Canada

WOOD BUFFALO NATIONAL PARK WATER QUALITY: *STATUS AND TRENDS FROM 1989-2006 IN THREE MAJOR RIVERS; ATHABASCA, PEACE AND SLAVE*

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WOOD BUFFALO NATIONAL PARK WATER QUALITY: STATUS AND TRENDS FROM 1989-2006 IN THREE MAJOR RIVERS; ATHABASCA, PEACE AND SLAVE

QUALITÉ DE L'EAU AU PARC NATIONAL DU CANADA WOOD BUFFALO: ÉTAT ET TENDANCES DE 1989 À 2006 POUR LES TROIS PRINCIPALES RIVIÈRES DE LA PAIX, DES ESCLAVES ET ATHABASCA

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Executive Summary

In this report we have presented and interpreted water quality data collected on the Athabasca, Peace, and Slave rivers at the boundaries of Wood Buffalo National Park between August 1989 and December 2006. We have summarized the large amount of water quality data available and provide detailed statistical summaries for the period of record as a reference for further studies and monitoring programs (Appendix 2). Patterns in water chemistry among the three watersheds are discussed, including comparisons to upstream source waters. Parameters with national guidelines or site specific objectives for the protection of aquatic life are evaluated for excursions, including metals, major ions, and nutrients. We provide site specific regression analyses for several parameters with suspended sediment concentration as measured by non-filterable residue. We report on the results of statistical temporal trend analyses (seasonal and yearly) conducted for 39 water quality parameters and discuss their relationship to: 1) river discharge, 2) specific time periods, and 3) season. More specific analyses were conducted to examine two issue driven concerns; changes in metal concentration in the Athabasca River, and nutrient concentrations in relation to ecosystem functioning at all stations. Finally, the monitoring program was reviewed for scientific validity, gaps and emerging issues with recommendations provided for ongoing Parks monitoring programs.

In general, water chemistry among the three sampling sites was similar, in that for all parameters, concentration ranges were overlapping. However, patterns between sites were apparent for many parameters and are discussed in detail in the body of the report. Dissolved oxygen was lowest, while total dissolved solids and most major ions were highest in the Athabasca River compared with the Peace and Slave rivers. Metals in the environment occur from natural sources in the soil, rocks and bottom sediments and therefore reflect the surrounding geology and hydrologic processing. In these rivers, total metal concentrations peak in May – July corresponding to the peak discharge and sediment loading. For all metals, ranges overlapped among sites, and for most, medians were similar.

A large component of this study focussed on evaluating trends through time to assess the chemical stability of these aquatic ecosystems over the previous two decades. For the physical and major ion parameters most analyses showed stability in concentration through time. Of the 50 analyses conducted over the entire period of record, only 16 showed changes in concentration and 5 of those showed no changes in the last decade. Changes in nutrient concentration were dependent on site and parameter. Carbon showed few changes through time. Trends in nitrogen concentration were similar in the Athabasca and Peace rivers; most dissolved forms displayed increasing concentrations, while in the Slave River, at least in the last decade, these parameters were showing decreasing trends. We detected no significant trends in phosphorus concentration in the Peace River but in both the Athabasca and Slave rivers, dissolved and total phosphorus concentrations increased over the period of record. The increases in nutrient concentration observed were largely driven by increases during winter months, under conditions of low flow, ice-cover. Finally, our results showed that, at least in part, the concentration trends in the Athabasca River are related to the changing discharge regime.

A more detailed summary of the results can be found in Section 5.0 however, the key findings and concerns raised in this study for these river reaches include;

- A change has occurred in the seasonal patterns of dissolved parameters in the Peace and Slave rivers which are due to the changes in river discharge patterns related to the construction of the William A. C. Bennett dam.
- Dissolved sulphate showed increasing trends at all sites but this is consistent with a broader regional change (Glozier et al., 2004b, Parker et al., 2009) for other northern rivers.

- ➢ Exceedences to CCME guidelines for total metal concentration were frequent but found to be directly related to the naturally high sediment loads in these rivers and probably have no negative effect on aquatic life.

- ➢ Total phosphorus and nitrogen showed exceedences to the Alberta guideline but, similar to total metals, all exceedences were associated with natural periods of high suspended sediment load.

- ➢ Site specific objectives for three parameters (dissolved oxygen, sulphate, total dissolved solids) developed under NREI (Donald et al., 2004) were met within the expected frequency.

- ➢ For the nine metal parameters for which trend analyses could be conducted on the Athabasca River, no increasing trends were evident.

Increasing nutrients along with decreasing river discharge appears to be the largest concern for the study reaches of the Athabasca and Slave rivers and downstream aquatic ecosystems. Increasing trends in phosphorus have resulted in a change in the trophic status (based on TP concentration) for these reaches by at least one and in some cases three trophic levels.

- ➢ A major short coming of the existing water quality monitoring program for Wood Buffalo National Park is the absence of data on some contaminants of concern. The monitoring program was established largely to assess general water chemistry and potential changes in nutrients due to point source inputs in upstream reaches. It is recommended that contaminants of concern be assessed in water samples in the future.

This joint Environment Canada – Parks Canada – Northwest Territories – Alberta Environment monitoring program has provided important data on water quality though time. However, some of the recommendations for future direction include:

- o Establishment of a consistent sampling frequency of 8X per year with sampling distributed among the three hydrological seasons identified in this report as follows; 2 in Spring/Summer (May – July), 2 during fall (August – October) and 4 during the longer winter period (November – April).
- o Establishment and maintenance of a consistent parameter list analyzed at all sites.
- o Measurements of a broader range of contaminants of concern from industrial sources within the basins should be added to the suite of parameters measured in water and perhaps in sediments. Examples of potential contaminants from pulp and paper effluents include dioxins, furans and sulphur compounds and from oil and gas activities include polynuclear aromatic hydrocarbons, polycyclic aromatic hydrocarbons, napthenic acid, chlorinated phenols.
- o As downstream ecosystems are a concern (specifically the Peace Athabasca Delta), it is recommended that additional sampling locations be considered for water quality and biota sampling within the delta.
- o With the completion of this report, regular, more focused assessments (e.g., nutrient trends) could be conducted to update the current long-term analyses presented in this report.
- o Site-specific objectives for metals and nutrients should be established for routine reporting. This could lead to the development of water quality indicators which could be reported more frequently.
- o Biota density and community composition should be considered for sites of interest.
- o Metal levels in indicator fish such as goldeye and walleye should be considered.

Résumé

Dans le présent rapport, nous avons présenté et interprété les données recueillies entre août 1989 et décembre 2006 sur la qualité de l'eau de la rivière de la Paix, la rivière des Esclaves et la rivière Athabasca qui se situent aux limites du Parc national du Canada Wood Buffalo. Nous avons résumé la grande quantité de données disponibles sur la qualité de l'eau et nous proposons des sommaires statistiques détaillés pour la période des relevés qui pourront servir de référence pour d'autres études et programmes de surveillance (annexe 2). Les tendances relatives aux propriétés chimiques de l'eau des trois bassins versants ont été étudiées, notamment en les comparant aux eaux sources d'amont. Des paramètres, basés sur des lignes directrices nationales ou des objectifs propres au site concernant la protection de la vie aquatique, ont été mesurés en fonction des excursions, notamment en ce qui a trait aux métaux, aux ions majeurs et aux éléments nutritifs. Nous présentons des analyses de régression propres au site pour plusieurs paramètres avec des concentrations de sédiments en suspension mesurées au moyen de résidus non filtrables. Nous recensons les résultats d'analyses statistiques des tendances temporelles (saisonnières et annuelles) réalisées pour 39 paramètres de la qualité de l'eau et nous étudions leur relation 1) au débit fluvial, 2) aux périodes de temps spécifiques et 3) à la saison. Des analyses plus précises ont été effectuées pour étudier deux enjeux préoccupants, à savoir les modifications de la concentration des métaux dans la rivière Athabasca et les concentrations en éléments nutritifs par rapport à l'écosystème présent à toutes les stations. Enfin, le programme de surveillance a été révisé pour mener une validation scientifique ainsi que pour définir les lacunes et les nouveaux enjeux, en tenant compte des recommandations prescrites pour les programmes actuels de surveillance des parcs.

D'une manière générale, les propriétés chimiques de l'eau étaient semblables aux trois sites d'échantillonnage, du fait que pour tous les paramètres, les fourchettes de concentration se recoupaient. Néanmoins, des tendances entre les différents sites étaient apparentes pour de nombreux paramètres, ce qui a été étudié en détail tout au long de ce rapport. C'est dans la rivière Athabasca, par rapport à la rivière de la Paix et la rivière des Esclaves, que la valeur de l'oxygène dissous était la plus basse et que, par contre, les valeurs étaient les plus hautes pour le total des solides dissous et la plupart des ions majeurs. Les métaux dans l'environnement proviennent de gisements naturels dans le sol, les roches et les sédiments benthiques et reflètent par conséquent la géologie environnante et le traitement hydrologique. Dans ces rivières, les concentrations totales en métaux atteignaient leur maximum entre les mois de mai et juillet, ce qui correspondait au débit de pointe et à la charge sédimentaire maximale. Pour tous les métaux, les fourchettes se recoupaient entre les sites et, pour la plupart, les médianes étaient semblables.

Une grande partie de cette étude était axée sur l'évaluation des tendances en fonction du temps pour mesurer la stabilité chimique de ces écosystèmes aquatiques pendant les deux précédentes décennies. En ce qui concerne les paramètres physiques et les ions majeurs, la plupart des analyses ont mis en évidence la stabilité de la concentration dans le temps. Sur les 50 analyses réalisées pendant toute la période des relevés, 16 seulement ont mis en évidence des modifications de concentration et cinq d'entre elles n'ont révélé aucune modification des concentrations au cours de la dernière décennie. Les modifications de la concentration en éléments nutritifs dépendaient du site et du paramètre. On n'a constaté que peu de changements en fonction du temps pour le carbone. Les tendances relatives aux concentrations en azote étaient semblables pour les rivières de la Paix et Athabasca; la plupart des formes dissoutes affichaient des concentrations à la hausse, tandis que pour la rivière des Esclaves, au moins au cours de la dernière décennie, ces paramètres suivaient des tendances à la baisse. Nous n'avons décelé aucune tendance significative des concentrations en phosphore dans la rivière de la Paix; par contre, dans la rivière Athabasca et la rivière des Esclaves, les concentrations de phosphore dissoute et totale ont augmenté au cours de la période des relevés. Les augmentations observées pour la concentration en éléments nutritifs résultent en grande partie d'augmentations ayant lieu pendant les mois d'hiver, dans des conditions de faible débit et de couverture de glace. En fin de compte, nos résultats ont montré qu'au moins en partie, les

tendances des concentrations dans la rivière Athabasca dépendent des variations du régime de débit.

Un sommaire plus détaillé de ces résultats se trouve au chapitre 5.0. Cependant, les conclusions essentielles et les questions soulevées par cette étude pour ces sections de rivières comprennent (...);

- Il y a eu une modification des tendances saisonnières des paramètres dissous de la rivière de la Paix et la rivière des Esclaves, en raison de variations dans les tendances de débit des rivières attribuables à la construction du barrage William A. C. Bennett.

- Pour les sulfates dissous, on a montré les tendances à la hausse sur tous les sites, mais c'est tout de même en cohérence avec un changement plus général au niveau régional (Glozier *et al.*, 2004b, et Parker *et al.*, 2009) qui touche d'autres rivières du Nord.

- Des dépassements par rapport aux lignes directrices du CCME en ce qui concerne les concentrations totales en métaux étaient fréquents, mais il s'est avéré qu'ils étaient directement liés aux charges sédimentaires naturellement élevées dans ces rivières et qu'ils n'avaient probablement aucune incidence négative sur la vie aquatique.

- On a mis en évidence des dépassements pour le phosphore total et l'azote total, par rapport aux lignes directrices du ministère de l'Environnement de l'Alberta; mais, comme pour le total des métaux, tous les dépassements étaient associés à des périodes où les charges sédimentaires de matières en suspension sont naturellement élevées.

- Les objectifs propres au site pour trois paramètres (l'oxygène dissous, le sulfate et le total des solides dissous) définis au titre de l'Initiative des écosystèmes des rivières du Nord (EIRN) (Donald *et al.*, 2004) ont été atteints à la fréquence attendue.

- En ce qui concerne les neuf paramètres relatifs aux métaux pour lesquels des analyses de tendance ont pu être faites dans la rivière Athabasca, aucune augmentation n'a été mise en évidence.

L'augmentation des éléments nutritifs tout comme la diminution du débit des rivières semblent la plus grande préoccupation pour les sections d'étude des rivières des Esclaves et Athabasca ainsi que pour les écosystèmes aquatiques en aval. Les tendances à la hausse concernant le phosphore ont occasionné une modification du statut trophique (basé sur la concentration totale de phosphore) pour ces éléments d'au moins un niveau trophique et, dans certains cas, trois niveaux trophiques.

- Une lacune majeure concernant le programme actuel de surveillance de la qualité de l'eau du Parc national Wood Buffalo est l'absence de données sur certains contaminants préoccupants. Le programme de surveillance a été établi en grande partie pour évaluer les propriétés chimiques générales et les variations potentielles en éléments nutritifs résultant d'un apport de pollution ponctuelle sur les sections en amont. Il est recommandé qu'à l'avenir les contaminants préoccupants soient évalués dans des échantillons d'eau.

Ce programme de surveillance mené en commun par Environnement Canada, Parcs Canada, les Territoires du Nord-Ouest et le ministère de l'Environnement de l'Alberta a fourni des données importantes sur la qualité de l'eau en fonction du temps. Cela dit, voici quelques recommandations à suivre pour les orientations futures :

- Établissement d'une fréquence systématique de huit échantillonnages par an, les échantillonnages se répartissant entre les trois saisons hydrologiques déterminées dans ce rapport comme suit : deux au printemps/été (de mai à juillet), deux à l'automne (d'août à octobre) et quatre durant la période d'hiver plus longue (de novembre à avril).

- Établissement et mise à jour d'une liste de paramètres pertinents analysés sur tous les sites.
- Il faudrait ajouter à la série des paramètres mesurés dans l'eau et peut-être dans les sédiments des mesures d'un spectre plus large de contaminants préoccupants issus de sources industrielles présentes dans les bassins. Les contaminants possibles provenant des effluents des usines de pâtes et papiers comprennent les dioxines, les furanes et les composés sulfurés; ceux provenant des installations de production pétrolière et gazière comprennent les hydrocarbures aromatiques polynucléaires, les hydrocarbures aromatiques polycycliques, les acides naphténiques et les phénols chlorés.
- Étant donné que les écosystèmes en aval sont une source de préoccupation (en particulier le delta des rivières de la Paix et Athabasca), il est recommandé de recourir à des sites d'échantillonnage supplémentaires pour mesurer la qualité de l'eau et le biote dans le delta.
- Après la rédaction de ce rapport, des évaluations régulières et plus ciblées (p. ex. les courbes des éléments nutritifs) pourraient être réalisées pour actualiser les analyses à long terme qui sont présentées dans ce rapport.
- Il conviendrait de fixer des objectifs propres aux sites concernant les métaux et les éléments nutritifs à utiliser pour la rédaction des rapports de routine. Cela pourrait aboutir à la mise au point d'indicateurs de la qualité de l'eau, lesquels pourraient être consignés plus fréquemment.
- La densité du biote et la composition des communautés devraient être prises en compte pour les sites d'intérêt.
- Les niveaux des métaux dans les poissons indicateurs, par exemple la laquaiche aux yeux d'or ou le doré jaune, doivent être pris en compte.

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1.0 Introduction

Long-term water quality monitoring is conducted by Environment Canada (EC) for two major purposes; 1) to obtain information on current water quality conditions including the identification of short-term but extreme conditions for parameters of concern, particularly for comparisons to guidelines, and 2) to provide information on water quality trends through time. The first can be referred to as status monitoring and can highlight conditions which may have more immediate impacts on ecosystem or human health and should be addressed with greater urgency. The parameters which are examined are limited to those applicable for this purpose. Of equal or greater importance, long-term trend analyses provide information regarding the direction of change in the environment and can contribute a significant component to the understanding of changes in water quality by water managers when making informed water management decisions.

At a Canadian Council of Ministers of the Environment (CCME) Water Quality Workshop in 2003, it was recognized that the “current level of concern and commitment to the protection and maintenance of water quality in Canada is unprecedented” (de Rosemond et al. 2003). Furthermore, for many parameters of concern, enhanced monitoring programs have repeatedly been identified as a key requirement to understanding and protecting Canadian aquatic ecosystems (Environment Canada 2001). Although long-term water quality monitoring programs in Canada are continually re-evaluated for scientific relevance against study objectives, and despite these recognized needs and concerns, a consistent reduction in the number of sampling sites and parameters being monitored has occurred throughout Canada over the previous several decades (Kent et al., 2003). The keys to maintaining national monitoring programs are two-fold. First, the reporting of results and their subsequent use to contribute to water management actions and secondly, the acknowledgement that historical background information is essential for contextual setting because samples predating an anthropogenic change in land use are unobtainable.

The condition of water in the lower reaches of the Slave River basin in Wood Buffalo National Park is the focus of this report. The Slave basin, which includes the Athabasca and Peace river basins, is a sub-basin of the Mackenzie River, the largest basin by area in Canada and one of the most studied watersheds in Canada. During the late 1980s, the Athabasca River and Peace River basins became focal points for industrial expansion in Alberta. The construction of several new pulp mills had begun, and plans for expansion of oil sands mining and refining near Fort McMurray were announced. Parks Canada raised concerns over the cumulative effects that developments within these basins may have on the water quality of the two major rivers entering Wood Buffalo National Park (WBNP). Of particular concern was the fragile ecosystem of the Peace-Athabasca Delta (PAD), which had been altered earlier by hydrologic changes brought about by construction on the Peace River of the William A. C. (W.A.C.) Bennett dam; completed in 1967. An additional concern in this National Park was for the health of Park residents, many of whom live “off the land”, using the major rivers and the delta as direct sources of food and water. Thus, a joint Park Canada – Environment Canada water quality monitoring program for the lower Athabasca, Peace and upper Slave rivers was initiated in 1989 (see details in Section 1.1).

In part to address questions posed by Parks Canada and other jurisdictions within the watersheds, a major research effort, the Northern River Basins Study (NRBS, 1991-1996), was initiated by the Governments of Canada, Alberta, and the North West Territories (NWT). The NRBS was comprised of 150 research and monitoring sub-projects, with topics ranging from industrial contaminants to traditional knowledge. The NRBS published its final report in 1996 (NRBS 1996) and contained a wide range of recommendations designed to protect the health of the northern rivers and those living along them. To address the recommendations of highest priority from NRBS, the Northern Rivers Ecosystem Initiative (NREI) was established to fund and expand the necessary research. The final NREI report was published in 2004 (NREI 2004). Additional studies specific to the functioning of the PAD have also been conducted over the past several decades. Many of these reports are available online (www.ec.gc.ca; www.pnr-rpn.ec.gc.ca/nature/ecosystems/nrei-iern/index.en.html).

The intent of this study is not to review the already large knowledge gained from these programs but rather to augment our understanding with a detailed analysis of the water quality information available from the joint EC-Parks monitoring program in the lower basin. An unpublished summary of this information was last produced in 1991 (Crosley person comm.) but did not include detailed statistical analyses. Several reports which provide background information were also produced through the Peace-Athabasca Technical Studies (e.g., MacMillan 1996). Although much of the monitoring data from these sites has been utilized by, and provided a significant contribution to many of the NRBS and NREI research oriented studies, a comprehensive analysis of the water quality data is needed. Therefore, in this report we present and interpret water quality data collected on the Athabasca, Peace, and Slave rivers at the boundaries of Wood Buffalo National Park between August 1989 and December 2006. As the National Parks Strategic Goals include the maintenance and restoration of aquatic ecosystems (Parks Canada 1997), the two main objectives of the water quality monitoring program when it was implemented (1989) included:

1. To provide an overview of status and trends in water quality in the three major watersheds entering and exiting the Wood Buffalo National Park.

2. To provide an assessment of the nutrient conditions of water entering and exiting the Park as a result of upstream point sources.

The nutrient focus is related to assessing potential impacts from nutrient inputs to the upstream reaches of the Athabasca and Peace rivers. Having reviewed these original objectives as well as current concerns, this report serves four major purposes. First, to provide a succinct source of information for water quality in these waters, we have summarized the large amount of water quality data available (>14500 records) and provide detailed statistical summaries for the period of record (Appendix 2). We also present and discuss the range and median concentrations of all water quality parameters and, for those of concern; we discuss the differences among the three watersheds in some detail, including comparisons to upstream source waters (Section 4.1). We also assess the range of concentrations for 11 metals against their respective CCME guidelines for the protection of aquatic life; provide correlations with suspended sediment concentrations, and recommendations regarding the development of site specific guidelines.

The second main purpose of this report was to determine if the water quality of these waters has changed over the period of record. We report on the results of statistical temporal trend analyses (seasonal and yearly) conducted for 30 water quality parameters. This is a major component of our analysis (Section 4.2) and is useful to identify seasonal changes in concentration for parameters which display long-term chemical stability (no change through period of record other than seasonal patterns), and those parameters which are increasing or decreasing in concentration through the 17 year period. In addition, we determined whether the changes in chemical concentration observed are, in part, related to changes in: 1) river discharge, 2) a particular period of time (entire period of record vs. latest decade), or 3) season.

The third component of this report (Section 4.3) examines two issue driven concerns which have been identified through earlier work and third party concerns. Metals have been raised as a potential concern in the Athabasca River in relation to potential impacts from the industrial activities associated with the Athabasca Tar Sands (Hatch and Price 2008). Although most of the data on metal concentrations in water are unsuitable for long-term trend analysis due to multiple changes in laboratory analytical technique, we report on trends for nine metals that metal data quality conditions and are also released to the atmosphere by these industrial activities. The second issue is the increasing nutrient concentration identified in this report and others (NRBS) for large, northern river systems with cumulative nutrient point source inputs. We examine the trends in nutrients in more detail and evaluate them against indicators of ecological trophic status.

Finally, the monitoring program was reviewed for scientific validity and gaps in information. We also make recommendations for improvements to the monitoring program to allow for a better ecological assessment of potential stressors, including the coordination with monitoring programs and research conducted by other agencies within the Slave River basin.

1.1 Wood Buffalo Water Quality Monitoring Program

Over the previous four decades Environment Canada and Parks Canada have monitored water quality to assess potential changes at sites on three major rivers in Wood Buffalo National Park. In 1967, following completion of the W.A.C. Bennett Dam, Environment Canada initiated water quality monitoring on the Peace River at Peace Point (Figure 1). Samples were collected monthly until 1976 at which time the sampling was discontinued. However, prompted by renewed concerns from Parks Canada over potential changes in water quality related to rapid growth in the forestry and pulp industries, monitoring at Peace Point was re-instated in August 1989. Concurrently, monitoring on the Athabasca River at 27 Baseline was initiated to provide water quality data for the Athabasca River at the upstream boundary of Wood Buffalo National Park (Table 1). The monitoring program on the Peace and Athabasca rivers is cost-shared between Parks Canada and the Prairie and Northern Water Quality Monitoring office of Environment Canada with sampling costs borne by Parks Canada, and analytical costs by Environment Canada.

Table 1: Long-term Water Quality Monitoring Locations within Wood Buffalo National Park.

Monitoring Station	Station ID	Latitude	Longitude	Drainage Area (km^2)	Period of Record*	No. of Samples
Athabasca River at 27 Baseline	AL07DD0001	58°10’21”	111°22’13”	154,880	1989 to 2006	148
Peace River at Peace Point	AL07KC0001	59°06’50”	112°25’35”	293,000	1967 to 1976 1989 to 2006	81 139
Slave River at Fitzgerald	AL07NB0001	59°52’10”	111°35’10”	615,000	1960 to 1967 1989 to 2006	35 124

**For the overall analysis in this report, data from August 1989 to December 2006 are presented*

A long-term water quality monitoring station on the Slave River at Fitzgerald, near the downstream boundary of WBNP (Figure 1), has been operational since 1960 under a separate agreement between Environment Canada, and the Department of Renewable Resources, Government of the NWT. Since 1995, the site has been operated in partnership with Alberta Environment.

During the first five years of monitoring program, on average, 9-11 samples per year were taken at each station. As the monitoring program was reviewed and modified, sample frequency was reduced to 6-8 samples per year on average for the period 1994-2006. All seasons were sampled in most years. A detailed examination of appropriate sampling frequency for trends and seasonality patterns is included in the recommendations section.

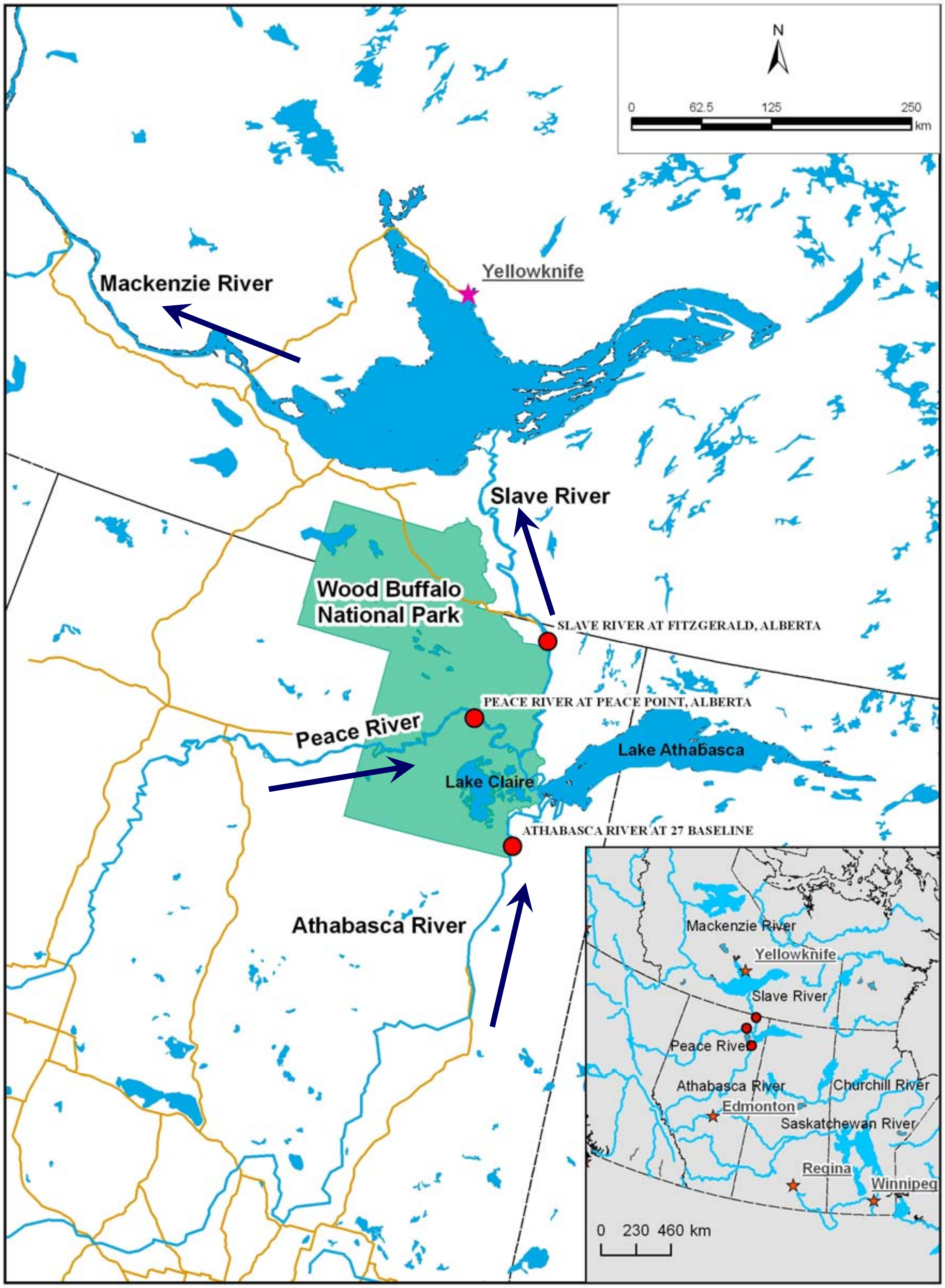


Figure 1: Long-term Water Quality Monitoring Locations near Wood Buffalo National Park.

