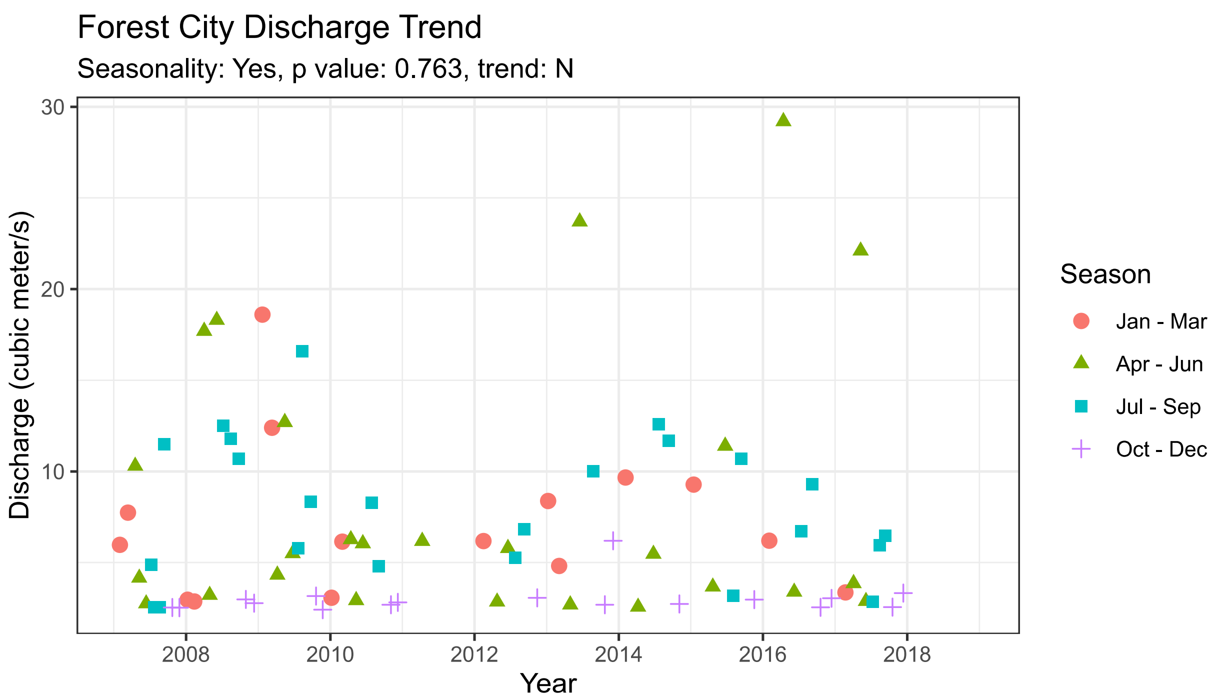


**Figure 6**. Seasonal Mann-Kendall trend test for discharge at Forest City.

## 4.3 Forest City Results

The dataset for Forest City revealed 13 statistically significant ($p < 0.05$) Mann-Kendall trends (**Table 1**) in 23 water quality parameters. Of those 13 parameters, six also showed significant seasonality in their values (K-W $p < 0.05$). Further interpretations of some of the trends observed at Forest City are described in the following section.

**Table 1**. Mann Kendall (seasonal) Trend Test Results for Forest City. Bolded and coloured rows have statistically significant ($p < 0.05$) trends. Trend notation: N; No trend, UP; significant upward trend and DOWN; significant downward trend.

| Variables | K-W p value | Seasonality Present? | Tau | M-K p value | Sen slope (unit/year) | Trend |
|---|---|---|---|---|---|---|
| **Alkalinity** | **0.005** | **Yes** | **0.324** | **0.007** | **0.044** | **UP** |
| Aluminum Total | 0.006 | Yes | 0.022 | 0.880 | 0.000 | N |
| Arsenic Total | 0.024 | Yes | -0.275 | 0.083 | -0.006 | N |
| **Calcium Total** | **0.014** | **Yes** | **-0.289** | **0.020** | **-0.015** | **DOWN** |
| **Carbon Total Organic** | **0.359** | **No** | **-0.405** | **0.000** | **-0.062** | **DOWN** |
| **Chloride Dissolved** | **0.180** | **No** | **-0.326** | **0.002** | **-0.017** | **DOWN** |
| Colour Apparent | 0.306 | No | 0.129 | 0.227 | 0.000 | N |
| Conductance (Field) | 0.256 | No | -0.119 | 0.327 | -0.121 | N |
| Copper Total | 0.305 | No | -0.027 | 0.850 | 0.000 | N |
| **Magnesium Total** | **0.000** | **Yes** | **-0.305** | **0.010** | **-0.002** | **DOWN** |
| **Manganese Total** | **0.000** | **Yes** | **0.303** | **0.009** | **0.100** | **UP** |
| **Nickel Total** | **0.302** | **No** | **-0.470** | **0.000** | **-0.011** | **DOWN** |
| Nitrogen Total | 0.394 | No | -0.179 | 0.082 | -0.001 | N |
| Oxygen Dissolved | 0.000 | Yes | 0.148 | 0.337 | 0.018 | N |
| **pH (Field)** | **0.006** | **Yes** | **-0.372** | **0.010** | **-0.075** | **DOWN** |
| **Sodium Total** | **0.001** | **Yes** | **-0.332** | **0.007** | **-0.010** | **DOWN** |
| **Specific Conductance** | **0.163** | **No** | **-0.462** | **0.000** | **-0.290** | **DOWN** |
| Strontium Total | 0.001 | Yes | -0.056 | 0.644 | 0.000 | N |
| **Sulphate Dissolved** | **0.332** | **No** | **-0.598** | **0.000** | **-0.070** | **DOWN** |
| **Titanium Total** | **0.134** | **No** | **-0.308** | **0.029** | **-0.019** | **DOWN** |
| **Turbidity** | **0.441** | **No** | **0.299** | **0.003** | **0.018** | **UP** |
| Turbidity (Field) | 0.894 | No | 0.045 | 0.667 | 0.000 | N |
| Zinc Total | 0.049 | Yes | -0.187 | 0.254 | -0.010 | N |

## 4.4 Interpreting Key Trends at Forest City

Due to Forest City's location in a sparsely populated and relatively undeveloped part of the watershed, minimal human influence is expected. Major anthropogenic influence at this site would therefore include acidic deposition originating from industrial activity upwind of the site, mainly in the Northeastern United States (Driscoll et al., 2001; ECCC, 2016a), and global atmospheric shifts such as climate change.

Many of the trends observed at this site likely relate to recovery from acidification, similar to other watersheds throughout Atlantic Canada as sulphate emissions have declined in upwind regions (ECCC, 2016a; Zhang et al., 2018). Reduced emissions and deposition within the watershed has resulted in decreasing sulphate concentrations and increasing alkalinity in the water that is indicative of a recovery in buffering capacity. Interestingly, field pH measurements show a decreasing trend that is not expected when a watershed is recovering from acidification. A decrease in field pH may instead be driven by increased atmospheric $CO_2$ that has been observed in freshwater reservoirs, and it is unclear how this may interact with recovery (Weiss et al., 2018).

Major ions including sodium, calcium, and magnesium show decreasing trends over the 12 year record. These trends are likely related to the watershed's recovery from acidification. Historical acidification mobilizes base cations in the watershed and leaves soils depleted of these major ions, while replenishment through weathering is slow. In particular, the calcium trend is notable as similar trends have been seen in other freshwater systems globally and because calcium is critical for the survival of many aquatic organisms (Weyhenmeyer et al., 2019).

There were no significant trends detected in either nitrogen or phosphorus and phosphorus concentrations were consistently low and near the detection limit. In general, the slopes of trends at Forest City are shallow and none are approaching their respective guideline values.

### *Alkalinity*

There has been a significant (and seasonal) increase in alkalinity at the Forest City site (**Figure 7**). Alkalinity is a measure of an aquatic system's capacity to resist change in pH that would make the water more acidic (i.e. buffering capacity). In systems such as the St. Croix River, alkalinity has been typically low due to the lack of carbonate rock weathering in the watershed and the natural discharges of tannic waters from wetlands that neutralize the alkalinity. An increase in alkalinity is beneficial to the aquatic life of the St. Croix River by providing buffering capacity. A decrease in atmospheric deposition (supported by decreasing sulphate concentrations) may have led to a decrease in acid-forming substance that can alter the natural acid-base balance in aquatic environments (CCME, 1987a).

