

Status and Trends of Flow, Water Quality and Suspended Sediment Quality in the Peel River Watershed

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Summary

The quantity and quality of water flowing within an undeveloped river, such as the Peel River and its tributaries, largely depends on the climate, relief, vegetation and geology of the surrounding watershed. Ignoring anthropogenic influences, the quantity and quality of water in the rivers reflects the cycle of the seasons, the rate of movement and volume of water that moves from the land into the river, and the amount and type of material, both particulate and dissolved, that the water transfers from the land of the watershed into the river.

The climate of the Peel River watershed is northern; there are long, cold, dark winters, and short cool summers with long days and abundant sunshine. In the spring, the days begin to lengthen, ice and snow rapidly start to melt and the creeks and rivers within the watershed quickly rise and flow faster. The pace of change during the 'spring freshet' is rapid because of the many mountain ranges, relatively few wetland areas, and almost continuous permafrost that occurs within the watershed. The dramatic relief within the watershed means that the spring melt-water runs down the mountainsides, rather than meandering slowly along a flat plain. The relative lack of wetlands and presence of permafrost means that there is only a limited area and depth in which melt-water can be stored, so that the spring melt-water typically runs quickly off the land rather than soaking into the ground and being released slowly over a long time period. The result is a 'spring freshet' that starts in the lower reaches of the Peel River during the early part of May each year, and reaches its peak flow only a week or two later. The timing of the spring freshet, though it is variable from year-to-year and can start anytime from late April to early June, does not appear to have undergone any consistent changes over the past 40 years. There has been no significant trend towards an earlier or later spring freshet in the lower reaches of the Peel River watershed. The intensity of the spring freshet is variable. The maximum flow rate during the spring freshet varies from year-to-year by over five-fold, though again, there has been no significant trend towards either an increased or decreased maximum flow, or total flow.

The same factors that contribute to the pace of the spring freshet, also make the watershed responsive to summer rains. Soon after a large rainfall, the river quickly rises and almost as quickly falls, as the water runs off the landscape. This period of the year is called the 'summer recession', and has perhaps the most changeable flow rates of any season within the Peel River. Following the summer recession, flow rates gradually decrease as the season progresses. Over the period of record, there has been a significant decrease in flow rates in June, during the early part of the summer recession. This perhaps suggests that the volume of spring rains have lessened over the years, or that the length of the spring freshet has decreased.

In the fall, as the days shorten and temperatures drop, flow within the river continues to decrease. Later, when ice and snow dominate the landscape, the Peel River continues to flow

lower and slower, and reaches its lowest point usually around the end of March or the beginning of April. Over the past 40 years, there has been no significant change in the timing of the lowest flow rates in the lower reaches of the Peel River. There have, however, been significant changes to the timing and amount of winter flow ("winter baseflow") in the Peel River. The beginning of the baseflow period has become significantly later in the year, which means that flow is significantly higher than it used to be for longer into the fall. There has also been a significant increase in the annual minimum flow rate, and the average rate of flow over the entire baseflow period. In the period from 2005 to 2010, though variable from year-to-year, the average rate of flow during the winter was about double what it was in the early 1970's. The increase in winter flow suggests that new hydrological flowpaths may have developed in recent years in association with warming permafrost. This suggestion is consistent with the observed decreases in flow rates during June; as winter flow increases there is perhaps less sustained flow during the late spring/early summer periods.

Despite the observed increases in winter flow in the Peel River above Fort McPherson, there has been no significant increase in the total amount of water flowing in the Peel River, measured over the whole year. This is because flow in winter ranges from about 50 to 100 m³/s, while flow in spring freshet can be higher than 8000 m³/s. The relatively large flow rates during the spring freshet mean that total yearly flow is dominated by the amount of water flowing in the Peel River during this period. The lack of a trend in total flow within the Peel River suggests that the total amount of water falling within the watershed, though variable from year-to-year, has not steadily increased or decreased over the past 40 years.

The dramatic changes in flow rates within the Peel River watershed have a dramatic effect on water quality. As river-flow rates change, the amount of sand, silt and clay suspended within the water also change. The levels of these particulates (collectively known as turbidity) in the Peel River above Fort McPherson are well above government (Canadian Council of Ministry of the Environment; CCME) guideline values for the protection of aquatic life, but they are natural to the Peel River so it is expected that the fish communities have adapted to their presence. Over the past 40 years, no significant changes in the turbidity levels in the Peel River above Fort McPherson Action (Canadian Council of Ministry of the Peel River so it is expected that the fish communities have adapted to their presence. Over the past 40 years, no significant changes in the turbidity levels in the Peel River above Fort McPherson have been observed.

The particles of sand, silt and clay that are washed into the river also contain metals, so that the total amount of metals tend to increase as the amount of particulates increase. During periods of high flow when lots of particulates are suspended in the water, total concentrations of metals including copper, iron, nickel and zinc are well above government guideline values for protection of aquatic life. Again, these conditions are natural to the Peel River so that fish communities are expected to be adapted to their presence. Additionally, metals that are bound to particles in the water do not appear readily soluble and so are not considered biologically available to the fish and the other animals that inhabit the river. It is generally considered that only the metals that are dissolved in the water that may cause effects. Because the amount of particulates within the river has not changed over the past 40 years, it is also expected that the amount of total metals has also not increased or decreased over the same time period.

The Peel River watershed is dominated by sedimentary rocks that contain calcium, magnesium, carbonate and sulphate. Because of this, as water runs off the land and into the many creeks and rivers within the watershed, large amounts of these four major ions are present in the water and define the water chemistry within the Peel River. These processes result in water that can be described as hard and alkaline. Within the watershed, the rivers contain relatively high concentrations of calcium, magnesium and sulphate, and relatively low concentrations of the major ions sodium, potassium and chloride. The sedimentary rocks also release large amounts of carbonate, so that the waters of the Peel River watershed have a pH greater than 7 and are highly buffered (that is, resistant to change in pH). This occurs over the entire watershed, so that the chemistry of the water is similar in all the major rivers, and unique to the Peel River watershed.

The concentration of major dissolved ions is also affected by changes in seasonal flow rates. During the spring freshet, the concentrations of most major ions decrease as they are diluted by melting ice and snow. As the summer progresses, concentrations of most major ions begin to increase, until they reach a maximum during the winter baseflow period. The seasonal pattern and flow in concentration for the major ions is opposite to the pattern displayed by total metals.

Over the past 40 years, there has been a significant increase in the concentration of dissolved calcium, magnesium and sulphate in the Peel River above Fort McPherson during spring freshet, summer recession and the winter baseflow period. This indicates that the amount of calcium, magnesium and sulphate that is moving from the land into the water has increased over the period of record for all seasons of the year. These observed increases suggest that the watershed landscape has changed over the past 40 years. The increase in summer concentrations of major ions is linked to the development of large permafrost disturbances which are making immense volumes of previously frozen materials available to chemical weathering, erosion and runoff into the river.

In contrast to the pattern shown by the major ions, the concentration of dissolved trace metals such as nickel, copper and zinc do not vary noticeably through the season. However, for these metals, the period of record is considerably shorter, because dissolved trace metals have only been measured since 2006. Also, the concentrations of the trace metals are relatively low compared with the major ions and in many cases are near the analytical detection limit that can be detected by the laboratory. This increases variability and may obscure seasonal relationships. With the current set of data, it is not possible to determine if there has been an increase or decrease in dissolved trace-metal concentrations over time. With continued monitoring, however, understanding of trends may be possible. Currently, only dissolved aluminum, cadmium, copper and lead have occasionally exceeded existing government water quality guidelines for the protection of aquatic life.

Within the industrial landscapes of the world, many organic chemicals are produced. These chemicals include pesticides and herbicides used in agriculture, and many other organic compounds used by industry for manufacture of plastics and other products of the industrial age. These chemicals can be toxic and persistent in the environment. Even though there is no

direct deposition of these chemicals within the Peel River watershed, many of these organic chemicals evaporate into the atmosphere and are capable of moving large distances from their sources with prevailing winds. These chemicals then tend to fall out of the atmosphere during rain or snow events, particularly in areas that are cold, such as mountains, and northern areas such as the Yukon. The Peel River watershed, being located in a cold and mountainous northern region, is therefore doubly vulnerable to deposition of these persistent and toxic chemicals. Because of this, efforts have been made to measure the concentration of these organic pollutants in the Peel River (above Fort McPherson). In the water, concentrations for most are below detection limits, and for others are well below guideline values. Currently, it does not appear that persistent organic pollutants are present as dissolved components in water within the Peel River. Within the suspended sediment of the Peel River (above Fort McPherson), several metals and hydrocarbon compounds have exceeded guideline values.

In this report, water quality baseline conditions have been defined for many water quality analytes of the Peel River above Fort McPherson. This information provides a benchmark for the development of site-specific water quality guidelines. Further, it will allow for comparisons to be made and for the detection of any future temporal trends and the effects of any developments that might occur within the region.

Stantec

STATUS AND TRENDS OF FLOW, WATER QUALITY AND SUSPENDED SEDIMENT QUALITY IN THE PEEL RIVER WATERSHED

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1.0 Introduction

On January 16, 2012, Stantec Consulting Ltd. was retained to produce a report discussing water quality and quantity in the Peel River watershed. The goal of the study was to provide information that might be used to address community concerns regarding water quality and quantity within the Peel River watershed, and to support development of site specific water quality guidelines for the Yukon/Northwest Territories Transboundary Agreement. In support of these goals, the objectives of the study were to develop an understanding of baseline water quality and quantity for the long term monitoring station: Peel River above Fort McPherson. This report defines the seasonal hydrological cycle, describes any seasonal differences in water chemistry and any temporal trends in water chemistry and/or hydrology for this station. In addition, this report also describes the spatial variability in water chemistry throughout the watershed, moving from the headwaters of the Peel River (Ogilvie and Blackstone Rivers) downstream to Fort McPherson.

To address these objectives, several comprehensive datasets were provided, including:

- 1) Flow data collected from the Peel River above Fort McPherson (1969 to 2010);
- 2) Water quality data collected from the Peel River above Fort McPherson (1960 to 2011);
- Suspended sediment quality data collected from the Peel River above Fort McPherson (2002 to 2012); and
- A set of water quality data collected from various sites throughout the Peel River Watershed in 1999 and once a year between 2002 and 2007

2.0 Study Area

The Peel River Watershed drains an area of approximately 70,600 km², and is located largely in the northern part of the Yukon Territory; from 64° to 67° north, and from 131° to 140° west (Figure 2-1). There are six major tributaries within the Peel River watershed, including the Ogilvie, Blackstone, Hart, Wind, Bonnet Plume and Snake Rivers (Kenyon and Whitley 2008). The Ogilvie and Blackstone Rivers flow east out of the Ogilvie Mountains and join to form the Peel River, and the Hart, Wind, Bonnet Plume and Snake Rivers flow north out of the Wernecke Mountains and join the Peel River downstream (Figure 2-1). Other, smaller tributaries arise out of the Richardson Mountains, and include the Caribou, Trail, Road, Satah and Vittrekwa Rivers.

Hydrological data collected between 1969 and 2010 indicates that flow of the Peel River above Fort McPherson averages 23 million dam³ per year while other tributaries range in flow from just over 300,000 to 3 million dam³ per year (Kenyon and Whitley 2008).

The headwaters of the Peel River watershed are located in the Taiga Cordillera Ecozone. This remote mountainous region "contains some of Canada's largest waterfalls, deepest canyons and wildest rivers" (Smith et al. 2004). This region encompasses the northernmost extent of the Rocky Mountains, but also contains rolling foothills, upland plateaus and low-lying basins (Czarnecki and Beavers 2002). The boreal forest reaches its northern limit here (Peepre and Locke 2008), and transitions to treeless Arctic tundra further north and at higher elevations. Summers are warm to cool with extended periods of daylight and average temperatures of 6 to 10°C depending on elevation and aspect. Winters are long and cold with little daylight and average temperatures approaching -25°C (Smith et al. 2004). The mean annual temperature ranges from -5 to -10°C. Annual precipitation ranges between 300 and 700 mm/yr and runoff is high relative to precipitation because of the underlying permafrost, high relief, relative lack of wetlands, and limited evapotranspiration. Sedimentary rocks such as sandstone, shale, limestone and dolomite dominate the Ecozone (Smith et al. 2004) and are important factors in determining the water chemistry of the Peel River and its tributaries.

The lower reaches of the Peel River are located in the Taiga Plains Ecozone, which is centered on the Mackenzie River valley (Peepre and Locke 2008). This part of the watershed is characterized by continuous permafrost, and extensive areas of low relief, low elevation peatlands (Smith et al. 2004). Summers are short and cool with average temperatures of approximately 10°C. Winters are long and cold and are typical of a high subarctic climate. Mean annual precipitation is approximately 300 mm/yr and runoff is low relative to precipitation because of the low relief and relatively extensive wetlands (Smith et al. 2004).

Wildlife in the watershed is diverse, and includes Dall Sheep, woodland and barren ground caribou, moose, mountain goat, black and grizzly bear, wolf, lynx, and a concentration of wolverine, among others (Smith et al. 2004). The watershed also contains 24 species of fish, including game fish such as Chum Salmon, Arctic Grayling, Dolly Varden, Lake Trout, Broad Whitefish, Lake Whitefish, Inconnu, Northern Pike, and Walleye (EDI Environmental 2006).

Slimy Sculpin are also present in the fast, boulder-strewn reaches of the watershed's many rivers. This is a potentially important species for future environmental monitoring efforts because of its sensitivity to pollutants and limited movement.

The Peel River watershed is almost completely undeveloped, except for the Dempster Highway that crosses the upper reaches of the basin (Figure 2-1) and historical mineral and oil and gas exploration. Currently, "*The water, wildlife and fisheries resources produced in the Peel Basin are used to support the traditional culture and subsistence lifestyle (hunting, trapping, fishing) of numerous residents within the area... [that]... include the Tetlit Gwich'in in Fort McPherson, the Inuvialuit in Aklavik, the Na-Cho Ny'a'k Dun in Mayo and the Tr'on Dek Hwech'in of Dawson City (Czarnecki and Beaver 2002)."*



Figure 2-1: Peel River Watershed (and Monitoring Stations)

3.0 Methods

Analytical methods were determined by dataset characteristics and the questions to be addressed by the study. Each of the datasets thus required a separate methodological approach. The three datasets included:

- Peel River above Fort McPherson (flow data)
- Peel River above Fort McPherson (water quality data and suspended sediment quality data)
- Peel River Watershed (numerous sites; water quality data)

3.1 FLOW - PEEL RIVER ABOVE FORT MCPHERSON

In addition to the 1969-2010 hydrometric data for Peel River at Fort McPherson that was provided to Stantec, an attempt was made to obtain the 2011 streamflow (Q) data from the Water Survey Canada (WSC) of Environment Canada archive hydrometric database. However, the streamflow data for Peel River above Fort McPherson are available only for the period from 1969 to 2010 from the WSC database (see Figure D-1 in Appendix D).

Stantec has reviewed the 1969 to 2010 streamflow data from the Peel River above Fort McPherson hydrometric station. The assessment indicated that there are a number of years where streamflow data are missing. Table 3-1 tabulates the years where streamflow data are missing, including the number of missing days in a particular year. The remaining years have year-round streamflow data that can be used for trends analysis for the Peel River.