2.0 Study Area

The three monitoring stations which are the focus of this report are all located on major tributaries of the Mackenzie River. The Mackenzie River basin is the largest watershed is Canada by area (1.8 million km^2), comprising 20% of the land mass of Canada and is second only to the St Lawrence River for river flow (average annual discharge 9,910 m^3/s, MMRB 2004). Being the largest basin in Canada, it is also very diverse in landscape including the Rocky Mountains in the west, Interior Plains and the Canadian Shield in the east. Vegetation ranges from mountain alpine meadows, boreal forest, peat lands and arctic taiga with 15 distinct Ecoregions identified (Ricketts et al., 1999). The tree line is the dividing line between the two major climatic zones in the basin, subarctic and arctic, and permafrost underlies about 75% of the basin. The three major tributaries discussed in this report, the Athabasca, Peace and Slave rivers, are located in the southern portion of the basin and together comprise nearly 60% of the Mackenzie by area. A major study focusing on the state of the aquatic ecosystem for the Mackenzie River basin released in 2004 summarizes the status of the basin and brings together the current knowledge for the basin (MMRB 2004).

2.1 Geographical Characteristics

Athabasca River

The Athabasca River (AR) arises from the Columbia Icefield located along the continental divide in Jasper National Park. The divide is also the source of headwaters to the Columbia and Saskatchewan rivers, and for this reason is referred to as the hydrologic apex of North America. From these headwaters the Athabasca River flows north-westerly for approximately 100 kilometres to the Jasper town site, and then turns and flows north-easterly for most of the 1040 river kilometres to Fort McMurray. At Fort McMurray, the Athabasca turns to the north for the last 300 kilometres to the mouth at Lake Athabasca, at which point it is a 6th order river (Figure 1).

Many tributaries enter the Athabasca River from the headwaters to the outlet. In the upper reaches these include the Sunwapta, Whirlpool, Astoria, Miette, Maligne, Snaring, Rocky and Snake Indian rivers. From Jasper to Athabasca several larger tributaries include the Berland, McCleod, Freeman, Pembina and Lesser Slave rivers. Between Athabasca and Fort McMurray, the Wandering, Hangingstone and Clearwater rivers enter from the southeast. North of Fort McMurray tributaries entering from both sides of the river include the Beaver, Steepbank, Muskeg, Mackay, Firebag and Richardson rivers. Many of these tributaries have water discharge records available at least during open water (http://scitech.pyr.ec.gc.ca/waterweb/main.asp).

Over the 1538 km of the river's course the character and its' surrounding topography changes greatly in it's decent of over 1000 m. In the upper section from the Columbia Icefield to Jasper, the Athabasca is shallow, high in velocity and steep in gradient (averaging 4 m/km). In this reach the river bed is dominated by gravel/cobble and the landscape changes from alpine to sub-alpine and then to montane. Along the remaining sections river slope gradually decreases from approximately 90 cm/km near Jasper to 40 cm/km at Athabasca finally to <20 cm/km below Fort McMurray. With lower slope and velocity, the river bed becomes progressively dominated by sand and silt substratum as the adjacent topography evolves from montane to rolling foothills and then to boreal forest. A series of three major rapids interrupts the flow of the river above Fort McMurray. At the Grand Rapids, the largest of the three, the Athabasca drops 11 m in a distance of 1.6 km. These rapids, a barrier to river transportation, replenish winter dissolved oxygen concentration throughout the lower reaches of the river. Beyond the 58th parallel, the Athabasca River (and further north its distributary, the Embarras River) form the eastern boundary of Wood Buffalo National Park. Delta-formed willow islands characterize the final kilometres to the river mouth at Lake Athabasca.

Peace River

The Peace River (PR) headwaters include numerous tributaries flowing from the B.C. Rockies into Williston Lake, which is British Columbia's largest reservoir with an area of 166,000 ha. Williston Lake was formed by construction of the W.A.C. Bennett Dam near Hudson's Hope, B.C. The dam, built by B.C. Hydro and completed in 1967, is one of the world's largest earth-fill dams, two km in length and nearly 200 m in height. When the dam was closed, the Peace River flooded the valleys of the Finlay and Parsnip rivers to form Williston Lake.

From the W.A.C. Bennett dam, the Peace River flows eastward past the town of Taylor, B.C and crosses the Alberta border at kilometre 160. The surrounding topography gradually changes from montane forest to prairie parkland for the next 650 km to Fort Vermilion. The Smoky River joins the Peace River just upstream of the town of Peace River. The Smoky River has it's headwaters in Jasper National Park, its major tributary, the Wapiti River, also has headwaters in the Rocky Mountains. Beyond the community of Paddle Prairie the river turns once more to the east past the town of Fort Vermilion. The Wabasca River joins the Peace approximately 50 km below Fort Vermilion. The Wabasca drains much of the south-eastern area of the Peace River basin. Beyond the confluence of the Wabasca River, the Peace River passes the Vermilion Chutes. The Peace drops 3.5 m through the Vermilion Chutes, posing an obstacle to river transportation and fish migration. The Peace River enters Wood Buffalo National Park at the Fifth Meridian, and continues its eastward flow, passing the small communities of Garden River and Peace Point. The Peace receives outflow from the Peace-Athabasca Delta and Lake Athabasca via the Chenal des Quatre Fourches, and at this point it is an 8th order stream, almost 2000 km in length. Over the course of the river the substratum is dominated by sand and gravel, with occasional islands and gravel bars.

Slave River

The Slave River (SR) begins at the confluence of the Peace River and the Rivière des Rochers. For most of its 434 kilometre course to the mouth at Great Slave Lake, the Slave River travels along the boundary between the Canadian Shield to the east and the sedimentary Taiga Plains to the west. Several smaller tributaries enter the Slave from the Canadian Shield to the east but at its mouth it is an 8th order river due to the larger upstream tributaries. Exposed bedrock can be found along the river as well as alluvial islands, abandoned channels and oxbow lakes (Culp et al., 2005). At Fitzgerald, the Slave River descends 35 m over a 30 km distance passing over a Precambrian sill of bedrock and crosses the border into the Northwest Territories.

2.2 Hydrologic Patterns

Mean discharge in the Athabasca River increases nearly 7-fold from the headwaters to Fort McMurray (mean discharge from 1989-2006 = 87 m^3/s at Jasper, 401 m^3/s at Athabasca and 577 m^3/s downstream of Fort McMurray). For the same period, the Peace River increases 1.6X from near the outlet of Williston Lake (1275 m^3/s) to the confluence (2080 m^3/s) and at that point is over three times the size of the Athabasca River. The Slave River had a mean discharge 3386 m^3/s at the outlet to Great Slave Lake, which includes additional inputs from the Birch River (a tributary to Lake Claire), and from Saskatchewan tributaries to Lake Athabasca. Note that, the discharge data for the Athabasca River is reported and used for the trend analyses are derived from the station downstream of Fort McMurray because it is the closest continuous discharge station on the Athabasca River. A discharge station closer to the mouth was in operation from 1971-1984 (ATHABASCA RIVER AT EMBARRAS, 07DD001) and flows during that period were within + 8.3% of the upstream station. The source for all river discharge data reported was the on-line Environment Canada Water Survey database (www.scitech.pyr.ec.gc.ca/waterweb).

Although total flow is clearly different, the annual patterns in discharge in the three rivers are similar with annual peak flows occurring between, May and July (Figure 2). Flow regulation in the Peace River has had a major effect on the magnitude of the peaks in discharge for both the Peace and Slave rivers. In Figure 2, three time periods are represented to illustrate the changing discharge patterns from 1960 to 2006.

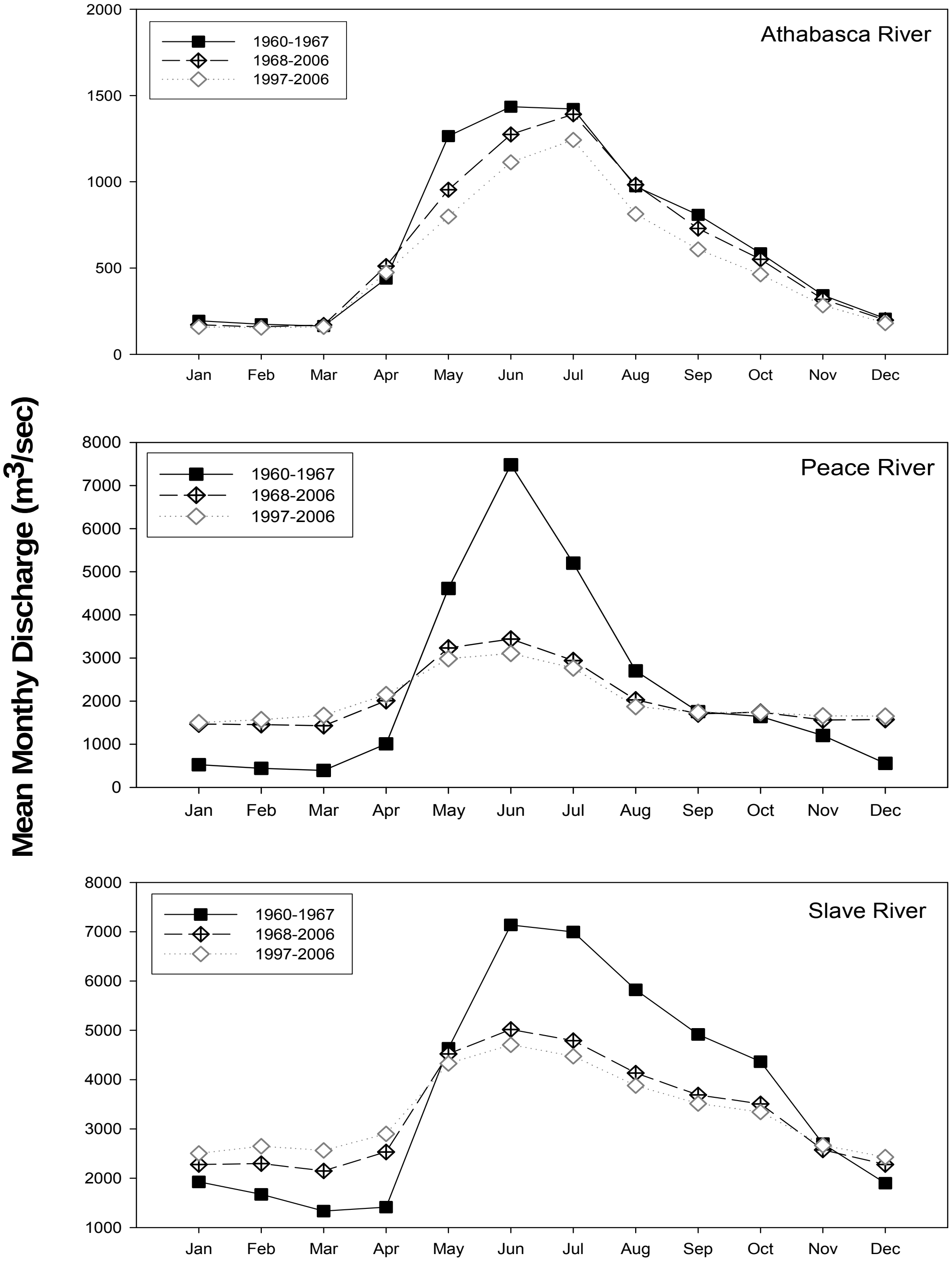


Figure 2: Monthly Mean Discharge for the Athabasca River below Fort McMurray, Peace River at Peace Point, and Slave River at Fitzgerald. Three time periods are depicted; Pre W.A.C. Bennett Dam (1960-1967), Post W.A.C. Bennett Dam (1968-2006) and the last decade (1997-2006).

The earliest period (1960-1967) is that period prior to closure of the W.A.C. Bennett dam. For the Peace and Slave rivers, the dam modified the pattern by dampening the peak spring/summer discharge (PR -42 % and SR -21%) and increasing the winter discharge (PR +63% and SR +35%). The same periods did not show any significant shifts in seasonal patterns for the Athabasca River. However, an overall reduction in discharge is evident in the Athabasca River and has been reported elsewhere. We explore yearly and seasonal patterns in discharge more fully in relation to changes in water chemistry in later sections (Sections 4.2.1 and 4.2.2).

Finally, a key feature associated with these rivers is the Peace-Athabasca Delta which was designated in 1982 as an internationally significant site for waterfowl habitat (NRBS 1996). Water flow through the PAD is complex and dependent on water levels within the contributing sources; direction of flow is at times reversed. When the level of Lake Athabasca is above that of two of the PAD's lakes (Claire and Mamawi), water flows westward into the delta; when levels are reversed water discharges from the PAD into Lake Athabasca and northern flowing tributaries of the Peace River. A similar situation occurs at the confluence of these rivers with the Peace. The three channels (Rivière des Rochers, Chenal des Quatre Fourches and Revillon Coupé) normally exiting the PAD and Lake Athabasca to flow north to the Peace River can reverse flow direction when flooding in the Peace River raises the water level above that of Lake Athabasca. These reversing flows contribute to flooding of the PAD's lakes and perched basins and hence the maintenance of the wetland habitat for waterfowl (Prowse and Conly 2000). These complex issues have been the subject of many studies and reports (NRBS 1996, NREI 2004, http://www.pnr-rpn.ec.gc.ca/nature/ecosystems/nrei-iern/index.en.html) which are only briefly covered by this description but are important to understand in the context of the interpretation of the water quality within the river reaches addressed by this report.

2.3 Land Use Patterns

Land use in the Peace and Athabasca River basins was previously summarized in the NRBS and NREI studies, excellent resources for further information (NRBS 1996, NREI 2004). Threats to the integrity of aquatic ecosystems in these river basins include; changes to land use from agricultural, forestry, mining (coal), hydrologic fragmentation, and point source industrial and municipal inputs. We have updated some of the information produced originally during those studies and provide more detailed information on population growth and land use as a background for discussion of water quality patterns.

The percent of land use (Figure 3) for the two basins (categories as defined in the Atlas of Canada www.atlas.nrcan.gc.ca/site/), are remarkably similar with the exception of a greater proportion of agricultural activities in the Peace River, centred in the Peace River country from the Grande Prairie area to Fort Vermillion. The Athabasca River basin has a higher proportion of Taiga/open lands, although agricultural lands are present in the south-eastern portion, along the Pembina River. Population density within the two basins is similar (<1 person/ km^2, Culp et al., 2005), however, population growth has been centred in two communities in Alberta, Fort McMurray and Grande Prairie (Table 2). For both of these communities the greatest population gain occurred over the most recent decade. The communities of Whitecourt, Slave Lake and Athabasca, in Alberta, and Fort St John, BC, also showed increases over the study period but the increases were more gradual and consistent through time. Taylor, BC, smaller in size than the other municipalities listed did show a large proportional increase in population.

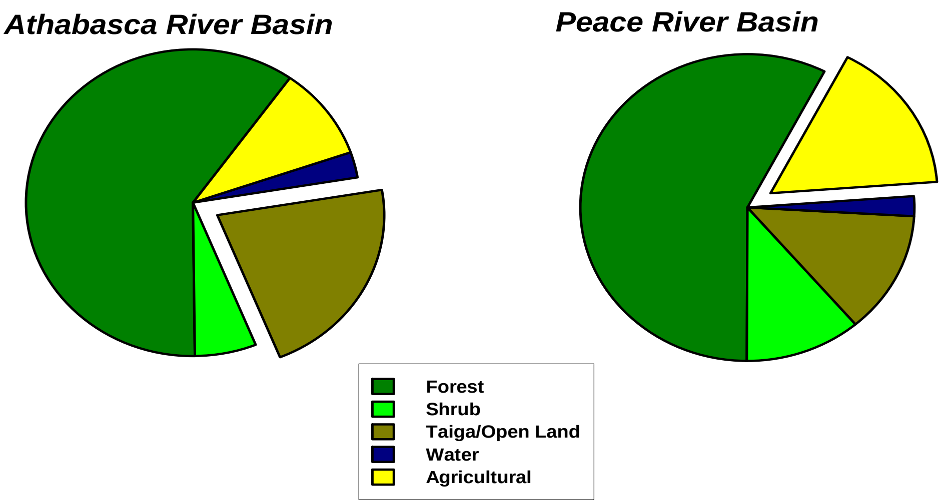


Figure 3: Proportion of Land use in the Athabasca and Peace river basins (*data source: www.atlas.nrcan.gc.ca*).

A total of ten pulp and/or paper mills discharge effluent into the Peace and Athabasca rivers, 5 in each basin (Table 3). In the Peace River basin, four mills operate on or near Williston Lake. These include Pope and Talbot (Mackenzie Pulp) and Abitibi-Bowater (Mackenzie Paper), which are located in the town of Mackenzie, B.C and are licensed to release effluent into Williston Lake. The third mill, Louisiana-Pacific, is located at the town of Chetwynd, B.C. but does not release effluent to Williston Lake. Canfor Forest Products (Taylor Pulp) discharges effluent into the Peace River at Taylor, BC, downstream of the dam outlet. Across the Alberta border, the Wapiti River, a major tributary of the Smoky (and then the Peace), receives bleach kraft effluent from the Weyerhaeuser pulp mill at Grande Prairie, 40 km upstream of the confluence with the Smoky River. Flowing northward, the Peace River receives effluent from the Diashowa-Marubeni kraft mill approximately 25 km downstream of the town of Peace River.

Two bleach kraft pulp mills operate along the Athabasca River, including the West Fraser in Hinton, the oldest pulp mill in Alberta, and Alberta-Pacific Pulp near Athabasca, the largest and newest pulp mill in the province. In additional to these two kraft mills, three CTMP (chemical-thermal-mechanical pulping) mills are in operation. Two of these mills are located in or near Whitecourt (Alberta Newsprint and Millar Western) and the third, Slave Lake Pulp, is situated on the Lesser Slave River near Slave Lake. All of the pulp mills on the Athabasca River are licensed to release effluent to the river. Effects of these effluents on aquatic ecosystems have been the focus of many of the NRBS (1996) and NREI (2004) studies and are discussed in relation to water quality trends in subsequent sections.

Table 2: Population of cities and towns located along the Athabasca and Peace rivers for the beginning (1989) midway (1997) and the end (2006) of the study period. Percentage change over the entire period as well as the earlier and later periods is provided (*data sources: www.municipalaffairs.alberta.ca/mc_offical_populations.cfm; /www.bcstats.gov.bc.ca/DATA/pop/popstart.asp*).

City/Town	**Population**					
	1989	**1997**	**2006**	**% Change 89-97**	**% Change 97-06**	**% Change 89-06**
Athabasca River Watershed						
Jasper, AB	4475	4691	4643	5	-1	4
Hinton, AB	9893	9961	9769	1	-2	-1
Edson, AB	7323	7399	8365	1	12	13
Whitecourt, AB	6560	7783	8747	16	11	25
Slave Lake, AB	5611	6553	6600	14	1	15
Athabasca, AB	1975	2313	2415	15	4	18
Fort McMurray, AB	33698	33078	61336	-2	46	45
Peace River Watershed						
Hudson Hope, BC	1026	1151	1066	11	-8	4
Fort St. John, BC	14040	15859	18249	12	13	23
Taylor, BC	767	1077	1444	29	25	47
Grande Prairie, AB	27208	31140	44631	13	30	39
Grande Cache, AB	3646	4441	3828	18	-16	5.0
Peace River, AB	6504	6536	6240	1	-5	-4

As of 2005 (the time period relevant to the current data analysis), there were three oil sands mines (Syncrude Energy, Suncor Energy, Shell Albian Sands) and two upgrading refineries (Syncrude Energy and Suncor Energy) operating north of Fort McMurray. However, since then additional mines have gone through start-up and plans for others are at various stages of approval, planning or construction. The amount of water which is allocated to be withdrawn within a given year by the six approved and/or operating oil sands mines (2005) is 453051 dam^3 which is equivalent to 2.5% of total annual flow in the Athabasca River at Fort McMurray over the study period (1989-2006) or 2.7% over the last decade (1997-2006) (www.scitech.pyr.ec.gc.ca/waterweb). The majority of these allocations (82%) are for water withdrawn directly from the Athabasca River. The other water sources include several tributaries to the Athabasca River (13%) and surface runoff (5%). The allocations for these six facilities account for over 60% of the water allocations for the entire Athabasca River basin (Schindler et al., 2007). However, as of 2005 only three projects were in operation and reported withdrawing approximately 98900 dam^3 or about 52% of their total allocation. While the oil sands mines and refineries do not release discharges from effluent tails ponds into the Athabasca River, atmospheric releases from the refineries and the close proximity of large tailings ponds to the Athabasca are ongoing concerns for stakeholders.

No industrial or municipal effluents enter the Slave River between the PAD and Fort Fitzgerald.

Table 3: List of Pulp and Paper Mills within the Athabasca and Peace river basins (updated from NRBS 1996 with information from www.ec.gc.ca; loadings from the NPRI substance release database www.ec.gc.ca/pdb/npri/npri_home_e.cfm).

Company Name/ Pulp Mill	**Details**					
	Receiving Water	**Location**	**Start Up**	**Product**	**2006 Loadings (Tonnes)**	
					TP	**NH3**
Athabasca River Watershed						
West Fraser Mills, Ltd[1] /Hinton Pulp	Athabasca River	Hinton, AB	1957	Bleached Kraft pulp	45	140
Alberta Newsrprint Co. Ltd.	Athabasca River	Whitecourt, AB	1990	Thermomechical pulp, de-inked paper	4	0.5
Millar Western Industries Ltd.	Athabasca River	Whitecourt, AB	1988	Bleached chemi-thermomechanical pulp	NA	1.0
Slave Lake Pulp Corporation	Lesser Slave River	Slave Lake, AB	1991	Bleached chemi-thermomechanical pulp	14	2.0
Alberta Pacific Forest Industries Inc.	Athabasca River	Near Grassland, AB	1993		41	148
Peace River Watershed						
Pope and Talbot Ltd. [2] /Mackenzie Pulp	Williston Lake	Mackenzie, BC	1972	Bleached Kraft Pulp	31	19.5
Abitibi Bowater Inc [3]/Mackenzie Paper	Williston Lake	Mackenzie, BC	1969	Mechanical Pulp, newsprint	0.2	10
Louisiana-Pacific	NA	Chetwynd, BC	1991	Bleached chemi-thermomechanical pulp	-------------------	
Canfor Forest Products Ltd. [4] / Taylor Pulp	Peace River	Taylor, BC	1988	Bleached chemi-thermomechanical pulp	27	NA
Weyerhaeuser Canada / Grande Prairie Operations	Wapiti River	Grande Prairie, AB	1973	Bleached Kraft Pulp	24	48
Daishowa-Marubeni	Peace River	Peace River, AB	1990	Bleached Kraft Pulp	NA	19.1

In previous documents these mills were listed as: [1] Weldwood of Canada; [2] Fletcher Challenge; [3] Finlay Forest Industries; and [4] Fibreco

3.0 Water Quality Monitoring Methods

Water quality monitoring at the three locations in Wood Buffalo National Park has been undertaken 4-12 times per year since 1989 (Appendix 2). A core group of parameters is analyzed at all three monitoring locations (Table 4). Some additions and deletions to the parameter lists have occurred over time, as laboratory techniques and equipment were improved, or as results and program requirements dictated. For analysis and discussion, the core parameters have been subdivided into four groups; physicals, major ions, nutrients, and metals. Dissolved metals were added to the parameter suite in 1999.

Table 4: List of Water Quality Parameters Analyzed.

Physicals	Major Ions	Nutrients	Metals	
			dissolved*	**total**
colour true	alkalinity total	carbon diss organic	aluminum*	
oxygen, dissolved	bicarbonate - C	carbon part organic	arsenic	
pH (F, L)	calcium	carbon total organic - C	barium*	barium
residue, nonfilterable	chloride	NH_3 dissolved	beryllium*	beryllium
specific conductance (F, L)	fluoride	Nitrogen NO_3-NO_2	boron	
turbidity	hardness total	Dissolved inorganic nitrogen - C	cadmium*	cadmium
	magnesium	nitrogen dissolved	chromium*	chromium
	potassium	nitrogen particulate	cobalt*	cobalt
	silica	nitrogen total - C	copper*	copper
	sodium	phosphorus dissolved	iron*	iron
	sulphate	phosphorus part - C	lead*	lead
	total dissolved solids - C	phosphorus total	lithium*	lithium
			manganese*	manganese
			molybdenum*	molybdenum
			nickel*	nickel
			selenium	
				silver
			strontium*	strontium
			vanadium*	vanadium
			zinc*	zinc

** Dissolved metals which have been analyzed since 1999 only.*
C Results for these variables are calculated from results of analyzed variables
F, L Variables which are measured in both the field (F) and the laboratory (L)

All samples were collected according to published field methods (Water Quality Branch 1983). For the Athabasca and Peace rivers, sample collection was performed by WBNP wardens stationed in Fort Chipewyan and/or Fort Smith while samples from the Slave River were collected by Environment Canada, Water Survey of Canada personnel. To facilitate inter-site comparisons, data collected during the period August 1989 to September 2006 are included in this report. Details on the frequency of sampling through this period are provided in Appendix 2. Monitoring of all three locations is ongoing as of this writing.