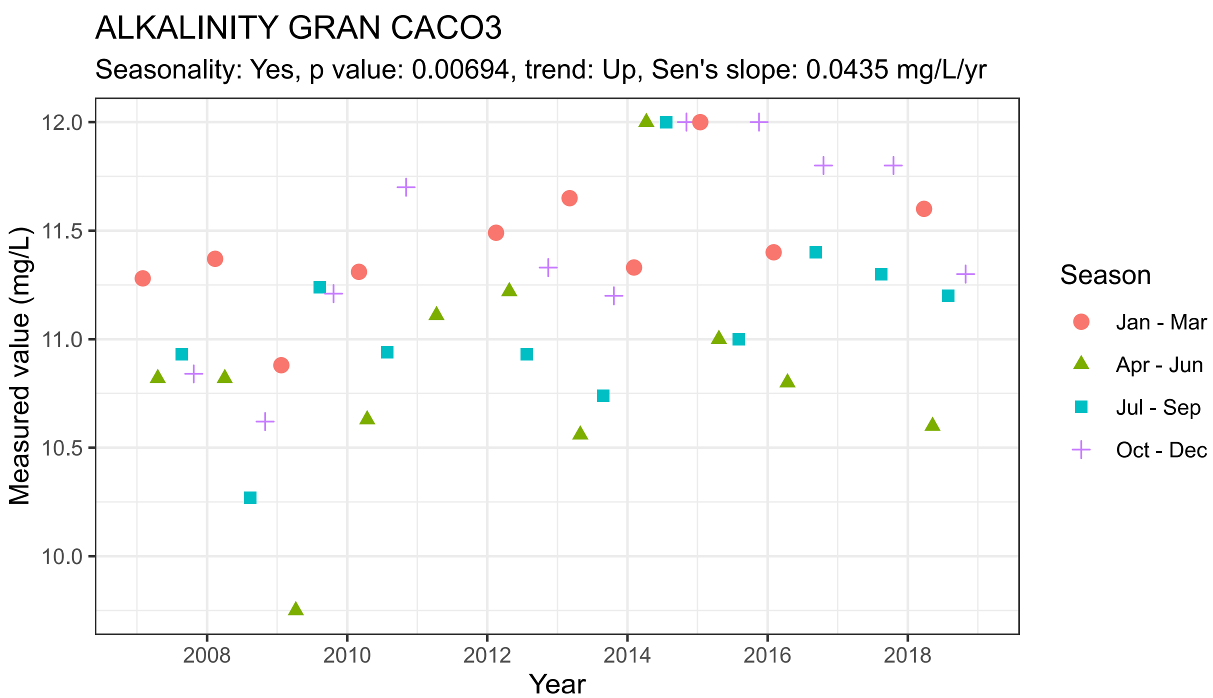


**Figure 7**. Measurements of alkalinity at Forest City from 2007 to 2018.

## *Sulphate*

Sulphate concentrations follow a significant decreasing trend over time at Forest City (**Figure 8**) and is only found at low concentrations. A survey of Atlantic Canada surface waters for sulphate from 1950-1985 had a range of sulphate concentrations from non-detect to 610 mg/L (based on 13646 samples) (CCME, 1987a), while values at Forest City ranged from 1.4 to 2.4 mg/L. Sulphate is commonly found in most water in Canada and anthropogenic sources include industrial discharges to the aquatic environment and atmospheric deposition via precipitation. In crystalline rock areas of North America, precipitation and subsequent leaching supplies nearly all the sulphate to surface waters The decrease in sulphate at Forest City is likely due to overall reductions in emissions upwind of the site, especially in the Northeastern United States (Zhang et al., 2018).

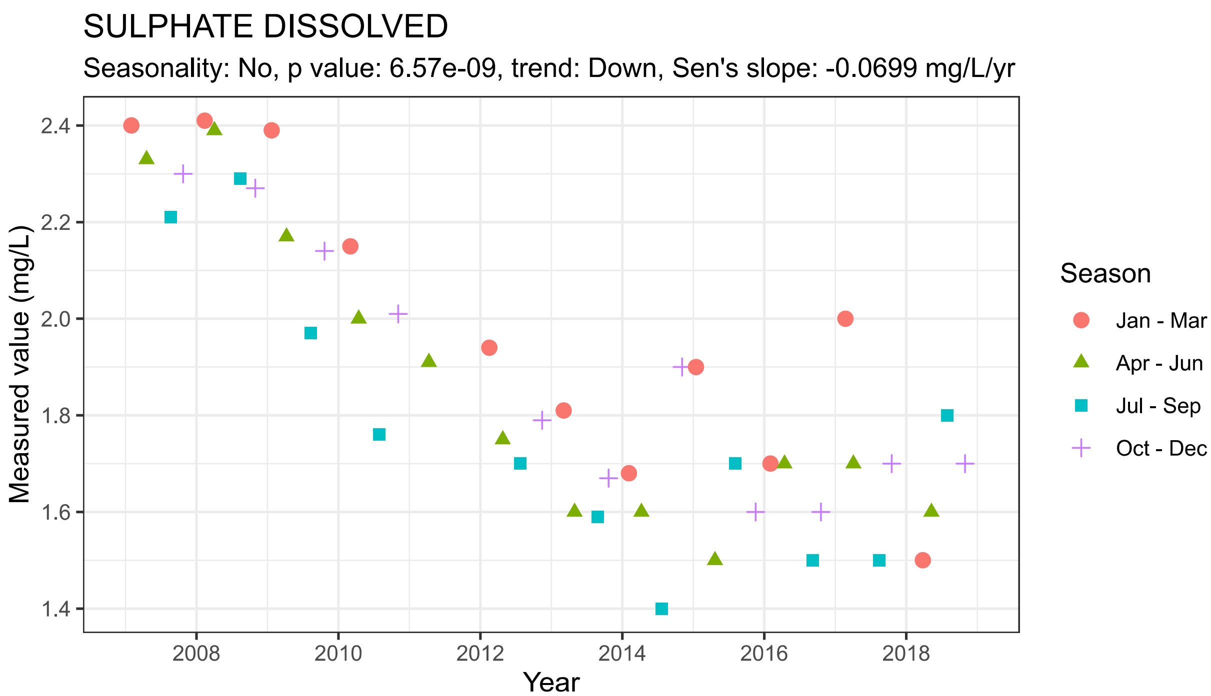


**Figure 8**. Concentrations of sulphate at Forest City from 2007 to 2018.

## *Calcium*

The trend in calcium concentrations at Forest City reveals a statistically significant decrease, although the slope is relatively shallow at 0.02 mg/L/year (**Figure 9**). Calcium is an essential element for aquatic organisms, as it is a key component for their growth and reproduction. Therefore, changes in calcium availability in freshwater environments are of concern, especially in light of recent and widespread declines in calcium (Weyhenmeyer et al., 2019). A critical threshold for the reproduction and survival of aquatic organisms was identified by Jeziorski et al. (2008) to be 1.5 mg/L. Although calcium concentrations at Forest City are high relative to this threshold (currently ~4 mg/L), trends should be monitored for further declines as the decreasing pH trend is likely to reduce the solubility of calcium, impacting its availability.

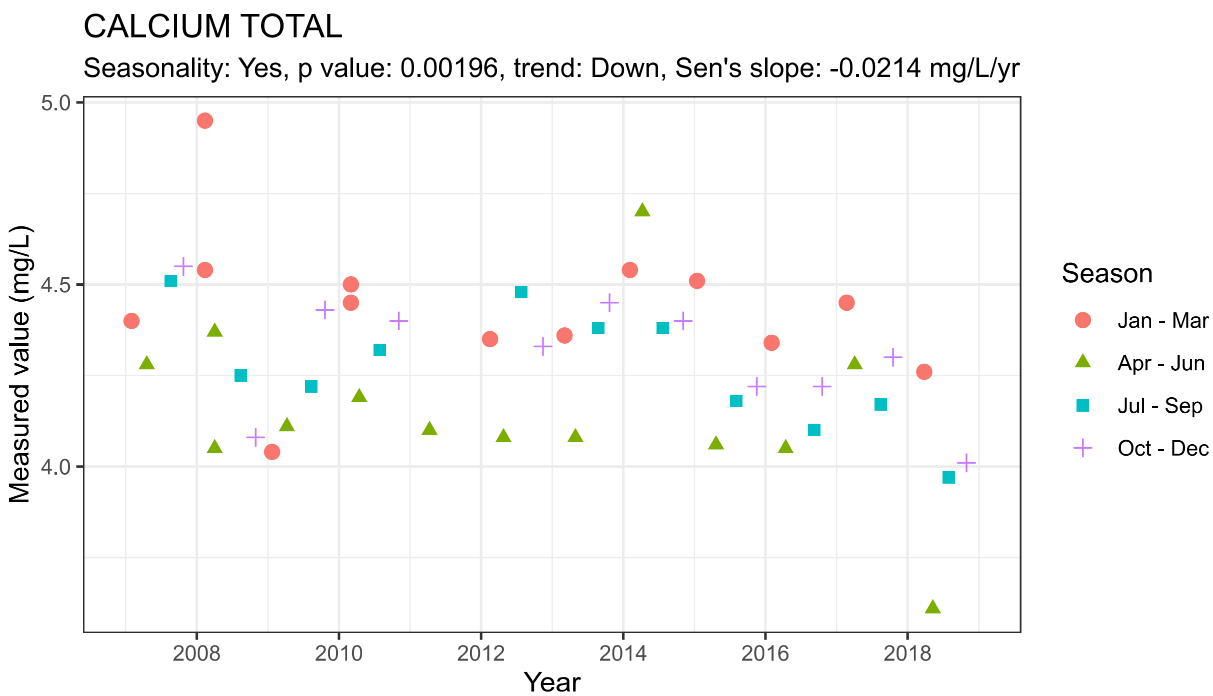


**Figure 9**. Concentrations of total calcium at Forest City from 2007 to 2018.

### *Chloride*

Chloride is widely distributed in the environment from both natural and anthropogenic sources. Natural sources include weathering of sedimentary or calcareous deposits, while anthropogenic sources include salting of roadways, and effluents from industrial or municipal wastewater plants (CCME, 2011). Chloride is declining at Forest City, and the highest concentrations of chloride occur in the winter season (January to March), a period where salt would be applied to roads (**Figure 10**). Even though road density is low in the upper watershed, a decrease in chloride at Forest City could be indicative of better managed application of salt to roadways (**Figure 11**). The CCME guidelines (short and long-term) for the protection of freshwater aquatic life are 120 and 640 mg/L respectively, and therefore chloride concentrations at Forest City (~1.5 mg/L) are not a threat to aquatic life (CCME, 2007).