Table 3-1: List of Missed Streamflow Data for Peel River at Fort McPherson				
Year No. of Missing Days Year No. of Missing				
1969	272	1974	69	
1970	55	1987	365	
1971	106	1997	61	
1972	18	1998	59	
1973	33	2004	1	

3.1.1 Trend Analysis

Generally, trends (positive or negative) in streamflow occur gradually (a trend) or abruptly (a 'step change'). Stantec assessed the trend in streamflow for the Peel River above Fort McPherson. The assessment was for the entire period of streamflow records (1969-2010) and for the last decade of streamflow records (2001-2010). Trend analyses were undertaken using linear regression (graphical trend analysis) and a Mann-Kendall test (Appendix A). An R² value was calculated using simple linear regression. Tests for significance (calculation of p values) were undertaken using the Mann-Kendall test. Trend analysis was undertaken for Peel River above Fort McPherson:

- Total annual streamflow
- Mean annual streamflow
- First Julian day above 1000 m³/s: the first day during freshet when flow rate increases to above 1,000 m³/s
- Annual maximum daily flow: the maximum daily flow rate in each year
 - Julian-calendar day of maximum freshet daily flow
- Annual minimum daily flow: the minimum daily flow rate in each year
 - Julian day of minimum daily flow
- Mean monthly streamflow to assess in depth any temporal changes in seasonality

In addition to the trends analysis, the following were calculated;

Definition of seasonal periods based on streamflow and turbidity (Table 3-2). This is an arbitrary framework overlain on a continuous and temporally variable natural process, but is useful for describing the progression of the seasons within the Peel River watershed, for the delineation of the seasonal variability in baseline chemistry, and for determining temporal trends on a seasonal basis. It is also convenient for use in determining optimal sampling dates. The start date of the spring freshet was defined as the first date when flow increased to greater than 300 m³/s, the start date of the summer recession was arbitrarily chosen as July 1st, and the start date of the winter baseflow was defined as the first date when flow decreased to less than 300 m³/s (Table 3-2). This delineation was based on the characteristics of flow increase during the spring, and the relationship between flow rate and turbidity.

Table 3-2: Definition of Seasonal Flow Periods					
Season Spring Freshet Summer/Fall Winter Baseflow					
Flow Rate	>300 m³/s	>300 m³/s	<300 m³/s		
Earliest Start Date	April 14	July 1	September 15		
Median Start Date	May 9		October 22		
Median End Date		October 22	May 9		
Latest End Date	June 30	November 23	May 24		
Trends Analysis	May-June	July-October	November-April		

Flow-Duration Curve (FDC): FDCs were constructed using available daily streamflow data in order to assess changes in the flow regime between the entire period of streamflow records (1969-2010) and for the last decade of streamflow data (2001-2010). This is useful to show the relationship between the magnitude and frequency of streamflow of the two periods. Moreover, it will highlight key streamflow features; such as the variability in the range of flows, changes in low and high flows. They also provide a measure of the percentage of time a given streamflow is equaled or exceeded over the daily time interval.

3.2 WATER QUALITY - PEEL RIVER ABOVE FORT MCPHERSON

The Peel River above Fort McPherson dataset, collected by Environment Canada and Aboriginal Affairs and Northern Development Canada (AANDC), provides the longest timeseries of surface water-chemistry data for the Peel River. The data can be divided into four sets of data, based on the measured variables. The four datasets include:

- Major Water Chemistry Variables
- Total and Dissolved Metals
- Nutrients
- Organic Compounds of Potential Concern

For each set of data, a quality-control check of the data was undertaken. This included determination and/or calculation of the following:

• Identification of anomalous data points.

- Identification of missing data points.
- Determination of ionic balance.
- The raw dataset contains duplicates and triplicates for some stations for the same date. The dataset was reduced through calculation of the average values.
- Reduction of dataset by year, and by analyte where, and if required.
- Rationalization of multiple analyte versions. This is especially important for the nitrogen and phosphorus datasets, each of which has multiples of categories, some of which are identical.

The purpose of the QA was to provide a core dataset for each category that was free of anomalous data, had a minimal amount of missing data, that had an equal number of data points for each sampling event, and that had one consistent record for each analyte.

3.2.1 Major Water Chemistry Variables

There are ten analytes within a 200-sample-event dataset spanning 1960 to 2011. These include; alkalinity, dissolved calcium, dissolved chloride, dissolved magnesium, pH, dissolved potassium, dissolved sodium, conductivity, dissolved sulphate, and turbidity. For each analyte, sampling period and analysis was not regular, so that there are missing time periods, relatively few samples from the freshet period, and there are from 6 to 31 missing values for each analyte within the 200 sampling events. The dataset was comprehensive enough to analyze the variables as follows:

- Definition of baseline chemistry using box and whisker plots. For each plot, the lower line represents the 25th percentile, the middle line represents the 50th percentile (median), and the upper line represents the 75th percentile of the data. The whiskers define the maximum and minimum observed values that were within 1.5X the interquartile range (distance between the 25th and 75th percentile). Values outside the whiskers are defined as outliers. Only the highest or lowest outliers were plotted for each boxplot. Box and whisker plots using data percentiles were used to define baseline chemistry because they are non-parametric and so make no assumptions regarding data structure, are resistant to the effect of outliers and values below detection limit, and provide clear outlier-cutoff values. For comparison, mean values were also included in each figure.
- Delineation of analyte concentration versus flow for the entire dataset, for flow rates less than 1,000 m³/s, and for flow rates less than 300 m³/s. These flow-rate cutoffs were selected as being important determinants of flow period (see Section 3.1.1 above). The purpose was to determine the relationship between concentration and flow rate.
- Delineation of concentration versus time for the period 1989 to 2010. The purpose was to clearly illustrate the relationship between concentration and time over the recent period of

record. The shorter period was chosen so that seasonal alterations could be delineated within the figure.

- Delineation of concentration by flow, separated by flow regime (baseflow, freshet and recession). The purpose was to examine and characterize the effect of flow rate and season on analyte concentration. Data were separated into winter baseflow, spring freshet and summer recession datasets. Each dataset was tested, and if model residuals conformed to assumptions of normality and equal variance, ANOVA was used to first detect a difference, and if one existed, it was followed with a posthoc Student's t multiple comparison. Major ions analyzed using these tests included pH, total alkalinity, conductivity, turbidity, calcium, magnesium, potassium, sodium, chloride and sulphate. If assumptions of normality and equal variance were not met, then non-parametric tests (Kruskal-Wallis) were performed on rank-transformed data. For the non-parametric post hoc multiple comparison, a Wilcoxon Each Pair test was used on rank-transformed data.
- An examination of trends over time for each analyte by flow regime. The first step in the trends analysis was to separate the data into their respective seasonal periods. The data for each year in each seasonal period were then averaged. This was necessary because the number of samples per year was variable. Finally, a Mann Kendall (Appendix A) trends test was used to determine if a statistically significant temporal trend was evident through the period of record and for the last 10 years. A Mann Kendall test was used because it is non-parametric and makes no assumptions regarding the structure of the data. Trends assessment was undertaken for the ten major ions listed previously. For those analytes that showed a highly significant trend over time, the percent change was calculated using the regression of concentration vs time. For the trends analysis, statistical significance (p-value) was defined as follows:
 - <0.05 marginally significant
 - <0.005 moderately significant
 - <0.001 highly significant
 - <0.0001 highly significant in all circumstances

A p-value of 0.05 is standard for statistical testing. This p-value indicates a marginally significant difference. For the major ions, ten variables were tested for trends. Because the probability of error increases as the number of tests increases, a second level of significance was established for testing of trends for the major ions. The value of 0.005 was calculated based on a Bonferroni correction, where $\alpha' = \alpha/n$, and;

- α = 0.05
- n = the number of analytes being tested (10)

- α' = the corrected p-value

For some groups of analyses, there were up to 30 time/variable combinations being tested. To ensure that the probability of finding an effect in error remained reasonable, a third and fourth level of significance was established (Table 3-3). It was considered that a p-value of <0.0001 indicated a highly significant result under all conditions (Table 3-3).

Table 3-3: The Probability of at Least One Type 1 Error at Three Test Levels				
P voluo	N (# tests)			
r-value	1	10	30	
0.05	5%	40%	78%	
0.005	0.5%	5%	14%	
0.001	0.1%	1%	3%	
0.0001	0.01%	0.1%	0.3%	

- For calcium (Ca), a loading rate calculation was also undertaken. The loading rate was calculated (for each seasonal period) as the mean Ca concentration multiplied by the mean flow rate and then multiplied by the duration of the seasonal period, for a value measured as tons Ca/yr. The yearly loading rate was calculated as the sum of the three seasonal loading rates.
- Comparison to chronic guideline values (Table 3-4), where applicable. Updated CCME water quality guidelines for 'The Protection of Aquatic Life' and Health Canada's drinking-water guidelines were used (CCME 2012), if available. For a few analytes (sulphate, cobalt, manganese and vanadium) the BC water-quality guidelines were adopted (BCMOE 2012). For turbidity, CCME guideline values are a narrative where, under clear flow conditions, a maximum increase of 8 NTUs from background levels are allowed for a short-term exposure (e.g., 24-h period), and a maximum average increase of 2 NTUs from background levels is allowed for a longer-term exposure (e.g., 30-d period). A maximum increase of 8 NTUs from background levels are between 8 and 80 NTUs, and turbidity should not increase by more than 10% of background levels when background is > 80 NTUs (CCME 2012). This guideline provides a useful strategy, given the variable and extreme turbidity levels recorded in the Peel River over the past 50 years. Turbidity provides an estimate of the amount of particulate material suspended in the water column. Turbidity can be caused by inorganic material, and/or organic components such as algae or dead algal cells.

Table 3-4: CCME Guidelines for the Protection of Aquatic Life and Health Canada Drinking Water Quality Guidelines for Treated Water						
Element	Symbol	Value ¹	Value ²	Units		
Aluminum	AI	100		ug/L		
Antimony	Sb		6	ug/L		
Arsenic	As	5	10	ug/L		
Barium	Ba		1000	ug/L		
Boron	В	1,500	5,000	ug/L		
Cadmium	Cd	0.054*	5	µg/L		
Chloride	CI	120,000		µg/L		
Chromium (VI)	Cr	1	50	µg/L		
Chromium (III)	Cr	8.9	50	µg/L		
Cobalt**	Со	4		µg/L		
Copper	Cu	3.87*		µg/L		
Iron	Fe	300		µg/L		
Lead	Pb	6.63*	10	µg/L		
Manganese**	Mn	1400		µg/L		
Mercury	Hg	0.026	1	µg/L		
Molybdenum	Мо	73		µg/L		
Nickel	Ni	148*		µg/L		
Selenium	Se	1	10	µg/L		
Silver	Ag	0.1		µg/L		
Sulphate**	SO4	100,000		µg/L		
Thallium	TI	0.8		µg/L		
Turbidity			1	NTU		
Vanadium**	V	6		μg/L		
Zinc	Zn	30		µg/L		
CCME guidelines accessed at: http://st-ts.ccme.ca/?chems =all&chapters=1						

*at a hardness of 178 mg/L as CaCO₃ **BC Guideline Value ¹ CCME Long term guideline values for the Protection of Aquatic Life

² Health Canada Drinking Water Guideline

3.2.2 Nutrients

For the purposes of this report, nutrients include dissolved organic carbon (DOC), total nitrogen (TN) and total phosphorus (TP). Total nitrogen was the sum of ammonia, nitrate, nitrite and particulate N. Analysis included the following:

- Definition of baseline chemistry using box and whisker plots. Analysis was undertaken for each variable in terms of baseflow, freshet and recession seasonal periods.
- An examination of the relationship between flow rate, season and concentration.
- Comparison to guideline values, where applicable.

3.2.3 Trace Metals

The longest record for trace metal analysis exists for total metals. After examination of the characteristics of the data, including apparent detection limits and completeness, data from 1983 to 2010 were used for analysis of baseline chemistry for total trace metals. Metals that were analyzed (selected because the majority of the data were above detection limits) include; Aluminum (Al), Barium (Ba), Beryllium (Be), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Lithium (Li), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), Lead (Pb), Strontium (Sr), Vanadium (V) and Zinc (Zn). For this set of data, analyses included the following:

- Relationship between concentration and turbidity. Because this relationship was highly significant for almost all total metals, it was not possible to undertake a trends analysis for each individual trace metal over the entire period of record, but it was considered that a trends analysis of turbidity (by seasonal period) also provided an indication of trends in total metal concentrations. To summarize the correlation between turbidity and total metal concentration, data for the metals that were correlated to turbidity were combined by normalizing each set of metal data to the highest concentration for that metal, and then summing all relative metal concentrations for each date. Because of the uneven distribution of data and the variable number of data points for any given turbidity level, seven turbidity categories were selected and a 'mean relative metal concentration' was then calculated for each turbidity category. The turbidity categories (as mean NTU) were; 3, 48, 145, 250, 402, 603 and 1138 NTU. The 'mean relative metal concentration' data were then plotted against turbidity and a "best fit" line was calculated.
- A trends analysis was undertaken for a select group of total metals during the winter baseflow period (only). Metals included AI, Cr, Cu, Fe, Li, Mn, Mo, Ni, Sr and Zn for the period from 1993 to 2010. Because of missing data, only twelve or thirteen years out of 18 possible were used in the trends analysis. This compromised the analysis and means the results should be interpreted cautiously.

- Calculation of the Water Quality Index (WQI; CCME 2001) was undertaken using the ten metals that were analyzed for both dissolved and total fractions and that have guideline values (AI, Cd, Cr, Co, Cu, Mn, Mo, Ni, Pb and Zn). The WQI is a tool that can be used to compare the water quality of two or more sites using the following categories (CCME 2001);
 - "Excellent" (CCME WQI 95-100). Water quality is protected with a virtual absence of threat or impairment. Conditions are very close to natural or pristine levels.
 - "Good" (CCME WQI 80-94). Water quality is protected with only a minor degree of threat or impairment. Conditions rarely depart from natural or desirable levels.
 - "Fair" (CCME WQI 65-79). Water quality is usually protected but occasionally threatened or impaired. Conditions sometimes depart from natural or desirable levels.
 - "Marginal" (CCME WQI 45-64). Water quality is frequently threatened or impaired. Conditions often depart from natural or desirable levels.
 - "Poor" (CCME WQI 0-44). Water quality is almost always threatened or impaired. Conditions usually depart from natural or desirable levels.

There is also a smaller dataset for dissolved metals collected from 2006 to present. For this set of data, analyses included the following:

- Definition of baseline chemistry using box and whisker plots. For each plot, the lower line represents the 25th percentile, the middle line represents the 50th percentile (median), and the upper line represents the 75th percentile of the data. The whiskers define the maximum and minimum observed values that were within 1.5X the interquartile range (distance between the 25th and 75th percentile). Values outside the whiskers are defined as outliers. Only the highest or lowest outliers were plotted for each boxplot. Box and whisker plots using data percentiles were used to define baseline chemistry because they are non-parametric and so make no assumptions regarding data structure, are resistant to the effect of outliers, and provide clear outlier-cutoff values. For comparison, mean values were also included in each figure and table.
- An examination of the relationship between flow rate, turbidity and dissolved concentration.
- Comparison to guideline values, where applicable (Table 3-4). As with the other categories, the most recent CCME guidelines for "The Protection of Aquatic Life" were used for comparison (CCME 2012). For determination of CCME guideline values for Cu, Cd, Ni and Pb, an average hardness of 178 mg/L CaCO3 was used for all calculations. BC guideline values (BCMOE 2012) were used for Mn and Co.