Samples from the Peace, Athabasca and Slave (up to 1991) rivers were analyzed at the National Laboratory for Environmental Testing (NLET) laboratories; in Saskatoon, Saskatchewan for nutrients and in Burlington, Ontario for metals and major ions. Beginning in 1992, water samples from the Slave River at Fitzgerald were analyzed at the Taiga Environmental Laboratory in Yellowknife. Published analytical protocols were used for all chemical analyses presented in this report (NAQUADAT, 1988, Taiga Environmental Laboratory 2005, www.nwt-tno.inac-ainc.gc.ca/taiga/index_e.htm).

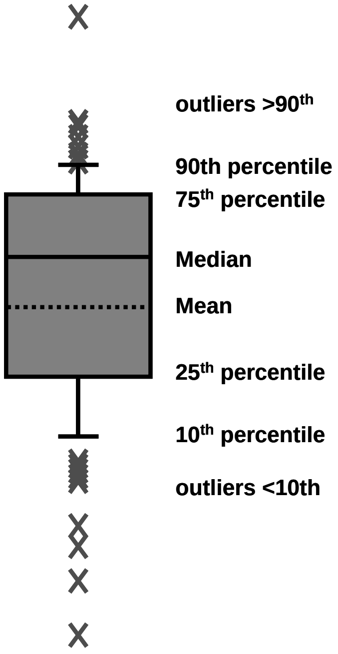
It should be noted that analytical methods for a number of parameters have changed over the years. These changes were implemented by the laboratories to lower detection limits, improve accuracy and precision, and to increase laboratory efficiency through automation. Most of these changes did not affect our statistical analyses. However, several analytical technique changes occurred over the period of record for which modification to the statistical approach were warranted. Specifically, these included:

1. Multiple changes in detection limits and analytical techniques for total and dissolved metals occurred throughout the study period (Appendix 2). Therefore statistical trend analyses were not conducted on the metal database as a whole. Some trend analyses were conducted to address specific issues (Section 4.3) but were limited to those metals that met data quality standards.

2. For the samples analyzed at the NLET Saskatoon laboratory, the analytical technique for dissolved nitrogen was changed from UV digestion to a higher recovering alkaline-persulphate digestion in October 1993. Although the dissolved nitrogen values are now more accurate, a clear step increase in concentrations was evident after this analytical change. Conversion factors between the two methods are not available (pers. comm. N.Yuen, EP Water Quality Laboratory, Saskatoon), and, thus, the trend analyses for dissolved and total nitrogen parameters were conducted for only the later time period (October 1993 to 2006).

Detailed statistical summaries (number of samples, mean, median, maximum, minimum, standard deviation, detection limit(s) and percent censored data) for the period 1989-2006 are provided in the Appendix 2, with subsets of data presented in tables and as box plots (see below) throughout the Results and Discussion.

Box and whisker plots (see example to the right) used in this report are defined as follows. The solid line within the larger box marks the median, dashed line the mean, and the lower and upper ends of the larger box are the 25th and 75th quartiles. The whiskers displayed are the 10th and 90thpercentiles. Outliers (more than the 10th or 90th percentiles) are small X's.



Statistical analyses and graphics were done using WQSTAT PLUS Version 1.56 (© NIC 1992-2004), SYSTAT Version 11 and Sigmplot Version 9.01 (© SYSTAT Software Inc, 2004). In cases where concentrations of 'less than detection limit' were reported by the laboratories, values equal to half of the detection limit have been used for statistical calculation and graphical presentation (Gilbert 1987). Although other more complex methods have emerged for the substituting of censored data (Helsel 2005), we chose this method as it remains the simplest and most commonly used in water quality reporting, and more importantly, for consistency with earlier reports in this series (Glozier et al., 2004b, 2006). Lastly, for the most part, detailed statistical analyses were only conducted for parameters with a high proportion of uncensored data (i.e., >70% of data measurements were above the method detection limit) so the method chosen would have minimal influence on results. For the parametric statistical analyses, data were examined for heteroscedasticity or departures from normality and when found, appropriate transformations were applied prior to analyses. For the temporal trend analyses, the effect of extreme outliers (>95th percentile) was examined by running the analyses with and without the data points in question. In fact, the significance of these non-parametric trend analyses were unaffected by the removal of outliers. Therefore reported statistical results and slopes are for the entire data set. We selected an $\alpha = 0.05$ for all analyses, report medians as a measure of central tendency to reduce the influence of high values, and report actual p values unless otherwise noted.

4.0 Results and Discussion

4.1 Descriptive Statistical Comparisons

4.1.1 Physical Parameters and Major Ions

Median concentrations are reported as a measure of central tendency for all physical parameters and major ions at the three monitoring sites for the period of record in Table 5. More detailed statistical summaries (including mean, median, maximum, minimum, 90th percentile and standard deviation) are included in the Appendix 2

Table 5: Median Concentrations of Physical Parameters and Major Ions (1989-2006).

Parameter	*units*	*Athabasca River at 27 Baseline*		*Peace River at Peace Point*		*Slave River at Fitzgerald*	
		n	Median	n	Median	n	Median
Physicals							
COLOUR TRUE	Rel units	133	25	124	23	122	30
OXYGEN DISSOLVED	mg/L	105	10.20	95	11.90	105	11.70
PH (L)	units	126	7.87	125	7.89	115	7.92
RESIDUE NONFILTRABLE	mg/L	146	31	138	58	41	45
SPECIFIC CONDUCTANCE (L)	usie/cm	123	294.00	127	235.00	115	219.00
TURBIDITY	ntu	148	17.20	139	32.60	120	55.00
Major Ions							
ALKALINITY TOTAL CACO3	mg/L	138	105.50	137	95.60	118	84.20
BICARBONATE (CALCD.)	mg/L	134	127.40	133	116.50		
CALCIUM DISSOLVED/FILTERED	mg/L	139	32.60	137	33.00	124	28.10
CHLORIDE DISSOLVED	mg/L	139	12.10	137	1.93	120	5.04
FLUORIDE DISSOLVED	mg/L	138	0.11	136	0.07	120	0.08
HARDNESS TOTAL (CALCD.) CACO3	mg/L	135	117.00	133	113.30	59	96.60
MAGNESIUM DISSOLVED/FILTERED	mg/L	139	8.56	137	7.51	124	6.58
POTASSIUM DISSOLVED/FILTERED	mg/L	139	1.20	136	0.70	124	0.86
SILICA	mg/L	138	5.41	106	4.04		
SODIUM DISSOLVED/FILTERED	mg/L	138	14.15	137	4.17	124	6.24
SULPHATE DISSOLVED	mg/L	138	23.40	137	20.70	120	18.05
TOTAL DISSOLVED SOLIDS (CALCD.)	mg/L	133	153.00	132	132.80	120	126.50

L=laboratory analyzed; CALCD.=calculated; n=number of samples

For pH and specific conductance, measurements are taken both in the field at the time of sampling, and in the laboratory at the time of sample analysis. Obtaining in-situ field measurements is preferred as changes can occur from the time of sampling to the time of measurement in the laboratory. For pH this can be due to changes in the equilibrium of carbonic acid or biological activity, therefore some differences are expected. However for many large data sets (Glozier et al., 2004b, 2006) field and laboratory values are often not significantly different. However, for the current data, frequent (4 of 6 comparisons) significant differences were observed for these pH and specific conductance between the field and laboratory analyses (paired t-test, $p<0.05$). These differences were not a result of predictable changes due to extended shipping times but due to the higher variability observed in field values, likely associated with difficulties in meter calibration in remote locations. No consistent directional trend was observed (i.e., field pH and conductivity could be higher or lower than laboratory values). Therefore, to reduce variability for statistical analyses and reporting, only laboratory values for pH and conductivity were used.

Median pH values at the monitoring locations were very similar and, in fact, ranged by less than 0.1 pH unit (7.87-7.92, Table 5). Values for true colour were similar for the AR and PR and slightly higher for the SR. All values were an order of magnitude higher than the values in mountain headwaters in Banff and Jasper National Parks including the upper Athabasca River (Glozier et al., 2004b). Water colour is attributed to varying light absorption characteristics of organic and inorganic materials such as humic substances, tannins, lignins, iron, and manganese. Sources can be both natural (organic decomposition, rock weathering) and anthropogenic (industrial effluents).

Dissolved oxygen (DO) results from the three sampling locations over the period of record showed similar ranges in concentration (Figure 4). However, these general plots do not reflect the diel variability typical with dissolved oxygen measurements and therefore interpretation was limited to spot measurements taken between 10:00 and 16:30 (mid-day). Diel variation in dissolved oxygen is related to daily cycles of photosynthesis/respiration while seasonal variation in DO is due to the inverse relationship between oxygen solubility and water temperature. Median DO concentrations for the period of record were 1.5 mg/L lower in the Athabasca River (10.2 mg/L) than medians in the Peace (11.9 mg/L) and Slave (11.7 mg/L) rivers (Table 5). The median dissolved oxygen concentrations at all sites ranged from 12-14 mg/L during winter and from 8-10 mg/L during the summer months while study period minima were: Athabasca River 7.2 mg/L (August 1989); Peace River 7.4 mg/L (August 1996); and Slave River 6.0 mg/L (June 1990).

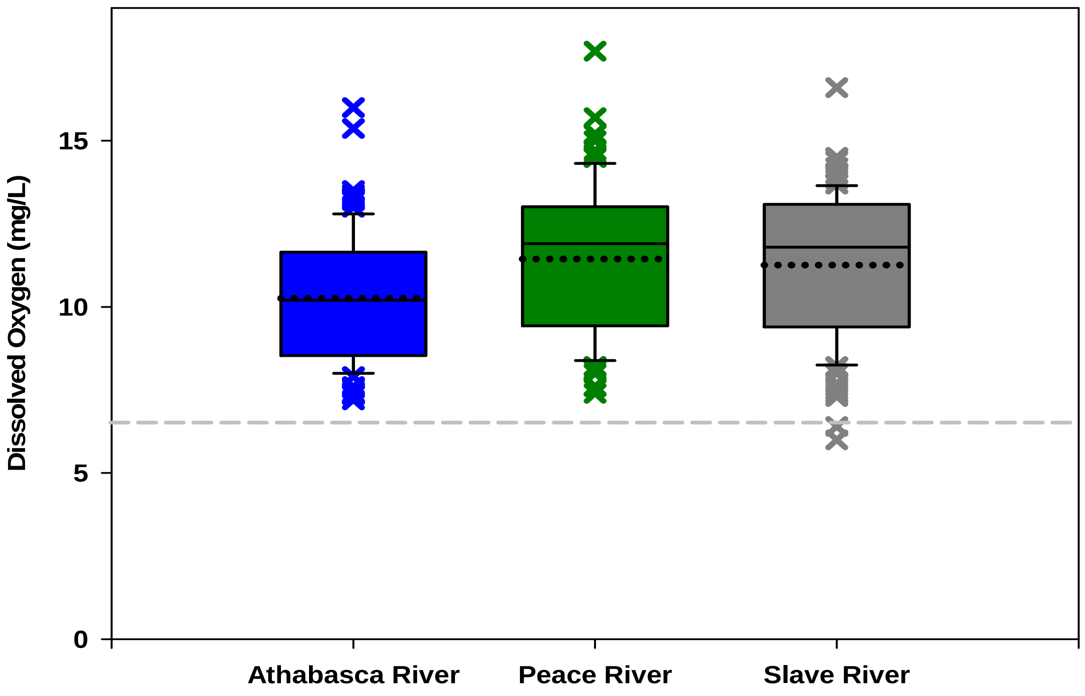


Figure 4: Dissolved Oxygen Concentrations for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2003). Dashed grey line is the CCME water quality guideline for dissolved oxygen (6.5 mg/L).

To protect aquatic life in Canadian water bodies, guidelines have been established by the *Canadian Council for Ministers of the Environment* (CCME, 1999). For dissolved oxygen, the guideline recommends that concentrations in the water column not fall below 6.5 mg L^{-1} to protect cold water adult fishes. For the more than 300 DO values, only two from the Slave River during summer, fell below this guideline (6.0 mg/L, 25/06/90 and 6.4 mg/L 21/07/1997). Donald et al, 1996, 2004, using a background approach, have suggested that, for theses waters, dissolved oxygen be >8.0mg/L in ≥ 90% of all samples as an indicator of normal water quality. This criterion was met for all sites. Although these concentrations do not pose a significant risk to cold water fishes based on the guidelines, the samples are spot, mid-day measurements and may not reflect true minima. In addition, research on the Athabasca River system regarding the relationship between water column and substrate dissolved oxygen indicates that water column guidelines are not necessarily protective of early life stages of fish and invertebrates residing in the substratum (Culp et al, 2004, Chambers et al, 2006). Therefore, continuation of a mid-day dissolved oxygen monitoring program, although informative of those conditions, should be viewed as a warning of changes through time in the ecosystem, but not as determinant of the current level of protection for aquatic biota.

Total dissolved solids (TDS) are calculated from the analytical results for major anions and cations dissolved in water. For the period of record, medians for TDS were greatest in the Athabasca River (153 mg/L) and similar in the Peace (130 mg/L) and Slave (127 mg/L) rivers (Figure 5). The Athabasca River showed approximately a 30% increase in TDS from the upstream Environment Canada sampling site at the boundary of Jasper National Park from 36 to 153 mg/L (Glozier et al., 2004b). This is not surprising considering the river distance (approximately 1300 km) between these sites and the chemical reactions which occur with longitudinal and geological changes (Webb and Walling 1996). Similar to dissolved oxygen indicator above, Donald et al, 1996, 2004, using a background approach, have suggested that, for these waters, total dissolved solids be <272 and 148 mg/L for the Athabasca and Peace rivers, respectively, in ≥ 90% of all samples. Samples from the Athabasca River met these criteria with only 6.8% of samples exceeding this value, while Peace River samples exceeded the site specific value in 10.6% of samples, just over the target suggested.

Major anions and cations used in the calculation of total dissolved solids, in order of predominance by equivalent weight include:

Anions: bicarbonate > sulphate > chloride > silica > fluoride (Athabasca and Slave rivers)
bicarbonate > sulphate > silica > chloride > fluoride (Peace River)

Cations: calcium > magnesium > sodium > potassium (Peace, Slave rivers)
calcium > sodium > magnesium > potassium (Athabasca River)

Based upon the ionic predominance, waters of the three major WBNP rivers are classified as calcium carbonate type, as are most major rivers in Canada (Benke and Cushing 2005). They are moderately hard waters, with total hardness <120 mg/L (study period medians) at all three locations. However, in the Athabasca River, hardness in low flow winter conditions typically increases and reaches the hard water classification (121-180mg/L) with values ranging from 150-165 mg/L. The Peace and Slave rivers show less seasonality (Section 4.4.1).

Specific conductance (25° C) is a measurement of the electrical conductivity of water and is directly related to the concentrations of ions present in water. TDS and specific conductance are directly related, according to the relationship *TDS = 0.5-0.6 x specific conductance*. The results for specific conductance at the WBNP locations show similar patterns to the TDS (Figure 5). Specific conductance was slightly higher in the Athabasca River (study period median 294 µsie/cm) than in the Peace (235 µsie/cm) and Slave (219 µsie/cm) rivers. A significant portion of the Slave River drainage is in the Canadian Shield. Waters from the Canadian Shield tend to be lower in dissolved materials than those from sedimentary basins

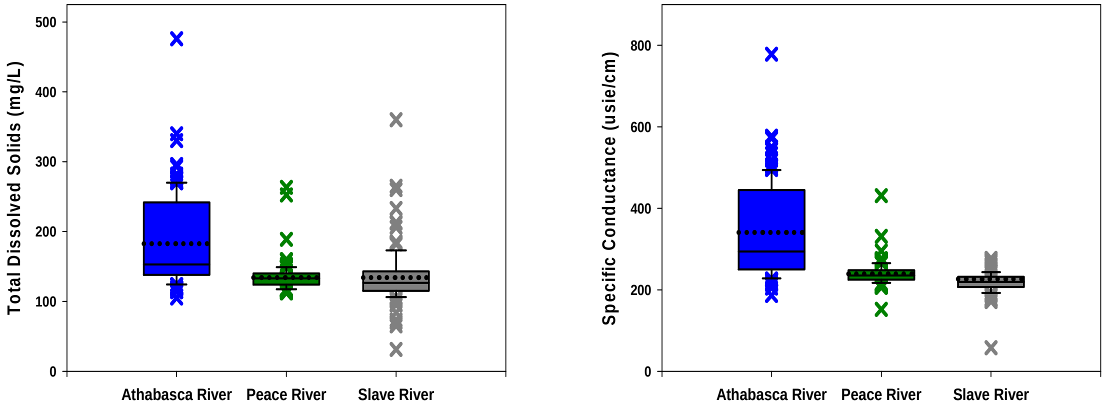


Figure 5: Total Dissolved Solids Concentration and Specific Conductance (Laboratory) for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

Sodium and chloride are two ions which are of interest due to their association with road salt and municipal sewage effluent (CEPA 2001, Schindler 2000). These two ions (as well as potassium, Table 5; Figure 6) showed similar geographical patterns with highest concentrations in the Athabasca River and lowest but more variable concentrations in the Peace River. The intermediary concentrations in the Slave River are explained (>91%) by the proportion of flow contributed from the two upstream rivers. In comparison to the mountain headwater sites in the Athabasca River (Glozier et al, 2004b), sodium and chloride concentrations increased 11 -17X, respectively, over the 1300 km of river. Increasing concentration due to geologic weathering, groundwater inputs, and river distance travelled from headwaters is expected between the two river sites.

The maximum chloride concentration observed throughout the period of record at all sites was 78.1 mg/L which is well below the No-Observed-Effect Concentration (NOEC) for early-life-stage fathead minnow tests (252mg/L) (CEPA 2001). Long-term temporal trends are further discussed in Section 4.2.2

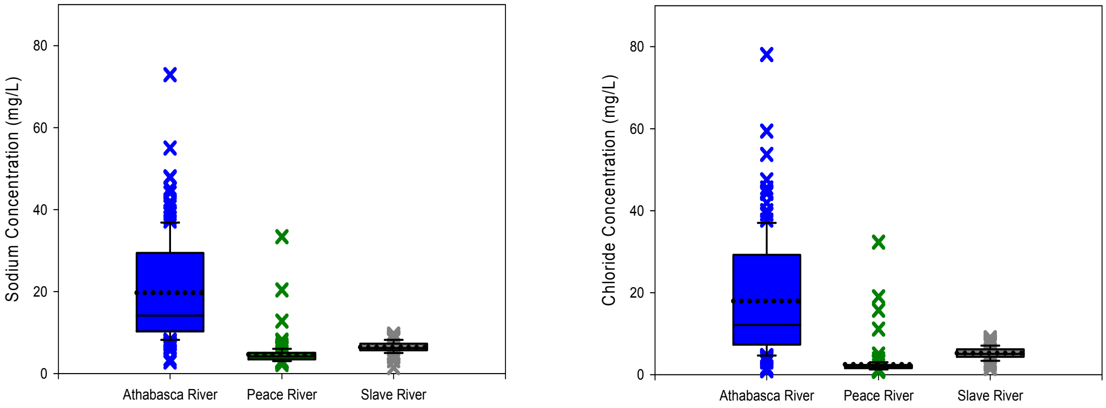


Figure 6: Dissolved Sodium and Chloride Concentrations for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

Dissolved sulphate exhibits a different pattern between the sites than the previous ions; similar, overlapping ranges in concentrations are evident (Figure 7) with decreasing concentrations in the following order; Athabasca, Peace and Slave rivers. The observed concentrations for these sites are well within those typical of natural water (2-80 mg/L, Chapman 1996). The sulphate indicator discussed in Donald et al., (1996, 2004) has been recently updated (Donald, per comm.) to dissolved sulphate concentrations being <39 and 30 mg/L for the Athabasca and Peace rivers, respectively, in ≥ 90% of all samples. Samples for the Athabasca River met these criteria with only 8.7% of samples exceeding the site specific objective while 10.2% of samples exceeded the objective for the Peace River indicator. Neither result suggesting a substantial departure from background conditions set forth in Donald et al. (1996, 2004). In Section 4.2.2, we examine temporal trends in sulphate concentration as it can be altered by municipal and industrial effluents inputs as well as atmospheric deposition (Chapman 1996), and has been used as a tracer for pulp mill effluents for environmental effects monitoring programs (www.ec.gc.ca/eem).

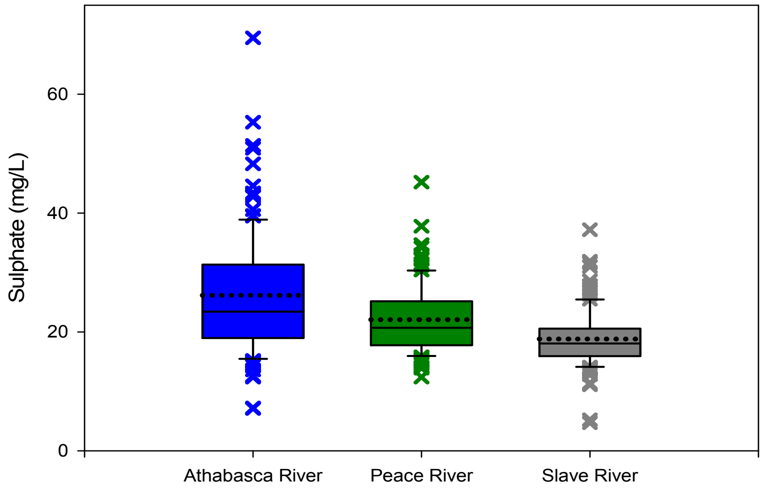


Figure 7: Dissolved Sulphate Concentrations for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

Non-filterable residue (NFR) is a measure of the concentration of suspended materials in water, including both inorganic and organic fractions and is also commonly referred to as Total Suspended Sediment (TSS). NFR is measured in water quality samples, in large part, as a supporting variable to assist interpreting other chemical constituents. These measurements should not be interpreted as a detailed suspended sediment study. High median NFR was recorded at all three locations, with median concentrations for the period of record from 30-50 mg/L (Table 5). NFR is highly variable as evident from the box plots (Figure 8) with many extreme values associated with high flow events and consequently the mean concentrations (dotted lines in Figure 8) are much greater than the median. Concentrations in these rivers are approximately 10x the concentrations observed in the headwaters (Glozier et al., 2004b). This increase is typical of rivers with mountainous headwaters which transition as they descend out of the foothills to lower-gradient main stem rivers (Benke and Cushing 2005).

Turbidity is measured with a meter which measures the scattering and absorption of incident light by suspended matter particles; slit, clay, particulate organic and inorganic material, soluble organic compounds, as well as microscopic biota. In many cases (Chapman 1996) turbidity can be used to estimate suspended matter in water (TSS or NFR), and our results for turbidity (laboratory) closely mirrored the results for NFR (Figure 8). In part, to examine redundancy in parameter analyses we performed regressions between NFR and turbidity for all samples where both parameters were measured. Not surprisingly, the relationships were all strong ($r^2 > 0.92$; Figure 9), however the slopes of the regressions differed between sites (ANCOVA, F = 44.59, df = 2, $p < 0.001$). The Peace and Slave rivers exhibited similar relationships with slopes of 0.86 and 0.82 respectively, but slope for the Turbidity – NFR relationship for the Athabasca River was significantly lower at 0.54. As the samples from the Athabasca and Peace rivers were analyzed in the same laboratory this is not likely an analytical difference but a difference in the characteristics of the suspended matter within the watersheds. Therefore, we provide these site specific conversion equations (Figure 9) for future studies, important for the Slave River as NFR measurements were terminated in April of 1993.

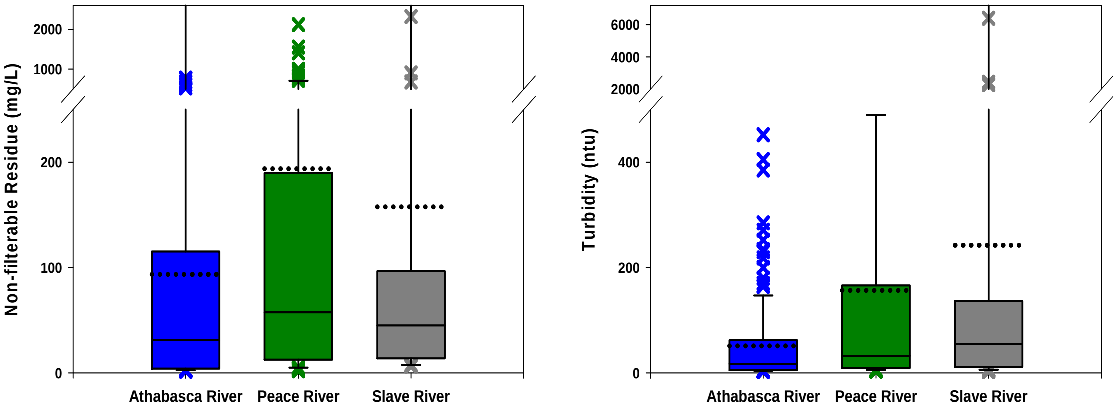


Figure 8: Non-Filtrable Residue Concentrations and Turbidity for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

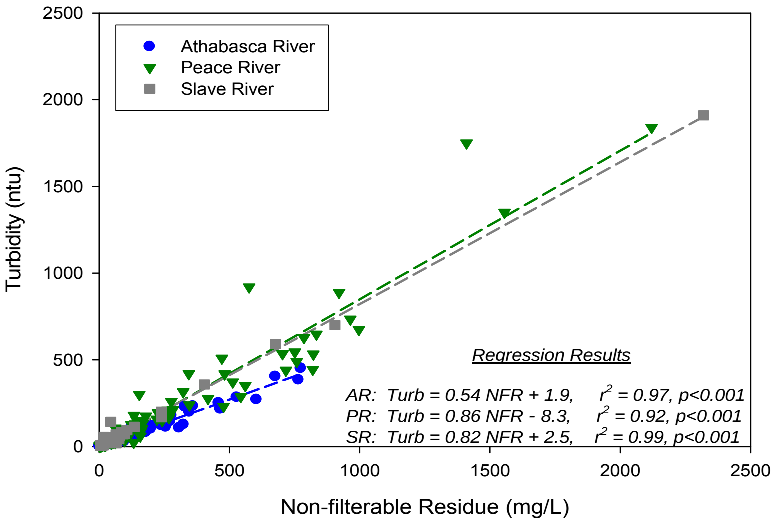


Figure 9: Relationship of Non-Filtrable Residue Concentrations and Turbidity for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

4.1.2 Nutrients

Plants require nitrogen, phosphorus, and carbon to live and grow, and for this reason these elements are referred to as nutrients. Atmospheric nitrogen is the most abundant natural source of nitrogen. Nitrogen-fixing bacteria or algae are required to convert atmospheric nitrogen to the dissolved forms, primarily nitrate and ammonia that are used by plants. Similarly, atmospheric carbon provides a vast source of carbon. Carbon dioxide dissolves in water primarily as bicarbonate ions in normal pH ranges, and is subsequently transformed into organic carbon by photosynthesis. The major source of natural phosphorus is through the weathering of phosphorus-bearing rock. Mineral phosphorus can be transformed to biologically available phosphate by chemical and biological transformation. Once nutrients are entrained into aquatic ecosystems, they undergo cycles of oxidation and reduction, as they move between the plant, animal, and sediment components of water bodies. A detailed summary of nutrient cycling and potential effects on the Canadian environment can be found in Chambers et al., (2001a).