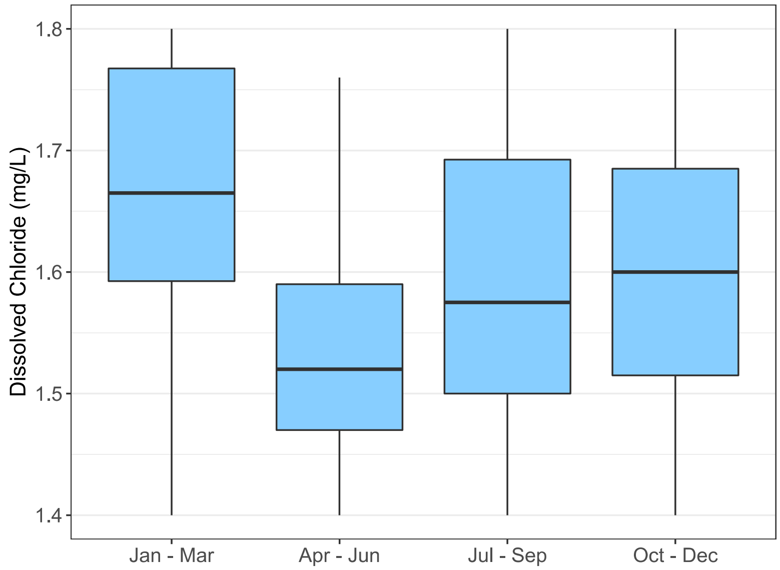


**Figure 10**. Box plots of chloride concentration at Forest City from 2007 to 2018 as a function of season.

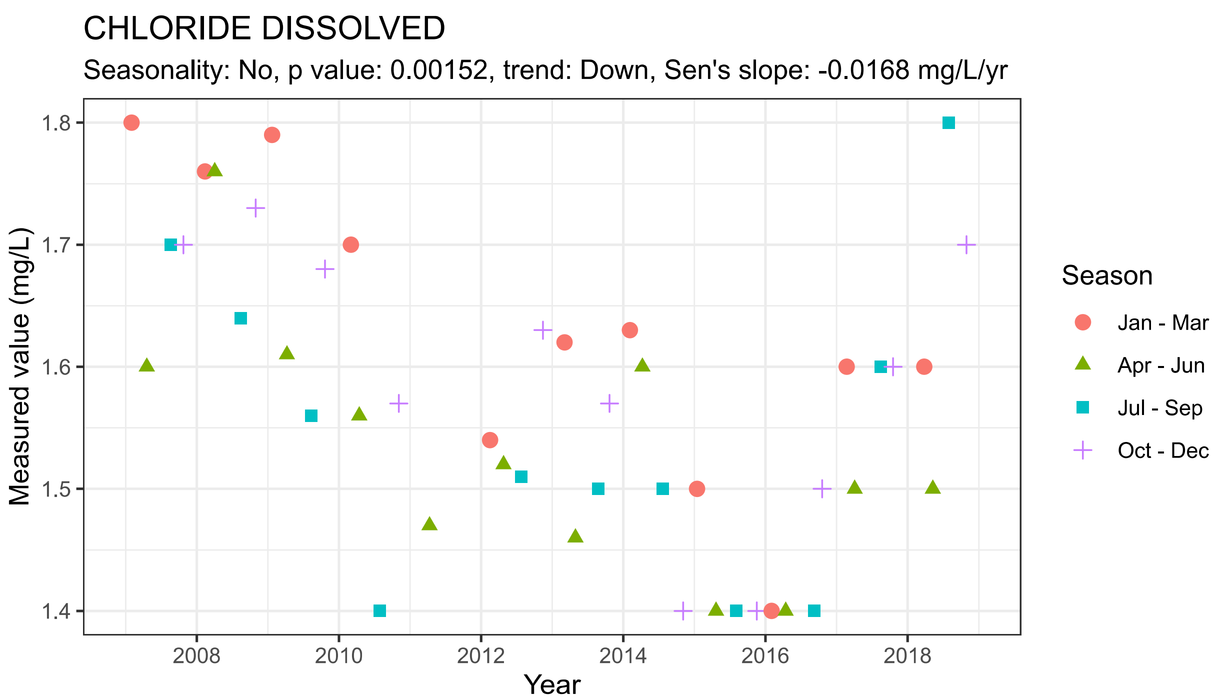


**Figure 11**. Concentrations of chloride at Forest City from 2007 to 2018.

### *Total Organic Carbon*

Total organic carbon (TOC) is calculated as the difference between the amount of total carbon and inorganic carbon present in a water sample. Detritus from plants and animals contribute organic carbon to the aquatic environment. In addition, anthropogenic sources of TOC in the aquatic environment have been reported from runoff from agricultural lands, municipal and industrial wastewater (especially from pulp and paper and meat processing plants) (CCME, 1987a). The trend analysis depicts a statistically significant decreasing trend in TOC at Forest City (**Figure 12**). Where Monteith et al. (2007) noted increases in TOC in freshwater environments for a wide range of geographic areas, Atlantic Canada was the only region studied that did not exhibit an increasing trend in TOC.

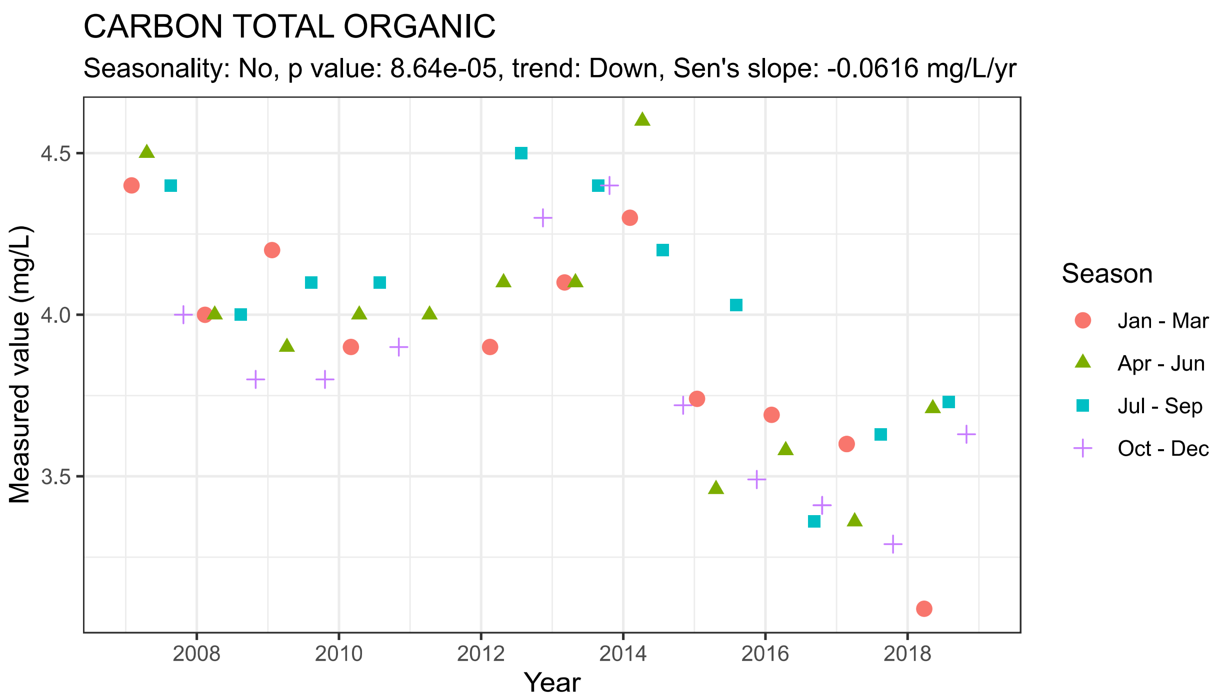


**Figure 12**. Concentrations of TOC at Forest City from 2007 to 2018.

### *Total Nitrogen*

There was no statistically significant trend in total nitrogen, although visually concentrations have decreased slightly from 2007 to 2018. Nitrogen is an essential nutrient for plants but may also be detrimental to aquatic life when it is in exceedance of guideline values. Total nitrogen accounts for all forms of nitrogen within water samples, and sources of total nitrogen include wastewater treatment plants, agricultural runoff, atmospheric deposition, and certain industrial discharges as well as natural sources.

The Forest City site drains a relatively undeveloped part of the St. Croix River Watershed where population densities are low (generally < 5 people/square km) and there is little industrial activity, which is reflected in the low total nitrogen concentrations. Dodds (1998) had calculated an oligotrophic-mesotrophic boundary value of 0.7mg/L for stream systems. The majority of total nitrogen samples at Forest City were below 0.2 mg/L and therefore this site in an oligotrophic state.

### *Total Phosphorus*

A trend analysis for total phosphorus at Forest City was not achievable as concentrations exhibited “blocky”-ness. The values were consistently near the detection limit (0.002 mg/L), leading to little variability in the measurements as seen in **Figure 13**. The values detected at Forest City are well below the guideline value of 0.03 mg/L (OMOE, 1994), and there were no exceedances of this trigger value at this site.

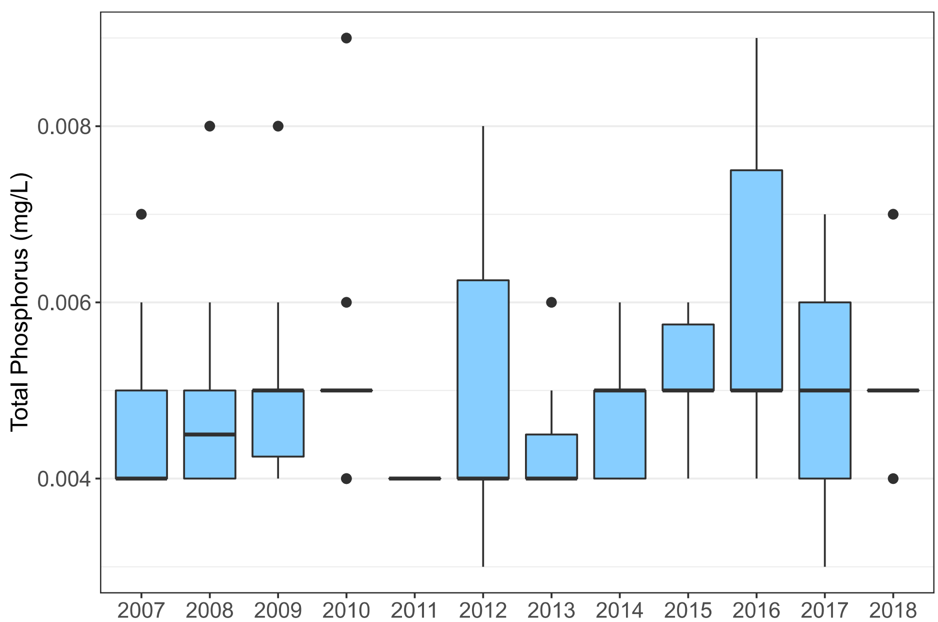


**Figure 13**. Box plots of yearly values of total phosphorus at Forest City.

### *Manganese*

Concentrations of manganese at Forest City exhibit a seasonal effect and a statistically significant increasing trend (**Table 1**). A manganese water quality guideline for the protection of aquatic life is currently in development. Concentrations of manganese at Forest City are very low relative to other sites within Atlantic Canada and the increasing trend is shallow, therefore manganese is not of concern here. Manganese leaches from soil in acidic conditions and its increasing trend may be related to the decrease in field pH at Forest City.