3.2.4 Organic Compounds of Potential Concern

This dataset includes a variety of organic compounds that are susceptible to long-range transport and subsequent deposition in arctic or alpine environments. The Peel River above Fort McPherson monitoring program includes the analyses of water and suspended sediment for human-made pollutants such as pesticides and polycyclic biphenyls (PCBs). Polycyclic aromatic hydrocarbons which have both natural and human sources are also measured in the water and suspended sediment of the Peel River above Fort McPherson. The organic compounds were compared to guideline values where possible.

Both surface water samples and centrifugate water samples were analyzed for organic compounds. The centrifugate water samples were collected with a centrifuge. The centrifuge separates the suspended sediment from the river water, and provides two types of samples:

- 1) Centrifugate water samples
- 2) Suspended sediment samples (see below)

3.3 SUSPENDED SEDIMENT QUALITY - PEEL RIVER ABOVE FORT MCPHERSON

Environment Canada's and Aboriginal Affairs and Northern Development Canada's (AANDC) monitoring programs also provide information regarding the levels of metals and organic compounds that are found in the suspended sediment of the Peel River above Fort McPherson. Suspended sediments are a good medium to look for organic compounds as metals and organic compounds tend to attach to these particles.

Where possible, results were compared to the CCME guidelines for the protection of aquatic life. Since suspended sediment guidelines do not exist, comparisons were made to the CCME bottom sediment guidelines.

3.4 WATER QUALITY - PEEL RIVER WATERSHED

Surface water quality samples were collected from 15 monitoring stations throughout the Peel River Watershed between 1999 and 2005. The dataset contains physical parameters, major ions, nutrients and trace (total and dissolved) metals. Data below detection limit (BDL) were common, and were assumed to be equal to the reported detection limits. For some parameters, multiple detection limits, differing by an order of magnitude, were reported (e.g., Cd and Ag). The raw dataset contains duplicates and triplicates for some stations for the same date. The dataset was reduced through calculation of the average values (Appendix E; Table E-1).

The dataset was checked by calculating charge balance. It is assumed that in an aquatic environment the positive and negative charges of the various analytes will be in balance. This can be checked by summing the milliequivalents (ie charges) for both the cations and anions. If the chemical analyses are accurate, then the sum of the positive charges (cations) and negative charges (anions) should be zero. If they are not zero, then the analyses have been inaccurate for one or more analytes. It is considered that a precision of $\pm 10\%$ is acceptable. However, the charge balance error was outside of a 10% threshold in 16 of 66 major ion analyses, which indicated an unacceptable accuracy for one or more parameters. However, because there was no possibility of re-analyzing the samples, the dataset remained uncorrected for further manipulation. The reduced dataset was further used to calculate a number of measurements including; median, average values and associated standard deviations for each station in the Peel River watershed. Pearson's correlation coefficients were calculated for selected parameters.

Due to the limited number of samples per station (usually < 5), it was decided to use averages and standard deviations for plotting, rather than producing box plots. Average values were also used to build pie charts for major ions for each station. Therefore, major differences observed in the watershed are generally based on comparison of the average values calculated between stations.

The analytes were compared with *Canadian Drinking Water Quality Guidelines* (CDWQ, Health Canada 2008) using Maximum Acceptable Concentrations (MAC) and Aesthetic Objectives (AO). *Canadian Council of Ministries of the Environment Guidelines for the Protection of the Freshwater Aquatic Life* (CCME, 2012) *and British Columbia Guidelines* (BCMOE 2012) were also used (Table 3-4).

4.0 Results

4.1 FLOW - PEEL RIVER ABOVE FORT MCPHERSON

Flow in the Peel River above Fort McPherson is marked by considerable seasonality (Figure 4-1). There is a relatively long period of 'baseflow' that occurs during the approximately seven to eight months of winter, considered here to be between approximately October 15th (Julian Day 288/289) and April 30th (Julian Day 120/121) when flow rates are generally well below 300 m³/s (Figure 4-1). Though somewhat arbitrary, the cutoff of 300 m³/s for baseflow was chosen because that is the maximum flow rate at which turbidity remains low (Figure 4-1). Once flows increase beyond this value, turbidity increases and water chemistry changes considerably.



Figure 4-1: Seasonal Flow Dynamics in the Peel River above Fort McPherson

Minimum flow rates occur in March and April, with April 1st (Julian Day 91/92) being the median date for minimum flow over the period of record (Figures 4-1 and 4-2). After the period of minimum flow, there is a slow increase over a period of weeks until a flow rate of 200 to 300 m³/s is reached. Over the period of record, the median date for the first day with flow rates over 300 m³/s is May 9/10(Julian Day 129/131; Figures 4-1 and 4-2). This is followed by the spring freshet, which due to the mountainous terrain, continuous permafrost, and relatively sparse wetlands, is an abrupt event (Figure 4-1). On average, flow rates increase from

<300 m³/s to over 1,000 m³/s in four to five days, with the median first day over 1,000 m³/s being May 14th (Julian Day 134/135; Figure 4-2). Annual peak freshet flows occur from one to two weeks later, with the median date being May 23rd (Julian Day 143/144; Figure 4-2). Over the period of record, freshet and peak flow rates have almost always occurred during May, though occasionally they have begun in April and ended in June (Appendix D; Table D-1). To accommodate the variability in onset and duration of freshet, it was considered that the spring freshet occurred between approximately April 15th and June 30th when flow rates were >300 m³/s. This somewhat arbitrary designation includes declining freshet flows that occur in June. After freshet peak flow, flow rates are variable with some large spikes in response to rain events, but gradually decreasing through the summer and fall until baseflow once again occurs (Figure 4-1). It was considered that the first day of the 'summer recession' occurred on July 1st (Julian Day 212/213) and lasted approximately until the end of October (Julian Day 304/305). The median first day for flow under 300 m³/s is October 22nd (Julian Day 295/296; Figure 4-2).





'Minimum Flow' is the day on which the lowest yearly flow is recorded. The spring freshet starts when the flow rate increases to above 1000 m^3 /s. 'Peak Flow' is the day on which the highest freshet flows are recorded. 'Start of Winter Baseflow' occurs when flows decrease to below 300 m^3 /s.

Over the period of record, there has been no significant trend for the Julian day on which minimum flow occurs, freshet begins or maximum freshet flow rates occur (Table 4-1). There has, however, been a marginally significant increase in the date on which baseflow begins in the fall (Table 4-1). The later date for the start of baseflow is consistent with the trend towards increasing seasonal baseflow (see below).

There is also considerable year to year variability in flow rates. Annual peak freshet flow rates below 2000 m³/s and over 8000 m³/s have been recorded (Figure 4-1). The highest peak flow rates apparently occur shortly after the peak spring flows (Figure 4-1), which perhaps indicates heavy spring runoff compounded by heavy spring rains

No significant trends in annual mean flow, or total annual flow for both the entire 40 years of record, and over the last decade (Table 4-1: Appendix D; Figure D-1 and D-2) were observed for the Peel River above Fort McPherson. The lack of trends indicates that the total volume of water flowing within the Peel River above Fort McPherson is the same now as it was 40 years ago, and suggests that overall the hydrological cycle has remained unchanged over the period of record.

Table 4-1: Mann-Kendall Trends Statistics for the "Peel River above Fort McPherson"					
Eleve Cotogony	1970-2010		2001-2010		
Flow Category	p-value	Significance	p-value	Significance	
Average Total	0.122	NS	0.601	NS	
Total Yearly	0.116	NS	0.601	NS	
Maximum Daily	0.861	NS	0.216	NS	
Minimum Daily	< 0.0001	*** (+)	0.484	NS	
Baseflow ¹	< 0.0001	*** (+)	1.000	NS	
Freshet ¹	0.361	NS	0.484	NS	
Recession ¹	0.917	NS	0.727	NS	
January	< 0.0001	*** (+)	0.601	NS	
February	< 0.0001	*** (+)	0.727	NS	
March	< 0.0001	*** (+)	0.484	NS	
April	< 0.0001	*** (+)	1.000	NS	
Мау	0.559	NS	0.291	NS	
June	0.003	** (-)	0.216	NS	
July	0.486	NS	1.000	NS	
August	0.385	NS	0.601	NS	
September	0.428	NS	0.862	NS	
October	0.025	* (+)	1.000	NS	
November	0.007	* (+)	0.727	NS	
December	< 0.0001	*** (+)	0.601	NS	
Date of Annual Minimum	0.089	NS			

Table 4-1: Mann-Kendall Trends Statistics for the "Peel River above Fort McPherson"				
Flow Category	1970-2010		2001-2010	
	p-value	Significance	p-value	Significance
Flow				
Date of First Day Above 1000 m ³ /s	0.100	NS		
Date of Peak Freshet Flow	0.064	NS		
Date of First Day Below 300 m ³ /s	0.006	* (+)		
¹ Baseflow: ~October 15 to ~April 30, and/or flow <300m ³ /s, Freshet: ~April 15 to June 30, and flow >300 m ³ /s, Summer Recession: July 1 to ~October 31, and flow >300 m ³ /s P-value: <0.05 = Marginally Significant (*), <0.005 = Moderately Significant (**), <0.0001 = Highly Significant (***)				

However, there has been a highly significant (p< 0.0001) positive trend in the annual minimum daily flow rate in the period 1970 to 2010 (Table 4-1: Figure 4-3: Appendix D; Figure D-3). It is apparent that the minimum volume of water flowing under the ice in winter has increased; in the period from 1970 to 1975, the annual minimum flow rate was approximately 50 m³/s, while over the past five years the minimum annual flow rate has been measured at approximately 100 m³/s (Figure 4-3).



Figure 4-3: Annual Daily Minimum Streamflow (Peel River above Fort McPherson; 1970-2010)

There has also been a highly significant (p<0.0001) increase in mean winter baseflow rate over the past 40 years (Figure 4-4; Table 4-1), which includes the date of minimum flow rate discussed above. In the period from 1970 to 1975, baseflow averaged approximately 75 m^3/s ,

while over the period 2005 to 2010, average baseflow was approximately 150 m³/s (Figure 4-4). Consistent with the increasing trend in baseflow, there have also been highly significant (p<0.0001) increases in mean monthly flow rates in the Peel River above Fort McPherson from December to April over the period of record (Table 4-1). These results suggest that groundwater and/or shallow subsurface flow¹ has increased in the watershed during the winter baseflow period and confirms a fundamental alteration in the seasonal timing of the hydrological cycle.



Figure 4-4: Mean Winter Baseflow (Peel River above Fort McPherson; 1970-2010)

In contrast to the increases seen in winter baseflow, there has been no significant alteration in flow rates overall during spring freshet, or during the summer recession flow period (Appendix D; Figures D5 and D6: Table 4-1), either over the period of record, or over the past 10 years. However, there has been a moderately significant (p<0.003) decrease in flow during June, which is the month immediately following the dates (i.e., May) of annual maximal flow (Table 4-1). A possible explanation is that declines in freshet flows occur more rapidly than in the past and/or that early summer precipitation has decreased over the same time period. The relatively rapid decline in freshet flows may be due to a smaller pre-freshet snowpack, which would be consistent with increased flow volumes during seasonal baseflow.

Above Fort McPherson, in the Peel River, there has been no significant increase in the annual maximum daily flow (Table 4-1; Appendix D, Figure D-7). Variability in flow rates during the spring freshet and summer recession periods has also not increased noticeably (Appendix D,

¹ Shallow subsurface flow refers to water moving above the permafrost table prior to completely freezing back in the winter.

Figures D-5 and D-6). This suggests that the frequency and occurrence of extreme events such as intense summer rainstorms, precipitous spring freshet melting events, and/or unusually large snowpack have not increased within the Peel River watershed. Consistent with this is the fact that the Q_{10} (which represents high flows) for the last decade is identical to the Q_{10} calculated for the period 1970-2010 (Figure 4-5).

In contrast, variability in minimum baseflow rates has been relatively large over the past 10 years (Figures 4-3 and 4-4), and this has been mirrored by an increase in the Q_{90} (which represents low flows) over the last decade versus the period of record (Figure 4-5). It is apparent that variability in flow rates in the winter has increased, and that winter baseflow conditions have become less predictable.



Figure 4-5: Flow Duration Curve for Peel River above Fort McPherson

The results of the hydrological flow and trends analysis suggests that the hydrological cycle within the Peel River watershed has not experienced a significant total increase in yearly flow over the past 40 years, but that the predictability and seasonal distribution of flow has changed. There has been an increase in winter baseflow over the period of record, and a corresponding decrease in flow during late spring freshet. Flow rates during the baseflow period have also increased in variability, such that there are larger year-to-year differences in baseflow. These results suggest that new hydrological flowpaths may have developed in association with warming permafrost (Kokelj and Burns, 2005).

4.2 WATER QUALITY - PEEL RIVER ABOVE FORT MCPHERSON

Water quality samples have been collected from the Peel River (above Fort McPherson). Samples have been collected by Environment Canada since 1960 and contains the largest and longest set of water chemistry data for the Peel River watershed. Analysis of the data is separated into four parts; Major Water Chemistry Variables, Dissolved and Total Trace Metals, Nutrients, and Organic Contaminants of Potential Concern. Analysis is variable for each section because of variability in the type and amount of available data.

4.2.1 Major Water Chemistry Variables

The major water chemistry variables include; turbidity, pH and conductivity, the cations calcium, magnesium, sodium and potassium, and the anions chloride, total alkalinity and sulphate. These are the variables that are at the highest concentration and therefore define the hardness, buffering capacity and ionic character of the water within the Peel River watershed. The concentration of the major ions within the Peel River can be considered to be the result of mechanical and chemical weathering, runoff flow, and groundwater flow within the larger watershed.

4.2.1.1 Turbidity and Total Suspended Solids

There are almost 45 years of turbidity and total suspended solids (TSS) data (Appendix C) collected from the Peel River above Fort McPherson (Figure 2-1). Turbidity is positively correlated to TSS ($R^2 = 0.79$), so for the purposes of this report, turbidity is the variable used to describe the characteristics of suspended material within the Peel River. It is expected that the major contributor to turbidity in the Peel River is the presence of inorganic clay, silt and sand particles suspended within the water column, and arising from both resuspension of sediments within the Peel River and mechanical weathering of upland watershed materials. Considering the mountainous terrain and the relatively sparse vegetation within much of the watershed, the amount of mechanical weathering is likely considerable. Within the Peel River, there is a strong positive log/log relationship between flow rate and turbidity (Figure 4-6). As flow increases, the amount of entrained particulate matter also increases. At flow rates below 300 m³/s, turbidity is consistently less than 10 NTU, and often measured at less than 1 NTU (Figure B-64; Table 4-2). Once flow rates increase further, turbidity begins to increase exponentially (Figure B-64). Over the period of record, the highest recorded turbidity has been measured at over 1,300 NTU at a flow rate of just over 5,000 m³/s (Figure 4-6; Table 4-2). The seasonal and yearly rhythm of flow within the Peel River, and the correlation between flow rate and turbidity, is of critical importance because the interplay between these two variables defines seasonal water chemistry within the Peel River for both major and trace ions.



Figure 4-6: The Relationship between Turbidity and Flow Rate (Peel River above Fort McPherson)

Because turbidity responds strongly to flow, there is a yearly seasonal trend in turbidity (Figure B-65), with a peak during the spring freshet (Figure 4-7). Plotting turbidity from 1989 to 2010 indicates the extreme seasonal variability that is observable over time, and also indicates considerable yearly variability (Figure B-65). In some years peak turbidity levels barely reach 200 NTU, while in other years turbidity exceeds 800 NTU (Figure B-65). During the winter baseflow period, turbidity is consistently less than 10 NTU and usually less than 1 NTU. At the onset of the spring freshet, turbidity increases and it is during this time that the highest turbidity levels have been recorded (Figure 4-7). Over the summer recession period, turbidity levels decline, particularly when flow rates fall to less than 1000 m³/s. However, during the recession, turbidity levels are the most variable (Table 4-2) and can reach levels comparable to the spring freshet (Figure 4-7), likely after heavy summer rainfall events when flow rates can increase sharply.