In a national report on threats to aquatic ecosystems in Canada, Chambers et al., (2001b) identified increased nitrogen and phosphorus as one of fifteen threats to sources of drinking water and aquatic ecosystem health in Canada. Nitrogen and phosphorus were designated as threats based on increases in the concentration of biologically available N and P constituents measured over the previous 60 years in Canadian aquatic ecosystems. Municipal effluent discharges were identified as the largest anthropogenic point source of nitrogen and phosphorus, although additional sources included septic systems, industrial inputs, and agricultural runoff. A key knowledge gap identified in their report was insufficient information from long-term continuous monitoring programs that would allow assessment of trends in nutrient concentrations in Canadian aquatic ecosystems.

This section summarizes the monitoring results for nutrient parameters in Wood Buffalo National Park over the period of record (Table 6).

Table 6: Median Concentrations of Nutrient Parameters (1989-2006).

Parameter		***Athabasca River at 27 Baseline***		***Peace River at Peace Point***		***Slave River at Fitzgerald***	
	units	**n**	**Median**	**n**	**Median**	**n**	**Median**
CARBON DISSOLVED ORGANIC	mg/L	147	8.6	137	5.2	119	5.4
CARBON PARTICULATE ORGANIC	mg/L	145	1.2	136	1.1	117	1.7
CARBON TOTAL ORGANIC (CALCD.)	mg/L	144	9.7	136	6.9	114	7.6
AMMONIA DISSOLVED	mg/L	139	0.034	138	0.013	81	0.016
NITROGEN DISSOLVED NO3 & NO2	mg/L	145	0.04	136	0.06	109	0.05
DISSOVLED INORGANIC NITROGEN (CALCD.)	mg/L	145	0.08	139	0.08	121	0.07
NITROGEN TOTAL DISSOLVED	mg/L	147	0.36	137	0.19	118	0.20
NITROGEN PARTICULATE	mg/L	146	0.11	136	0.11	116	0.16
NITROGEN TOTAL (CALCD.)	mg/L	145	0.54	136	0.34	114	0.36
PHOSPHOROUS TOTAL DISSOLVED	mg/L	147	0.016	136	0.007	122	0.011
PHOSPHOROUS PARTICULATE (CALCD.)	mg/L	148	0.038	136	0.047	120	0.070
PHOSPHOROUS TOTAL	mg/L	148	0.050	139	0.056	121	0.078

CALCD. = Calculated from analyzed parameters

Carbon

Organic carbon can enter surface waters from anthropogenic sources or via natural photosynthetic pathways. Concentrations of dissolved organic carbon (DOC) vary with photosynthetic cycles and with bacterial breakdown of organic matter, and are related to the biochemical oxygen demand of water bodies. Median concentrations of DOC during the study period ranged from 5.2–8.6 mg/L (Table 6) while median total organic carbon (TOC) ranged from 6.9-9.7 mg/L. DOC makes up the majority of the TOC (71-89%). Box plots illustrate similar ranges in carbon concentrations between all sites with higher concentrations observed in the Athabasca River (Figure 10). The highest TOC concentration (77.7 mg/L) occurred on 29/07/2001 in the Slave River and was associated with the highest turbidity measurement at that site (6400 NTU).

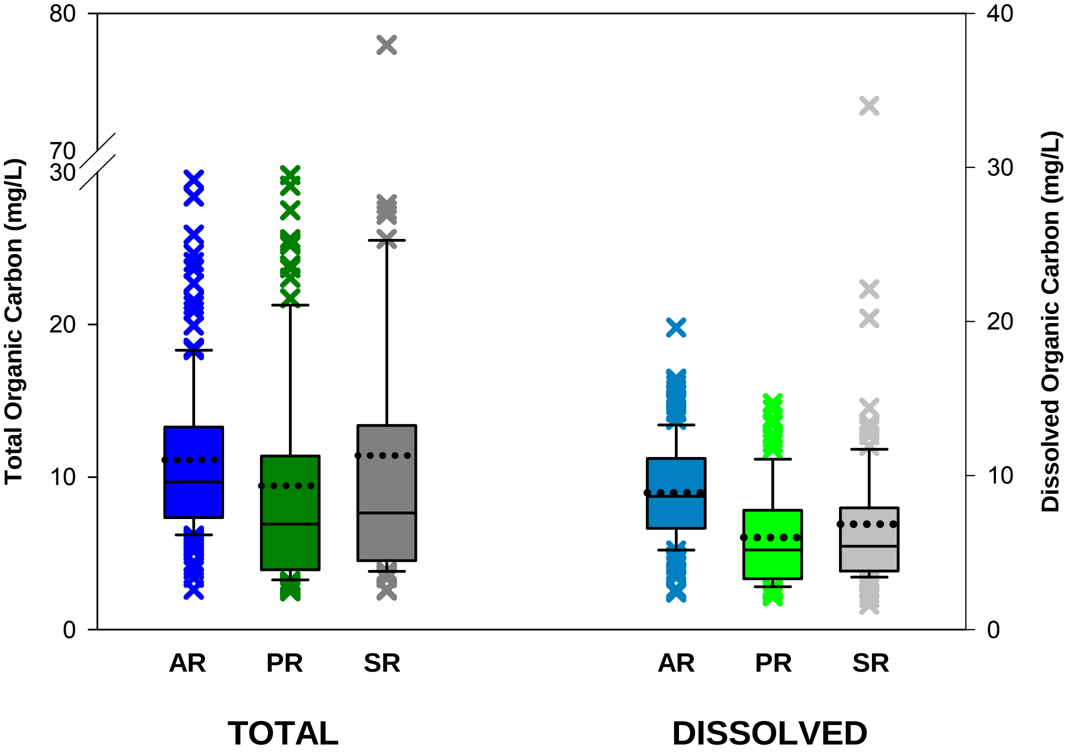


Figure 10: Total and Dissolved Organic Carbon; Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

Nitrogen

Nitrogen variables analyzed include dissolved ammonia, nitrate-nitrite (NO_3-NO_2), dissolved nitrogen (DN), and particulate nitrogen (PN). Total nitrogen (TN) was calculated from the sum of DN + PN while dissolved inorganic nitrogen (DIN) was calculated from the sum of ammonia and NO_3-NO_2. Dissolved nitrogen is largely bio-available, and includes NO_3-NO_2, ammonia, and dissolved organic forms. The major sources of DN to surface waters include municipal effluent discharge, atmospheric transport, and bacterial breakdown of in-stream organic matter of either natural or anthropogenic source.

The median TN and DIN concentrations for the period of record were 1.6-1.8 times higher, in the Athabasca River when compared to the Peace and Slave rivers (Table 6, Figure 11). Maximum TN concentrations recorded were as follows: Athabasca River 1.7 mg/L (Aug 1989); Peace River 4.0 mg/L (June 2001); Slave River 7.0 mg/L (July 2001). The Alberta Environment Surface Water Quality Guideline of 1.0 mg/L (Alberta Environment 1999) was exceeded on a number of occasion's at all three WBNP stations (exceedences rates; AR 6.2%, PR 15.4%, and SR 16.7%; Figure 11). Exceedences to the TN guideline tended to occur during high discharge periods, coinciding with higher PN, likely related to the presence of natural erosional particulate matter. In fact, for the samples with TN exceedence, the particulate nitrogen was 61, 76 and 73% of total nitrogen for the AR, PR and SR, respectively.

In contrast, the medians for PN at the three locations are similar: Athabasca River 0.11 mg/L; Peace River 0.11 mg/L; and Slave River 0.16 mg/L. Based on median values, PN makes up less than half of the total nitrogen at 20, 32 and 44% in the AR, PR and SR, respectively (other than during the high discharge periods noted above). PN includes numerous plant and animal breakdown products and is unavailable to algae during photosynthesis, though breakdown to available dissolved nitrogen forms can be rapid.

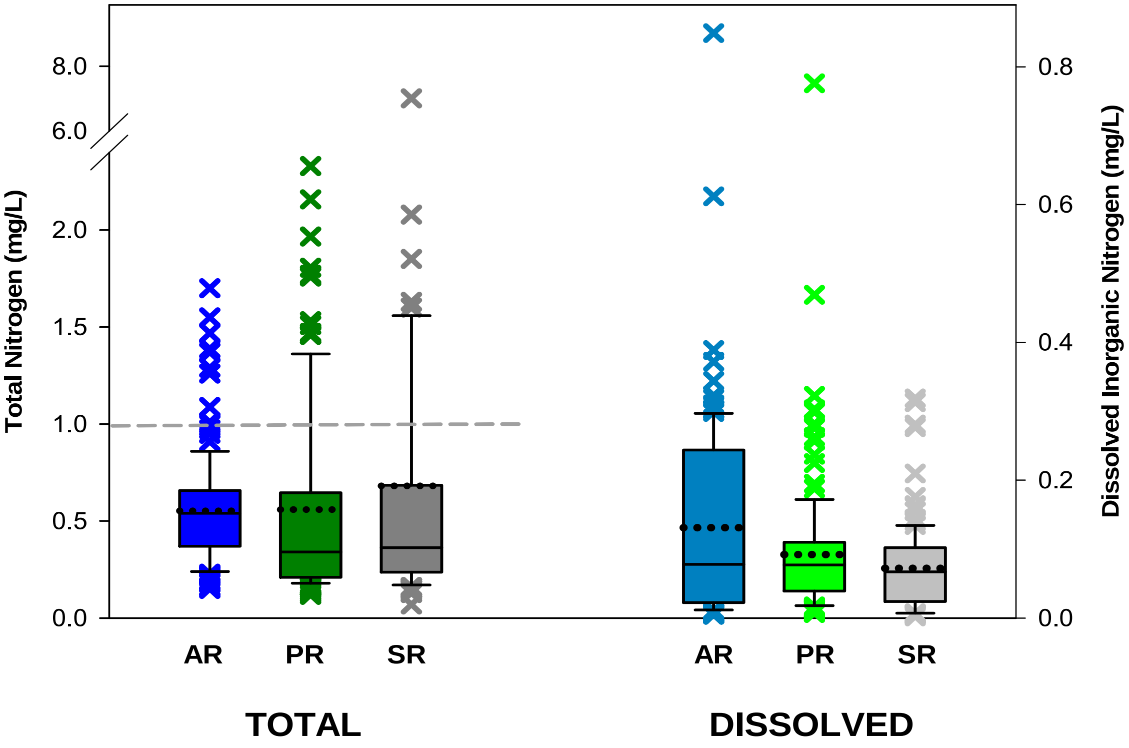


Figure 11: Total and Dissolved Inorganic Nitrogen; Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006). Dashed grey line is the Alberta water quality objective for Total Nitrogen (1.0 mg/L).

Of the dissolved nitrogen measured in these waters, between 11% (Athabasca River) and 32% (Peace River) was NO_3-NO_2. Dissolved ammonia (Table 6) was characteristically low at the three monitoring locations, with medians for the study period between 0.01 mg/L (Peace River) and 0.03 mg/L (Athabasca River). The maximum concentration recorded for dissolved ammonia at the WBNP locations was 0.695 mg/L (Peace River, April 1992), which is below the guideline of 1.23

mg/L for total ammonia-N (CEQG 2002) based on the pH and temperature of the water at collection.

Phosphorus

Phosphorus variables included dissolved phosphorus (DP) and total phosphorus (TP), with particulate phosphorus calculated by subtraction (TP – DP). DP is largely bio-available, and includes inorganic phosphates and dissolved organic phosphorus compounds. DP can enter surface waters directly from wastewater treatment plants and non-point source municipal and agricultural runoff. DP can also be produced by biological breakdown of particulate organic matter from natural or anthropogenic sources.

Median total phosphorus concentrations for the study period were lowest for the Athabasca River, higher by an additional 12% in the Peace and by an additional 40% in the Slave River (Figure 12). The Alberta Water Quality Guideline for TP (0.05 mg/L) was exceeded on numerous occasions at all three WBNP locations (exceedences rates; AR 50.0%, PR 53%, and SR 61%; Figure 12). In contrast to carbon and nitrogen, particulate phosphorus made up the majority of the total phosphorus concentrations; 76, 84, and 90 % for the AR, PR, and SR, respectively. Not surprisingly then, the same increasing pattern among sites was observed for particulate phosphorus (Table 6).

However, dissolved phosphorus concentrations showed a different pattern among sites. Dissolved phosphorus medians were highest for the Athabasca River, lower in the Peace River and elevated again in the Slave River. Higher variability was observed in the Peace and Slave rivers with several high outliers (maximum Slave River DP = 0.343 mg/L).

Regression analyses indicated that the relationships between DP and TP were weak (r^2 values <0.09) while the relationships between TP and PP were strongly significant, with r^2 values of 0.99 ($\rho<0.001$) at all three monitoring locations.

Since the particulate phosphorus appears to be driving total concentrations we examined the relationship between total phosphorus and non-filterable residue in the Athabasca and Peace rivers and, as there was limited NFR data available, total phosphorus and turbidity in the Slave River. All regressions were significant ($p<0.001$), with r^2 values between 0.72 and 0.85, thus over 70% of the variation in total phosphorus concentrations can be explained by the variation in suspended sediment concentration (NFR). Interestingly, all slopes for these regression were identical, and for TP-NFR in the Athabasca and Peace rivers not significantly different (ANCOVA, F=1.92, df = 1, *p*=0.17). Therefore, the combined regression equation could be applicable for either river. The regression equations are as follows:

Athabasca River: ***TP = 0.001 NFR + 0.038***; n= 146, r^2 = 0.72
Peace River ***TP = 0.001 NFR + 0.030***; n = 136, r^2 = 0.85
AR + SR combined ***TP = 0.001 NFR + 0.033***; n = 282, r^2 = 0.83
Slave River ***TP = 0.001 Turb + 0.054***; n = 115, r^2 = 0.83

To illustrate these relationships, we plotted the Athabasca River data and in addition, indicated which samples were taken during high flow; high sediment load conditions (Figure 13). For the Athabasca River, as is typical in these rivers, >80% of the total phosphorus exceedences to the Alberta guideline are associated with these high discharge, high sediment conditions. Currently, there are no provincial or federal water quality guidelines for dissolved phosphorus, the most readily bio-available form of phosphorus. Trends in phosphorus and their importance for ecological status and functioning are explored in Section 4.2.3.

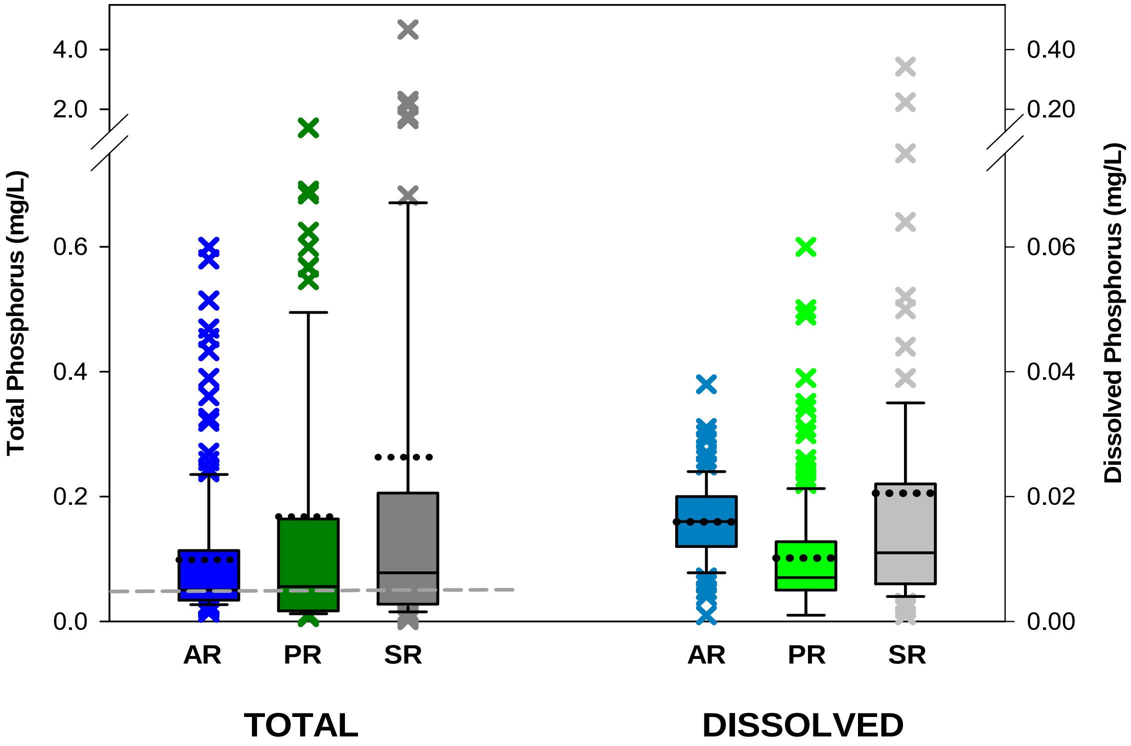
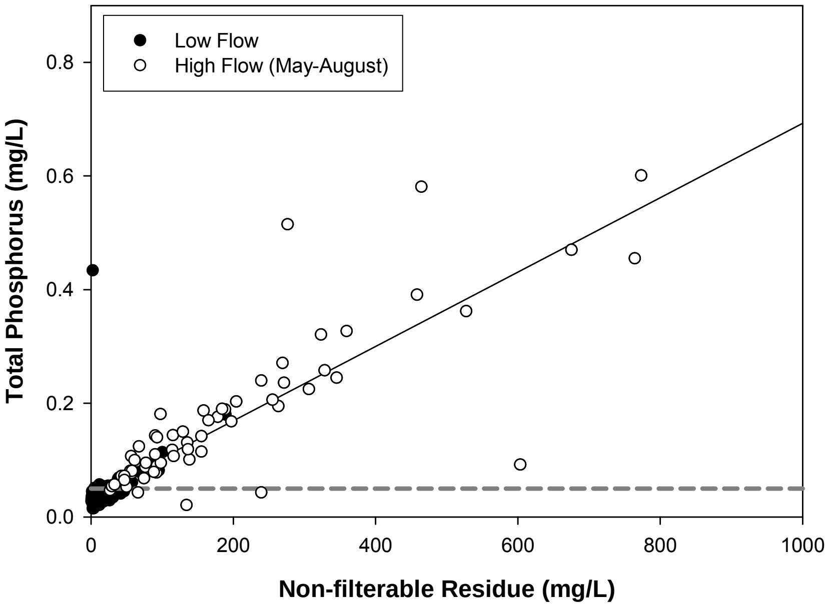


Figure 12: Total and Dissolved Phosphorus; Athabasca River (AR) at 27 Baseline, Peace River (PR) at Peace Point, and Slave River (SR) at Fitzgerald (1989-2006). Dashed grey line is the Alberta water quality objective for Total Phosphorus (0.05 mg/L). Note that the left axis for total phosphorus is 10X the scale for the right dissolved phosphorus axis.

A) All data for period of record



B) Expanded view of data < 100 mg/L NFR

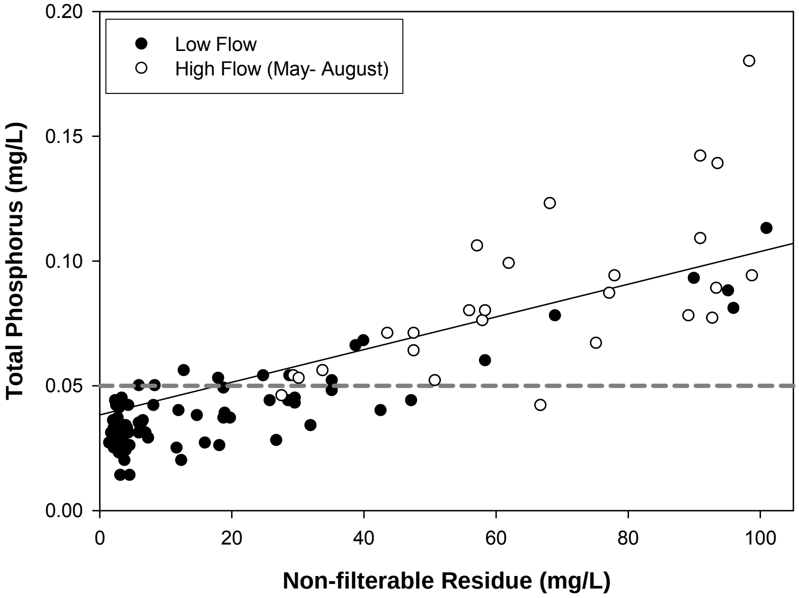


Figure 13: Relationship between Total Phosphorus and Non-Filterable Residue at Athabasca River at 27 Baseline for A) all data, B) samples with <100 mg/L non-filterable residue. Samples from low flow and high flow discharge periods indicated. Dashed grey line is the Alberta water quality objective for Total Phosphorus (0.05mg/L).

4.1.3 Dissolved and Total Metals

Sources of metals in surface waters can be natural and/or related to human activities. Natural sources of metals include leaching from soil and rock and re-suspension of metals entrained in bottom sediments. Human-related sources of metals include municipal and industrial effluents, accidental spills, atmospheric deposition and non-point sources.

The Wood Buffalo National Park sampling program includes the analysis of water samples for 21 metallic elements for which medians and number of samples are reported (Table 7). Total and dissolved metals were analyzed for the Athabasca and Peace rivers but for the Slave only total metal analysis is available. Total metal analysis includes a strong acid digestion step on an unfiltered sample, and as a result total metals include both ions dissolved in water and those extracted from suspended sediment particles. Analysis for dissolved metals involves filtration prior to acid digestion and thus includes only the fraction of the metal element dissolved in water. Dissolved metals are usually considered to be the fraction that is, biologically, most readily available to aquatic organisms.

Although over the period of record total metals have been consistently measured at all sites resulting in well over 100 samples, measurement of the dissolved component was not initiated until May of 1999. Thus, there were far fewer samples over the period of record (<60). The exception is dissolved Arsenic in the Athabasca River which has been measured at that site since 1989. Total mercury was removed from the analytical request list in 2002 because of inadequate field techniques, and therefore discussion of results for mercury are not included (statistical summaries are provided in the Appendix 2 for completeness). Some metal variables were analyzed by up to four analytical techniques, each having different detection limits and potentially differing recoveries. Finally, for eight of the dissolved (aluminium, beryllium, cadmium, chromium, cobalt, lead, vanadium, and zinc) and three of the total (beryllium, mercury, silver) metals, over 30% (see Appendix 2) of the samples had values recorded as less than the detection limit. Therefore, for these parameters with a high proportion of censored data the statistical summaries should be viewed with caution. Finally, for many metal parameters the usefulness for determination of temporal trend has been reduced due to these changes in analytical methods, laboratories, and detection limits. Therefore, only a limited set of metals were examined for temporal trend analyses in the Athabasca River (Section 4.2.4).

While trace concentrations of a number of metals are required for plant and animal nutrition, high concentrations are generally undesirable and can be harmful or toxic to aquatic organisms. Guidelines for the protection of aquatic life for a number of total metals have been published by the CCME (1999). Several of the metals for which guidelines have been developed (lead, arsenic, cadmium) are also included on the CEPA toxic substances list (CEPA 2003). The CCME water quality guidelines for metals to date have been developed for total metals, even though the dissolved metal component is more biologically available. This was, in part, because total metals analyses were, until recently, more commonly analyzed than dissolved metals, and partly due to the presumed positive relationship between total and dissolved fractions. For those metal elements which have CCME guidelines, the number of excursions (i.e., number of samples for which the metal concentration was greater than the guideline) are summarized in Table 8. For arsenic and selenium, compliance with the total metal guideline was checked against concentrations of dissolved arsenic and selenium (the only data available for these parameters).

Excursions to the CCME guidelines for arsenic, chromium, molybdenum, nickel, and selenium were infrequent (<1%, Table 8). Compliance with the total arsenic and total selenium guidelines were checked against the results for dissolved arsenic and selenium. The three excursions for these dissolved metals were at the Slave River with no unusual conditions or seasonal patterns identified for the samples in question.

Table 7: Median Concentrations of Dissolved and Total Metal Parameters (1989-2006). Most dissolved metals were analyzed starting in 1999. Dissolved arsenic (AR and SR), boron (AR and PR) and selenium (AR, PR, and SR) have been analyzed since 1989.