### *Nickel*

Nickel has a CCME water quality guideline that is dependent on water hardness (CCME, 1987b). Hardness at Forest City is approximately 25 mg/L, which corresponds to a guideline value of 25 µg/L. Nickel concentrations at Forest City show a statistically significant decreasing trend (**Table 1**) and concentrations there (0.1 – 0.3 µg/L) are well below the guideline. Therefore, nickel is not a parameter of concern at Forest City.

## 4.5 Milltown Results

Of 30 parameters tested, the dataset for Milltown contained four statistically significant ($p < 0.05$) Mann-Kendall trends, for chromium, total nitrogen, titanium, and vanadium (**Table 2**). Of those parameters, total nitrogen, and titanium exhibited seasonality in their values (K-W $p < 0.05$). Further interpretations of some of the trends observed at Milltown are described below in the following section.

**Table 2**. Kruskal-Wallis seasonality test and Mann Kendall trend test results for Milltown. Bold and coloured rows have statistically significant ($p < 0.05$) trends. Trend notation: N; No trend, UP; significant upward trend and DOWN; significant downward trend.

| Variables | K-W p value | Seasonality Present? | Tau | M-K p value | Sen slope (unit/year) | Trend |
|---|---|---|---|---|---|---|
| Alkalinity | 0.000 | Yes | 0.029 | 0.828 | 0.012 | N |
| Aluminum Total | 0.119 | No | -0.071 | 0.486 | -0.948 | N |
| Arsenic Total | 0.000 | Yes | -0.019 | 0.947 | 0.000 | N |
| Barium Total | 0.000 | Yes | -0.059 | 0.616 | 0.000 | N |
| Calcium Total | 0.000 | Yes | -0.057 | 0.659 | -0.028 | N |
| Carbon Total Organic | 0.003 | Yes | -0.150 | 0.191 | -0.050 | N |
| Chloride Dissolved | 0.000 | Yes | 0.047 | 0.698 | 0.018 | N |
| **Chromium Total** | **0.219** | **No** | **-0.297** | **0.019** | **-0.008** | **DOWN** |
| Colour Apparent | 0.290 | No | 0.155 | 0.132 | 0.836 | N |
| Conductance (Field) | 0.000 | Yes | -0.038 | 0.829 | -0.600 | N |
| Copper Total | 0.268 | No | 0.086 | 0.506 | 0.004 | N |
| Dissolved Nitrogen Nitrate | 0.000 | Yes | 0.033 | 0.803 | 0.000 | N |
| Iron Total | 0.043 | Yes | -0.095 | 0.415 | -0.003 | N |
| Lead Total | 0.028 | Yes | -0.114 | 0.471 | -0.002 | N |
| Magnesium Total | 0.001 | Yes | -0.143 | 0.243 | -0.007 | N |
| Manganese Total | 0.001 | Yes | -0.028 | 0.832 | -0.200 | N |
| **Nitrogen Total** | **0.000** | **Yes** | **0.352** | **0.002** | **0.008** | **UP** |
| Oxygen Dissolved | 0.000 | Yes | -0.038 | 0.827 | -0.019 | N |
| pH (Field) | 0.077 | No | -0.188 | 0.136 | -0.059 | N |
| Phosphorus Total | 0.000 | Yes | 0.032 | 0.802 | 0.000 | N |
| Potassium Total | 0.002 | Yes | 0.052 | 0.695 | 0.000 | N |
| Sodium Total | 0.000 | Yes | 0.029 | 0.841 | 0.032 | N |
| Specific Conductance | 0.000 | Yes | -0.028 | 0.832 | -0.100 | N |
| Strontium Total | 0.000 | Yes | -0.024 | 0.860 | -0.017 | N |
| Sulphate Dissolved | 0.000 | Yes | -0.154 | 0.179 | -0.128 | N |
| **Titanium Total** | **0.047** | **Yes** | **-0.345** | **0.035** | **-0.061** | **DOWN** |
| Turbidity | 0.241 | No | 0.192 | 0.059 | 0.040 | N |
| Turbidity (Field) | 0.488 | No | 0.010 | 0.941 | 0.000 | N |
| **Vanadium Total** | **0.268** | **No** | **-0.288** | **0.024** | **-0.021** | **DOWN** |
| Zinc Total | 0.05 | Yes | -0.031 | 0.892 | -0.029 | N |

## 4.6 Interpreting Key Trends at Milltown

Milltown faces major and constant influences from both the pulp mill at Baileyville as well as the Baileyville municipal wastewater treatment plant (WWTP). The pulp mill is the stronger influence of the two, discharging much greater volumes of effluents than the WWTP (EPA, 2019b,c). Changes in water quality parameters at this site will likely be heavily influenced by these facilities (Environment Canada, 1987). Other anthropogenic impacts on water quality here include combined sewer overflow (CSO) events at St. Stephen, New Brunswick and Calais, Maine, although both towns have enacted plans to reduce the frequency of CSO outflow events (ISCRWB, 2018). Recent increases in anadromous alewife returns may also contribute to changes in nutrient concentrations at this site through the transport of marine-derived nutrients.

In comparison with Forest City, fewer trends were detected at Milltown and the main trends were detected in total nitrogen and several metals (chromium, vanadium, titanium). In general, slopes for all trends were shallow at this site and no trends are approaching guideline values.

### *Total Nitrogen*

Total nitrogen at Milltown shows a statistically significant increasing trend over the past 12 years (**Figures 14**). Interestingly the median concentrations in 2017 and 2018 (**Figure 15**) are much greater than the likely range of variation (first to third quartile) seen in the years prior to 2017. Furthermore, the median values in individual years increase progressively from 2008 to 2018. A seasonal effect is also evident in **Figure 16**, where the summer and fall seasons have higher median values and compared to the spring and winter seasons.

Discharge and temperature conditions at this site may be contributing to the increased total nitrogen concentrations. Low summer discharges from 2016 to 2018 were observed at Baring, Maine (approximately 9 km upstream), while summer temperatures have been higher in this period as well. Other potential influences include changes in industrial operations upstream or the recent, abundant alewife returns to the lower portions of the St. Croix River, as anadromous fish can transport marine-derived nutrients into river systems during spawning periods (Barber et al., 2018).

Although the concentration of total nitrogen is increasing, annual median values still fall short of classifying this system as mesotrophic as per the recommendations of Dodds (1998). Dodds (1998) had calculated an oligotrophic-mesotrophic boundary value of 0.7 mg/L. The box plots (**Figure 15**) show the highest median occurring in 2017-2018 as approximately 0.45 mg/L, which is well below the boundary. However, total nitrogen at Milltown has increased by approximately 0.1 mg/L over the past 12 years, a magnitude of change that could cause a shift in the river's trophic state in the next few decades if it is sustained.