Figure 4-7: The Relationship between Season, Flow & Turbidity (Peel River above Fort McPherson)

Definition of baseline conditions for turbidity is difficult because of the correlation of turbidity with flow, and because of the large variability in flow rate through seasonal and yearly cycles (Figure 4-1). However, baseline conditions can be described for seasonal periods with the understanding of the inherent uncertainty in the definition of baseline due to the considerable variability within any seasonal period (Table 4-2). The Coefficient of Variation (CV) for turbidity reflects this variability; the CV values for turbidity are greater than for all other major ions. There is also a relatively large difference between the median and mean turbidity values (Tables 4-2 & 4-3 & 4-5); the median is considerably less in all three periods. This indicates the presence of 'anomalous' or 'rare' high turbidity values in all seasons.

Within the period of record, turbidity values vary from 0.6 NTU to 1340 NTU (Table 4-2). The median turbidity in the Peel River above Fort McPherson is 1.7 NTU for winter baseflow, 236 NTU for spring freshet, and 38 NTU for the summer recession (Figure 4-8: Table 4-2). Upper cutoff values are 3.6 NTU for winter baseflow, 947 NTU for spring freshet, and 264 for summer recession (Figure 4-8: Table 4-2). Levels of turbidity above these cutoff values occur within each season (defined as values above 'Max' in Table 4-2), and indicate unusual conditions within the Peel River and/or sampling error, though any such determination, as discussed, should be made with caution (Table 4-2). Statistical analysis indicates that the differences in turbidity between the three seasons are highly significant (p<0.0001; Figure 4-8; Table 4-3).



Figure 4-8:Baseline Conditions for Turbidity (Peel River above Fort McPherson).

The (letters) indicate	significance	categories
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Table 4-2	Table 4-2: Peel River above Fort McPherson (1960-2010) Baseline Water Chemistry (mg/L) for Major Ions												
Analyte	Season	N ¹	BDL	Min	Low	25%	50%	75%	High	Max	Mean	STD	CV
	Baseflow	85	0	210	280	350	390	414	500	520	378	28	7
Conductivity	Freshet	38	0	103	103	190	240	262	345	345	234	50	21
	Recession	66	0	135	205	290	338	379	512	512	336	64	19
	Baseflow	77	0	7.5	7.5	7.8	7.9	8.0	8.2	8.4	7.9	0.2	3
рН	Freshet	34	0	6.7	7.4	7.7	7.9	8.0	8.2	8.2	7.8	0.3	4
	Recession	61	0	7.5	7.8	8.0	8.1	8.2	8.5	8.6	8.1	0.2	2
	Baseflow	76	0	0.6	0.6	1.2	1.7	2.6	3.6	20	2.5	3.2	128
Turbidity	Freshet	36	0	50	50	160	236	494	942	1340	354	285	81
	Recession	61	0	1.0	1.0	17	38	119	264	1210	116	219	189
	Baseflow	76	0	98	130	143	150	155	163	174	146	14	10
l otal Alkalinity	Freshet	32	0	52	52	75	82	93	117	117	82	14	17
, and an inty	Recession	57	0	88	88	105	117	124	136	136	115	12	10
	Baseflow	81	0	37	46	51	54	57	63	63	53	5	9
Dissolved	Freshet	34	0	22	22	29	32	35	43	43	32	5	16
	Recession	66	0	25	31	41	46	50	58	58	45	6	13

Table 4-2	Table 4-2: Peel River above Fort McPherson (1960-2010) Baseline Water Chemistry (mg/L) for Major Ions												
Analyte	Season	N ¹	BDL	Min	Low	25%	50%	75%	High	Max	Mean	STD	CV
	Baseflow	81	0	9.6	14	16	17	18	20	20	17	1.9	11
Dissolved	Freshet	33	0	5.8	5.8	7.8	9.4	11	14	14	9.4	2.3	24
magneelam	Recession	61	0	7.8	9.9	13	15	16	21	21	15	2.3	15
	Baseflow	81	0	3.9	3.9	4.8	5.1	5.4	6.3	10.6	5.4	1.2	22
Dissolved	Freshet	34	0	1.8	1.8	2.4	2.7	3.2	4.3	6.7	2.9	1.0	34
Soulum	Recession	66	0	2.5	2.5	3.8	4.5	5.1	6.5	12.5	4.6	1.4	30
	Baseflow	81	0	0.40	0.40	0.50	0.53	0.60	0.75	1.19	0.58	0.14	24
Dissolved	Freshet	34	0	0.25	0.40	0.56	0.63	0.74	0.92	1.11	0.66	0.14	21
1 otaootani	Recession	66	0	0.25	0.40	0.50	0.54	0.60	0.75	1.02	0.56	0.13	23
	Baseflow	80	0	32	32	48	54	66	89	89	57	13	23
Dissolved	Freshet	34	0	18	18	29	38	47	61	78	40	13	33
Cuprato	Recession	67	0	21	21	43	57	72	100	100	58	19	33
	Baseflow	80	0	2.3	2.3	3.4	3.7	4.2	5.0	12.0	4.0	1.6	40
Dissolved Chloride	Freshet	34	0	0.8	0.8	1.0	1.3	1.6	2.2	7.6	1.5	1.1	73
	Recession	67	0	1.0	1.0	1.5	1.8	2.1	2.9	3.7	1.8	0.5	28

1. N= number of samples; BDL = number of samples Below Detection Limit; Min = the lowest recorded value; Low = the lower limit of baseline chemistry beyond which the data is considered an outlier; 25% = the 25th percentile of the data; 50%= the median of the data; 75% = the 75th percentile of the data; High = the upper limit of baseline chemistry beyond which the data is considered an outlier; Max = the highest recorded value; Mean = the average of the data; STD = standard deviation; CV = coefficient of variation (STD/Mean)

Table 4-3: Sta	tistical Summary	for Seasonal I	Differences of	Major Ions (1	960-2010)
Analyte	Season	Mean	Median	P-value	Range ¹
	Baseflow	378	390		A
Conductivity	Freshet	234	240	<0.0001	С
	Recession	336	338		В
	Baseflow	7.9	7.9		В
рН	Freshet	7.8	7.9	<0.0001	В
	Recession	8.1	8.1		A
	Baseflow	2.5	1.7		С
Turbidity	Freshet	354	236	<0.0001	A
	Recession	116	38		В
	Baseflow	53	54		A
Dissolved Calcium	Freshet	32	32	<0.0001	С
	Recession	45 46			В
Dissolved Magnesium	Baseflow	17	17	<0.0001	A

Table 4-3: Sta	atistical Summary	y for Seasonal	Differences of	f Major Ions (1	960-2010)
Analyte	Season	Mean	Median	P-value	Range ¹
	Freshet	9.4	9.4		С
	Recession	15	15		В
Dissolved Sodium	Baseflow	5.4	5.1	<0.0001	А
	Freshet	2.9	2.7		С
	Recession	4.6	4.5		В
	Baseflow	0.58	0.53		В
Dissolved Potassium	Freshet	0.66	0.63	0.0003	А
	Recession	0.56	0.54		В
	Baseflow	57	54		А
Dissolved Sulphate	Freshet	40	38	<0.0001	В
	Recession	58	57		А
	Baseflow	4.0	3.7		А
Dissolved Chloride	Freshet	1.5	1.3	<0.0001	С
	Recession	1.8	1.8		В
	Baseflow	146	150		А
Total Alkalinity	Freshet	82	82	<0.0001	С
	Recession	115	117]	В
¹ Range = Significance ca	ategories. Differen	t letters indicate	the flow period	ds are significar	ntly different.

Because of the significant increases in flow during winter baseflow, and because of the significant reductions in flow during the beginning of the summer recession in June (Table 4-1), it is reasonable to expect that significant trends in turbidity might also have occurred over the period of record.

Trends analysis, however, indicates that there have been no trends in turbidity (either increasing or decreasing) for either the spring freshet or the summer recession, and that there has been only a marginally significant positive trend in turbidity during winter baseflow (Table 4-4). The increasing trend in winter baseflow, however, is not an important consideration in the overall chemistry of the Peel River, because the turbidity levels during the winter baseflow period are relatively low, and the small observed increases in turbidity are not likely to alter the chemistry of other ions.

	Table 4	-4: Pe	el River abo	ve Fort Mc	Pherson (1960	-2010) Trends	s Analysis fo	or Major Ion	IS	
Analyte	Season	N ¹	1979-2010 P-value	Direction	Comparison- wise Significance	Experiment- wise Significance	2001-2010 P-value	Direction	Comparison- wise Significance	Experiment- wise Significance
Conductivity	Baseflow	29	0.151		NS	NS	0.038	+	*	NS
	Recession	30	0.021	+	*	NS	0.142		NS	NS
рН	Baseflow	26	0.076		NS	NS				
	Recession	30	0.017	+	*	NS	0.126		NS	NS
Turbidity	Baseflow	27	0.026	+	*	NS				
	Freshet	21	0.225		NS	NS	0.024	-	*	NS
	Recession	30	0.058		NS	NS	0.174		NS	NS
Dissolved Calcium	Baseflow	27	<0.0001	+18%	***	***	0.542		NS	NS
	Freshet	19	0.0095	+16%	*	NS	0.054		NS	NS
	Recession	30	<0.001	+21%	***	**	0.265		NS	NS
Dissolved Magnesium	Baseflow	27	<0.001	+19%	***	**	0.301		NS	NS
	Freshet	19	0.0016	+50%	**	*	0.076		NS	NS
	Recession	30	0.0011	+23%	**	*	0.142		NS	NS
Dissolved Sodium	Baseflow	27	0.015	+	*	NS	0.377		NS	NS
	Recession	30	0.056		NS	NS	0.054		NS	NS
Dissolved Potassium	Baseflow	27	0.265		NS	NS	0.417		NS	NS
	Recession	30	0.071		NS	NS	0.464		NS	NS
Total Alkalinity	Baseflow	25	0.264		NS	NS				
	Recession	29	0.440		NS	NS	0.542		NS	NS
Dissolved Sulphate	Baseflow	27	<0.0001	+47%	***	***	0.377		NS	NS
	Freshet	19	0.0025	+75%	**	*	0.301		NS	NS
	Recession	30	<0.0001	+77%	***	***	0.237		NS	NS
Dissolved Chloride	Baseflow	27	0.164		NS	NS	0.377		NS	NS
	Recession	30	0.123		NS	NS	0.36		NS	NS
Comparison * <0.05 Experiment * <0.005 ** <0.001										

4.2.1.2 Major lons

As mentioned above, the interplay between season, turbidity and surface and groundwater flow within the Peel River also profoundly affects the chemistry of all other major ions. Calcium is the dominant cation within the Peel River watershed (Table 4-2) and is appropriate for use as an example to illustrate the interaction between season, turbidity, flow and ionic concentration.



Figure 4-9: The Relationship between Flow and Dissolved Calcium Concentration

The concentration of calcium within the Peel River is variable over time, with values ranging from a low of 22 mg/L and a high of 63 mg/L (Table 4-2). Through the period of record, the overall variability has resulted in a coefficient of variation (standard deviation/mean) of 20% for estimation of calcium concentration (Table 4-5). Variability of the other major ions is comparable, with the notable exceptions for pH which varies little, and turbidity, which exhibits extreme variability over the period of record (Table 4-5). The consistency of pH values and variability of turbidity are not surprising given: 1) the high buffering capacity within the watershed that stabilizes pH; and 2) the variability in flow that affects turbidity. The concordance of median and mean values, however, is surprising. Water-chemistry data often exhibit non-normal distributions, with occasional high values skewing mean values upwards. This is observed for turbidity, but for none of the other major ions (Table 4-5).

The open circles indicate the data points used in the linear regression to define maximum concentration.

Table 4-5:	Table 4-5: Peel River above Fort McPherson Comparison of Mean and for Median Major Ions Coofficient of												
Analyte	Median	Mean	Standard Deviation	Coefficient of Variation									
Conductivity	345	334	79	24									
рН	8.0	7.9	0.2	3									
Turbidity	14	116	225	194									
Total Alkalinity	124	123	28	23									
Dissolved Calcium	48	46	9.5	20									
Dissolved Magnesium	16	15	3.5	24									
Dissolved Sodium	4.8	4.6	1.5	33									
Dissolved Potassium	0.54	0.59	0.14	24									
Dissolved Sulphate	53	54	17	31									
Dissolved Chloride	2.3	2.7	1.7	60									

In contrast to turbidity, there is a decrease in the concentration of dissolved calcium (Figure 4-9) with increasing flow. This suggests that the main source of dissolved calcium in the Peel River above Fort McPherson is from chemical weathering in the watershed. That is, calcium dissolves into runoff as precipitation occurs and percolates through the watershed soils, then enters the river through surface and/or groundwater flow. During periods of very high flow, the rate of dissolution appears to decrease. During periods of low flow, the rate of dissolution increases or the relative contribution of groundwater to total flow increases. The same relationship holds for the cation magnesium; the anions sulphate, chloride and total alkalinity, and conductivity (Figures B-68 to 83; Table 4-3).

The relationship between flow and ion concentration, however, is not so much related to the mean calcium concentration for any given flow rate, but rather to the maximum concentration for any given flow rate (Figure 4-9). As the flow rate increases, the maximum calcium concentration decreases in a linear relationship. At lower flow rates, the concentration is variable and can range from high to low values, but at higher flow rates the highest recorded calcium concentrations progressively decrease (Figure 4-9). The form of this relationship indicates that the calcium concentration is not so much altered by turbidity, but by an interaction between the flow itself and chemical weathering processes. The relationship is not as obvious at flow rates less than 1000 m³/s and particularly so at flow rates less than 300 m³/s (Figure B-66). At the lower flow rates, calcium concentrations vary from less than 40 mg/L to over 60 mg/L (Figure 4-9). The reason for this relatively large variability in calcium concentration is unclear. It might be related to year over year fluctuations in chemical weathering, alterations in groundwater

interaction, or perhaps changes over time in analytical procedures. Whatever the cause, the result is that outliers in calcium concentration are at low rather than high concentration (Table 4-2). This is somewhat unusual for water-chemistry data. Magnesium, sodium, sulphate and conductivity follow the same pattern (Figures B-68 to 83). For total alkalinity and chloride, although their concentrations also decrease at increasing flow rates, there is an exponential decrease in concentration with increased flow (Figures B-68 and 70). The reasons for the slightly different relationship between flow and concentration for these two variables are unknown.

In contrast are the responses of pH and potassium to changes in flow rate (Figures B-76 and 78). Potassium concentrations increase slightly during periods of high flow, and pH is relatively stable, regardless of flow. It is perhaps expected that the pH would be relatively stable within the watershed (as mentioned above), particularly considering the relatively high buffering capacity (i.e., total alkalinity) within the Peel River, but the different response of potassium to flow indicates that the source of potassium within the watershed is fundamentally different than for the other major cations. Potassium is at a relatively low concentration (Table 4-2) and, as mentioned, increases slightly in concentration during the spring freshet (Figure B-79; Table 4-3). This suggests that the major source of potassium within the watershed is related to seasonal fluctuations in turbidity rather than flow rate and/or groundwater interactions. It appears that potassium is dominantly associated with particulate material (Table 4-16) and undergoes dissolution into the water column during periods of high turbidity/flow, rather than entering the water through chemical weathering within the watershed. This response is similar to that seen for total trace metals, though in the latter case the trace ions do not appear particularly soluble (see Section 4.1.2 below).