Parameter		***Athabasca River at 27 Baseline***		***Peace River at Peace Point***		***Slave River at Fitzgerald***	
	units	**n**	**Median**	**n**	**Median**	**n**	**Median**
ALUMINUM DISSOLVED*	**mg/L**	57	0.01	55	0.01		
ALUMINUM TOTAL	**mg/L**	99	0.39	101	0.55	75	1.33
ARSENIC DISSOLVED	**mg/L**	141	0.0003	55	0.0003	108	0.0003
BARIUM DISSOLVED	**mg/L**	57	0.05	55	0.05		
BARIUM TOTAL	**mg/L**	138	0.06	139	0.07	117	0.07
BERYLLIUM DISSOLVED*	**mg/L**	57	0.000008	55	0.000008		
BERYLLIUM TOTAL*	**mg/L**	97	0.000025	100	0.000025	76	0.000043
BORON DISSOLVED	**mg/L**	139	0.024	131	0.009	22	0.015
CADMIUM DISSOLVED*	**mg/L**	57	0.0002	55	0.0002		
CADMIUM TOTAL	**mg/L**	138	0.0001	139	0.0001	118	0.0002
CHROMIUM DISSOLVED*	**mg/L**	57	0.0001	55	0.0001		
CHROMIUM TOTAL	**mg/L**	99	0.001	101	0.001	76	0.002
COBALT DISSOLVED*	**mg/L**	57	0.0001	55	0.0001		
COBALT TOTAL	**mg/L**	138	0.0004	139	0.0006	116	0.0011
COPPER DISSOLVED	**mg/L**	57	0.001	55	0.001		
COPPER TOTAL	**mg/L**	138	0.002	139	0.003	118	0.004
IRON DISSOLVED*	**mg/L**	57	0.11	55	0.04		
IRON TOTAL	**mg/L**	97	0.9	100	1.1	76	2.8
LEAD DISSOLVED*	**mg/L**	57	0.0003	55	0.0003		
LEAD TOTAL	**mg/L**	138	0.001	139	0.001	118	0.002
LITHIUM DISSOLVED	**mg/L**	57	0.006	55	0.004		
LITHIUM TOTAL	**mg/L**	97	0.010	100	0.006	76	0.007
MANGANESE DISSOLVED	**mg/L**	57	0.001	55	0.001		
MANGANESE TOTAL	**mg/L**	97	0.054	100	0.034	76	0.060
MOLYBDENUM DISSOLVED	**mg/L**	57	0.001	55	0.001	76	0.001
MOLYBDENUM TOTAL	**mg/L**	97	0.001	100	0.001		
NICKEL DISSOLVED	**mg/L**	57	0.001	55	0.001		
NICKEL TOTAL	**mg/L**	138	0.002	139	0.003	118	0.004
SELENIUM DISSOLVED	**mg/L**	141	0.0001	131	0.0003	103	0.0002
SILVER TOTAL*	**mg/L**	54	0.00003	58	0.00005	58	0.00005
STRONTIUM DISSOLVED	**mg/L**	57	0.19	55	0.13		
STRONTIUM TOTAL	**mg/L**	97	0.21	100	0.14	76	0.14
VANADIUM DISSOLVED*	**mg/L**	57	0.0005	55	0.0004		
VANADIUM TOTAL	**mg/L**	138	0.001	139	0.001	116	0.003
ZINC DISSOLVED*	**mg/L**	57	0.001	55	0.001		
ZINC TOTAL	**mg/L**	138	0.005	139	0.007	118	0.011

* *metals with > 30% of analyses resulting in values < the method detection limit*

Table 8: Exceedences to CCME Water Quality Guidelines for the Protection of Aquatic Life for Total Metals over the Period of Record (1989-2006). Overall % Exceedences calculated across all sites and samples.

Parameter	Objective	Foot Note	Overall % Exceedences	***Athabasca River at 27 Baseline***		***Peace River at Peace Point***		***Slave River at Fitzgerald***	
				Excursions	**n**	**Excursions**	**n**	**Excursions**	**n**
Aluminum - T	100 ug/L	1	81	66	99	83	101	74	75
Arsenic - D	5 ug/L	2	<1	0	141	0	55	2	108
Cadmium – T**	0.017 ug/L	3	76	99	138	114	139	88	118
Chromium - T	50 ug/L	4	<1	0	99	1	101	1	76
Copper - T	2-4 ug/L	5	53	58	138	71	139	79	118
Iron - T	300 ug/L		87	90	97	77	100	71	76
Lead - T	1-7 ug/L	6	36	33	138	54	139	55	118
Molybdenum - T	73 ug/L	7	0	0	97	0	100	0	76
Nickel - T	25-150 ug/L	8	<1	0	138	0	139	1	118
Selenium - D	1 ug/L	9	<1	0	141	0	131	1	103
Zinc - T	30 ug/L		15	7	138	30	139	24	118

T=total; **D**-dissolved; **n**=total number of samples;

****** Detection limit for cadmium was higher than CCME guideline from 1989-2003; values< DL were assumed to be less than the guideline

1. CEQG 2002. PFAL. This objective applicable at pH >6.5, [calcium] >4 mg/L; [DOC] >2 mg/L
2. CEQG 2002. PFAL. Objective is applicable to total arsenic.
3. CEQG 2002. PFAL. The detection limit for total cadmium was 0.1 μg/L during the study period.
4. CEQG 2002. MAC Maximum acceptable concentration for total chromium
5. CEQG 2002. PFAL. 2 μg/L at [total hardness] 0-120 mg/L; 3 μg/L at [total hardness] 120-180 mg/L; 4 μg/L at [total hardness] >180 mg/L.
6. CEQG 2002. PFAL. 1 μg/L at [total hardness] 0-60 mg/L, 2 μg/L at [total hardness] 60-120 mg/L, 4 μg/L at [total hardness] 120-180 mg/L, 7 μg/L at [total hardness] >180 mg/L.
7. CEQG 2002. Interim objective.
8. CEQG 2002. PFAL. 25 μg/L at [total hardness] 0-60 mg/L, 65 μg/L at [total hardness] 60-120 mg/L, 110 μg/L at [total hardness] 120-180 mg/L, 150 μg/L at [total hardness] >180 mg/L .

9 CEQG 2002. PFAL. Objective is for total selenium.

Excursion rates among the three sites for the same parameters were very nearly identical, an interesting observation considering the differing environmental stresses on the three rivers. Overall exceedences rates to the guidelines for total aluminium, iron, copper and cadmium were all greater than 50%, while overall exceedences for lead and zinc were less than 36% (Table 8). The CCME guideline for total aluminium (0.1 mg/L for waters having pH>6.5) has been recommended to protect the growth and survival of fish, particularly early developmental stages. Excursions to the total aluminium guideline (Figure 14, dashed line) were frequent at all three stations, with a 67% excursion rate in the Athabasca River, 82% in the Peace River, and 99% (all but one sample) in the Slave River. The maximum values for total aluminium were one to two orders of magnitude greater than the guideline (Athabasca River - 7.14 mg/L; Peace River - 68.7 mg/L and Slave River - 48.7 mg/L). Median values are greatest in the Slave River; however outliers and boxes overlap for all three sites (Figure 14). Dissolved Aluminium concentrations had similar ranges in the Athabasca and Peace rivers (Figure 14) with many (>42%) below the detection limit (0.02 mg/L) and all well below the total guideline.

The CCREM guideline for total iron, established at 0.3 mg/L based upon toxicity of iron to fish and invertebrates, was exceeded in 92% of samples from the Athabasca River, 77% from the Peace River, and 93% for the Slave River. Study maxima for total iron were 13.9 mg/L (Athabasca River), 61.7 mg/L (Peace River), and 128 mg/L (Slave River), substantially greater (>2 orders of magnitude) than the guideline. Patterns among sites (Figure 14) were similar to total aluminium; however, dissolved iron appears to be generally higher in the Athabasca River than in the Peace; all results for iron were above the detection limit (Appendix 2).

Total copper concentrations was assessed against the CCREM guideline of 2-4 µg/L (dependent on water hardness, Table 8) based upon toxicity of copper to various fish species. The total copper guideline was exceeded in 42% of samples from Athabasca River, 51% of samples from Peace River, and 67% of samples from Slave River. Maxima recorded during the study were as follows: Athabasca River (19 µg/L), Peace River (56 µg/L), and Slave River (97 µg/L). Patterns in exceedence rates between sites were mirrored in the concentration ranges, medians and outliers with marginal increases from the Athabasca River to the Peace and Slave, rivers respectively (Figure 15). Similarly, dissolved copper concentrations tended to be greater in the Peace than the Athabasca with concentration in a few of the samples (<10) being greater than the guideline for total copper, all of which were taken during the open water period,.

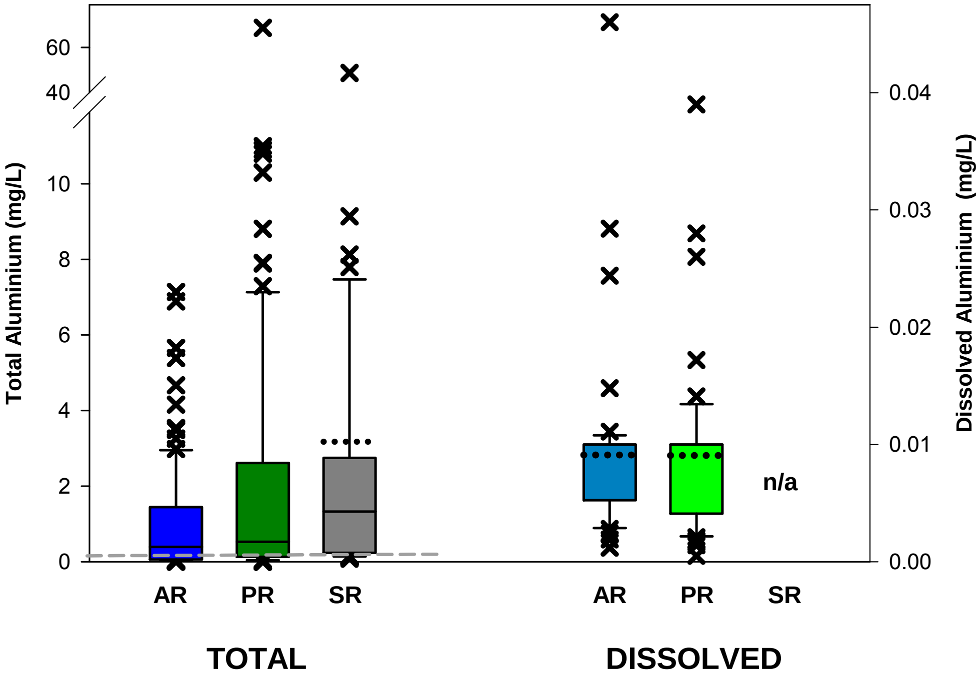
The freshwater aquatic life CCREM guideline for total cadmium is set at 0.017 µg/L (Table 8). A serious problem in assessing total cadmium exceedences with our data was that the analytical detection limit (0.1 ug/L) for samples prior to 2003 was greater than this guideline. Many samples during this earlier period were less than this detection limit; 24, 17, and 25 % for the AR, PR, and SR, respectively. Post April 2003, detection limits were revised with a new analytical method that lowered the detection limit to 0.001ug/L. No samples post April 2003 were below the new detection limit. Therefore, to calculate exceedence rates for total cadmium, any samples below detection limit prior to 2003 were assumed to "pass" as the true value is unknown and substituting 0.5X DL would result in all samples being considered in exceedence.

With the above caveat, post 2002 the total cadmium guideline was exceeded in 72% of samples from Athabasca River, 82% from Peace River, and 75% from Slave River. The maximum concentration of total cadmium was 1.6 µg/L (Athabasca River), 6.3 µg/L (Peace River), and 15 µg/L (Slave River). As with the previous metals discussed, total cadmium concentrations had the greatest range, and highest median values in the Slave River (Table 5, Figure 15). Dissolved cadmium concentrations were similar in the Athabasca and Peace rivers, however the detection limit for this fraction (1 ug/L) for the pre May 2003 period was higher than the total cadmium detection limit and, in fact, 45% of samples were determined to be less than this detection limit. The relationship between the detection limits and guidelines are illustrated in Figure 15 to help demonstrate this issue and ensure caution is taken when interpreting the cadmium data.

The CCREM guideline for total lead (1-7 ug/L), developed to protect lead-sensitive fish and invertebrate species, was exceeded in 24% of samples from the Athabasca River, 39% from Peace River, and 47% of samples from Slave River (Table 8). Maximum concentrations for total lead during the study period were 86 µg/L (Athabasca River), 46 µg/L (Peace River), and 51 µg/L (Slave River). Little difference in total or dissolved lead concentrations was observed between sites (Table 8, Appendix 2).

Finally, the published CCREM guideline for total zinc of 30 µg/L is based on acute and chronic toxicity to invertebrates and early fish life stages. The guideline was exceeded in 5% of samples from Athabasca River, 22% from Peace River, and 20% of samples from Slave River. Maximum concentrations reported were 50 µg/L (Athabasca River), 279 µg/L (Peace River), and 560 µg/L (Slave River). The CCREM guideline for total zinc was exceeded by in one sample for dissolved zinc from the Peace River (32 µg/L). Dissolved zinc concentrations from both the Athabasca River and Peace River were generally at or near the detection limit of 2 µg/L.

Basic statistics for other metals not already discussed are included in Table 7 and in the Appendix 2. Differences among sites were minimal other than for boron, lithium, and strontium which tended to be greater in the Athabasca River than in the other sites.



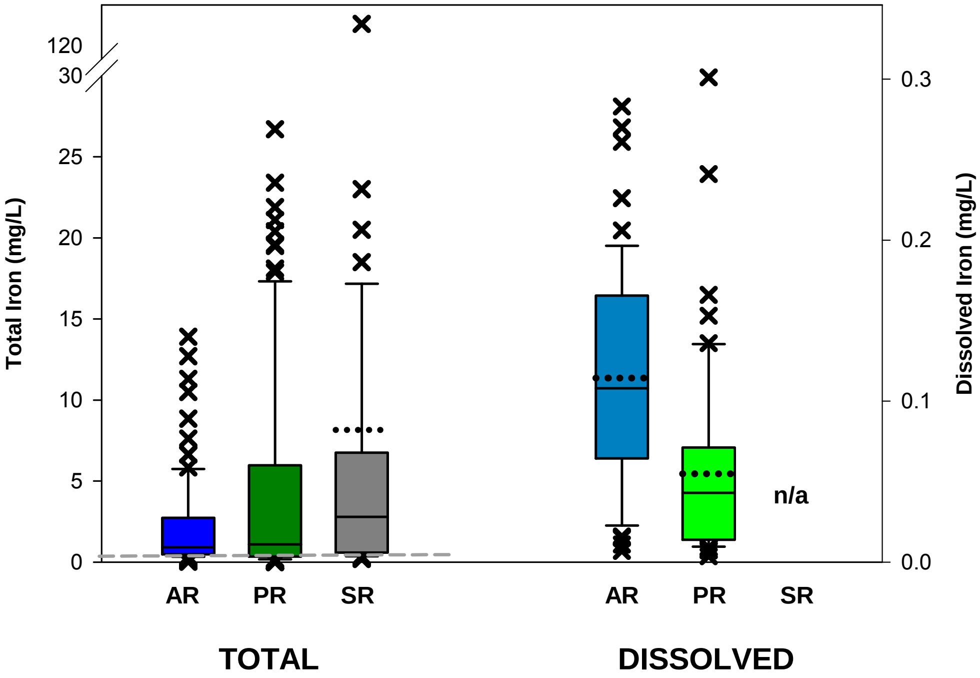


Figure 14: Total and Dissolved Aluminium and Iron; Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006). Dashed grey lines are the CCME water quality objectives for Total Aluminium (0.1 mg/L), and Iron (0.3 mg/L).

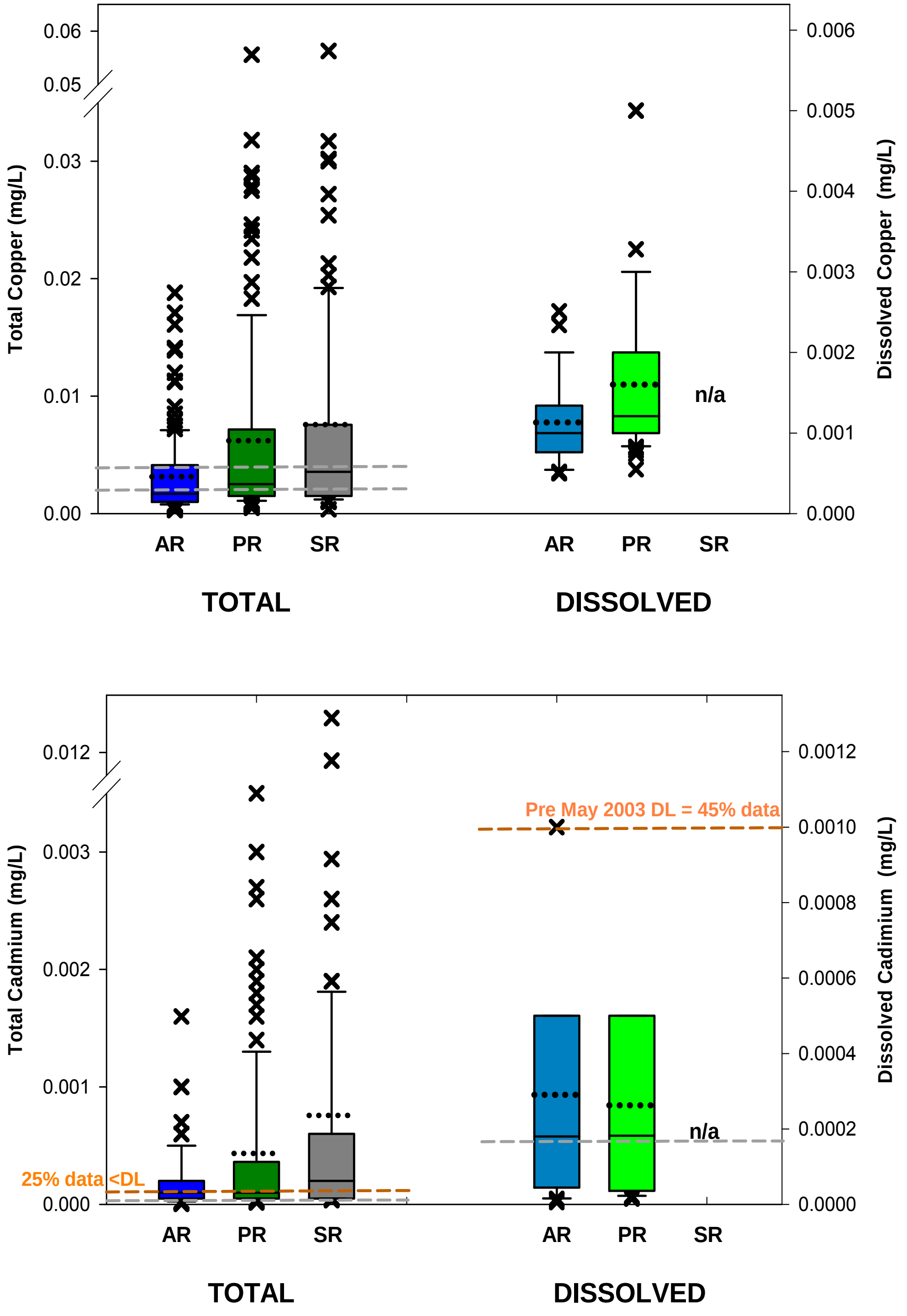


Figure 15: Total and Dissolved Copper and Cadmium; Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006). Dashed grey lines are the CCME water quality objective for Total Aluminium (0.1 mg/L), Copper (2-4 ug/L) and Iron (0.3 mg/L).

As identified, many of the total metals at these sites exceed national guidelines on a frequent basis which could raise concerns regarding the risk to aquatic ecosystems. However, we hypothesized that the majority of the total metals in these rivers are associated with sediment, and hence not readily available to biota. Therefore, we examined the seasonality of exceedences as well as the relationship between these parameters and suspended sediment as reflected in the NFR concentrations.

Seasonality was determined as described more fully in Section 4.2.1 and we found that the majority of all exceedences occurred during the spring and summer months when discharge and sediment load are high. Total aluminium seasonality (Figure 16), representative of most total metals, exhibited peak concentrations in the spring and summer months (May – July) and in fact mirrors the pattern in NFR (Figure 16). Although exceedences were recorded throughout all seasons, the vast majority occurred during the open water period.

Similar to total phosphorus (Section 4.1.2), for those total metals with high exceedence rates, we found significant relationships between total metals and the total suspended sediment (NFR) in the Athabasca and Peace rivers (see total copper example Figure 17). Although the strongest relationships were found between NFR and total iron (r^2 >0.91, Table 9), r^2 values were greater than 0.75 for all metals examined except for cadmium. The regression statistics for total cadmium indicate moderately strong relationships between the two variables (r^2=0.43-0.68) and as previous discussed for total cadmium, a high proportion of censored data (17-25%) may have reduced the accuracy and thus the strength of these relationships. As there was limited NFR data measured with the water quality sample in the Slave River, relationships between total metal and turbidity were examined. These results are included in Table 9 and reveal similar patterns to the NFR – total metal results for the Athabasca and Peace rivers.

Table 9: Regression results for total metals and NFR for the Athabasca and Peace rivers and total metals and turbidity for the Slave River. All regressions were significant at p<0.001.

Parameter	***Athabasca River at 27 Baseline***		***Peace River at Peace Point***		***Slave River at Fitzgerald***	
	r^2	**n**	**r^2**	**n**	**r^2**	**n**
Aluminum - T	0.85	98	0.76	97	0.85	70
Cadmium – T	0.43	136	0.68	134	0.67	111
Copper - T	0.85	134	0.93	134	0.87	112
Iron - T	0.93	96	0.92	97	0.91	71
Lead - T	0.89	135	0.85	134	0.74	112
Zinc - T	0.85	136	0.76	134	0.78	112

Finally, given the significant relationships between NFR and total metals, we also examined the strength of relationships between total and dissolved metals and, not surprising, in these aquatic ecosystems they were very weak. For example, the relationship between dissolved and total iron was found to be weak and non-significant in both the Athabasca River (n=17, r^2=0.16, ρ=0.07) and Peace River (n=23, r^2=0.08, ρ=0.20), as were the relationships between total copper and dissolved copper in both the Athabasca River (n=21, r^2=0.13, ρ=0.11) and Peace River (n=23, r^2=0.12, ρ=0.10). Therefore, the presumption of relationship between total and dissolved metals for application against total metal guidelines did not hold in these high sediment laden river systems.

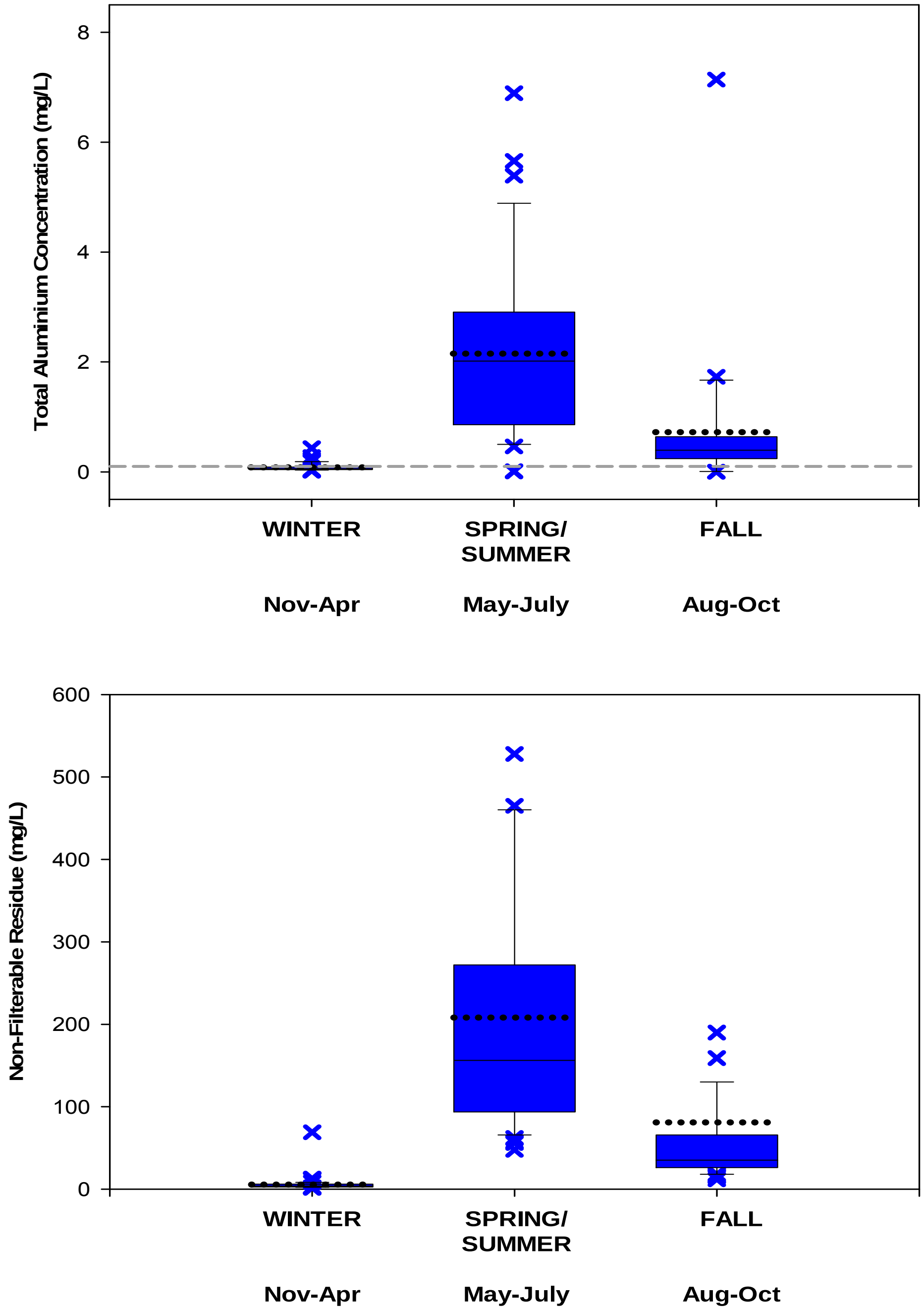
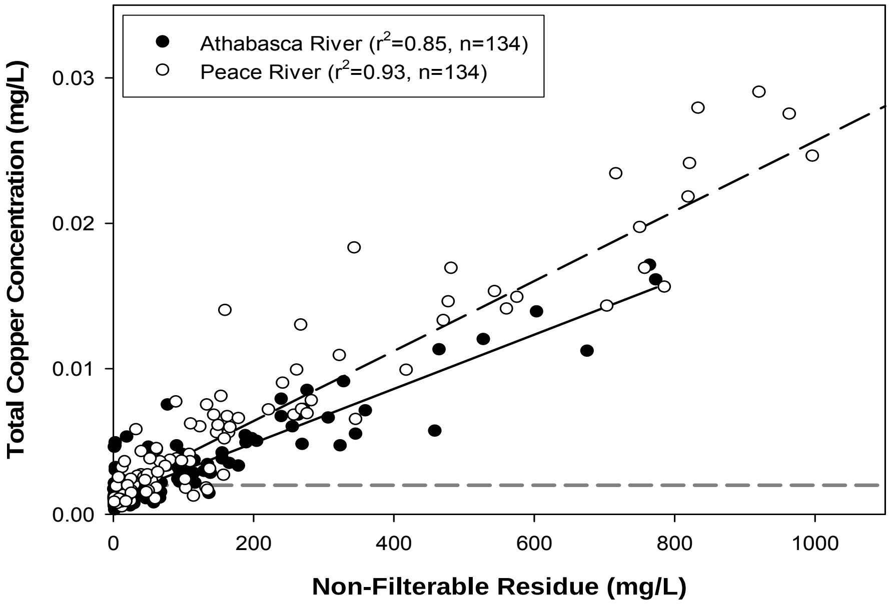


Figure 16: Seasonality in Total Aluminium and NFR for the Athabasca River at 27 Baseline (1989-2006). Dashed grey lines are the CCME water quality objective for Total Aluminium (0.1 mg/L).