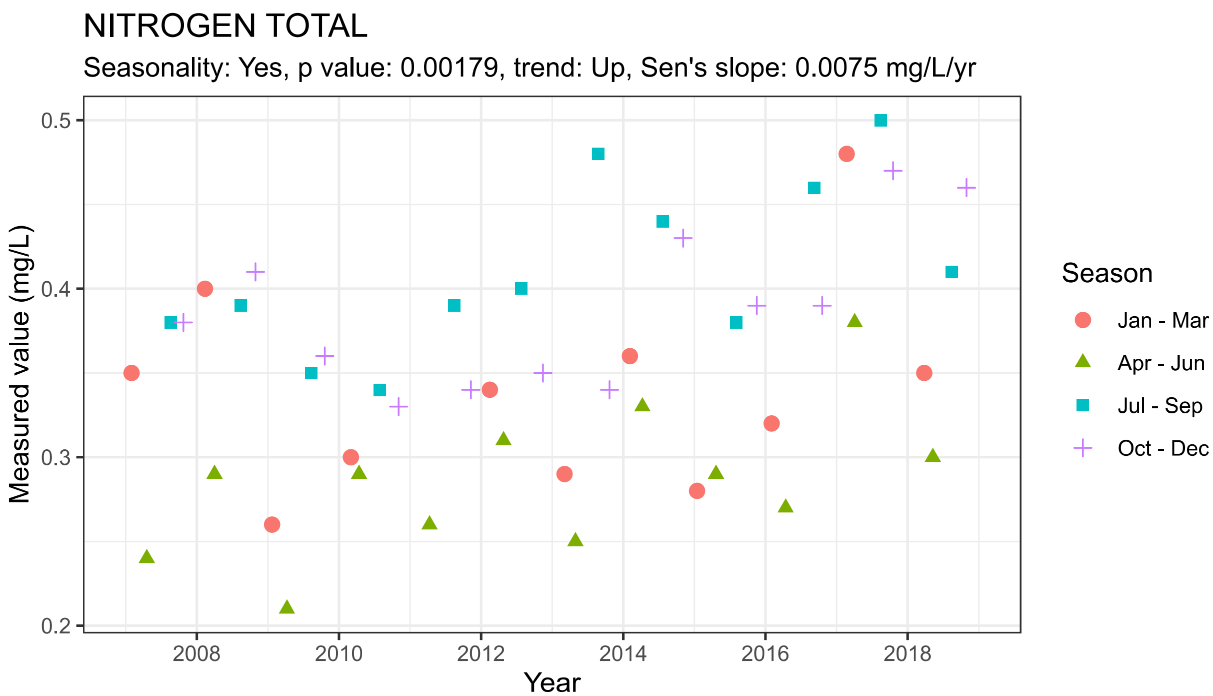


**Figure 14**. Concentrations of total nitrogen at Milltown from 2007 to 2018.

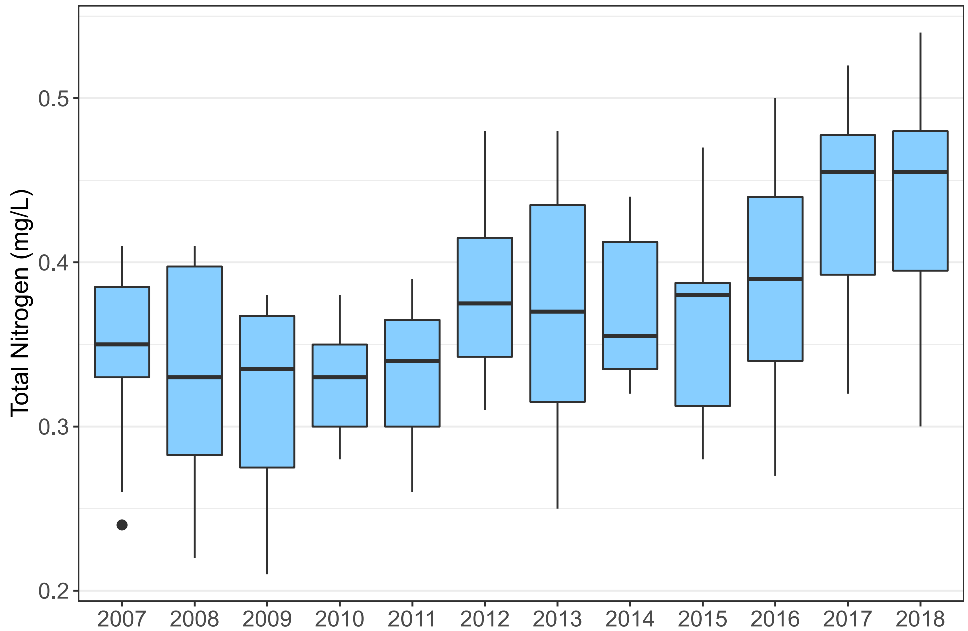


**Figure 15**. Box plots of yearly values of total nitrogen at Milltown.

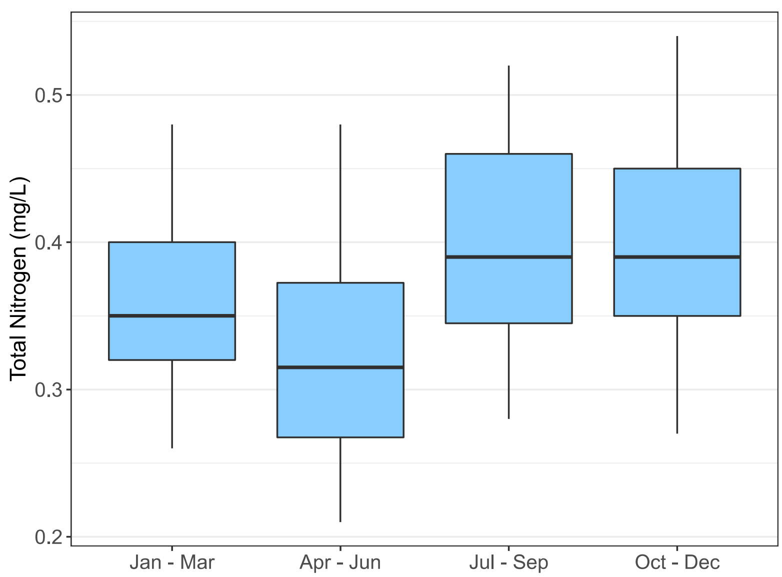


**Figure 16**. Box plots of total nitrogen at Milltown from 2007 to 2018 as a function of seasons.

*Total Phosphorus*

Phosphorus is an essential nutrient for all living organisms and is commonly the first limiting nutrient in biological productivity. However, elevated phosphorus concentrations may adversely affect aquatic ecosystems (CCME, 2004). For example, excessive phosphorus can lead to nuisance algal blooms. Sources of phosphorus in an aquatic ecosystem are varied and may include naturally occuring phosphorus in rock, discharge from wastewater treatment plants, runoff from fertilized lawns or cropland, disturbed land areas, and runoff from animal manure storage.

Total phosphorus measured at Milltown appears to be increasing visually but is not significant statistically (M-K p = 0.802) (**Figure 17**).

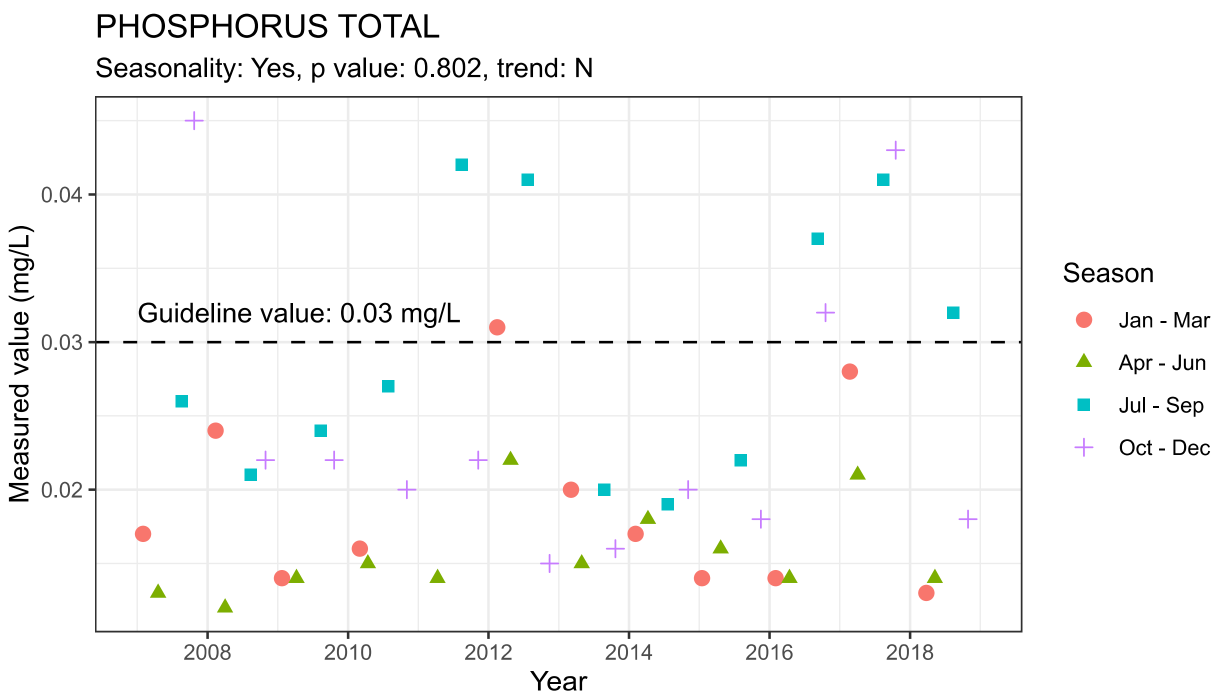


**Figure 17**. Concentrations of total nitrogen at Milltown from 2007 to 2018.

Although there is no statistically significant increasing trend for phosphorus at Milltown, the median values and scatter of the data around the medians were the highest ever measured in the last three years in Milltown (**Figure 18**). Furthermore, the median value observed for phosphorus in 2018 (**Figure 18**) is above the guideline value (0.03 mg/L) recommended by the Ontario Ministry of the Environment (OMOE, 1994). **Figure 19** shows that the highest concentrations of total phosphorus occured during the summer season, where the majority of concentrations above the 0.03 mg/L guideline value were also observed (**Figure 19**).

These results suggest that although no trend exists over the 12 year record, elevated phosphorus values in the past three years may be indicative of an emerging trend. Potential factors include anadromous migrations of alewife, which are known to import nutrients into freshwater systems (West et al., 2010; Barber et al., 2018), or variation in discharge from the WWTP and pulp mill upstream. Meanwhile, higher phosphorus concentrations during the summer may be related to lower summer discharge in the past several years as observed at Baring, Maine or anthropogenic sources such as CSO events near this site.