Figure 4-10: The Effect of Season and Flow Rate on Calcium Concentration

Not unexpectedly, there are consistent and significant alterations in calcium concentration on a seasonal basis (Figure 4-10 and 4-11; Table 4-3). Concentrations are relatively high during

winter baseflow and drop precipitously at the onset of spring freshet (Figure 4-10 and 4-11; Table 4-3). Once the spring freshet progresses, calcium concentrations within the Peel River begin to increase and it is noteworthy that the increases occur over time regardless of flow rates (Figures 4-10 and 4-11; Table 4-3). During the summer recession, for instance, there appears to be little difference in Ca concentration between samples taken during periods of high flow or periods of low flow (Figure 4-10 and 4-11; Table 4-3). This suggests that the decrease in Ca concentration observed at the start of the spring freshet is caused not so much by the increased flow, but by the lack of chemical weathering in early spring when the watershed material is frozen and unavailable for dissolution reactions. Once the snow and ice melt, then chemical weathering processes and groundwater interactions likely dominate and slowly increase concentration occurs during the summer recession, not coincidentally during the period with the greatest variability in flow rates (Figure 4-10 and 4-11; Table 4-3) and also likely the greatest amount of chemical weathering and groundwater flows.

The significant seasonal pattern observed for calcium is also observed for the cations magnesium and sodium, and the anions chloride, total alkalinity and sulphate, but not for pH or potassium (Figures B-68 to 83; Table 4-3). This differentiation of pH and K is consistent with the separate relationship observed for flow rate. This suggests, again, that the processes that determine the level of these variables are different than for the other major ions.

Water chemistry data for the major ions is adequate for definition of baseline conditions within the lower reaches of the Peel River (Table 4-2). There is a mostly consistent yearly record of concentration for all major variables over a period of approximately 30 years, the data can be conveniently separated by season, and there appears to be relative consistency in concentration over time for most seasonal periods and for most variables (though not all, see below).



Figure 4-11: The Effect of Season and Time on Dissolved Calcium Concentration in the Peel River above Fort McPherson

The (letters) indicate significance categories (cf. Table 4-3).

For calcium, the median concentration within the lower reaches of the Peel River is 54 mg/L for winter baseflow, 32 mg/L for spring freshet, and 46 mg/L for the summer recession (Figure 4-11:Table 4-2). Upper cutoff values are 63 mg/L for winter baseflow, 43 mg/L for spring freshet, and 58 mg/L for summer recession (Figure 4-11:Table 4-2). Lower cutoff values are 46 mg/L for winter baseflow, 22 mg/L for spring freshet, 31 mg/L for summer recession. Levels of calcium above or below these cutoff values would be considered outliers, but for Ca these occur only rarely within the period of record and only for the lower cutoff values (Table 4-2). Statistical analysis indicates that the differences in calcium concentration between the three seasons are highly significant (p<0.0001; Figure 4-11; Table 4-3). The lowest concentrations, as discussed, occur during the spring freshet and the highest concentrations occur during winter baseflow (Figure 4-11). Identical patterns are observed for conductivity, magnesium, sodium, sulphate, chloride and total alkalinity (Table 4-3). The opposite pattern is observed for turbidity (see Section 4.2.1.1) and potassium.

Trends analysis indicates that there are moderately to highly significant positive trends over the period of record for calcium, magnesium and sulphate (Table 4-4). Moreover, over the period of record the concentrations of these three ions have increased in all three seasonal periods; 15-20% for calcium, 20-50% for magnesium, and 50-75% for sulphate (Table 4-4). For calcium, the concentration data are variable from year-to-year, but are clearest for the winter baseflow season (Figure B-84; Figure 4-12). The significant trends suggest that the amount of chemical weathering within the watershed has consistently increased year after year, and/or that the

contribution of groundwater to total flow has also increased. It is expected that groundwater would have a higher concentration of the major ions due to the longer contact with watershed material and the greater opportunity for chemical weathering. Either of these processes would result in the observed increases, particularly for cations (Kokelj and Burns 2005). Burns and Kokelj (2005) suggest that the increase in concentrations of major ions (particularly during the summer) is linked to the development of large permafrost disturbances which are making immense volumes of previously frozen materials available to chemical weathering, erosion and runoff into the river.





Figure 4-12: Calcium Concentration (A) and Loading Rate (B) over the Period of Record in the Peel River above Fort McPherson

Despite the significant trend in calcium concentration, there has been no observable increase in loading rate (Figure 4-12B). This is somewhat unexpected, but suggests that the considerable variability in flow from year-to-year obscures the relationship between calcium concentration and calcium loading rate.

4.2.2 Total Trace Metals

Of the fifteen trace metals that were analyzed for total concentration, all but one were positively correlated to turbidity, with correlation coefficients ranging from 0.38 for Cd, to 0.96 for Al (Appendix B: Figures B-49 to B-63). The lower correlation coefficients were generally associated with trace metals that were at or near the detection limit (e.g., Cd). The data indicate that the amount of total trace metals increases as the amount of entrained particulates (i.e. turbidity) increases, though the combined trace metal data (Figure 4-13) indicate that the correlation between turbidity and total trace metal concentration is not linear for many of the metals. These include AI, Be, Co, Cr, Cu, Li, Mn, Ni, Pb, and Zn (Appendix B: Figures B-49 to B-63). As turbidity increases, there is a proportionately lower increase in metal concentration. This suggests that the character of the particles changes as turbidity increases. Considering that turbidity is positively correlated to flow rate (Figure 4-6), this suggests that at high flow rates and high turbidity there are fewer metals associated with the particulate fraction than at low flow rates and low turbidity. This is reasonable, considering that at relatively low flow rates it is likely that silts and clays dominate, while at higher flow rates, proportionately larger particles become entrained within the water column. Smaller particles have higher cation exchange capacity, and so would be expected to contain relatively higher metal concentrations.

Metals for which the best fit line was linear included Ba, Cd, Mo, and V. The data suggest that these metals may be at a relatively low concentration within the particulate fraction, and variability within the data perhaps obscures the relationship between particle size and metal content. Alternatively, it is possible that concentrations of these cations are independent of particle size.





Open circles are the combined daily metal relative concentrations. Closed circles are the 'mean relative metal concentration' data with which the regression was calculated. The relationship is polynomial, so should not be extrapolated.

The lone exception to the relationship between turbidity and concentration was total Sr, the concentration of which varied throughout the year in the same way as the major ions (Appendix B: Figure B-63). This suggests that Sr is not a major component of the inorganic particulate material entrained within the Peel River, but rather enters the river through weathering and runoff from within the watershed.

Because total metals are correlated to turbidity, it is difficult to undertake a trends analysis or to define 'baseline' chemistry for total metals. Turbidity is highly variable seasonally, so trends analysis and definition of baseline can only be calculated within narrowly defined turbidity limits. This constraint is further exacerbated by the sporadic sampling that has been undertaken over time for even the most complete set of data, so that there are simply not enough data for any defined level of turbidity. Perhaps the one exception is chemistry data for winter baseflow, which is relatively extensive due to the length of the winter baseflow period. Trends analysis on winter baseflow indicates there have been no trends in total metal concentration for nine of the ten metals for which there were enough data (Table 4-6). The one exception was Li, which has significantly decreased over the period of record (Table 4-6). These results, however, must be interpreted with caution, because even for these ten metals, trends analysis was only undertaken for 12 or 13 years out of an 18-year record. The gaps in data compromise the validity of the trends analysis. Because the amount of particulates within the river has not changed significantly over the past 40 years (Table 4.4), it is also expected that the amount of total metals has also not increased or decreased over the same time period.

Table 4	Table 4-6: Peel River above Fort McPherson Trends Analysis for Total Metals in the Winter Baseflow Period											
Total Metal	Season	N1	1993-2010 p-value	Direction	Comparison wise Significance	Experiment wise Significance						
Aluminum	Baseflow	12	0.250		NS	NS						
Chromium	Baseflow	13	0.271		NS	NS						
Copper	Baseflow	13	0.590		NS	NS						
Iron	Baseflow	13	0.737		NS	NS						
Lithium	Baseflow	13	0.002	-	**	*						
Manganese	Baseflow	13	0.435		NS	NS						
Molybdenum	Baseflow	13	0.495		NS	NS						
Nickel	Baseflow	13	0.100		NS	NS						
Strontium	Baseflow	13	0.426		NS	NS						
Zinc	Baseflow	12	0.947		NS	NS						
1. Out of a total	of 18 years.	The missing d	ata compromis	ses the trends	analysis.							

During periods of high flow, when turbidity and particulate load are considerable, total concentrations of aluminum, copper, zinc and many other metals are well above government guideline values for protection of aquatic life (Table 4-7).

Table 4-7: CCME With	Table 4-7: CCME Chronic Guideline Values for the Protection of Aquatic Life Compared With Maximum Dissolved and Total Metal Concentrations											
Element	Symbol	Guideline Value ¹	Units	Max. Diss. [Me ⁺] ⁴	Max. Total [Me [⁺]]							
Aluminum	AI	100*	ug/L	127	19967							
Cadmium	Cd	0.054 ²	ug/L	0.231	5.6							
Chromium (VI)	Cr	1	ug/L	0.61	30.1							
Cobalt ³	Со	4	ug/L	0.49	14.6							
Copper	Cu	3.87 ²	ug/L	4.43	38.7							
Iron	Fe	300	ug/L	259	59833							
Lead	Pb	6.63 ²	ug/L	69	22.6							
Manganese ³	Mn	1400	ug/L	37	476							

Table 4-7: CCME With	Chronic Guide Maximum Diss	line Values for solved and Tota	the Protection Il Metal Conce	of Aquatic Life	e Compared							
Element	Symbol	Guideline Value ¹	Units	Max. Diss. [Me⁺] ⁴	Max. Total [Me [⁺]]							
Molybdenum	Мо	73	ug/L	1.27	3.47							
Nickel	lickel Ni 148 ² ug/L 5.91 49.5											
Vanadium	inadium V 6 ³ ug/L 0.5 71											
Zinc	Zn 30 ug/L 16 198											
¹ Long-term guideline valu ts.ccme.ca/?chems=all&ch ² Calculated at a hardness ³ BC Guideline Value (BCM ⁴ [Me ⁺] = Metal concentration	¹ Long-term guideline value for the Protection of Aquatic Life. CCME values accessed at; http://st- ts.ccme.ca/?chems=all&chapters=1 ² Calculated at a hardness of 178 mg/L as CaCO ₃ ³ BC Guideline Value (BCMOE 2012) ⁴ [Me ⁺] – Metal concentration											
* dissolved metal guideline NOTE: Period of Record for Dissolved Metals (2006 to 2011); Period of Record for Total Metals (1983 or 1993 to 2011)												

The guideline value for copper, for example, is approximately 3-4 ug/L, while the highest concentration of total copper was measured at almost 40 ug/L (Table 4-7; Figure 4-14). This is a considerable exceedance of the CCME guideline value, and most of the metals that have guideline values show similarly high concentrations of total metals. The exceptions are Mn, Mo and Ni which are all below guideline at even the highest total concentration (Table 4-7).



Figure 4-14: The Relationship between Turbidity and Copper at Peel River above Fort McPherson

Red data points are considered outliers for the purposes of describing the correlation. The 'outlier' samples were consistently different for almost all the metal data examined. The red line is the CCME guideline for Protection of Aquatic Life.

These conditions, however, are natural to the Peel River, so that fish communities are expected to be adapted to the presence of elevated total metal concentrations. In addition, metals bound to particles in the water are not considered biologically available to the aquatic communities that inhabit the Peel River watershed; it is generally considered that only metals actually dissolved in the water can cause toxicity (e.g., Vigneault and Gopalapillai 2009). Note that most dissolved metal concentrations except Al, Cd, Cu and Pb were always below the total metal guideline. Related to this concept is the expectation that metals bound to the particulate fraction do not easily exchange with the dissolved fraction. If this is the case, then the concentration, turbidity or flow rate (see Section 4.2.3 below).

Water quality based on total vs dissolved metal concentration can be compared using the Water Quality Index (WQI). Calculation of the WQI (CCME 2001) indicates that water in the lower reaches of the Peel River is considered 'marginal' (60%) using total metals, but is considered 'good to excellent' (94%) using dissolved metals. For total metals, water quality is considered threatened or impaired, with conditions that 'often depart from natural or desirable levels', while for dissolved metals, conditions are considered to be 'very close to natural or pristine levels'. Considering the relatively pristine condition of the Peel River watershed, it is clear that total metal concentrations do not reflect the health of the watershed.

4.2.3 Dissolved Trace Metals

The chemistry of dissolved trace metals is relatively complex. The marked seasonality of flow within the Peel River watershed potentially reduces trace metal concentrations through dilution with spring melt water, and the marked seasonality of turbidity and total metal concentration potentially increases dissolved concentrations through exchange between particulate and dissolved fractions. The former dynamic is identical to that observed for major ions and is considered to be caused by variation in the amount of weathering versus flow through the seasons. The latter dynamic is caused by equilibrium reactions that might occur between the dissolved and particulate trace metal fractions. The interplay between these two processes potentially creates a variety of responses, depending on the metal. These relationships are further obscured for this particular dataset because of the limited amount of dissolved metal data, and its relatively low precision.

Of the 22 metals that were analyzed for dissolved concentration, 20 showed a decreasing trend in the dissolved/total ratio as turbidity increased (Appendix B, Figures B-1 to B-44). For most metals, such as cobalt, the dissolved/total ratio decreased rapidly as turbidity increased and then continued to decrease at a lower rate at higher turbidity levels (Figure 4-15). This is the relationship that might be expected if the metals bound to the particulate fraction do not readily exchange with the dissolved fraction. The exceptions to this relationship were for B, Li and Sr where there was a negative linear correlation between turbidity and the dissolved/total ratio, and for Mo and Sb where there was no obvious relationship. For Mo and Sb, the dissolved/total ratios were approximately 1 regardless of turbidity (Appendix B, Figure B-29 and B-37), and there was little increase in total Mo as the turbidity increased (Appendix B, Figure B-58). This suggests that the particulate fraction within the lower reaches of the Peel River contains relatively low amounts of Mo (Figure E-8) and Sb (Figure E-6) and consequently almost all is in the dissolved fraction regardless of turbidity levels.



Figure 4-15: The Relationship between Turbidity and the Dissolved/Total Ratio for Cobalt at Peel River above Fort McPherson

It was expected that the dissolved/total ratio would be close to 1 at the lowest levels of turbidity, because in clear water conditions there should be almost no particulates to bind metals (eg Figure 4-15). This was observed for many, but not all metals (Appendix B: Figures B-1 to B-44). For instance, the maximum dissolved/total ratio for AI was less than 0.35 (Appendix B, Figure B-1). Other metals with low dissolved/total ratios at low turbidity were Be, Ce, Cs, Fe, Pb, and V (Appendix B: Figure B-1 to B-44). The reasons for this are unclear, but may be due to sampling and/or analytical error. There were also several instances where the dissolved/total ratio was greater than 1, which can only be caused by lack of analytical precision and accuracy.