A) All data for period of record



B) Expanded view of data < 200 mg/L NFR

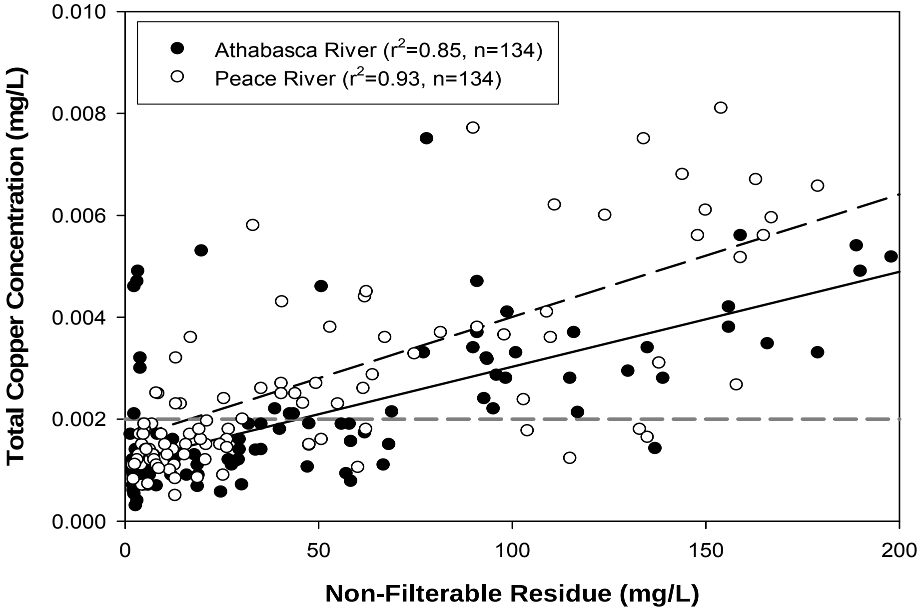


Figure 17: Relationship between Total Copper and Non-Filterable Residue at Athabasca River at 27 Baseline for A) all data, B) samples with <200 mg/L non-filterable residue. Samples from low flow and high flow discharge periods indicated. Dashed grey line is the CCME guideline for total copper (0.002 mg/L) for waters with total hardness 0-120 mg/L.

In summary, the CCME water quality guidelines were developed for total metals though dissolved metals are generally considered to be more important biologically. The decision to base the CCME guidelines on total metals was largely because, until recently, total metals were much more commonly analyzed than dissolved metals. As well, many of the CCREM guidelines were derived from work which had been done on the Great Lakes, where suspended sediment is a less important determinant of total metals concentrations than in rivers prone to seasonal sediment loading events. The results from this study have shown that the relationship between total and dissolved metal fractions is typically weak, which invalidates the applicability of total metals guidelines to the aquatic health of these river systems. Total metal concentrations in these waters are driven by suspended sediment load, associated with natural erosional processes. Therefore, the excursions reported here are not deemed of concern for the biota naturally inhabiting these waters or for downstream, receiving ecosystems (i.e., PAD). The presence of sediment bound metals is a natural component of the ecosystem. However, we strongly suggest the development of site specific guidelines (CCME 2003) for dissolved metals as the most appropriate approach to evaluating whether high metal concentrations in these ecosystems should be identified as a concern. We also examine a limited set of metals for trend analyses in Section 4.3.

4.2 Temporal Trends

The foremost objective of many surface water quality monitoring programs is the determination of trends through time (temporal). Temporal trends can occur on several temporal scales including diel (daily), seasonal (annual), and long-term (over a number of years). Seasonal and diel trends in water quality are primarily related to natural patterns in plant and animal life processes, water discharge, water temperature; while long-term trends can reflect both natural changes and/or changes due to anthropogenic impacts. Therefore, key objectives for monitoring programs include addressing the following questions:

- Is water chemistry changing through time?
- Are the observed changes attributable to natural patterns or anthropogenic influences? and
- Could observed changes in water chemistry impact the biological integrity of the aquatic ecosystem?

We addressed these questions for the three monitoring sites by examining trends at two temporal scales. First, seasonal patterns, which occur yearly regardless of longer term trends, were examined as an aid to understanding the natural patterns of chemical concentration in these aquatic ecosystems and if these patterns have been altered by human activities. Second, long-term temporal patterns of parameter concentration were examined and comparisons among sites of observed trends allowed assessments of potential anthropogenic impacts. Finally, potential impacts on trophic status of these ecosystems are addressed in Section 4.3 by examining levels and ratios of nitrogen and phosphorus concentrations to determine potential impacts on biotic integrity.

4.2.1 Seasonality in Water Quality

Natural changes in water chemistry through the year correspond largely to changes in the hydrologic regime within a basin. The definition of "seasons" for examining water quality patterns is tied to the hydrologic patterns as well as the observed concentration patterns. Seasonal discharge patterns were similar within the three basins (Figure 2), with all sites displaying typical runoff patterns of extended peak discharge through the summer months. Although, as noted previously (Section 2.0), these patterns have been dampened in both the Peace and Slave rivers with the completion of the W.A.C. Bennett Dam, the general patterns remain consistent for the definition of seasons. Therefore, considering the northern climate and the fact that seasonality of many variables is discharge-related, the following seasons were chosen to be most applicable to WBNP:

Spring/Summer	May - July	rising limb & peak of hydrograph
Fall	August - October	falling limb of hydrograph
Winter	November - April	ice covered, base flow

Clearly these time periods are dissimilar in length but represent periods which are distinct hydrologically. Importantly, the appropriateness of these seasonal definitions was confirmed by reviewing monthly frequency graphs for key chemical parameters and the resultant seasonal box plots (see examples presented in Figure 18). Clearly, hydrologic and chemical water quality seasons in northern rivers are neither equal in length nor related to the calendar seasons and we choose to follow patterns derived from the data rather than force arbitrarily defined seasonal definitions. After the seasons were defined and general patterns confirmed, the existence of significant seasonal patterns in water chemistry was statistically determined using the seasonality function within WQSTAT PLUS (version 1.56, ©NIC 2003). This analysis is a non-parametric Kruskal-Wallis (K-W) test where a significant result ($p<0.05$) indicates that at least one season has a significantly different median concentration than one or more other seasons.

Significant seasonality was evident in the majority of water quality parameters tested. Two significant seasonality patterns emerged (Figure 18). First, many parameters exhibited a pattern inverse to the hydrograph, with minimum concentrations occurring during high discharge periods (spring/summer) and maximum concentrations occurring in low flow winter months. These patterns are called Winter Concentration Peaks and designated with a “W” (Table 10; Figure 18A). The second seasonal pattern observed had maximum concentrations occurring in conjunction with high summer discharge levels (Table 10, “S”; Figure 18B). Typically, the parameters associated with this pattern are positively correlated with discharge and sediment concentration. The final pattern was one of no seasonality (Figure 18C). On occasion for the Peace and Slave rivers, two seasons displayed similar median concentrations, higher than the third season. In these cases both “peak” seasons are indicated in the tables.

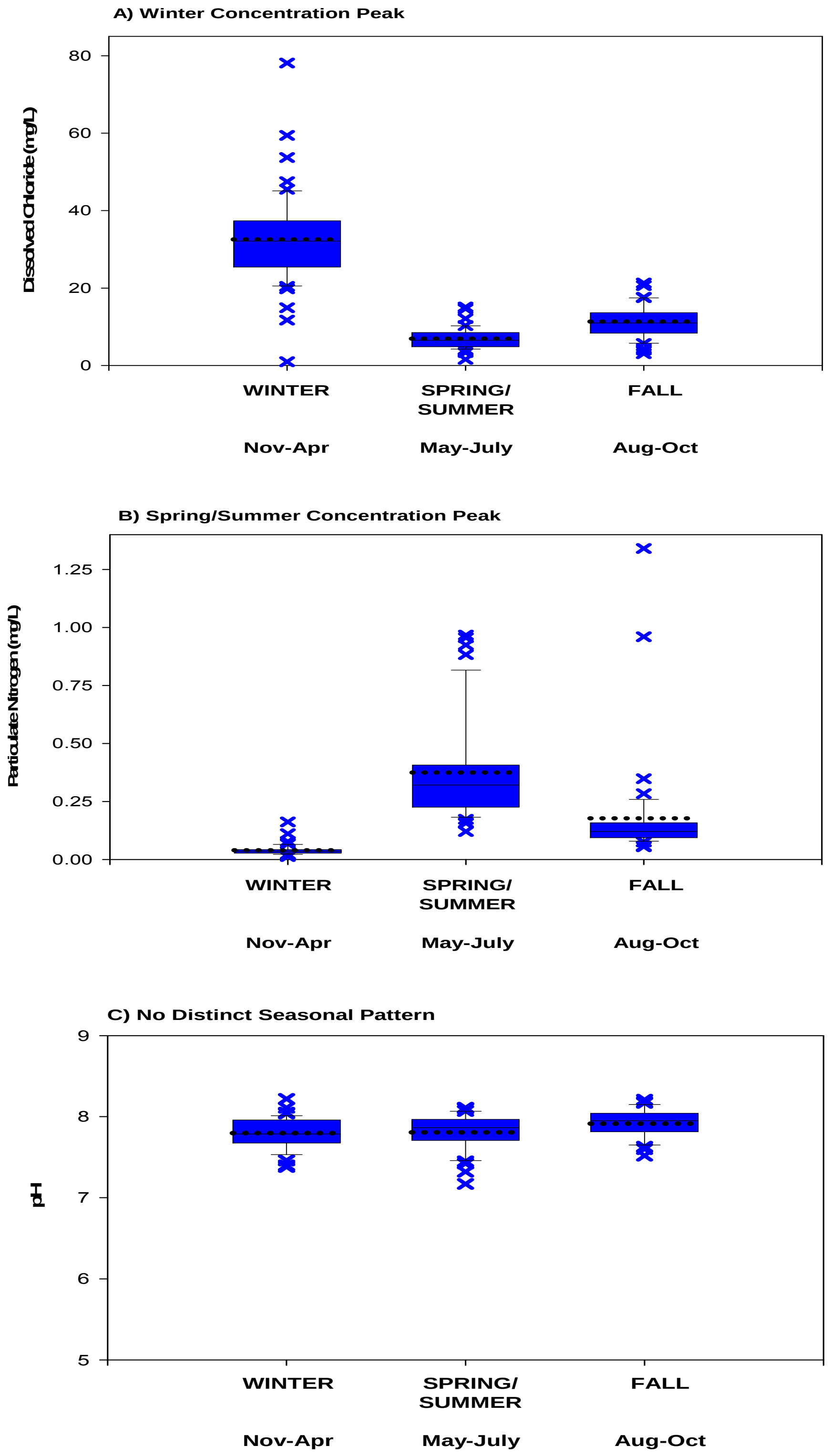
In the Athabasca River seasonality displayed was typical of unregulated northern rivers (Tables 10 and 11), with dissolved parameter concentrations varying inversely with discharge. Particulate and total parameter concentrations displayed peak concentrations during the hydrologic peaks. Seasonality patterns displayed in the Athabasca River at 27 Baseline were similar to other northern, mountain rivers (Bow, North Saskatchewan and upper Athabasca rivers, Glozier et al, 2004b) and largely result from natural processes. A dilution effect occurs during the spring and summer, when lower-mineralized water from snow melt and rainfall runoff make up the majority of river flow. During winter, discharge in natural streams is primarily from groundwater sources. Groundwater tends to be ‘older’ water which has been in contact with soils and rock for longer periods of time, and therefore has higher concentrations of dissolved constituents. Parameters which are directly related to sediment load (turbidity, NFR, colour, particulate and total nutrients) reached maximum concentrations during the high discharge summer period. Winter maxima in dissolved oxygen are also typical (Glozier et al 2004b) and are due to the solubility relationship between dissolved oxygen and temperature (see Medding et al. 2004 and Culp et al. 2004a for comprehensive reviews of dissolved oxygen relationships in northern rivers). The only parameter not showing distinct seasonality was pH, with a small range among the three seasons (range in seasonal median values 7.8-7.95 pH units).

Seasonality results for the Peace and Slave rivers differed substantially from the typical, flow-driven, natural patterns (Tables 10 and 11) observed at the Athabasca River site and the other rivers mentioned previously (Glozier et al., 2004b). While the parameters associated with particulate matter, as well as pH and dissolved oxygen, showed the expected seasonal pattern, most of the dissolved components exhibited either a complete reversal in seasonality (i.e., peaks in summer instead of winter) or a less distinct pattern (similar high concentrations in two seasons). The major ions, all with distinct winter patterns in the Athabasca River, showed various and less distinctive patterns in both the Peace and Slave rivers (Table 10). In fact, three parameters showed no significant seasonality in the Slave River (alkalinity, hardness and magnesium). The dissolved forms of nitrogen and phosphorus, which display peak concentrations in winter for the Athabasca River, displayed either summer peaks, joint summer/winter peaks (i.e., minimal fall concentrations), or no pattern (Table 11). The only exceptions to this change in seasonality for dissolved constituents occurred in the Peace River for chloride and silica which displayed winter-high seasonality.

Table 10: Summary of Kruskal-Wallis Seasonality Analyses for Major Ions and Physical Parameters. Where two seasons are identified as "peak", this was indicative of two seasonal medians being similar and not distinct enough to determine a single peak season but with both displaying higher concentrations than the third season. Detailed statistical results are presented in the Appendix 3.

Parameter	***Athabasca River at 27 Baseline*** **S / F / W**	***Peace River at Peace Point*** **S / F / W**	***Slave River at Fitzgerald*** **S / F / W**
Physical Parameters			
Colour, True	S	S	S
Oxygen, Dissolved	W	W	W
pH (lab)	--------------------	--------------------	--------------------
Residue, Nonfilterable	S	S	S
Specific Conductance (lab)	W	S F	--------------------
Turbidity	S	S	S
Major Ions			
Alkalinity, Total	W	S F	--------------------
Bicarbonate	W	S F	*n/a*
Calcium	W	S F	S
Chloride	W	W	F W
Fluoride	W	S	S
Hardness, Total	W	S F	--------------------
Magnesium	W	S F	--------------------
Potassium	W	S	S
Silica	W	W	*n/a*
Sodium	W	S	F
Sulphate	W	S	S
Total Dissolved Solids	W	S F	S

S = significant seasonality (p<0.05) with high concentrations during Spring/Summer
F = significant seasonality (p<0.05) with high concentrations during Fall
W = significant seasonality (p<0.05) with high concentrations during winter
"------" = no significant seasonality (p>0.05)



A) Winter Concentration Peak

B) Spring/Summer Concentration Peak

C) No Distinct Seasonal Pattern

Figure 18: Patterns in Seasonality from the Athabasca River for A) winter peaks; dissolved chloride B) spring/summer peaks; particulate nitrogen, C) no seasonality; pH.

The major reason for these differences is the altered flow regime brought about by W.A.C. Bennett Dam, which retains water in Williston Lake during the spring and summer high discharge period for release during electrical generation in the winter months. The effects of this altered flow regime on several aspects of downstream ecosystems, including the hydrologic, ecological, and geomorphology features of the Peace and Slave rivers as well as the PAD have been examined in detail elsewhere (Prowse et al., 2002, English et al., 1997, Church 1995). In this report we demonstrate these changes with the hydrographs in Figure 2 and the percentage change in monthly discharge (Figure 19) which clearly shows the effect on seasonal discharge patterns in the Peace and Slave rivers since closure of the W.A.C. Bennett Dam in 1967. During winter, flows in the Peace are on average 163% above pre-dam discharges, while in the open water period (spring/summer and fall seasons) discharges are 25% below pre-dam discharges. This pattern is evident in the Slave River with similar changes in the open water period (-23%) but the overall % increase in winter flows is much lower (+35%), in part due to the additional influences of Lake Athabasca. As a result of these extreme flow alterations, waters from the open water seasons are held back and become mixed in Williston Lake and the subsequent increases in winter releases result in the changes in seasonality observed in dissolved ion concentrations (dampened or reversed seasonality). The overall seasonal patterns for particulate parameters do not appear to be affected by this change in flow regime as physical scouring still occurs with the higher open water flows. Maximum concentrations reached during these times are likely lower than during pre-dam periods; however water quality data for the Peace River pre-dam closure are unavailable (Table 1).

Table 11: Summary of Kruskal-Wallis Seasonality Analyses for Nutrient Parameters. Where two seasons are identified as “peak”, this was indicative of two seasonal medians being similar and not distinct enough to determine a single peak season but with both displaying higher concentrations than the third season. Detailed statistical results are presented in the Appendix 3.

Parameter	***Athabasca River at 27 Baseline***			***Peace River at Peace Point***			***Slave River at Fitzgerald***		
	S	**F**	**W**	**S**	**F**	**W**	**S**	**F**	**W**
Carbon, Dissolved Organic	S			S			S		
Carbon, Particulate Organic	S			S			S		
Carbon, Total Organic	S			S			S		
Ammonia, Dissolved			W	S			--------------------		
Nitrogen, NO23			W	S		W	S		W
Nitrogen, Diss Inorganic			W	S		W	S		W
Nitrogen, Total Dissolved			W	S			S		W
Nitrogen, Particulate	S			S			S		
Nitrogen, Total	S			S			S		
Phosphorous, Dissolved			W	S			S		
Phosphorous, Particulate	S			S			S		
Phosphorous, Total	S			S			S		

S = significant seasonality (p<0.05) with high concentrations during Spring/Summer

F = significant seasonality (p<0.05) with high concentrations during Fall

W = significant seasonality (p<0.05) with high concentrations during winter

"------" = no significant seasonality (p>0.05)

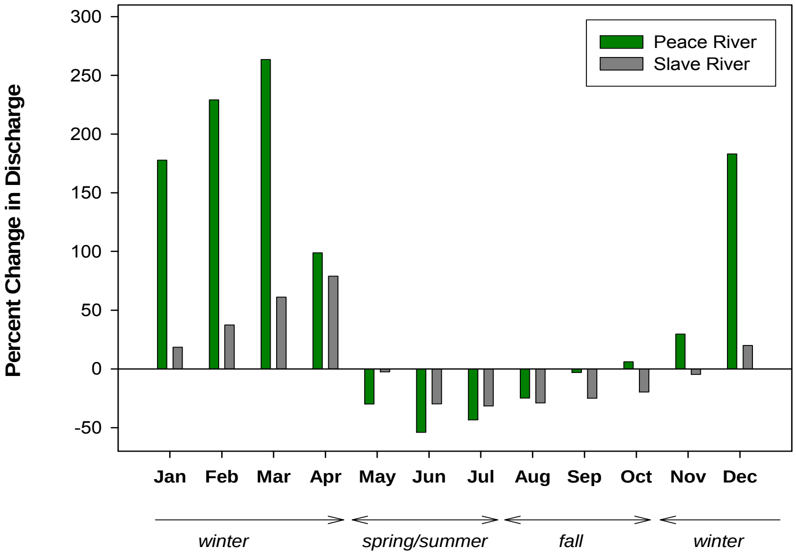


Figure 19: Percent change in median monthly discharge between the pre W.A.C. Bennett Dam Closure (1960-1967) and post closure (1968-2006) for the Peace and Slave rivers.

A final note of interest is included regarding the seasonal patterns for carbon concentrations. The seasonality patterns for total and particulate organic carbon were the same as those in other rivers, with summer peak concentrations. However, the pattern for dissolved organic carbon in these study reaches of peak concentrations in summer was unexpected as it is opposite to the pattern of winter peaks observed in the Bow, North Saskatchewan and upper Athabasca rivers (Glozier et al., 2004b). There are natural and anthropogenic sources in these watersheds for DOC. As dissolved organic carbon is a common constituent present in pulp mill and municipal effluents (Glozier et al., 2004c and unpublished data), both of which discharge into reaches above the Athabasca and Peace River sites in this study, there may be a correlation between the change in seasonality and these industrial inputs. However, the many peatland and bogs in the lower reaches of these rivers which thaw in summer months and have a large sink of DOC may also contribute to the seasonality shift for this parameter from the upper to lower reaches through seepage or overland flow. With the potential of DOC being readily available during the summer growing season as a carbon source for the base of aquatic food webs, particularly microbial components, it is recommended that this difference in seasonal pattern be examined more closely to determine if this is a natural pattern in these lower reaches.

4.2.2 Long-Term Temporal Trends

Long-term temporal trend analyses were run on a total 29 water quality parameters including physical parameters, major ions, and nutrients. All parameters chosen for trend analyses had long and relatively continuous records at all monitoring locations. As a quality control step, the time series graphs were examined for potential steps in the data (e.g., April 1993, April 2003) which may have occurred in conjunction with known changes in analytical techniques. If steps were found related to these changes, the trend analyses were split or truncated so that the trend for the time period examined was not compromised. For example, for dissolved and total nitrogen the period of record analysed for trends was from October 1993 – 2006, as the change in dissolved nitrogen technique resulted in higher recovery rates post 09/2003 (Section 3.0). Although the complete metal suite was not analyzed for overall patterns in trends due to data quality issues (frequent results of ‘less than detection limit’ and changing analytical techniques), a limited set of metal parameters are examined in Section 4.3 to address issue specific concerns.

As most parameters consistently exhibited significant seasonality (Section 4.4.1), the trend analysis method used was the Seasonal Mann-Kendall test (WQSTAT PLUS version 1.56, ©NIC 2003). This is a non-parametric test which does not rely on assumptions of the distribution in the data set. The Seasonal Mann-Kendall determines the significance of an observed trend when seasonality is present and estimates the magnitude of the trend (Sen’s slope). For those few parameters which did not exhibit significant seasonality, the Mann-Kendall trend analysis was applied.

As sampling frequency changed somewhat through the study period, a quality control check was performed to determine if there was any influence of these changes on trend results. In the first five years of the monitoring program (1989-1993), on average, 10 samples per year were obtained. This effort was reduced to an average of 7 samples/year across all stations for the period 1994-2006. We re-examined 18 trend results (5 parameters across the 3 stations), 13 showing increasing trends, 5 showing no change, removed samples in the first five year period to match the distribution of samples (total number and seasonal distribution) in the later period, and re-ran the analyses. Of these 18 trend analyses with reduced sampling in the earlier period, only one analysis result changed in significance level from increasing to non-significant (i.e., 5.5% of analyses). This number is just outside the expected percentage of Type 1 statistical errors considering an alpha value of 0.05. In addition, the change in Z value from 2.02 to 1.93, with a $Z_{critical}$ value of 1.96, means that the result remains very near to significance. Therefore, we are confident that the overall trend analyses presented utilizing all data available is within the regular statistical rigor of expected Type 1 errors, and, as with all statistical analyses, those results near to statistical critical values be simply viewed with caution.

For all parameters, trends were examined for the entire period of record (1989-2006) available. An additional question, which is often asked of water managers, is “what has been occurring in the ecosystem in the most *recent* period of record”; in the case of trend analyses usually the last decade. Therefore, we also examined trends for the most recent decade (1997-2006) to determine if the trend results observed over the entire period were still evident in the most recent decade. The results for the most recent decade are only displayed if they differed from the period of record (Tables 12 and 13). Finally, the influence of changes in river discharge on the concentration trends was examined by flow-weighting the data and re-running the trend analyses (Tables 15 and 16).

The significance and direction of trends are simplified for presentation (see Table 12) by symbolically representing significant ($p<0.05$) increasing (↑), decreasing (↓), and non-significant trends (↔). Details of the statistical results are included in the Appendix 3.

Trends through the Period of Record and Last Decade

Physical Parameters

For the physical parameters examined, the trend results were generally similar between sites (Table 12). Specific conductance showed no significant changes during the study period at any sites, nor did non-filterable residue, turbidity and colour (Athabasca and Peace rivers). Colour at the Slave River did exhibit increasing values over the entire period of record (slope = +0.278 Rel. Units / year), however, when the last decade was examined, no significant trend was detected ($p>0.20$). The overall increasing trend was influenced largely by lower values, which occurred more frequently pre-1993, and a series of higher values in the mid to late 1990s. Mann-Whitney non-parametric tests indicated a significant increase in colour between the first and last decade with median values by increasing by 25% from 22.5 to 30.0 (Rel Units) which could be related to cumulative effluent inputs over time or changes in the hydrologic regime in the Peace-Athabasca delta.

Dissolved oxygen concentrations increased at a rate of +0.05 mg/L/year in the Athabasca River and +0.07 mg/L/year in both the Peace and Slave rivers (Figure 20). As noted previously, only two values in the Slave River were below the CCME (1999) guideline of 6.5mg/L but the sampling program was not designed to assess daily minima given that all sampling occurred during the daylight hours when oxygen is expected to be at its diel peak coinciding with peak photosynthetic activity. As these increasing trends in dissolved oxygen were found at all sites, additional studies on trends in algal productivity and/or respiration may be of interest (Culp et al., 2004, Wassenaar et al. 1999). A similarly increasing trend (slope = 0.03 mg/L/year) for DO was found at the Bow River site downstream of the municipal effluent inputs where increased productivity was noted (Bowman et. al., 2005, Chambers and Watson 2006). Unfortunately, due to difficulties in obtaining and maintaining dissolved oxygen field meters, sampling for DO has been extremely limited since 2003. Recommendations regarding the monitoring for dissolved oxygen are discussed in Section 5.0.