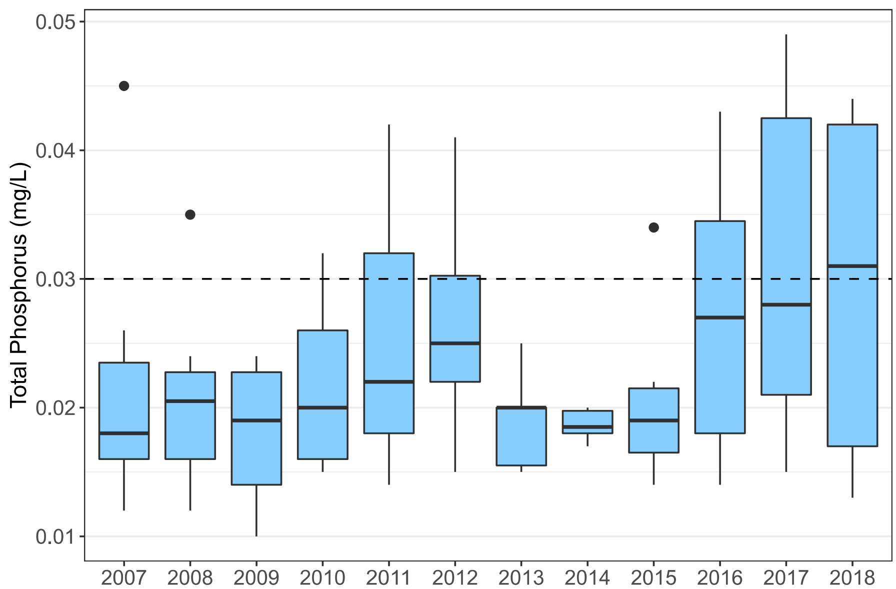


**Figure 18**. Box plots of yearly values of total phosphorus at Milltown.

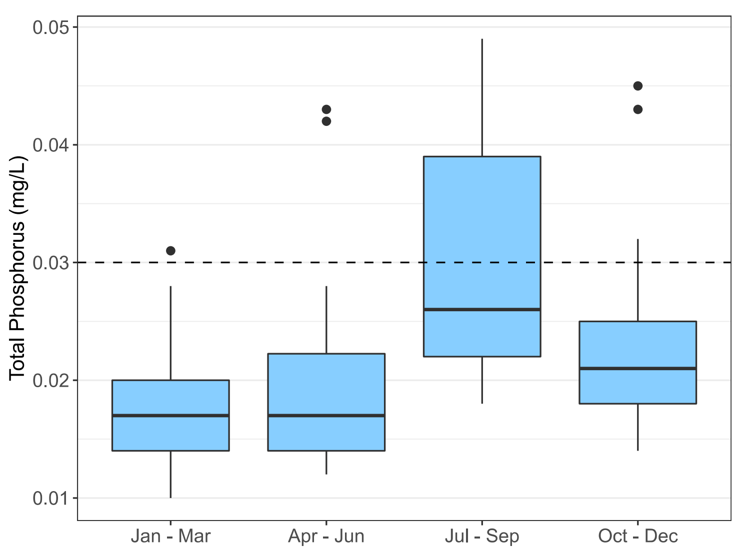


**Figure 19**. Box plots of total phosphorus at Milltown from 2007 to 2018 as a function of seasons.

### *Vanadium*

The main source of vanadium in surface waters is atmospheric deposition; especially from facilities that combust fossil fuels (ECCC, 2016b). For this site, sources likely include industrial emissions upwind of the watershed. The decreasing trend is significant and values have decreased by approximately 0.17 µg/L in the last eight years (**Figure 20**). In comparison, the Canadian water quality guideline for vanadium in freshwater is 120 µg/L (ECCC, 2016b). Due to the decreasing trend, an absence of local sources, and values well below the guideline, vanadium changes at Milltown are not of concern.

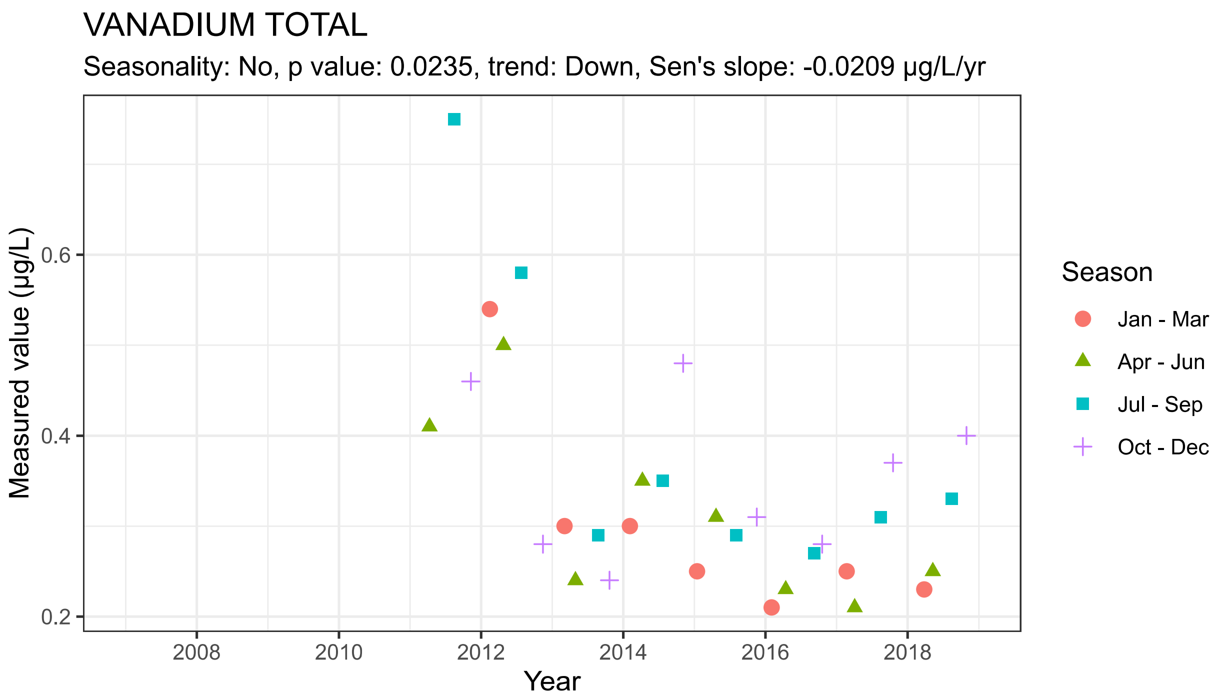


**Figure 20**. Concentrations of vanadium at Milltown from 2011 to 2018.

## 4.7 Trends in Water Temperature

ECCC operates real-time continuous monitoring stations at Milltown and Forest City that collect hourly measurements of several physical parameters at these sites, including water temperature. Extended periods of high water temperature are of concern for aquatic organisms such as salmonids.

Because hourly temperature data does not lend itself well to the same trend analysis methods used for water chemistry, instead we present the number of continuous days where daily mean water temperatures exceed 20 °C (**Table 3**). Data were not available for the years 2011 and 2012 at Forest City. The number of continuous days with water temperature over 20 °C at Milltown was relatively consistent, with the exception of warmer summers in 2015 and 2018. The record was shorter at Forest City, where three of the last four years had more than 80 days where water temperature exceeded 20 °C. It appears that the number of warm days is increasing at Forest City, though more in depth analysis is required.

**Table 3**. Number of continuous days where daily mean water temperatures exceeded 20 °C.

| | **2011** | **2012** | **2013** | **2014** | **2015** | **2016** | **2017** | **2018** |
|---|---|---|---|---|---|---|---|---|
| **Milltown** | 76 | 78 | 77 | 77 | 93 | 71 | 69 | 98 |
| **Forest City** | | | 69 | 73 | 89 | 79 | 83 | 85 |

# 5 Comparisons of Parameters at Milltown and Forest City

Concentrations of water quality parameters in the last five years (2014 – 2018) are shown to be very different between the less disturbed, upstream Forest City site and the downstream Milltown site. With the exception of a few parameters (alkalinity, calcium, dissolved oxygen, and pH), values for metals, major ions, and nutrients are much greater at Milltown (**Figure 21**). Contributions from industrial and municipal sources likely account for much of this difference, while those parameters that do not differ are more closely related to the geology of the region. Variability in concentrations are also much greater at Milltown than at Forest City. This is likely a factor of Forest City's location at the outflow of East Grand Lake where the flow regime remains relatively consistent throughout the year.

Comparisons of water chemistry along the St. Croix River in the 1987 technical report (Environment Canada, 1987) yielded similar results. The report states that higher concentrations of major ions caused by effluent from the pulp mill at Baileyville are diluted by the time they reach the Milltown site, and concentrations are generally one to five times the background levels (i.e. concentrations at Forest City).

Three parameters have values that are frequently near and occasionally exceed guideline levels: total aluminum, total iron, and total phosphorus. In addition, all values that exceeded these guidelines were recorded at the Milltown site. More than half of aluminum values at Milltown in the past five years exceeded the guideline value (100 µg/L for waters > pH 6.5), while phosphorus exceedances (0.03 mg/L) occurred in just over 25% of the samples and the iron guideline (300 µg/L) was only exceeded twice. The elevated total aluminum concentrations at Milltown are not a major concern as much of the aluminum in Atlantic Canada is complexed with organic material and not in a bioavailable form (Dennis and Clair, 2012). As previously mentioned, recent exceedances of phosphorus could indicate an emerging trend and be detrimental to water quality.

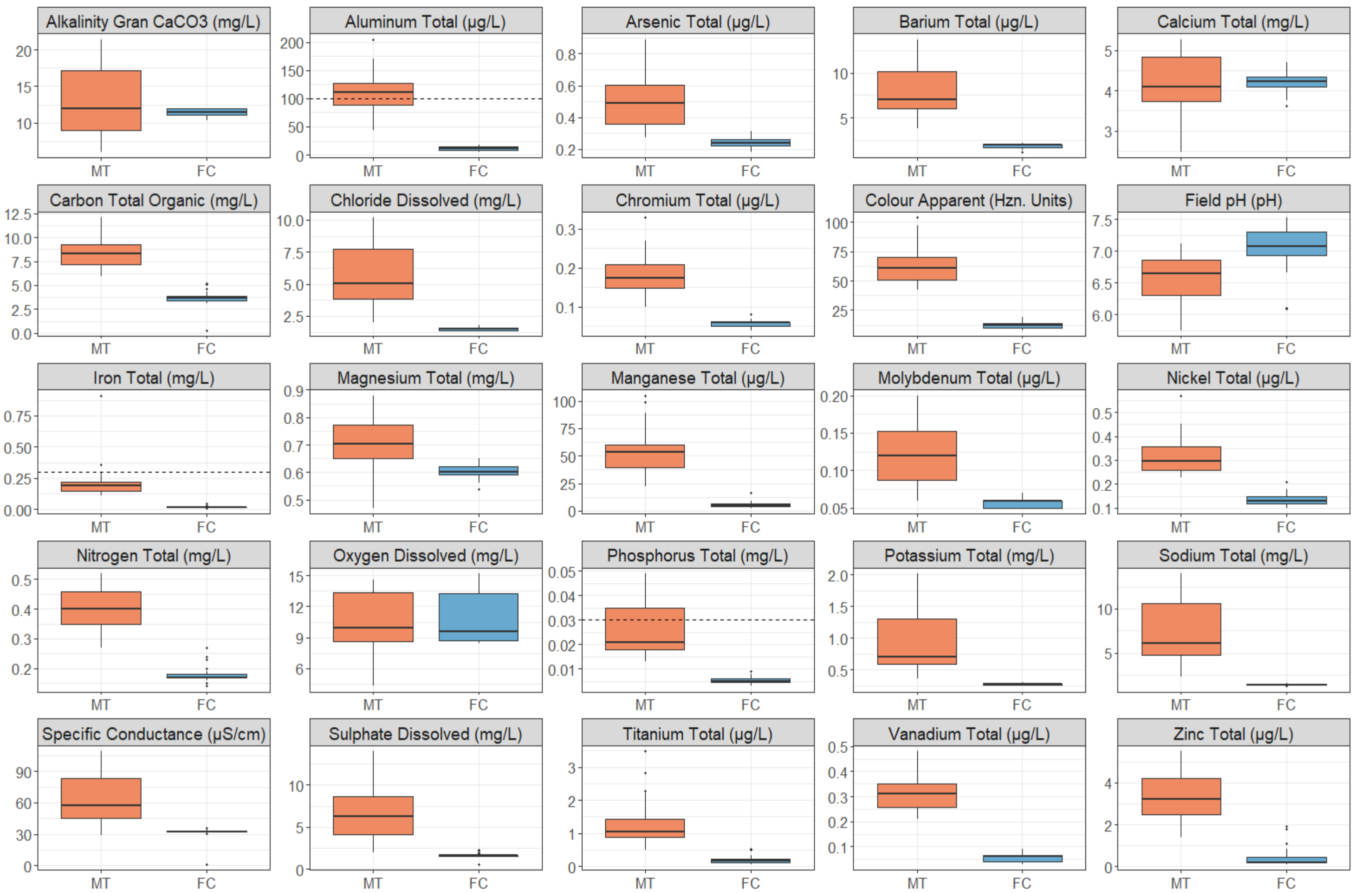


**Figure 21**. Box plots comparing water quality parameters at Milltown and Forest City obtained at all site visits from 2014 to 2018. Parameters shown here were ones that passed the trend analysis screening at both sites. Guideline values for aluminum, iron, and phosphorus are indicated by the dashed lines.