Of the 22 metals and ions that were analyzed for dissolved concentration, 20 are not correlated with flow within the Peel River (Appendix B: Figure B-1 to B-44). Copper, for instance, varies consistently between 0.4 and 4 ug/L, regardless of flow rate (Figure 4-16). This suggests that there is no seasonality to dissolved trace metal concentration within the lower reaches of the Peel River. This is an unexpected result, because, as mentioned above, it is reasonable to consider that either concentrations fall as flow increases during freshet (as for the major ions), or concentrations rise due to equilibrium reactions between the dissolved and particulate metal fractions. However, dissolved metals have only been measured since 2006, so the dataset for dissolved metals is relatively limited. In addition, dissolved trace metal concentrations are relatively variable over time within the dataset (Table 4-6). For instance, the coefficient of variation for trace metals averages over 50%, and varies from 14 to 351% (Table 4-6). The causes of the variability are unknown, but are perhaps indicative of the difficulties inherent in measuring dissolved fractions at low concentration. The variability and lack of precision are important to recognize, however, because they perhaps obscure any subtle seasonal

relationships, and ultimately affect definition of baseline conditions. It may also be important to review sampling and analytical protocols to ensure data quality.

Finally, there were no positive correlations between flow and dissolved metal concentration (Appendix B: Figure B-1 to B-44), consistent with the concept of a low rate of exchange between particulate and dissolved metal fractions. This again suggests that particulate metal fractions are not biologically available and are unlikely to cause toxicity within the watershed.



Figure 4-16: Relationship between Flow Rate and Dissolved Copper Concentration in the Peel River above Fort McPherson



The two exceptions to the lack of correlation of flow with concentration are for dissolved Ba and Sr, which were both negatively correlated to flow and were similar to the relationship found between flow and concentration for the major ions (Figure 4-9). This suggests that the major source of Ba and Sr is from weathering and runoff, and that the particulate fraction in the Peel River above Fort McPherson contains relatively insoluble Ba and Sr (Figure E-6). Consistent with this, the concentration of total Ba is relatively constant as the turbidity increases (Appendix B, Figure B-50), and the concentration of total Sr actually decreases at increased flow rates (Appendix B, Figure B-63).

Baseline conditions for dissolved trace element concentrations have been described for 22 elements using box and whisker plots (Table 4-8; Appendix B, Figure B-45). The plots define the median, various data percentiles, and the upper and lower limits of baseline conditions (Table 4-8). For instance, the upper limit of dissolved metal concentration is 106 μ g/L for Al, 3.56 μ g/L for Cu and 4.71 μ g/L for Ni (Table 4-8; Figure 4-17). The upper baseline limit is above

the guideline for AI, just below the guideline for Cu and well below the guideline for Ni (Table 4-7). These three metals describe the range of upper limit values compared with CCME guidelines, but most elements are below guideline (for those with established guideline values). The exceptions are AI and Cu as noted, and also Cd and Pb.



Figure 4-17: Baseline Chemistry for Dissolved AI, Cu & Zn in the Peel River above Fort McPherson

Many of the metals also contain outliers (shown as red diamonds), defined as data points greater than 1.5 times above or below the inter-quartile range (25th to 75th percentile; Figure 4-17; Table 4-8). Outliers may be real and may describe actual unusual conditions, but are often caused by sampling error, analytical error and/or transcription errors, and they can seriously skew understanding of baseline chemistry or temporal trends, particularly if means and standard deviations are used. For instance, upper limits for lead are uncertain, because of the extremely high outlier values that have been measured for Pb (Appendix B; Figure B-45). It is important to understand and define outlier-cutoff concentrations under baseline conditions, because one of the effects of development is to increase variability, and defined cutoff values allow for recognition of such potential increases.

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STATUS AND TRENDS OF FLOW, WATER QUALITY AND SUSPENDED SEDIMENT QUALITY IN THE PEEL RIVER WATERSHED

	Table 4-8: Peel River above Fort McPherson Baseline Water Chemistry (µg/L) for Dissolved Trace Metals													
Analyte (µg/L)	Symbol	CCME*	N	BDL**	Min	Low	25%	50%	75%	High	Max	Mean	STD	C۷
Aluminum	AI	100	19	0	6	6	30	53	67	106	127	54	36	0.67
Arsenic	As	5	19	0	0.12	0.12	0.27	0.33	0.37	0.53	0.53	0.31	0.11	0.36
Boron	В	1500	19	0	6.7	6.7	8.1	9.5	12.1	15.9	15.9	10.0	2.5	0.25
Barium	Ва		19	0	42	42	56	62	79	85	85	66	14	0.22
Beryllium	Be		19	0	0.001	0.001	0.003	0.007	0.008	0.013	0.013	0.006	0.004	0.57
Cadmium	Cd	0.054	19	0	0.021	0.021	0.028	0.043	0.087	0.141	0.231	0.069	0.060	0.87
Cerium	Ce		19	0	0.007	0.007	0.067	0.125	0.148	0.263	0.263	0.116	0.074	0.64
Cobalt	Со	4	19	0	0.041	0.041	0.072	0.136	0.197	0.372	0.490	0.161	0.120	0.75
Chromium	Cr	1	19	0	0.113	0.113	0.151	0.166	0.230	0.259	0.610	0.220	0.123	0.56
Cesium	Cs		19	1	0.003	0.003	0.006	0.010	0.017	0.030	0.030	0.013	0.009	0.68
Copper	Cu	3.87	19	0	0.40	0.40	1.29	1.99	2.53	3.56	4.43	2.02	0.98	0.48
Iron	Fe	300	19	0	16	16	92	123	163	259	259	127	70	0.55
Lithium	Li		19	0	2.8	3.7	5.0	5.7	6.3	7.0	8.2	5.6	1.3	0.24
Manganese	Mn	1400	19	0	3.5	3.5	5.9	8.3	11	18	37	9.9	7.6	0.77
Molybdenum	Мо	73	19	0	0.63	0.90	0.95	1.06	1.12	1.22	1.22	1.04	0.15	0.14
Nickel	Ni	148	19	0	1.24	1.24	1.54	2.58	3.24	4.71	5.91	2.59	1.33	0.51
Lead	Pb	6.63	19	0	0.043	0.043	0.096	0.12	0.31	2.32	69	4.49	16	3.51
Rubidium	Rb		19	0	0.31	0.31	0.40	0.45	0.57	0.77	0.97	0.51	0.16	0.32
Antimony	Sb		19	0	0.14	0.14	0.18	0.21	0.26	0.29	0.58	0.23	0.09	0.40
Strontium	Sr		19	0	72	72	133	162	184	255	255	158	43	0.28
Vanadium	V		19	0	0.12	0.12	0.22	0.33	0.41	0.49	0.49	0.32	0.12	0.38
Zinc	Zn	30	19	0	1.4	1.4	2.0	4.4	5.9	7.9	16	4.8	3.9	0.82
* CCME auideline f	or the prote	ction of agu	uatic life at	a hardness	s of 178 m	J/L CaCO ₃	50%	$= 50^{\text{th}} \text{ perc}$	entile of th	e entire da	taset (med	ian)		

** Below Detection Limit

Shading = values exceeding CCME guideline

Min = lowest observed value in the entire dataset

Low = lowest value within 1.5 x the interquartile $(25^{th} \text{ to } 75^{th} \%)$

 $25\% = 25^{\text{th}}$ percentile of the entire dataset

High = highest value within 1.5 x the interquartile $(25^{th} \text{ to } 75^{th} \%)$

Max = highest observed value in the dataset

STD = Standard Deviation

CV = Coefficient of Variation (STD/Mean)

With the current set of data, it is not possible to determine if there has been an increase or decrease in dissolved trace-metal concentration over time. With continued monitoring, however, understanding of trends may be possible at some point in the future. This is important, because if dissolved trace metals increase in concentration, particularly those that are already near guideline values, they have the potential to become toxic and harm fish and other aquatic organisms within the Peel River watershed.

4.2.4 Nutrients

For the purposes of this discussion, nutrients include dissolved organic carbon (DOC), total nitrogen (TN) and total phosphorus (TP). For all three of these analytes, concentration is positively correlated to flow rate (Appendix B: Figure B85, 87 & 89) and turbidity (Appendix B: Figure B91). During periods of high flow (spring freshet and summer recession), nutrient concentrations reach their maximum levels but are highly variable (Figure 4-18). This relationship means that the nutrient concentrations increase during the spring freshet and then slowly decrease until reaching a consistent minimum during winter baseflow (Figure 4-18). The seasonal pattern is the same as that seen for turbidity and opposite to the seasonal pattern for most of the other major ions (Section 4.2.1). The seasonal differences in concentration suggest that all three nutrients are associated with particulate material within the Peel River. This is perhaps expected for TN and TP, because the particulate fraction for both nutrients generally dominates. For DOC, however, the positive correlation with flow/turbidity is less easily understood, unless algal productivity increases during the summer season. However, given the complete lack of phytoplankton and chlorophyll a data, algal community structure, biomass and productivity within the Peel River are unknown at the present time.



Figure 4-18: The Effect of Season and Flow Rate on Total Phosphorus Concentration

Within the period of record, concentrations vary from 0.3 mg/L to 24.6 mg/L for DOC, 0.07 to 3.71 mg/L for TN, and 2 to 1880 μ g/L for TP (Table 4-9). Within any given seasonal period for the three nutrients, variability is relatively high, with CV values ranging from 39 to 122% (Table 4-9). This indicates that nutrient concentrations within the river are changeable, even within a seasonal period.

Table 4-9:	9: Peel River above Fort McPherson (Site O) Baseline Water Chemistry for Dissolved Organic Carbon (DOC), Total Nitrogen (TN) and Total Phosphorus (TP)												
Analyte	Season	Ν	BDL	Min	Low	25%	50%	75%	High	Max	Mean	STD	CV
	Baseflow	68	0	0.3	0.3	1.2	1.5	2.4	3.9	13.5	2.3	2.4	104
DOC (mg/L)	Freshet	33	0	1.8	1.8	4.7	6.6	8.9	13.7	16.0	7.1	3.5	50
(119/1)	Recession	52	0	0.8	0.8	2.5	3.4	5.1	8.6	24.6	4.3	3.4	80
Total	Baseflow	68	0	0.13	0.13	0.20	0.23	0.28	0.40	0.65	0.26	0.10	39
Nitrogen	Freshet	32	0	0.14	0.14	0.55	0.90	1.34	2.08	2.08	0.98	0.57	59
(mg/L)	Recession	51	0	0.07	0.07	0.22	0.33	0.52	0.96	3.71	0.55	0.62	113
Total	Baseflow	72	0	2	2	6	8	13	23	200	10	6	60
Phosphorus (µg/L)	Freshet	33	0	70	70	208	517	820	1360	1880	613	430	70
	Recession	50	0	20	20	49	86	185	390	1070	173	211	122

Nevertheless, the DOC, TN and TP data are sufficient for definition of baseline conditions (Table 4-9). The median baseflow nutrient concentrations within the lower reaches of the Peel River are 1.5 mg/L for DOC, 0.23 mg/L for TN, and 8 ug/L for TP (Figure 4-19: Table 4-9; Appendix B; Figure 86, 88 & 90). Median concentrations are considerably higher and more variable during spring freshet and intermediate during the summer recession (e.g., Figure 4-19). Nutrient concentrations above the defined cutoff values occur within each season (defined as values above 'High' in Table 4-9), and indicate unusual conditions within the Peel River and/or sampling error, though any such determination, as discussed, should be made with caution (Table 4-9). In contrast, there were no outliers at low concentration, which is generally typical of water-chemistry data.



Figure 4-19: Definition of Seasonal Baseline Concentrations for Total Phosphorus

Nitrogen and/or phosphorus are considered the nutrients most often limiting primary productivity in aquatic ecosystems (Wetzel 1983). Based on TN and TP concentrations, aquatic ecosystems can be classified on the basis of their primary productivity. Water bodies are considered "oligotrophic" when TN, TP and productivity are low, "mesotrophic" when productivity is intermediate, and "eutrophic" when TN, TP and productivity are high (Wetzel 1983). Classification of water bodies within these categories has been developed, most commonly for lentic systems (e.g., Carlson 1996), but also for lotic systems such as the Peel River and its tributaries (Dodds et al. 1998).

Table 4-10: Trophic Status in Lotic Systems Related to TN and TP Concentrations											
Trophic Status	Total Nitrogen (mg/L)	Total Phosphorus (µg/L)									
Oligotrophic	<0.7	<25									
Mesotrophic	0.7 – 1.5	25 – 75									
Eutrophic	>1.5	>75									
Source: Dodds et al. 1998											

Because of the seasonal variability of the TN and TP data, trophic status within the lower reaches of the Peel River changes throughout the year. During the winter baseflow period, the Peel River can be considered oligotrophic, with even the defined high cutoff concentrations (75%) of TN and TP below the threshold of mesotrophy (Figure 4-19, Tables 4-9 and 4-10). In contrast, the Peel River would be classified as eutrophic during the spring freshet, when concentrations of TN and TP are above the threshold value for eutrophy (Figure 4-19, Tables 4-9 and 4-10). This suggests that the nutrient conditions for considerable algal productivity are present within the Peel River during the spring and summer months. However, given the turbulence and turbidity within the river, algal biomass may never actually increase to potential. If future flows and turbidity levels decrease at some point in the future, perhaps due to climate change or hydroelectric development, then the potential for increased algal biomass within the river should be understood to exist (e.g., Bormans et al. 2004, 2005).



Figure 4-20: The Relationship between Turbidity and TN:TP Ratio in the Peel River above Fort McPherson

Algal community structure is partially influenced by the ratio of nitrogen to phosphorus (Elser 1999). At low TN:TP ratios, the potential for blue green algal blooms exists, while at high TN:TP ratios, blue green algae are often an insignificant component of the algal community. Increased abundance of blue green algae is of concern because of its toxicity and bloom-forming ability. While there are many factors that can influence community structure, it is considered that a TN:TP ratio less than 30 by weight (Smith 1983) increases the potential for blue green algal blooms. Within the Peel River there appears to be a marked seasonality to TN:TP ratios. During periods of high turbidity and high flow, the TN:TP ratio is consistently less than 10:1, while during periods of low turbidity and low flow the ratio increases to greater than 100:1 (Figure 4-20). The data suggest that there is disproportionate increase in Total P as flows and turbidity increase. The threshold for the change from high to low TN:TP ratio occurs at a flow rate of approximately 900 m³/s and a turbidity of approximately 55 NTU (Figure 4-6; Figure 4-20). This flow rate occurs yearly at the threshold of the spring freshet, when flows rapidly increase from $<300 \text{ m}^3$ /s to $>1000 \text{ m}^3$ /s over a period of four or five days (Section 4.1). The seasonal alteration in TN:TP ratio suggests that the Peel River watershed is potentially nitrogen limited in the spring freshet and summer recession, during periods of high flow/turbidity, and potentially phosphorus limited in baseflow conditions during periods of low flow/turbidity.

4.3 WATER AND SUSPENDED SEDIMENT QUALITY – PEEL RIVER ABOVE FORT MCPHERSON

4.3.1 Organic Compounds of Potential Concern

Organic chemicals produced by industrial society are often highly toxic and persistent in the environment. Also, many of these organic chemicals are volatile, evaporate into the atmosphere and are capable of moving large distances with prevailing winds. These chemicals then tend to fall out of the atmosphere during rain or snow events, particularly in areas that are cold, such as mountains, and in northern areas such as the Yukon. The Peel River watershed, being located in a cold and mountainous northern region, is therefore doubly vulnerable to deposition of these persistent and toxic chemicals.