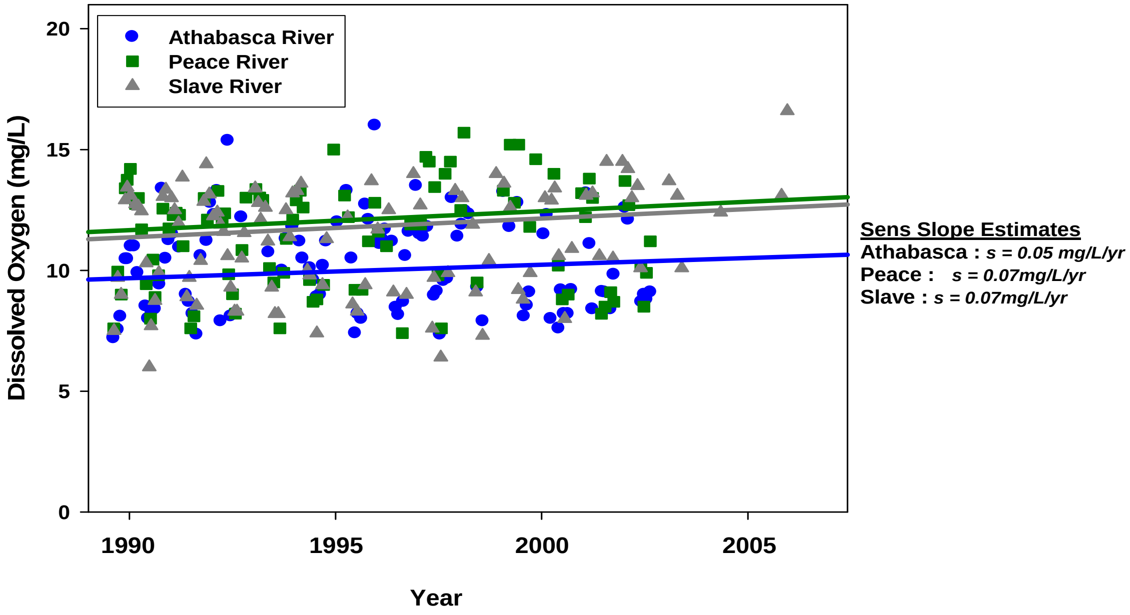


Figure 20: Long-term Temporal Trends for Dissolved Oxygen for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2003). Note, limited data available post 2003.

Finally, pH values increased significantly at all three sites all with slopes of 0.01 pH units/year. As this slope would result in an increase of only 0.1 pH units over the course of a decade, and all pH values were well within aquatic life guidelines, this is not considered an important change to the environment. However, as pH units are based on a logarithmic scale, the one fold change in a decade is actually a 10 fold change so this remains an important parameter to continue to monitor for further changes. Discrepancies between lab and field measurements noted in Section 4.1.1 should be resolved.

Table 12: Summary of Seasonal Mann Kendall Trend results for Major Ions and Physical Parameters. Detailed statistical results are presented in the Appendix 3. Where trend results were the same regardless of time periods, a single frame indicating the results is provided. *↑ = a significant increasing trend through time (p<0.05); ↓ = a significant decreasing trend through time (p<0.05); ↔ = a non-significant increase or decrease through time (p>0.05); n/a = data not available at this site.*

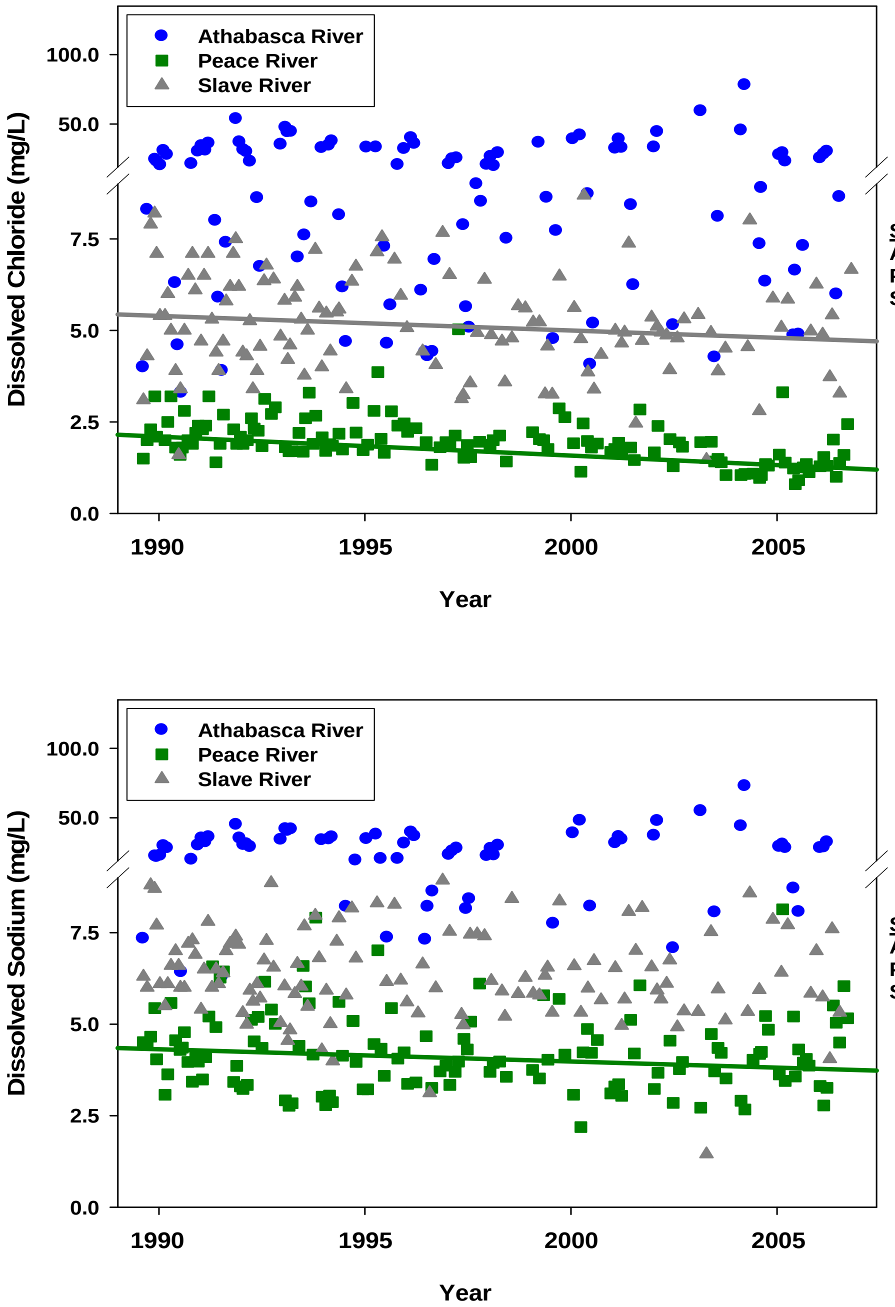
Parameter	**Athabasca River at 27 Baseline**		**Peace River at Peace Point**		**Slave River at Fitzgerald**	
	Period of Record 89-06	**Current Decade 97-06**	**Period of Record 89-06**	**Current Decade 97-06**	**Period of Record 89-06**	**Current Decade 97-06**
Physicals						
Colour, True	↔		↔		↑	↔
Oxygen, Dissolved	↑		↑		↑	
pH (lab)	↑		↑		↑	
Residue, Nonfilterable	↔		↔		*n/a*	
Specific Cond. (lab)	↔		↔		↔	
Turbidity	↔		↔		↔	
Major Ions						
Alkalinity , Total	↔		↔		↔	
Bicarbonate	↔		↔		*n/a*	
Calcium	↔		↔		↔	
Chloride	↔		↓		↓	
Fluoride	↑		↔		↔	
Hardness, Total	↔		↔		*n/a*	
Magnesium	↔		↔		↔	
Potassium	↑	↔	↔		↔	
Silica	↔		↑		*n/a*	
Sodium	↔		↓		↔	
Sulphate	↑	↔	↑	↔	↑	↔
Total Dissolved Solids	↔		↔		↔	↓

Major Ions

Of the 12 parameters in the major ion grouping, five, (calcium, magnesium, alkalinity, bicarbonate, and total hardness) displayed no trends at any sites through the period of record or in the last decade (Table 12). An additional two parameters (fluoride and potassium) showed non-significant trends in the Peace and Slave rivers but increasing trends in the Athabasca River over the period of record (slopes = 0.001 and 0.01 mg/L/yr, respectively). However, the increasing trend for potassium was not evident in the later decade. The overall trend in potassium in the Athabasca River was influenced by greater increases in the first decade with a slope for the 1989-1998 period (0.053 mg/L/yr) being 5X greater than over the entire period of record. Silica showed increasing trends only in the Peace River with a slope of 0.03 mg/L/year.

Sodium and Chloride were examined in more detail as large differences in concentration among sites were already noted (Section 4.1.1). In the Athabasca River where concentrations were highest, no significant trends were observed (Table 12, Figure 21). Chloride concentrations exhibited decreasing trends in both the Peace and Slave rivers (slopes; -0.05 and -0.04 mg/L/yr, respectively) and, while sodium concentrations also showed decreases in both rivers, the trend was only significantly in the Peace River (slope = -0.03 mg/L/yr). The statistical significance of these analyses was maintained regardless of the time period examined. These trends are in contrast to those observed previously for sodium and chloride in upstream reaches of the Bow and North Saskatchewan rivers, where increasing trends were noted (Glozier et al. 2004b). In fact, many of the ions (nearly 70% of all tests run) in those rivers showed consistent increasing trends from 1973-2002. Also of note, is that the sum of all ions, total dissolved solids, in these previous studies showed consistent increasing concentration through time, while in the current study, increasing TDS was not observed at any site (Table 12). In the Slave River, decreasing TDS was observed for the previous decade and was initially observed in 1993 onwards. This time period also corresponded to an obvious increase in annual TDS variability. The reasons for this increase in variability are uncertain, but it is likely that it is related to the variability in major ion trends (increasing, decreasing, stable) and resultant change in composition in these waters as analytical techniques did not differ through the period of record.

Dissolved sulphate, on the other hand showed consistent increasing concentrations over the period of record with slopes ranging from 0.19 to 0.30 mg/L/year (Figure 22). This is a similar result to those in the Bow and North Saskatchewan rivers and the upstream reaches of the Athabasca River, which had increasing concentrations in all study reaches with similar slopes (0.14-0.27 mg/L/yr). An interesting finding for dissolved sulphate was that at all three sites, when the trends were examined for the last decade, the trend was not significant. Thus the increase in sulphate in these rivers occurred in the earlier period of record and although concentrations remains elevated compared to previous concentration they are no longer increasing. The consistency of increasing sulphate concentrations across all study reaches monitored, including upstream reference reaches in the mountain parks, suggests that this is a signal of global or landscape level changes in water chemistry and not a direct result of point source inputs.



Sens Slope Estimates
Athabasca : ***ns***
Peace : ***s = - 0.05 mg/L/yr***
Slave : ***s = - 0.04 mg/L/yr***

Sens Slope Estimates
Athabasca : ***ns***
Peace : ***s = - 0.03 mg/L/yr***
Slave : ***ns***

Figure 21: Long-term Temporal Trends for Chloride and Sodium for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006). Only significant trends are plotted.

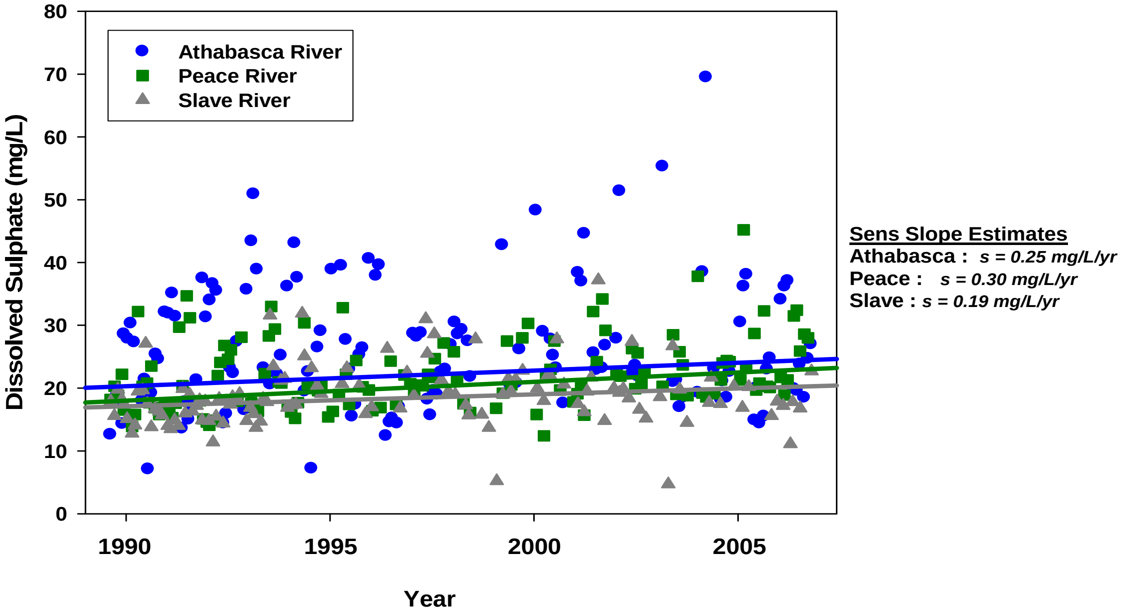


Figure 22: Long-term Temporal Trends for Sulphate for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

Nutrients

When we examined nutrient trends over the entire period of record and for the most recent decade the majority (>70%) of the analyses were consistent regardless of time period (Table 13). In addition, for those parameters which displayed differences in trend results between the two time periods, the changes in results were consistent between sites.

More specifically, the carbon parameters, at all sites, displayed the same trend result, regardless of time period and there was few changes through time. Changes detected included a decreasing trend in dissolved organic carbon concentration (slope = -0.069 mg/L/yr) at the Peace River and an increasing trend in particulate organic carbon (slope = 0.036 mg/L/yr) at the Slave River.

The nitrogen constituents showed more variable results. In comparisons between sites, the results for the Athabasca and Peace rivers were very similar. Total nitrogen, particulate nitrogen, and dissolved nitrogen displayed no significant changes through time at either site. Dissolved inorganic nitrogen and nitrate-nitrite showed increasing trends when the entire period of record was examined (all slopes ~ 0.001 mg/L/yr); however, for the most recent decade the trend became non-significant. For nitrate-nitrite in the Athabasca River, a high percentage (36%) of < DL values should raise caution when interpreting this trend. This was the only nutrient which had this data qualifier (Appendix 2). Total ammonia in the Athabasca River showed a reversing pattern (increasing trend over the period of record but a decreasing trend in the last decade), while in the Peace River a significant trend was not recorded for ammonia at $p < 0.05$. Interestingly, although not statistically significant, for both nitrate-nitrite and DIN, the non-significant trends in the last decade displayed a negative direction compared to the positive direction for the entire period of record, thus, somewhat consistent the dissolved ammonia results. In contrast, the nitrogen parameters in the Slave River showed either no trend or a decreasing trend; no increasing trends were evident. Nitrate-nitrite, ammonia, dissolved inorganic nitrogen and particulate nitrogen all showed no trend over the entire period of record. Total and dissolved nitrogen showed decreasing trends for the period of record tested (post 09/93 data only) and dissolved inorganic nitrogen displayed a decreasing trend over the last decade (all slopes ~ -0.015 mg/L/yr). Thus, in general the dissolved nitrogen components in the Athabasca and Peace rivers showed increasing trends over the entire period of record, but which were not evident or reversed direction when the most recent decade is examined, while in the Slave River these constituents generally showed non-significant or decreasing trends.

In comparisons of phosphorus trends between sites, different patterns emerge. The trend results are most similar between the Athabasca and Slave rivers than with the Peace River (Table 13) Phosphorus concentrations in the Peace River had no significant changes over the period of record or over the last decade. In the Athabasca and Slave rivers, only particulate phosphorus showed non-significant trends. Total (Figure 23) and dissolved phosphorus showed increasing trends for the period of record in both the Athabasca and Slave rivers with slopes of; total phosphorus, 0.0005 (AR), 0.0016 (SR) mg/L/yr, and dissolved phosphorus 0.0002 (AR) and 0.0004 (SR) mg/L/yr. For all these cases, when the last decade is examined, the trend becomes non-significant and for both parameters in the Slave and dissolved phosphorus in the Athabasca, the direction of slope calculated was reversed (negative, although non-significant). The slope for total phosphorus in the Athabasca remained similar (0.0004 mg/L/yr) although it is non-significant for the last decade.

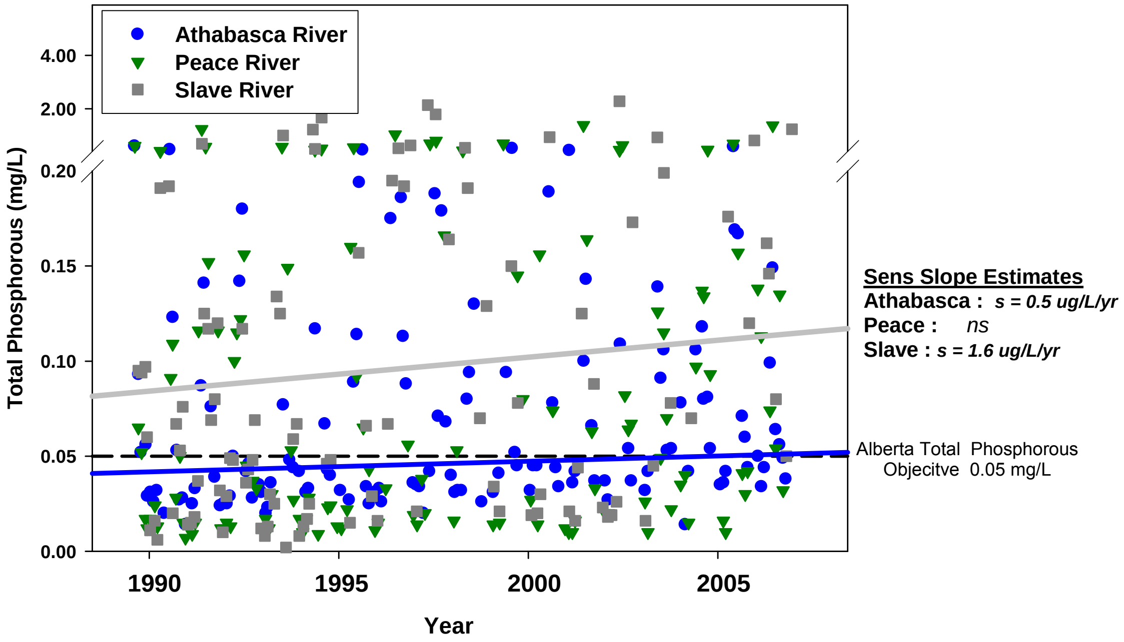


Figure 23: Long-term Temporal Trends for Total Phosphorous for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

Table 13: Summary of Seasonal Mann Kendall Trend results for Nutrients . Detailed statistical results are presented in the Appendix 3. ↑ *= a significant increasing trend through time ($p<0.05$); ↓ = a significant decreasing trend through time ($p<0.05$); ↔ = a non-significant increase or decrease through time ($p>0.05$)*; ↑* *Significant at $p<0.10$; n/a =no data available at this site.*

<table>
<tr><th>Parameter</th><th colspan="2">Athabasca River at 27 Baseline</th><th colspan="2">Peace River at Peace Point</th><th colspan="2">Slave River at Fitzgerald</th></tr>
<tr><th></th><th>Period of Record 89-06</th><th>Current Decade 97-06</th><th>Period of Record 89-06</th><th>Current Decade 97-06</th><th>Period of Record 89-06</th><th>Current Decade 97-06</th></tr>
<tr><td><i>Carbon</i></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Carbon, Dissolved Organic</td><td colspan="2">↔</td><td colspan="2">↓</td><td colspan="2">↔</td></tr>
<tr><td>Carbon, Particulate Organic</td><td colspan="2">↔</td><td colspan="2">↔</td><td colspan="2">↑</td></tr>
<tr><td>Carbon, Total Organic</td><td colspan="2">↔</td><td colspan="2">↔</td><td colspan="2">↔</td></tr>
<tr><td><i>Nitrogen</i></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Ammonia, Dissolved</td><td>↑</td><td>↓</td><td colspan="2">↔↑*</td><td colspan="2">↔</td></tr>
<tr><td>Nitrogen, NO23</td><td>↑</td><td>↔</td><td>↑</td><td>↔</td><td colspan="2">↔</td></tr>
<tr><td>Nitrogen, Dissolved Inorganic</td><td>↑</td><td>↔</td><td>↑</td><td>↔</td><td>↔</td><td>↓</td></tr>
<tr><td>Nitrogen, Total Dissolved <i>post 09/93</i></td><td colspan="2">↔</td><td colspan="2">↔</td><td colspan="2">↓</td></tr>
<tr><td>Nitrogen, Particulate</td><td colspan="2">↔</td><td colspan="2">↔</td><td colspan="2">↔</td></tr>
<tr><td>Nitrogen Total <i>post 09/93</i></td><td colspan="2">↔</td><td colspan="2">↔</td><td colspan="2">↓</td></tr>
<tr><td><i>Phosphorus</i></td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Phosphorus, Dissolved</td><td>↑</td><td>↔</td><td colspan="2">↔</td><td>↑</td><td>↔</td></tr>
<tr><td>Phosphorus, Particulate</td><td colspan="2">↔</td><td colspan="2">↔</td><td colspan="2">↔</td></tr>
<tr><td>Phosphorus, Total</td><td>↑</td><td>↔</td><td colspan="2">↔</td><td>↑</td><td>↔</td></tr>
</table>

In summary, carbon parameters showed few changes through time in concentration at any sites and none that were evident in the last decade. Nitrogen trends were most similar for the Athabasca and Peace rivers and not consistent with the Slave, Further investigation is recommended to determine the relationship between ecosystem processing, landscape or point source influences on these differences in nitrogen trends.

In contrast, phosphorus trends were most similar between the Athabasca and Slave rivers. This was somewhat surprising considering the small proportion of flow the Athabasca River contributes to Slave River flow (<20%). With percentage of flow taken into account some simple calculations indicate that the majority (88%) of dissolved phosphorus entering the Slave River from the two source-rivers could be accounted for by simple addition. However, only 64% of the particulate phosphorus was accounted for in a similar manner, suggesting that for particulate phosphorus, other processes (e.g., deposition in the delta) are influencing the concentrations reaching the Slave River. Detailed hydrologic modelling of these systems have been presented elsewhere (Peters et.al., 2006, Pietroniro et al., 2006, Toth et al., 2006), and these basic percentage calculations do not presume to supersede those studies, but rather to demonstrate that the processes affecting transport of phosphorus through the Peace-Athabasca Delta differ depending on the form (particulate vs dissolved) and hence watershed management actions should be specific to the form of concern.

Effect of River Discharge on Concentration Trends

Where river discharge information is available, the contribution of changes in discharge over time to the temporal trends observed can be determined by flow-weighting the data and re-running the analysis (WQStat – flow weighting option). This process requires a daily discharge value for each concentration measurement and essentially adjusts the concentration data to remove the contribution due to changing flow. This analysis was completed for all parameters at all sites with co-located discharge data for the Peace and Slave rivers.

For the Athabasca River, the closest discharge station with the appropriate period of record was the station “Athabasca River below Fort McMurray” (Station ID 07DA001); nearly 300 km upstream of the water quality site. Therefore, to perform flow weighted trend analyses for the Athabasca River we assumed that no significant changes in river discharge occurred between the water quality and discharge stations, or, at the least, that no significant changes in discharge *patterns* occurred between the stations. When we compared the only historic (1971-1984) discharge data available for a site closer to the current water quality site (i.e., Athabasca River at Embarras Airport, Station 07DD001) we found that the mean discharge differed by only 8.3% (higher discharge at the furthest downstream site). So although discharge has changed in the Athabasca River (Schindler and Donahue 2006, Schindler et al., 2007) over the period of record, as long as the *pattern* of change is similar between these two sites and considering that this is the only data available, we were satisfied with our reasoning for using the discharge data from the upstream site in the Athabasca River. However, interpretation of the results of analyses should be conducted with a caution regarding this assumption particularly given that there were three oil sands projects with licences for water withdrawal and with minimal return flow over the study period in this section of the Athabasca River (Schindler et al., 2007).

River Discharge

The first step in our analysis was to determine if the flow data associated with the dates of the samples has changed through time. These results should not be interpreted as a detailed analysis of changes in flow regime as the dates included are limited to those for which water quality samples were obtained, however, it is the relevant analysis in this context. All three rivers exhibited negative slopes for discharge through the period of record but only the Athabasca River exhibited significant changes in river discharge (slope = -6.51 m^3/s/year, $p < 0.05$). This slope would indicate approximately a 23% reduction in median flow over the 17 year period of record which is similar to previously noted changes (Schindler and Donahue 2006, Schindler et al., 2007, Toth et al., 2006). Furthermore, when we examined the changes in discharge over five decades (Figure 24; Table 14), it becomes clear that the biggest change has occurred in the most recent decade, during the open water period (May-October). Winter flows have also been reduced and thus the seasonal pattern of discharge appears to be unaltered. Therefore the results of our statistical trend analysis, although limited to the dates of water chemistry sampling, are consistent with overall changes in Athabasca River flows.

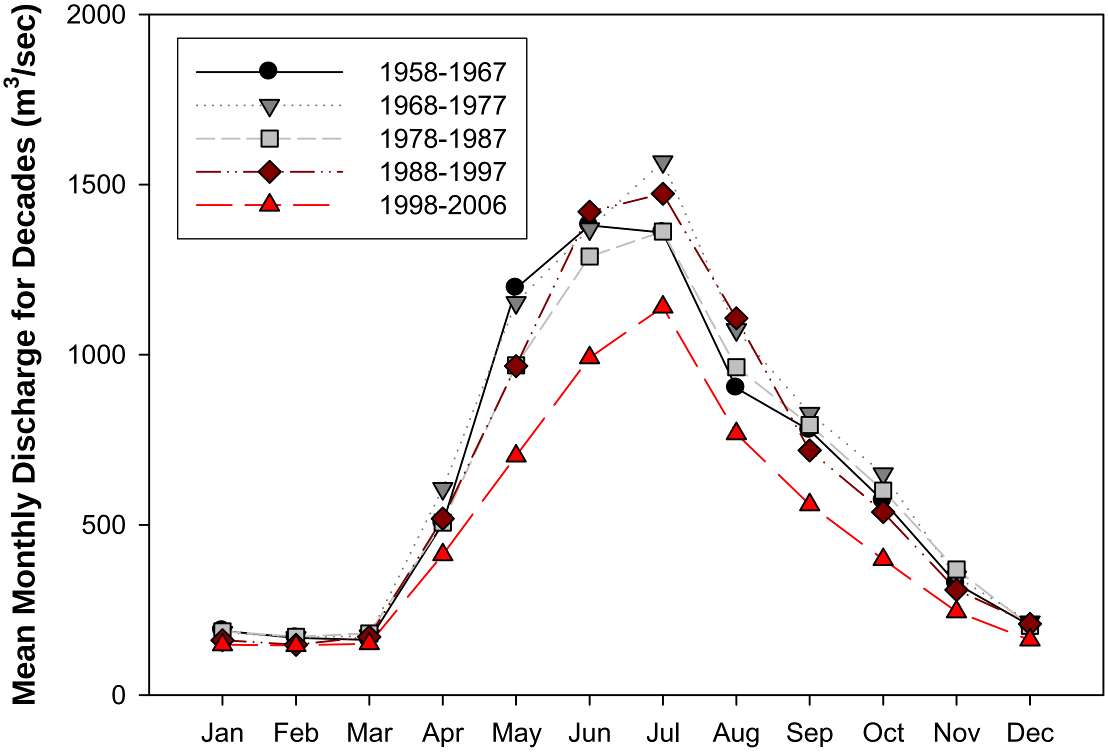


Figure 24: Monthly mean discharge for the Athabasca River below Fort McMurray plotted separately for the previous five decades.