# 6 Conclusions and Recommendations

Overall, this trend analysis method identified several recent long-term trends in water quality parameters at the Forest City and Milltown.

At Forest City, the less disturbed site, there are a large number of trends in water quality parameters. However, the trends generally have shallow slopes and none of the increasing trends are approaching guideline limits or levels of concern for aquatic life. Many of these trends are likely associated with changes in atmospheric deposition, such as those expected during a watershed's recovery from acidification including increasing alkalinity, decreasing dissolved sulphate, and decreases in major ions (calcium, magnesium, sodium, chloride) that have been depleted by historical acidic deposition. The decreasing trend in calcium does not warrant immediate concern, as the trend slope is shallow and concentrations are well above the suggested critical level for aquatic life. However, calcium concentrations should be monitored for changes in the rate of this trend in the near future.

The Milltown site, which has experienced continuous influences from industrial and municipal effluents over the years, displayed fewer significant trends. The main trend observed here has been an increase in total nitrogen, which may be indicative of changes in mill or municipal discharges. Greater returns of anadromous alewife may also be contributing to this trend. Meanwhile the shallow decreasing trends in metals may be related to improvements to mill operations over time.

Currently, samples are taken at the two sites approximately six times per year. Because these samples are taken during trips primarily geared towards deploying, cleaning, and retrieving sondes at the automated stations, the timing of samples varies between years. Future trend analyses would benefit from a more consistent sampling schedule, and we suggest one that aligns with the four seasons identified from discharge patterns. Four of the six samples per year should be taken in February, April, July, and October respectively while the remaining samples can be scheduled as necessary. This will ensure samples that are representative of seasonal influences.

The recent increases in nitrogen and the observations of phosphorus above the NB guideline at Milltown point to an issue that needs to be more closely monitored and potentially addressed – the potential for a shift in the system towards more eutrophic conditions and an increase in the risk of algal blooms. As such, future projects could involve more in depth investigations of nutrients in the St. Croix River Watershed.

A review of existing monitoring data by other groups and agencies within the watershed, such as the St. Croix River Waterway Commission, can identify where current efforts are concentrated and where gaps in monitoring exist. Targeted monitoring of nutrients at select sites and during key periods such as the spring and fall can help create a clearer picture of the nutrient dynamics in the watershed. For example, sampling could occur at major tributaries, dams, and suspected point sources along the St. Croix River in order to investigate level of inputs from various parts of the watershed. In addition, extra parameters such as more nutrient forms (i.e. total Kjeldahl nitrogen, dissolved phosphorus) could also be included in analyses at the long-term monitoring sites to determine the amount of bioavailable nutrients in the St. Croix River watershed.

Finally, the application of an aggregated stress index, such as the Watershed Stressor Index (WSI) developed by the Nature Conservancy of Canada, can help identify small watershed units within the St. Croix watershed that are under greater pressure from anthropogenic stressors. An aggregated index like the WSI uses geospatial data for a range of stressors including point source pollution, land use, river crossings, and barriers to fish passage to produce scores for individual watershed units. These scores can then be used to prioritize units within the watershed for conservation or monitoring activities.

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# Appendix 1: Summary Statistics for Forest City

| Forest City (NB01AR0151) | Count | Min | Max | Median | St. Dev. | # Censored | % Censored | Date Range |
|---|---|---|---|---|---|---|---|---|
| Alkalinity Gran $CaCO_3$ | 86 | 2 | 12 | 11.2 | 1.122 | 1 | 1.2 | 2007-2018 |
| Alkalinity Total $CaCO_3$ | 89 | 10.4 | 20 | 20 | 2.863 | 75 | 84.3 | 2007-2018 |
| Aluminum Total | 92 | 4 | 22 | 10.75 | 4.047 | 1 | 1.1 | 2007-2018 |
| Antimony Total | 90 | 0.02 | 0.1 | 0.04 | 0.033 | 36 | 40 | 2007-2018 |
| Arsenic Total | 90 | 0.05 | 0.5 | 0.255 | 0.066 | 2 | 2.2 | 2007-2018 |
| Barium Total | 92 | 1 | 3 | 2 | 0.281 | 2 | 2.2 | 2007-2018 |
| Beryllium Total | 90 | 0.005 | 0.1 | 0.01 | 0.045 | 90 | 100 | 2007-2018 |
| Boron Total | 49 | 1.1 | 10.2 | 10 | 2.846 | 42 | 85.7 | 2011-2018 |
| Cadmium Total | 90 | 0.01 | 0.1 | 0.02 | 0.04 | 89 | 98.9 | 2007-2018 |
| Calcium Total | 80 | 0.01 | 4.95 | 4.245 | 0.523 | 1 | 1.3 | 2007-2018 |
| Carbon Dissolved Organic | 33 | 2.9 | 4.5 | 3.9 | 0.391 | 0 | 0 | 2007-2010 |
| Carbon Total Organic | 97 | 0.3 | 5.9 | 3.93 | 0.568 | 0 | 0 | 2007-2018 |
| Chloride Dissolved | 90 | 0.1 | 1.8 | 1.57 | 0.193 | 1 | 1.1 | 2007-2018 |
| Chromium Total | 90 | 0.02 | 0.4 | 0.07 | 0.169 | 38 | 42.2 | 2007-2018 |
| Cobalt Total | 90 | 0.01 | 0.1 | 0.01 | 0.044 | 82 | 91.1 | 2007-2018 |
| Colour Apparent | 87 | 5 | 44 | 12 | 4.445 | 5 | 5.7 | 2007-2018 |
| Conductance (Field) | 71 | 27.3 | 35.6 | 32.8 | 1.68 | 0 | 0 | 2007-2016 |
| Copper Total | 90 | 0.01 | 0.56 | 0.29 | 0.068 | 5 | 5.6 | 2007-2018 |
| Dissolved Nitrogen Nitrate | 90 | 0.01 | 0.07 | 0.02 | 0.007 | 75 | 83.3 | 2007-2018 |
| Iron Total | 92 | 0 | 0.05 | 0.02 | 0.005 | 55 | 59.8 | 2007-2018 |
| Lead Total | 90 | 0.02 | 0.22 | 0.03 | 0.038 | 80 | 88.9 | 2007-2018 |
| Magnesium Total | 80 | 0.05 | 1 | 0.61 | 0.082 | 1 | 1.3 | 2007-2018 |
| Manganese Total | 92 | 1 | 16.6 | 4.65 | 1.998 | 1 | 1.1 | 2007-2018 |
| Molybdenum Total | 90 | 0.01 | 0.7 | 0.06 | 0.073 | 33 | 36.7 | 2007-2018 |
| Nickel Total | 90 | 0.01 | 5.8 | 0.14 | 0.598 | 5 | 5.6 | 2007-2018 |
| Nitrogen Total | 90 | 0.02 | 0.27 | 0.17 | 0.032 | 2 | 2.2 | 2007-2018 |
| Nitrogen Total Dissolved | 32 | 0.11 | 0.21 | 0.16 | 0.024 | 0 | 0 | 2007-2014 |
| Oxygen Dissolved | 73 | 5.24 | 15.19 | 10.56 | 2.206 | 0 | 0 | 2007-2016 |
| $O_2$ % Saturation | 68 | 58.9 | 113.5 | 98.4 | 6.402 | 0 | 0 | 2007-2016 |
| pH | 90 | 5.86 | 7.53 | 7.37 | 0.183 | 0 | 0 | 2007-2018 |
| pH (Field) | 70 | 5.62 | 8.58 | 7.185 | 0.544 | 0 | 0 | 2007-2016 |
| Phosphorus Total | 90 | 0.002 | 0.009 | 0.005 | 0.001 | 1 | 1.1 | 2007-2018 |
| Potassium Total | 80 | 0 | 0.41 | 0.4 | 0.072 | 43 | 53.8 | 2007-2018 |
| Selenium Total | 77 | 0.03 | 0.2 | 0.05 | 0.03 | 24 | 31.2 | 2008-2018 |
| Silver Total | 90 | 0 | 0.1 | 0.01 | 0.045 | 90 | 100 | 2007-2018 |
| Sodium Total | 80 | 0.02 | 1.7 | 1.46 | 0.186 | 1 | 1.3 | 2007-2018 |
| Specific Conductance | 90 | 1.2 | 37 | 33.6 | 3.733 | 0 | 0 | 2007-2018 |
| Strontium Total | 92 | 1 | 25 | 22.85 | 2.51 | 1 | 1.1 | 2007-2018 |
| Sulphate Dissolved | 90 | 0.6 | 2.41 | 1.9 | 0.324 | 0 | 0 | 2007-2018 |
| Temp. Water (Field) | 71 | -0.03 | 26.01 | 11.15 | 8.543 | 0 | 0 | 2007-2016 |
| Thallium Total | 77 | 0.01 | 0.1 | 0.01 | 0.042 | 77 | 100 | 2008-2018 |
| Tin Total | 77 | 0.02 | 0.2 | 0.05 | 0.031 | 75 | 97.4 | 2008-2018 |
| Titanium Total | 84 | 0.05 | 0.7 | 0.2 | 0.13 | 6 | 7.1 | 2007-2018 |
| Turbidity | 90 | 0.1 | 2.8 | 0.4 | 0.4 | 0 | 0 | 2007-2018 |
| Turbidity (Field) | 71 | -0.8 | 38.7 | 0 | 4.649 | 0 | 0 | 2007-2016 |
| Uranium Total | 77 | 0.01 | 0.1 | 0.03 | 0.035 | 25 | 32.5 | 2008-2018 |
| Vanadium Total | 90 | 0.02 | 0.1 | 0.08 | 0.023 | 29 | 32.2 | 2007-2018 |
| Zinc Total | 90 | 0.05 | 3.13 | 0.3 | 0.417 | 31 | 34.4 | 2007-2018 |