4.3.2 Pesticides and Polychlorinated Biphenyls (PCBs)

The Peel River above Fort McPherson monitoring program includes the analyses of water and suspended sediment for human-made pollutants such as pesticides and polychlorinated biphenyls (PCBs) (Appendix C; Tables C5, 6, 7, and 11).

Where possible, results were compared to the CCME guidelines for the protection of aquatic life (TEL and PEL). Since suspended sediment guidelines do not exist, comparisons were made to the CCME bottom sediment guidelines to provide some context.

Since 2002, 10 Peel River water and suspended sediment samples have been analyzed for 38 different pesticides. Pesticides include chemicals like DDT (dichloro-diphenyl-trichloroethane)

and herbicides such as 2,4-D (dichlorophenoxy acetic acid). None of these chemicals were found in any of the water samples. However 2,4-D was found once in 2004 whereas PP-DDE and methoxychlor were each found once in 2012.

2,4-D is a herbicide commonly used to control weeds on lawns. Today, it is the third-most widely used herbicide in North America. PP-DDE is a breakdown product of DDT, a chemical that was used in North America until 1972 to control pests. DDT is still used by some tropical countries to control malaria. Methoxychlor was first developed as a replacement for DDT. It has been used to control various pests including the beetles that spread Dutch elm disease. As these chemicals are not used in the region, lab contamination or atmospheric transport is the most probable source for them.

In each instance, the concentrations of the pesticides detected in the suspended sediment samples collected from the Peel River were low. The one time, PP-DDE was detected, the value measured 6.5 ug/kg. This is slightly below the CCME aquatic life guideline (TEL; 6.75 ug/kg) that represents the value where an effect could occur. CCME guidelines do not exist for 2,4-D and methoxychlor. In general, the available data suggest that pesticide concentrations within the Peel River are very low at this time.

Of the water samples collected from 2002-2007 (n=8), total PCBs have not been detected. However, a few individual congeners have been detected in the suspended sediment samples. A PCB congener is a single, unique chemical compound in the PCB category. Each suspended sediment sample (n=8) was analyzed for 209 different PCB congeners. The congeners are very useful because they can be measured by the laboratory at exceptionally low detection limits. The sum of the individual congeners in the eight samples of the Peel River ranged from 0.07-0.4 ppb. The recommended guideline is 34.1 ppb. Based on the laboratory report and the kinds of PCBs found, atmospheric transport is the most likely source.

4.3.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs), on the other hand, have been found more often and at higher concentrations than pesticides and PCBs. This is partly because PAHs have natural sources (e.g., forest fires, natural oil and gas deposits), as well as human sources (e.g., industrial projects, urban runoff and burning of fossil fuels).

Several hydrocarbons have been detected in the water samples collected from the Peel River above Fort McPherson. On all occasions, the concentrations have been below the CCME guidelines for the protection of aquatic life.

From 2002 and 2007, 10 Peel River suspended sediment samples were analyzed for 19 different hydrocarbon compounds; all of which have been detected on one occasion of more. Of these 19 compounds, CCME guidelines exist for 12 PAH compounds (Table 4-11). Although some PAH values have exceeded the threshold effect level (TEL), all results were lower than the probable effect level (PEL), at which adverse effects are predicted to occur frequently (CCME, 2001).

Table 4-11: CCME TEL and PEL Guideline Values for the Protection of Aquatic Life Compared with Maximum PAH Concentration (2002-2007)												
PAH Compound	CCME Guideline (TEL / PEL)	Units	Range	Date of Max Conc								
Acenaphthene	6.71 / 88.9	ug/kg	<10-20	August 2007								
Acenaphthylene	5.87 / 128	ug/kg	<314	July 2007								
Anthracene	46.9 / 245	ug/kg	<3-28	July 2007								
Benz(a)anthracene	31.7 / 385	ug/kg	<10-88	July 2007								
Benzo(a)pyrene	31.9 / 782	ug/kg	<10-82	July 2007								
Chrysene	57.1 / 862	ug/kg	<10-74	July 2007								
Dibenz(a,h)anthracene	6.22 / 135	ug/kg	<10-47	August 2007								
Fluoranthene	111 / 2355	ug/kg	<10-146	July 2007								
Fluorene	21.2 / 144	ug/kg	<10-33	July 2007								
Naphthalene	34.6 / 391	ug/kg	30-95	July 2007								
Phenanthrene	41.9 / 515	ug/kg	60-220	July 2007								
Pyrene	53/875	ug/kg	10-146	July 2007								

In June 2012, the analyses of alkylated PAHs were added to the monitoring program. Alkylated PAHs are PAH compounds containing a straight side chain. Several of these were detected in the samples that were collected during 2012. This does not mean that there are more hydrocarbons in the river now than there were before. What it means is that these alkylated hydrocarbon compounds are good indicators of hydrocarbons in the river and will continue to be a part of the monitoring program so that future levels can be compared to them.

4.3.4 Metals

The suspended sediment samples collected from the Peel River above Fort McPherson were analyzed for up to twenty-eight metals. The major constituents of the entrained sediment included iron, calcium, aluminum, magnesium and potassium (Table 4-12). The relatively high potassium content is consistent with the positive relationship between potassium concentration and turbidity discussed above (Section 4-2). Average values were above the ISQG for arsenic, cadmium and zinc and individual data points were above ISQG for Cu and Cr. It is clear that metal content within watershed materials is naturally substantial.

Та	ble 4-12:	Metal Con	itent (mg/kg)	in the Suspe	e Suspended Sediments Collected from the Peel River Above Fort McPherson							
Ameluda		CCME				Maan	OTD					
Analyte	DL	PEL	ISQG	Jul-02	Jun-03	Aug-04	Jun-05	Aug-06	Jun-07	wean	510	
Iron (Fe)	200			33600	27300	29600	30200	36700	29800	31200	3369	
Calcium (Ca)	100			17800	19900	6200	37000	9600	18500	18167	10719	
Aluminum (Al)	50			13300	9100	12300	12900	16900	11800	12717	2529	
Magnesium (Mg)	10			9040	10600	4830	17200	6490	10800	9827	4304	
Potassium (K)	20			2090	1440	2910	2660	3400	2400	2483	679	
Barium (Ba)	5			672	525	660	1010	779	525	695	182	
Manganese (Mn)	0.5			377	340	162	498	335	360	345	108	
Sodium (Na)	20			190	200	300	400	300	300	282	78	
Zinc (Zn)	5	315	123	149	172	138	175	186	208	171	25	
Strontium (Sr)	1			54	58	61	81	73	69	66	10	
Vanadium (V)	0.1			43	39	53	64	67	55	54	11	
Nickel (Ni)	0.5			46	45	38	48	48	53	47	4.8	
Copper (Cu)	2	197	35.7	31	34	35	32	38	39	35	3.1	
Chromium (Cr)	0.2	90	37.3	34	26	30	41	34	30	32	5.3	
Lead (Pb)	0.5	91.3	35	18	14	17	17	18	17	17	1.5	
Cobalt (Co)	0.1			13	12	10	13	15	14	13	1.6	
Arsenic (As)	0.5	17	5.9	11	13	15	12	13	13	13	1.3	
Boron (B)	2			9.0	6.0	15	15	18	13	13	4.4	
Titanium (Ti)	0.5			6.4	9.0	11	19	11	13	12	4.3	
Molybdenum (Mo)	0.1			1.4	2.3	3.1	2.5	1.8	2.1	2.2	0.59	
Selenium (Se)	0.2			0.9	1.6	1.4	1.4	1.3	1.7	1.4	0.28	
Uranium (U)	0.1			1.1	1.3	1.2	1.6	1.2	1.4	1.3	0.17	
Cadmium (Cd)	0.1	3.5	0.6	0.50	0.90	0.50	0.90	0.60	1.00	0.73	0.23	
Beryllium (Be)	0.2			0.60	0.50	0.70	0.80	0.90	0.80	0.72	0.15	
Thallium (TI)	0.05			0.30	0.29	0.53	0.39	0.45	0.39	0.39	0.09	

Tab	tent (mg/kg) i	in the Susper	nded Sedime	nts Collected	from the Pee	el River Abov	e Fort McPhe	erson			
Analyte	Ы	ССМЕ				Meen	etD				
		PEL	ISQG	Jul-02	Jun-03	Aug-04	Jun-05	Aug-06	Jun-07	wean	310
Tin (Sn)	0.1			<0.1	<2	<2	<2	<2	<2	BDL	
Bismuth (Bi)	0.5			<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	BDL	
Silver (Ag)	0.1			<0.1	<0.2	<0.2	<0.2	0.2	<0.2	BDL	
Major Constituents are F	e, Ca, Al, Mg,	К									
Mean > ISQG are Zn, As	s, Cd										
Date > ISQG are Cu, Cr											
High K is consistent with increased K with increased turbidity/flow											
July and August 2007 samples are different, with suspect data for some analytes (e.g., Ca)											
Shading = Value above t	the Interim Sec	diment Quality	/ Guideline (IS	QG)							

4.4 WATER QUALITY - PEEL RIVER WATERSHED

Water samples were collected from 15 monitoring stations located throughout the Peel River Watershed (Sites A to O; Figure 2-1) between 1999 and 2005. Sampling effort was variable across the monitoring stations, which resulted in seasonal differences between sites and over time. The dataset contains physical parameters such as pH, TSS, TDS, turbidity, conductivity, as well as major ions, nutrients and total and dissolved trace metals.

Peel Riv	Peel River Watershed Water Quality Sampling Locations									
А	Ogilvie River above Engineer Creek									
В	Ogilvie River near Mouth									
С	Blackstone River near Champion Lake									
D	Blackstone River near Mouth									
Е	Peel River above Hart River									
F	Hart River near Hungry Lake									
G	Peel River above Canyon Creek									
Н	Wind River near Mouth									
I	Peel River above the Bonnet Plume River									
J	Bonnet Plume River above Gillespie Creek									
К	Bonnet Plume River above Mouth									
L	Peel River above Snake River									
М	Snake River above Mouth									
Ν	Peel River above Caribou River									
N ₁	Caribou River above Mouth									
0	Peel River above Fort McPherson									



4.4.1 Major Water Chemistry Parameters

Within the Peel River watershed, flow rate is a major determinant of water chemistry in general, and turbidity, which is correlated to flow, exerts a major effect on total trace metal chemistry (Section 4.2). Throughout the Peel River watershed, there is considerable variability in both flow and turbidity amongst sites and sampling dates (Table 4-13). Flow rates at the Peel River above Fort McPherson vary from 77 to 1870 m³/s amongst the various sample dates, and turbidity varies from less than 1 NTU, to over 300 NTU over the same time period (Table 4-13). Turbidity within the various tributaries is also variable, with an increase from the headwaters downstream, and with the highest values found in the Bonnet Plume and Snake rivers (Table 4-12; Figure 4-21). The Bonnet Plume River watershed consists of unconsolidated deposits (Smith et al. 2004), which are easily eroded relative to the bedrock underlying upstream tributaries. Unconsolidated deposits release significantly more suspended sediments than consolidated rock, particularly in high flow events.



Figure 4-21: Comparison of turbidity levels throughout the Peel River Watershed on June 26, 2003 (Flow Rate at Fort McPherson on June 26, 2003 measured: 936 m³/s)

Grey bars represent turbidity levels in the furthest downstream section of tributaries, while blue bars represent turbidity levels in the Ogilvie/Peel River mainstem. Water samples were collected on June 26, 2003 (see Table 4-12)

The variability in flow/turbidity will necessarily increase variability for many water chemistry parameters, and may ultimately obscure potential upstream/downstream relationships within the watershed. A notable exception is pH, which is consistently 8.2 from upstream to downstream (Figure E-1). Despite the variability in the other parameters, baseline water chemistry

throughout the watershed has been defined, primarily through calculation of average and standard deviation (Tables 4-13, 14 and 15). There are not enough data to calculate median and cutoff values as was done for the Peel River above Fort McPherson (Site O) sampling location (Section 4.2). None of the major water chemistry parameters exceeded CCME guideline values for the protection of aquatic life, though guideline values were exceeded for some of the total and dissolved metals (Tables 4-13, 14 and 15).

Calcium (Ca), magnesium (Mg), bicarbonate (HCO_3^- ; calculated from alkalinity) and sulphate ($SO_4^{2^-}$) are the dominant ions in the Peel River watershed from upstream to downstream and in all major tributaries, with Ca and bicarbonate occurring at slightly higher concentrations (Figures 4-22 and 4-23). Other major ions, such as sodium (Na), potassium (K), and chloride (Cl), generally comprise less than 3% of the total ion concentration (Figures 44-22 and 4-23). The dominance of the Ca cation and bicarbonate anion within the Peel River and its tributaries is the result of the wide-spread prevalence of limestone and dolomite within the watershed (Figure 2-1) and the chemical weathering of these carbonate minerals (Kenyon and Whitley 2008).

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STATUS AND TRENDS OF FLOW, WATER QUALITY AND SUSPENDED SEDIMENT QUALITY IN THE PEEL RIVER WATERSHED

Table 4-13: Turbidity (NTU) in the Peel River Watershed															
Sample Date	A	в	с	D	E	F	G	н	I	к	L	м	N	0	'O' Flow (m ³ /s)
9-Mar-99	0.25	0.20	0.50	0.20	0.20	0.30	0.20	0.10	0.15	0.20	0.30	0.75	127	0.90	77
29-Jul-02	7.7	5.6	4.0	0.90	5.6	12	14	64	46	167	107	331	260	174	1280
26-Jun-03	1.1	3.0	1.0	1.2	2.2	1.1	2.0	5.9	9.0	31	16	38	25	47	936
27-Aug-04		0.31		0.17	0.38	0.29	0.31	1.5	1.9	2.6	3.2	6.5	7.9	182	375
16-Jun-05														123	1870
12-Jul-05		0.27		0.18	0.28	0.67	0.55	4.8	2.9	1.6	3.0	5.3	3.5	22	842
10-Aug-05														49	680
Mean	3.0	1.9	1.8	0.5	1.7	2.9	3.4	15	12	40	26	76	85	85	866
STD	4.1	2.4	1.9	0.5	2.3	5.1	6.0	28	19	72	46	143	110	74	589
CV	135	128	103	92	134	178	175	179	161	178	177	188	130	86	68

Blue values are for tributaries of the Ogilvie/Peel River, including the Blackstone (C/D), Hart (F), Wind (H), Bonnet Plume (K), and Snake (M) Rivers (See Figure 2-1 for locations). Green shading indicates outliers within the dataset.



Figure 4-22: Major Ion Compositions of Major Rivers in the Peel River Watershed (Stations A-H)


Figure 4-23: Major Ion Compositions of Major Rivers in the Peel River Watershed (Stations I-O)

Within the watershed, Ca concentrations range from 31 to 85 mg/L with the highest values and greatest variability occurring in the Ogilvie (A/B) River (Figure 4-24). The concentrations of Ca in the Blackstone (C/D), Hart (F), and Wind (H) Rivers (Figure 4-24) are slightly lower than in the Peel as they join, and appear to stabilize the average Ca concentration downstream in the Peel River to approximately 45 to 50 mg/L (Figure 4-24). The concentration in the Snake River (M) is relatively high and variable compared to many of the other sites. This pattern is observed for many other analytes (Figures E-1 to E-5), and suggests that weathering in the Snake River watershed is highly variable.



Figure 4-24: Calcium Concentrations in the Peel River Watershed

The blue data points are those moving from upstream (A) to downstream (O) in the Ogilvie/Peel Rivers. The white dots are from tributaries as described in Figure 2-1 and include the Blackstone (C/D), Hart (F), Wind (H), Bonnet Plume (K) and Snake (M) Rivers.