# Appendix 2: Summary Statistics for Milltown

| Milltown (NB01AR0021) | Count | Min | Max | Median | St. Dev. | # Censored | % Censored | Date range |
|---|---|---|---|---|---|---|---|---|
| Alkalinity Gran CaCO3 | 88 | 5.34 | 21.4 | 10.775 | 3.874 | 0 | 0 | 2007-2018 |
| Alkalinity Total CaCO3 | 90 | 6.37 | 22.6 | 20 | 2.864 | 73 | 81.1 | 2007-2018 |
| Aluminum Dissolved | 31 | 36.9 | 162 | 82 | 28.96 | 0 | 0 | 2007-2010 |
| Aluminum Total | 93 | 43 | 211.8 | 113.2 | 32.12 | 0 | 0 | 2007-2018 |
| Antimony Total | 92 | 0.03 | 0.22 | 0.05 | 0.033 | 37 | 40.2 | 2007-2018 |
| Arsenic Total | 92 | 0.1 | 0.89 | 0.445 | 0.156 | 2 | 2.2 | 2007-2018 |
| Barium Total | 93 | 3 | 15.9 | 7 | 2.932 | 0 | 0 | 2007-2018 |
| Beryllium Dissolved | 28 | 0.1 | 1 | 1 | 0.397 | 28 | 100 | 2008-2010 |
| Beryllium Total | 92 | 0.005 | 0.1 | 0.0135 | 0.044 | 53 | 57.6 | 2007-2018 |
| Boron Total | 51 | 2.9 | 10.2 | 10 | 2.204 | 43 | 84.3 | 2011-2018 |
| Cadmium Dissolved | 38 | 0.1 | 3 | 1 | 1.395 | 37 | 97.4 | 2007-2010 |
| Cadmium Total | 92 | 0.01 | 0.1 | 0.06 | 0.035 | 43 | 46.7 | 2007-2018 |
| Calcium Dissolved | 32 | 2.25 | 6.82 | 4.24 | 1.145 | 0 | 0 | 2007-2010 |
| Calcium Total | 82 | 2.33 | 6.14 | 4.06 | 0.872 | 0 | 0 | 2007-2018 |
| Carbon Dissolved Organic | 33 | 5.6 | 12.8 | 8.1 | 1.957 | 0 | 0 | 2007-2010 |
| Carbon Total Organic | 100 | 5.97 | 13.8 | 8.45 | 1.638 | 0 | 0 | 2007-2018 |
| Chloride Dissolved | 92 | 1.5 | 10.2 | 4.4 | 2.202 | 0 | 0 | 2007-2018 |
| Chromium Dissolved | 38 | 0.4 | 2 | 2 | 0.803 | 36 | 94.7 | 2007-2010 |
| Chromium Total | 92 | 0.1 | 0.6 | 0.25 | 0.122 | 31 | 33.7 | 2007-2018 |
| Cobalt Dissolved | 38 | 0.1 | 5 | 3 | 2.353 | 38 | 100 | 2007-2010 |
| Cobalt Total | 92 | 0.01 | 0.15 | 0.08 | 0.029 | 33 | 35.9 | 2007-2018 |
| Colour Apparent | 89 | 21 | 104 | 60 | 15.90 | 0 | 0 | 2007-2018 |
| Conductance (Field) | 67 | 22.6 | 100.2 | 50.4 | 19.74 | 0 | 0 | 2007-2016 |
| Copper Dissolved | 38 | 0.2 | 2 | 2 | 0.781 | 21 | 55.3 | 2007-2010 |
| Copper Total | 92 | 0.2 | 1.4 | 0.45 | 0.186 | 2 | 2.2 | 2007-2018 |
| Dissolved Nitrogen Nitrate | 92 | 0.01 | 0.18 | 0.05 | 0.032 | 9 | 9.8 | 2007-2018 |
| Iron Dissolved | 31 | 0.05 | 0.19 | 0.1 | 0.042 | 0 | 0 | 2007-2010 |
| Iron Total | 93 | 0.08 | 0.911 | 0.19 | 0.095 | 0 | 0 | 2007-2018 |
| Lead Dissolved | 38 | 0.1 | 20 | 10 | 8.399 | 30 | 78.9 | 2007-2010 |
| Lead Total | 92 | 0.06 | 1.6 | 0.15 | 0.208 | 1 | 1.1 | 2007-2018 |
| Magnesium Dissolved | 32 | 0.46 | 0.97 | 0.7 | 0.122 | 0 | 0 | 2007-2010 |
| Magnesium Total | 82 | 0.469 | 1.05 | 0.7 | 0.107 | 0 | 0 | 2007-2018 |
| Manganese Dissolved | 31 | 8 | 74 | 26 | 14.85 | 0 | 0 | 2007-2010 |
| Manganese Total | 93 | 19 | 105 | 48 | 19.33 | 0 | 0 | 2007-2018 |
| Molybdenum Dissolved | 28 | 0.1 | 5 | 5 | 2.11 | 28 | 100 | 2008-2010 |
| Molybdenum Total | 92 | 0.06 | 0.5 | 0.1 | 0.055 | 31 | 33.7 | 2007-2018 |
| Nickel Dissolved | 38 | 0.3 | 6 | 4 | 2.659 | 21 | 55.3 | 2007-2010 |
| Nickel Total | 92 | 0.1 | 1.72 | 0.41 | 0.293 | 1 | 1.1 | 2007-2018 |
| Nitrogen Total | 92 | 0.21 | 0.52 | 0.36 | 0.071 | 0 | 0 | 2007-2018 |
| Nitrogen Total Dissolved | 32 | 0.22 | 0.47 | 0.34 | 0.069 | 0 | 0 | 2007-2014 |
| Oxygen Dissolved | 70 | 4.3 | 38.7 | 10.755 | 4.107 | 0 | 0 | 2007-2016 |
| $O_2$ % Saturation | 65 | 44.9 | 108.3 | 98.2 | 7.246 | 0 | 0 | 2007-2016 |
| pH | 92 | 6.64 | 7.64 | 7.205 | 0.193 | 0 | 0 | 2007-2018 |
| pH (Field) | 66 | 0.86 | 8.16 | 6.82 | 1.262 | 0 | 0 | 2007-2016 |
| Phosphorus Total | 92 | 0.01 | 0.049 | 0.02 | 0.009 | 0 | 0 | 2007-2018 |
| Potassium Total | 82 | 0.1 | 2.02 | 0.7 | 0.423 | 4 | 4.9 | 2007-2018 |
| Selenium Total | 80 | 0.03 | 0.2 | 0.06 | 0.027 | 20 | 25 | 2008-2018 |
| Silver Dissolved | 28 | 0.1 | 2 | 2 | 0.83 | 28 | 100 | 2008-2010 |
| Silver Total | 92 | 0 | 0.1 | 0.01 | 0.045 | 91 | 98.9 | 2007-2018 |
| Sodium Total | 82 | 1.6 | 14 | 5.71 | 3.266 | 0 | 0 | 2007-2018 |
| Specific Conductance | 92 | 25.4 | 109 | 54.8 | 21.76 | 0 | 0 | 2007-2018 |
| Strontium Total | 93 | 11 | 28.9 | 20 | 4.252 | 0 | 0 | 2007-2018 |
| Sulphate Dissolved | 92 | 1.59 | 14 | 6.09 | 3.055 | 0 | 0 | 2007-2018 |
| Temp. Water (Field) | 63 | -0.17 | 25.65 | 10.99 | 8.785 | 0 | 0 | 2007-2016 |
| Thallium Total | 80 | 0.01 | 0.1 | 0.01 | 0.041 | 80 | 100 | 2008-2018 |
| Tin Total | 80 | 0.02 | 0.1 | 0.05 | 0.027 | 78 | 97.5 | 2008-2018 |
| Titanium Dissolved | 28 | 0.4 | 1 | 1 | 0.19 | 20 | 71.4 | 2008-2010 |
| Titanium Total | 85 | 0.1 | 4.17 | 1.1 | 0.643 | 1 | 1.2 | 2007-2018 |
| Turbidity | 92 | 0.2 | 29.6 | 1.3 | 3.024 | 0 | 0 | 2007-2018 |
| Turbidity (Field) | 67 | 0 | 41 | 0.7 | 6.004 | 0 | 0 | 2007-2016 |
| Uranium Total | 80 | 0.05 | 0.1 | 0.08 | 0.016 | 25 | 31.3 | 2008-2018 |
| Vanadium Dissolved | 38 | 0.2 | 4 | 4 | 1.752 | 21 | 55.3 | 2007-2010 |
| Vanadium Total | 92 | 0.1 | 0.8 | 0.385 | 0.154 | 1 | 1.1 | 2007-2018 |
| Zinc Dissolved | 38 | 1.2 | 14 | 2.75 | 2.807 | 6 | 15.8 | 2007-2010 |
| Zinc Total | 92 | 0.3 | 33 | 3.18 | 5.315 | 1 | 1.1 | 2007-2018 |

# Appendix 3: Example of a "blocky" parameter