The concentration of Mg is somewhat lower than Ca, and ranges from 6.9 to 28 mg/L within the watershed (Figure E-3; Table E-1). Elevated average concentrations of magnesium (>20 mg/L) are associated with the Ogilvie (A/B), Bonnet Plume (K) and Snake (M) rivers (Figure E-3).

Sodium and K, as mentioned, are minor components within the watershed, and range between 1.3 and 14 mg/L for Na, and 0.1 to 1.7 mg/L for K (Table E-1). The Na concentration in the Ogilvie River (A/B) is considerably higher than at other sites, so that the Ogilvie River contributes a major amount of Na in the Peel River (Figure E-3). The source of Na within the Ogilvie River is likely from chemical weathering of saline beds in the Ogilvie formation that are exposed near Sapper Hill (Smith et al. 2004).

The dominant anion in the Peel River watershed is bicarbonate (Figures 4-22 and 4-23). Bicarbonate is not usually measured in water, but can be determined through measurement of total alkalinity for most natural waters, including the Peel River watershed. Therefore, alkalinity is used as a surrogate for the bicarbonate ion. Total alkalinity ranges from 77 to 198 mg/L (Table E-1), with average values between 100 and 150 mg/L (Table 4-12). The highest total

alkalinity is observed upstream in the Ogilvie River (A/B), though alkalinity is relatively consistent throughout the watershed (Figure E-4). Alkalinity originates in part from the dissolution of calcium carbonates, which is the dominant component of the limestone and dolomites that occur in the Ogilvie Mountains and Taiga Ranges (Figure 2-1). Concentrations of sulphate are lower, and range from 16 to 230 mg/L (Table E-1). Elevated average sulphate concentrations are observed in the Ogilvie (A/B), Snake (M) and Bonnet Plume (K) Rivers (Figure E-4). The lowest anion concentrations were found for Cl, which range from 0.4 to 8.5 mg/L (Table E-1). The highest chloride values were observed in the Ogilvie (A/B) and Bonnet Plume (K) Rivers (Figure E-4). Similar to sodium, chloride is generally sourced from saline beds occurring in marine sedimentary rocks.

Patterns of ionic composition of dissolved chemical components within the watershed are summarized by conductivity and/or TDS, which are correlated as shown in a previous report (Czarnecki and Beavers, 2002). Unlike the pattern of increasing turbidity (or TSS) from headwaters downstream, conductivity patterns are subtle and reflect concentrations of major ions. There is a relatively high conductivity in the Ogilvie River (A/B) and lower concentrations in the other tributaries moving downstream (Figure 4-25). The exception is the Snake River (M), which has greater variability and higher average concentration than other tributaries and the Peel River (Figure 4-25). This relationship, as mentioned, is consistent with that seen for Ca (Figure 44-24), and for many of the other major ions (Figures E-1 to E-4).





The blue data points are those moving upstream (A) to downstream (O) in the Ogilvie/Peel Rivers. The white dots are from tributaries as described in Figure 2-1 and include the Blackstone (C/D), Hart (F), Wind (H), Bonnet Plume (K) and Snake (M) Rivers.

4.4.2 Nutrients

For the purposes of this discussion, major nutrients are considered to be phosphorus (total and dissolved), the various forms of nitrogen (nitrate, nitrite, ammonia), and organic carbon (total and dissolved). Reactive silica was measured only at Station O and is therefore not considered in this section.

Nitrate/nitrite nitrogen concentrations range from 0.04 to 0.3 mg/L in the watershed and are also highly variable (Figure E-5). This precludes a detailed analysis of differences in concentration through the watershed. Ammonia concentrations are low, and follow the general pattern of an increase moving downstream that is observed for turbidity (Figures E-5 and E-2). This suggests that ammonia may be associated with the particulate fraction within the watershed. Total organic carbon is relatively high in the Ogilvie (A/B) and Blackstone (C/D) Rivers and then consistent throughout the watershed (Figure E-5). Dissolved organic carbon ranges from 1 to 5 mg/L and shows no spatial pattern within the watershed (Figure E-5). Concentrations of total phosphorous vary from 0.006 to 0.56 mg/L (Table E-1), with extreme values occasionally observed between the mouth of the Bonnet Plume River and Fort McPherson (Figure E-5). As with ammonia, the downstream increase is consistent with the increased turbidity in the lower reaches of the watershed.

4.4.3 Metals (total and dissolved)

Trace metals are minor, but important components of natural waters. They often work as micronutrients for aquatic organisms, but can also be toxic if present in high concentrations and available forms. This section is focused on metals that are regulated by the stipulated guidelines (Table 3-4). These include AI, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Hg, Ni, Se, Ag, TI, U, and Zn. The total metal guidelines are compared to both the particulate and dissolved (biologically available) form of the metals.

The chemistry of dissolved and total metals is complex. The marked seasonality of flow within the Peel River watershed (Section 4.1) potentially reduces trace metal concentrations through dilution with spring melt water, and the marked seasonality of turbidity and total metal concentration (Section 4.2) potentially increases dissolved concentrations through exchange between particulate and dissolved fractions. The former dynamic is identical to that observed for major ions and is considered to be caused by variation in the amount of weathering versus flow through the seasons. The latter dynamic is caused by equilibrium reactions that might occur between the dissolved and particulate trace metal fractions. The interplay between these two processes potentially creates a variety of responses, depending on the metal. These relationships are further obscured for this particular dataset because of the limited amount of data, and the variability in flow and turbidity between sample periods and within the watershed.

Despite these confounding factors, watershed relationships for the trace elements are apparent for many of the elements. For Ba, Cu, Mn, Ni and Zn the dissolved fraction dominates in upstream portions of the watershed and at some point downstream, the particulate fraction increases substantially (Figures E-6 to E-9). Average values of total manganese, for example,

increase by approximately an order of magnitude from the upper reaches downstream while dissolved concentrations increase only slightly (Figure 4-26).



Figure 4-26: Dissolved and Total Manganese in the Peel River Watershed

The increase in total concentration occurs downstream of the Wind River (H) for Mn, downstream of the Bonnet Plume River (K) for Cu, Ni, and Zn, and downstream of the Snake River (M) for Ba (Figures E-6 to E-9). This indicates that the various tributaries contain suspended solids with variable chemistry, likely due to differences in geology within each subbasin. For instance, elevated concentrations of dissolved copper in the headwaters of Ogilvie River are possibly associated with natural sulfide oxidation that has been documented in the vicinity of Engineer Creek (Kwong and Whitely 1992). For other metals, the particulate fraction dominates throughout the watershed. These include AI, Co, Cr, and Fe (Figures E-6 to E-9). These metals also increase in concentration moving downstream, consistent with increases in turbidity associated with higher flow rates. Aluminum, for instance, is likely associated with clay particles throughout the watershed and is positively correlated to turbidity (Section 4.3; Figure B-49). There are also two metals (Sb and Mo) that occur predominantly as dissolved metals throughout the watershed (Figure E-6, E-8). It is likely that these two metals are at low concentration within the suspended sediment fraction entrained within the Peel River and tributaries (Section 4.2.3). The upstream source of Mo and Sb is likely from the weathering of sulfide minerals, which are abundant in the Jones Ridge and Canol formations that are exposed in the Ogilvie Mountains (Smith et al. 2004).

As discussed in Section 4.2.3 (Table 4-7) for the downstream portion of the Peel River, the total metal concentration of many metals exceeds guideline values for the protection of aquatic life throughout the watershed. Metals that consistently exceed guideline values within the watershed include AI, Cr, Cu, Fe, and Pb (Figure E6 to E-9). As discussed, however, it is not expected that these metal levels are toxic within the watershed, because it is considered that

only the dissolved metals are biologically available. In contrast, dissolved concentrations for almost all trace elements were below applicable guideline values almost all the time. Exceptions included dissolved AI, Cd, Cr, Cu, Ag, and Zn, which occasionally exceeded guideline values (Table E-1).

Selenium occurs naturally in coal deposits found in the Camic formation and in the sulfide rich shales of the Canol formation, both of which occur in the Ogilvie Mountains (Smith et al., 2004). Concentrations of Se are often above the guideline value of 1 ug/L (Table E-1), but the data are compromised by high detection limits (1-10 ug/L). A concerted effort to analyze Se using low detection limits would perhaps be useful.

5.0 Key Observations

5.1 FLOW - PEEL RIVER ABOVE FORT MCPHERSON

- There were considerable differences found in seasonal flow:
 - Seasonal flow periods were differentiated by Julian day and flow rate:
 - Spring freshet ~April 15 to June 30, AND flow >300 m³/s
 - Summer recession July 1 to ~ October 30, AND flow >300 m³/s
 - Winter baseflow ~October 15 to ~ April 30, AND/OR flow <300 m³/s
- Significant temporal trends in flow are evident:
 - There has been a significant increase in winter baseflow over the entire period of record.
 - There has been a significant increase in annual minimum flow rate, although with considerable year-to-year variability.
 - There has been a significant decrease in flow rate during late spring freshet in the month of June.

5.2 WATER QUALITY - PEEL RIVER ABOVE FORT MCPHERSON

5.2.1 Major Water-Chemistry Parameters

- Consistent seasonal differences occurred in concentration, related to flow rate and season:
 - The lowest concentrations occurred during spring freshet.
 - Slightly higher concentrations occurred during the recession of flow through the summer.
 - Highest concentrations occurred during winter baseflow.
- Positive and increasing temporal trends were observed for sulphate, magnesium and calcium for the entire period of record (1980 to 2010), but not for the last ten years.
- Inconsistent and/or marginally significant trends were observed for a few other analytes/time periods.
- Turbidity CCME guidelines were routinely exceeded. For the other major water chemistry parameters, where guidelines exist, no guidelines were exceeded.

5.2.2 Total Metals

- Concentrations were strongly and positively correlated to turbidity.
- Long term trend analysis was limited to winter baseflow data for total Al, Cr, Cu, Fe, Li, Mn, Mo, Ni, Sr and Zn. There were no statistically significant temporal trends except for lithium, which showed a marginally significant decreasing temporal trend.
- For most total metals, concentrations were considerably above guideline values, though particulate metals are considered not bioavailable.

5.2.3 Dissolved Metals

- There were consistent seasonal differences in dissolved/total ratio related to flow rate and season:
 - Higher relative concentrations of dissolved metals occurred during winter baseflow.
 - Lower relative concentrations of dissolved metals occurred as flow rate increased.
- There was no relationship between seasonal flow rate and dissolved concentration for most dissolved metals.
 - Dissolved metal concentrations were occasionally above CCME guideline for Protection of Freshwater Aquatic Life for a few metals, including: Al, Cd, Cu, and Pb.
- Temporal trends analysis was not possible with the current dataset for dissolved metals.

5.2.4 Nutrients

- The Peel River trophic status (based on TP and/or TN) is changeable. During periods of high flow it is considered potentially eutrophic, and during periods of low flow it is considered potentially oligotrophic.
- During the spring freshet and summer recession, the Peel River appears to be potentially nitrogen limited, though with the high turbidity levels at this time, it may be that light is actually the factor limiting productivity.

5.2.5 Organic Compounds of Potential Concern

• Concentrations of organic compounds were low in the water samples collected at Peel River above Fort McPherson, though the samples had not been collected at the optimum time, nor in the optimum medium (e.g., snow samples collected in March/April).

5.3 SUSPENDED SEDIMENT QUALITY - PEEL RIVER ABOVE FORT MCPHERSON

- Of these 19 hydrocarbons compounds measured in the suspended sediment of the Peel River (above Fort McPherson), CCME guidelines exist for 12 PAH compounds. Although several PAH values have exceeded the threshold effect level (TEL), all results were lower than the probable effect level (PEL), at which adverse effects are predicted to occur frequently
- The total amount of PCB compounds was very low. Levels were below the TEL guideline.
- Average values of metals were above the TEL guidelines for arsenic, cadmium and zinc; individual data points were above TEL guidelines for copper and chromium.

5.4 WATER QUALITY - PEEL RIVER WATERSHED

- The Peel River and its tributaries are alkaline (pH = 7.9-8.4) with total dissolved solids generally ranging from 170 to 300 mg/L.
- Calcium (Ca), magnesium (Mg), bicarbonate (HCO₃⁻) and sulphate (SO₄²⁻) are the dominant major ions in the Peel River watershed. Calcium, Mg and HCO₃⁻ are produced by dissolution of carbonate rocks such as limestone and dolomite, whereas sulphate is generated from the weathering of gypsum lenses and oxidation of sulfide-rich rocks.
- Turbidity increases from the headwaters of the Peel River downstream. The Bonnet Plume and Snake Rivers appear to contribute a considerable sediment load.
- Trace metals are divided into three major groups based on the dominant form of occurrence within the Peel River watershed:
 - AI, Co, Cr, and Fe are generally present in the particulate form.
 - Dissolved Ba, Cu, Mn, Ni and Zn dominate in the headwaters of the Peel River, whereas the particulate form of these metals becomes dominant in the middle and lower watershed.
 - Sb and Mo are generally present in the dissolved fraction within the watershed.
- Concentrations of total Al, Cr, Cu, Fe, and Pb consistently exceed CCME FAL guideline values.
- Dissolved Al, Cd, Cr, Cu, Ag, Se and Zn occasionally exceed the CCME FAL Guideline. In some cases, dissolved Al and Mn concentrations are above the CDWQ aesthetic objective.
- Analytical results for Se, Ag, Hg and TI are consistently reported as below detection limit. It
 is recommended that detection limits for these elements be reduced to below guideline
 values.

6.0 Recommendations

- Format the data as a flat file and enter into a database.
- For optimal sampling of persistent organic pollutants of potential concern, collect snow samples in March, just before spring freshet (Kelly et al. 2009, Jacques Whitford 2008). Snow sampling will provide aerial deposition rates.
- Review trace metal sampling and analytical procedures to ensure maximum precision and accuracy.
- Measure Chla in water samples.
- Lower the detection limit for P, Se, Ag, Hg and TI.
- Sample each flow period on a regular basis:
 - Baseflow in February/March.
 - Freshet in May after/during peak flow if this is safely possible.
 - Recession in late August. This is the most difficult period to time correctly because of the variability in flow and the continuous alteration of ion concentration through the season.
- Consider development of risk-based site-specific protective criteria based on *in situ* bioassay studies for all parameters (e.g., total metals) which are naturally, and consistently, greater than "guideline" values in selected areas (e.g., above Fort McPherson).
- Consider development of reach-specific seasonal nutrient limitations consistent with understandings of the switch from oligotrophy to eutrophy, or from N-limitations in spring to P-limitations during winter.

7.0 Closure

This report was prepared on behalf of *Aboriginal Affairs and Northern Development Canada*. The report may not be relied upon by any other person or entity without the express written consent of Stantec Consulting Ltd. and *Aboriginal Affairs and Northern Development Canada*.

Any use which a third party makes of this report, or any reliance on decisions made based on it, is the responsibility of such third parties. Stantec Consulting Ltd. accepts no responsibility for damages, if any, suffered by any third party as a result of decisions made or actions based on this report.

The information and conclusions contained in this report are based upon work undertaken by trained professional and technical staff in accordance with accepted scientific practices current at the time the work was performed. The conclusions and recommendations presented represent the best judgment of Stantec Consulting Ltd. based on the data obtained from the work and on the site conditions encountered at the time the work was performed at the specific sampling, testing, and/or observation locations.

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