Table 14: Changes in Athabasca River discharge in three seasons from the earliest period of record (1958) to present (2006). Seasons are defined as in Section 4.2.1. The complete discharge data set was used in these calculations and obtained from http://scitech.pyr.ec.gc.ca/waterweb/main.asp.

Season	**Mean Discharge m^3/s**	**Mean Discharge m^3/s (% change from 1st decade of record)**			
Decade	**58-67**	**68-77**	**78-87**	**88-97**	**98-06**
Entire Year	644	695 **(+7.7)**	633 **(-1.8)**	645 **(+0.03)**	485 **(-25.0)**
Spring/Summer	1312	1363 **(+4.0)**	1206 **(-8.0)**	1287 **(-1.9)**	944 **(-28.0)**
Fall	750	851 **(+13.4)**	786 **(+4.8)**	788 **(+5.1)**	575 **(-23.3)**
Winter	259	282 **(+9.1)**	270 **(+4.2)**	253 **(-2.4)**	211 **(-18.7)**

Flow-weighted concentration trends

Considering the non-significant changes in flow for the Peace and Slave rivers, when the concentrations for the water quality parameters were flow weighted, and the trend analyses re-run with the adjusted values, little to no change in the results were found. Therefore the details are not presented.

However, when the Athabasca River data was flow-adjusted many of the trend results differed, indicating that the changing flow regime accounted for a portion of the concentration trend (Table 15). In considering these results it is important to note that, in general, particulate parameters tend to be positively correlated with flow and dissolved parameters negatively correlated. Therefore, with a decreasing flow regime, for trend analyses performed without a flow correction, we would expect concurrent decreasing trends in particulates and increasing trends in dissolved components. As presented above, trends for the dissolved constituents were either increasing or non-significant. When the influence of decreasing flows in the last decade was removed by flow weighting and the trend analyses re-run, the dissolved nutrient compounds which had previously displayed increasing trends showed no trend through time. In addition, many of the non-significant trends in dissolved major ions changed to decreasing trends through time when flow adjusted values were used. Alternately, for all of the particulate parameters, trend results changed from non-significant to increasing with flow-adjusted values. These changes are consistent with the expected direction of change for the slope of the relationships upon flow-weighting. However, the landscape explanation for the decreasing dissolved ion concentrations after removal of the influence of changes in flow is unclear. Therefore, the concentration trends observed in the Athabasca River are, at least in part, due to the changing flow regime and if the flow regime continues to change as predicted (Schindler et al., 2007, Pietroniro et al., 2006, Toth et al., 2006), concentrations may also continue to change and potentially alter the ecosystem characteristics for which the endemic biological communities are adapted. These potential changes could be accelerated if increases in water withdrawals or cumulative point source inputs in upstream reaches results in the river approaching its assimilative capacity.

Table 15: Summary of Seasonal Mann Kendall Trend results for Major Ions and Physical Parameters with flow-weighting. Where results of analyses did not differ with flow adjusted values the table cells are merged. Detailed statistical results are presented in the Appendix 3. ↑ *= a significant increasing trend through time (p<0.05);* ↓ *= a significant decreasing trend through time (p<0.05);* ↔ *= a non-significant increase or decrease through time (p>0.05); n/a =no data available at this site.*

Parameter	**Athabasca River at 27 Baseline**	
	Concentration Trend	**Flow Adjusted Trend**
River Discharge	↓	***NA***
Physicals		
Colour, True	↔	
Oxygen, Dissolved	↑	↔
pH (lab)	↑	
Residue, Nonfilterable	↔	↑
Specific. Cond. (lab)	↔	↓
Turbidity	↔	↑
Major Ions		
Alkalinity, Total	↔	↓
Bicarbonate	↔	↓
Calcium	↔	↓
Chloride	↔	↓
Fluoride	↑	↔
Hardness, Total	↔	↓
Magnesium	↔	↓
Potassium	↑	
Silica	↔	↓
Sodium	↔	
Sulphate	↑	↔
Total Dissolved Solids	↔	

Table 16: Summary of Seasonal Mann Kendall Trend results for Nutrients with flow-weighting. Detailed statistical results are presented in the Appendix 3. Where results of analyses did not differ with flow adjusted values the table cells are merged. ↑ *= a significant increasing trend through time (p<0.05); ↓ = a significant decreasing trend through time (p<0.05); ↔ = a non-significant increase or decrease through time (p>0.05); n/a =no data available at this site.*

<table>
<tr><th>Parameter</th><th colspan="2">Athabasca River at 27 Baseline</th></tr>
<tr><td></td><td>Concentration Trend</td><td>Flow Adjusted Trend</td></tr>
<tr><td><i>River Discharge</i></td><td>↓</td><td><i>NA</i></td></tr>
<tr><td colspan="3"><i>Nutrients</i></td></tr>
<tr><td>Carbon, Dissolved Organic</td><td colspan="2">↔</td></tr>
<tr><td>Carbon, Particulate Organic</td><td>↔</td><td>↑</td></tr>
<tr><td>Carbon, Total Organic</td><td colspan="2">↔</td></tr>
<tr><td colspan="3"></td></tr>
<tr><td>Ammonia, Dissolved</td><td>↑</td><td>↔</td></tr>
<tr><td>Nitrogen, NO23</td><td>↑</td><td>↔</td></tr>
<tr><td>Nitrogen, Dissolved Inorganic</td><td>↑</td><td>↔</td></tr>
<tr><td>Nitrogen, Total Dissolved
<i>post 09/93</i></td><td colspan="2">↔</td></tr>
<tr><td>Nitrogen, Particulate</td><td>↔</td><td>↑</td></tr>
<tr><td>Nitrogen Total
<i>post 09/93</i></td><td colspan="2">↔</td></tr>
<tr><td colspan="3"></td></tr>
<tr><td>Phosphorus, Dissolved</td><td>↑</td><td>↔</td></tr>
<tr><td>Phosphorus, Particulate</td><td>↔</td><td>↑</td></tr>
<tr><td>Phosphorus, Total</td><td colspan="2">↑</td></tr>
</table>

4.3 Supplementary Analyses for Issues of Concern

4.3.1 Metals in the Athabasca River – *Trend Analyses of Select Parameters*

Recently, several reports regarding water quality in the Athabasca River in relation to potential impacts from the industrial activities associated with the Athabasca Oil Sands have been raised by several groups (Timoney 2007 and Hatch and Price 2008). Metals have been identified as a potential contaminant from these activities. However, as stated previously (Sections 3.0 and 4.2) the full suite of metals measured in this study have limited use for long-term trend analyses due to the multiple changes in analytical technique changes, and detection limits. However, to address the concerns raised, we reviewed the metal concentration data in detail and selected a limited set of parameters which, 1) have been identified as metals of concern in these previous reports, 2) are released to the atmosphere from tar sands activities (NPRI substance release database www.ec.gc.ca/pdb/npri/npri_home_e.cfm), but, 3) also meet data quality standards which allowed statistical trend analyses. The quality control criteria for data screening included; <30% of censored data with less than detection results, no apparent step changes due to changes in detection limits or analytical changes (April 1993, April 2003), a time frame of at least 8 years (although 10 years is usually recommended this would limit the analysis to total metals), and consistent sampling over the period of record in all seasons. For dissolved arsenic, an analytical technique change which occurred in April of 2003 appears to have increased recovery rates and thus the trend analysis was truncated in 2002. Given these criteria we conducted trend analyses on three dissolved metals and six total metals for the Athabasca River sampling station.

All three dissolved metals as well as total vanadium showed no trends through time (Table 17). For dissolved copper and iron the period of record only spanned a total of 8 years and thus we may not have a sufficient data record at this point and this analysis should be re-examined in future. For total copper, iron, nickel, and zinc, trends over the period of record were decreasing in concentration. For 3 of these the concentration trends were related to decreasing discharge in the Athabasca River as the flow adjusted concentrations showed no trends through time. Trends in lead concentration were unaffected by changes in discharge.

To compare these results with a site which is not likely affected by the atmospheric deposition or potential leaching from tailings ponds associated with the oil sands (Hatch and Price 2008), we also conducted trend analyses on the same metals from the Peace River station. Considering that discharge in the Peace River has not changed significantly over the period of analysis, we would not expect identical results for those parameters influenced by changes in flow in the Athabasca River. Therefore, the valid comparison is between the concentration trend results from the Peace River and the flow adjusted trends in the Athabasca River. In this comparison, the results are the same in terms of significance and direction of trends. Furthermore, when we compared the *direction* of concentration trends between the Peace and Athabasca rivers, although little is significant in the Peace River, the direction of the trend is similar (downward for total metals).

We also examined a limited set of data from a station upstream of the oil sands operations (data source; Alberta Environment, envext02.env.gov.ab.ca/crystal/aenv/viewreport.csp, detailed data not presented) and found that for total copper and dissolved iron, trend results were consistent with the Athabasca River site at 27 baseline (decreasing and unchanging, respectively).

Therefore, from our analyses conducted on a limited parameter list, it is clear that for the sampling station in the Athabasca River ~90 km downstream of the oil sands activities, total metal concentrations are decreasing likely related to changes in discharge, while dissolved metals are unchanging. These results are similar to findings in other reports for the main stem (Conly et al., 2002, Crosley 1996) and tributaries of the Athabasca River (Conly et al., 2007). In addition, these trends are consistent with sites which would not be suspected of having incurred impacts from the oil sands operations. However, as stated in the 5 year review of the RAMP program (Glozier et al., 2004a), the distance of this site downstream of the oil sands activities without sites at intermediary locations does not allow for concrete conclusions regarding the potential for effects on the Athabasca River as a whole. Recommendations for improvements to monitoring programs are included in Section 5.0 which may allow for a more comprehensive evaluation of potential effects from upstream industries.

Table 17: Summary of Seasonal Mann Kendall Trend results for a Limited set of Metal Parameters. Concentration and flow-weighting trends are presented for the period of record (1989-2006) unless otherwise indicated. Detailed statistical results are presented in the Appendix 3. Where results of analyses did not differ with flow adjusted values the table cells are merged. *↑ = a significant increasing trend through time ($p<0.05$); ↓ = a significant decreasing trend through time ($p<0.05$); ↔ = a non-significant increase or decrease through time ($p>0.05$); n/a =no data available at this site.*

Parameter	**Athabasca River at 27 Baseline**		**Peace River at Peace Point**
	Concentration Trend	**Flow Adjusted Trend**	**Concentration Trend**
Dissolved Metals			
Arsenic *89-02*	↔		*n/a*
Copper *99-06*	↔		↔
Iron *99-06*	↔		↔
Total Metals			
Copper	↓	↔	↔
Iron *93-06*	↓	↔	↔
Lead	↓		↓
Nickel	↓	↔	↔
Vanadium	↔		↔
Zinc	↓	↔	↔

4.3.2 Trophic Status – *Potential Effects of Trends*

Plant and animal productivity, growth, and diversity in aquatic ecosystems are controlled by several factors including water temperature, light, and nutrient concentration. The nutrient available in shortest supply, referred to as the limiting nutrient, is a particularly important determinant to ecosystem productivity. Elevated levels of nutrients in aquatic ecosystems are considered non-toxic stressors, but they can lead to significant changes in the trophic status of rivers (Chambers et al., 2006, Cash et al., 2004, Chambers and Guy 2004, Culp et al., 2004b, Chambers et al. 2001a). A moderate nutrient addition often leads to stimulation in growth and diversity of aquatic plants, invertebrates, and fish. Excessive or prolonged additions can result in more deleterious changes in plant growth and a resultant change in the trophic status and community composition of the aquatic ecosystem. Naturally occurring concentrations of nutrients range greatly depending on the ecosystem and geographic region and hence the effects of nutrient can range from mild to extreme eutrophication. For these reasons, it is not appropriate to advocate for a single nitrogen or phosphorous guideline (Chambers and Guy 2004, Environment Canada 2004), as is the case for toxicity related water quality parameters. Several jurisdictions have published site or regional nutrient guidelines (Table 18).

A document outlining a framework for the management of phosphorous in Canada (Environment Canada 2004) presents a standardized approach for setting site specific phosphorus guidelines. This document provides an excellent review of nutrient issues in Canada and establishes trigger ranges for trophic status of Canadian aquatic ecosystems. Although it is not the intention of this report to review and develop site specific guidelines for nutrients for the Wood Buffalo National Park, we suggest, that the CCME phosphorous framework be considered for the future development of meaningful site specific nutrient guidelines for the Parks' monitoring locations. In this framework establishing background nutrient concentrations are a key step, and for these sites this includes examination of temporal trends. Therefore, in this section we examine the trend characteristics for nitrogen and phosphorus in further detail and place them in the context of potential impacts on natural trophic status of these aquatic ecosystems. The results of this work can be used directly by the Park without significantly more effort to develop site specific objectives.

To determine whether either phosphorous or nitrogen were limiting in the Wood Buffalo Park study area, an approach outlined by Chambers and Guy (2004) has been used. They examined and compared four approaches to determining nutrient limitation conditions, three of which involve experimental or field collection of biotic material. The fourth approach requires comparisons of phosphorous and nitrogen concentrations and ratios to published values associated with nutrient limitation. As chemical concentrations were the only data available for this report we used the later approach as follows:

1. DIN:DP molar ratios were calculated and compared with ranges associated with nitrogen limitation (<10), nitrogen and phosphorous co-limitation (10-32), and phosphorous limitation (>32) (Kahlert 1998).

2. Concentrations of dissolved inorganic nitrogen (calculated from NO_3-NO_2 + dissolved ammonia) were compared to concentrations indicated in the literature as potentially limiting (<0.035 mg/L) (Borchardt 1996).

3. Concentrations of dissolved phosphorous were compared to concentrations indicated in the literature as potentially limiting (<0.005 mg/L SRP) (Bothwell 1989).

To conclude that an aquatic ecosystem is limited by either or both nutrients, a combination of the appropriate ratio and absolute concentration must both fall into the nutrient limited category. For example, the N:P molar ratio may be 45, indicating phosphorous limitation. However, if the phosphorous concentration is >5 µg/L, phosphorous limitation would not necessarily be indicated. Although other studies indicate differing nitrogen and phosphorus levels for limitation (Table 18), the levels used in determining nutrient limitation status in the National parks were those followed by Chambers and Guy (2004) in the Wapiti River, Alberta.

Considering the parameters available in our data set there were several limitations in applying this N:P ratio approach. First, as we did not have access to results for soluble reactive phosphorus (SRP), we used our best proxy, total dissolved phosphorus (TDP). Therefore, conditions indicative of phosphorous saturation may be over stated, as SRP concentrations would be less than TDP concentrations. Secondly, dissolved inorganic nitrogen (DIN) is calculated by summing the concentrations of NO_3+NO_2 and ammonia. Fortunately, these calculations do not include DN, for which an analytical technique change occurred in September, 1993. As a result, the entire monitoring period could be evaluated without concern of a step function in the data set. In most cases, NO_3+NO_2 and ammonia were both available for the calculation. In cases where ammonia data were not available, 0.5 X DL was substituted to allow the calculation. Even with these limitations the approach remains of value in determining trends in nutrient limitation at the three monitoring sites.

Table 18: Summary of Nitrogen and Phosphorus Guidelines or Site Specific Objectives for several Canadian Jurisdictions, Experimentally Derived Nutrient Saturation Levels, Environment Canada 2004 and Dodds et al, 1998 trophic status categories.

Available Nutrient Concentration Information	**TP mg/L**	**TN mg/L**
Published Nutrient Guidelines/ Objectives		
EC (2004)	Framework for deriving Site Specific Guidelines	------------
Manitoba (Williamson 2001)	0.050	
Alberta (AE 1999)	0.050	1.0
Saskatchewan (SERM 1997)		1.0
Ontario (OMEE 1994) for streams and rivers	0.030	
Interim Ontario (OME 1998) & Quebec (MEFQ 1998)	50% above "background"	
Chambers et al, 2006 Upper Athabasca	0.017	0.27
Mid Athabasca	0.027	0.55
Lower Athabasca ** proposed reach specific 90th %*	0.051	0.32
Published Nutrient Saturation Levels		
Dodds et al. 2002	0.030	0.040
Dodds et al. 1997	0.055	0.470
Bothwell 1989	0.005(TDP)	------------
Borchardt 1996		0.035 (DIN)
Lohman et al. 1992	0.021	0.250
Chambers and Guy 2004	0.003 (TDP)	0.065 (DIN)
Cash et al., 2004	0.008 (ortho-P)	0.080 (NO_3+NO_2)
Trophic Status Trigger Ranges (EC 2004)		
Ultra-oligotrophic	< 0.004	------------
Oligotrophic	0.004-0.010	------------
Mesotrophic	0.010-0.020	------------
Meso-eutrophic	0.020-0.035	------------
Eutrophic	0.035-0.100	------------
Hyper-eutrophic	> 0.100	------------
Trophic Status Ranges for Rivers (Dodds et al., 1998)		
Oligotrophic	<0.025	<0.7
Mesotrophic	0.025-0.075	0.7-1.5
Eutrophic	>0.075	>1.5

DIN:DP ratios in all three stations sampled were distributed among the three nutrient limitation categories (Figure 25) and displayed significant seasonality ($p < 0.05$) with maximum ratios occurring in winter. For the Peace River the values were evenly split (30-37% per category). However, for both the Athabasca and Slave Rivers a greater proportion of samples (48 and 59%, respectively) fell within the nitrogen limitation category (DIN: DP ratio of <10). Less than 20 % of samples for these rivers fell within the phosphorus limitation category, indicating that if nutrients were limiting it would likely be nitrogen rather than phosphorus. Mean and median ratios (Table 19) indicate that a strong trend for either nitrogen or phosphorus limitation is not present at these sites as the values are largely in the mid-range.

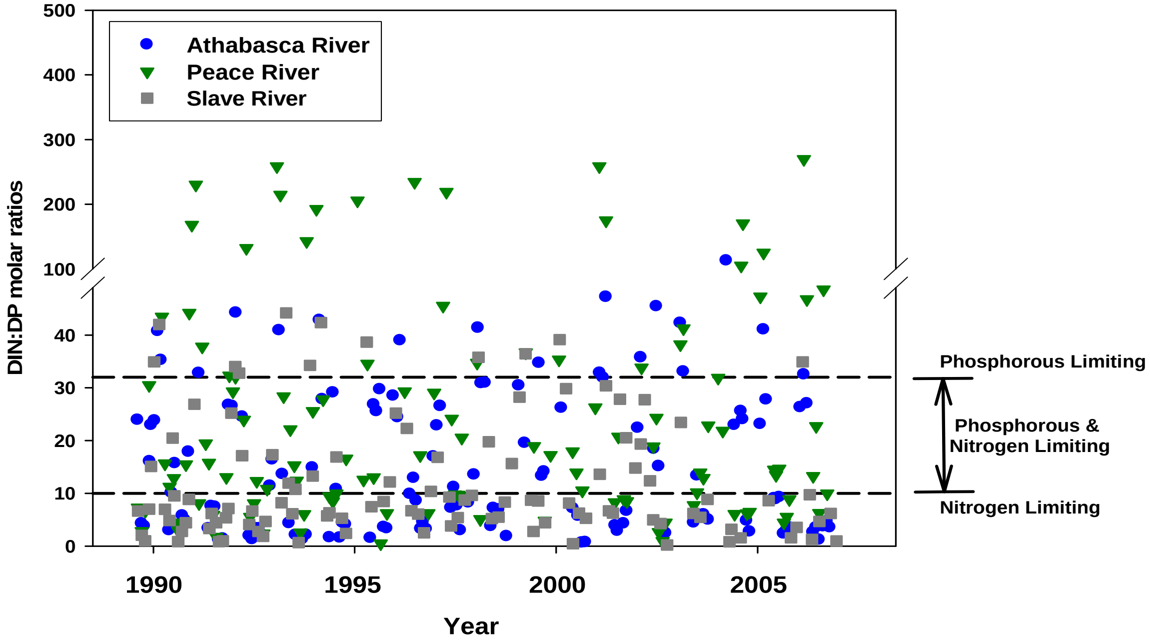
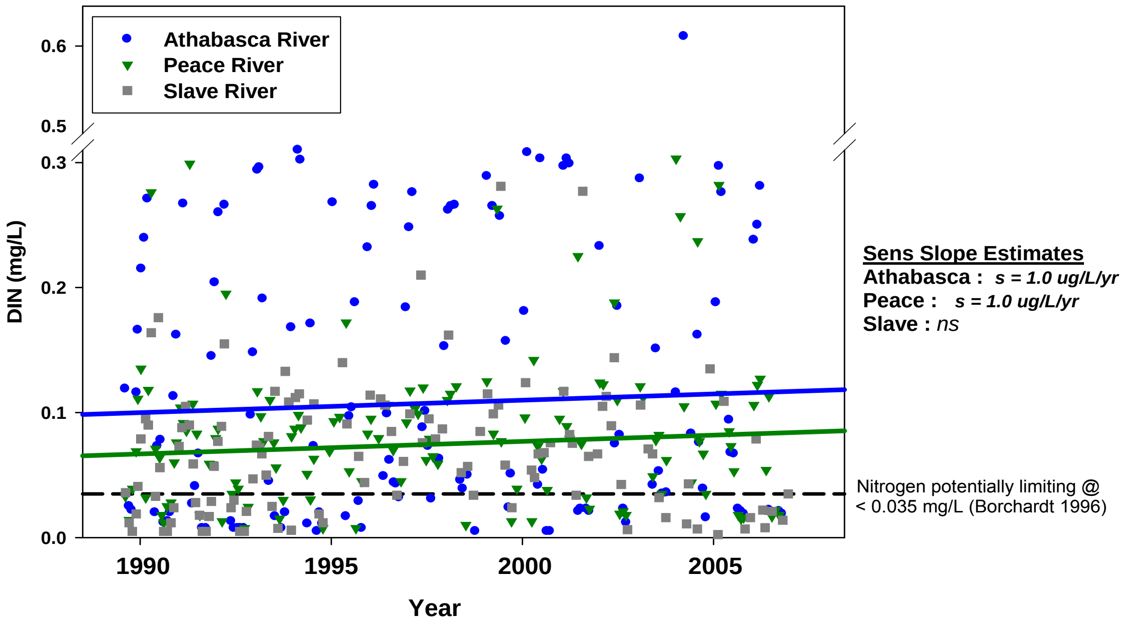


Figure 25: Long-term Temporal Trends at All Sites for N:P Ratios for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

When we examine the DIN and DP concentrations (Figure 26), it is apparent that even though at times the ratios may indicate limitation of one nutrient over the other, the concentrations are largely not nutrient limiting. DIN concentrations were higher than the potentially limiting concentration proposed by Borchardt (1996) of 0.035 mg/L in greater than 65% of samples (i.e., AR 68%; PR 78%; SR 67%). As discussed in the previous section, DIN concentrations showed significant seasonality for all three stations with peak concentrations occurring in winter.
In examinations of dissolved phosphorus concentrations in relation to nutrient limitation (Figure 26B), over 75% of all samples (i.e., AR 98%; PR 76% and SR 88%) were greater than the proposed phosphorus limiting concentration (0.005 mg/L, Bothwell 1989) for rivers. As with DIN, dissolved phosphorus did display seasonality at all sites; peak concentrations occurred in the winter in the Athabasca River but in the spring/summer for both the Peace and Slave rivers (Table11).

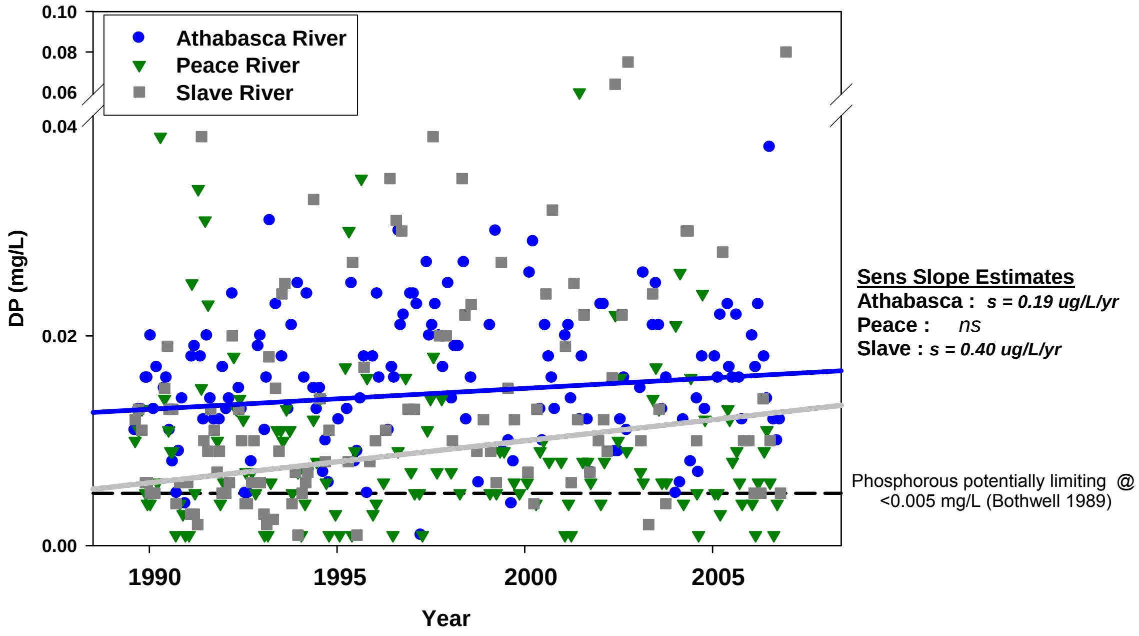
A) Dissolved Inorganic Nitrogen Concentration at Reference Stations



Sens Slope Estimates
Athabasca : ***s = 1.0 ug/L/yr***
Peace : ***s = 1.0 ug/L/yr***
Slave : *ns*

Nitrogen potentially limiting @ < 0.035 mg/L (Borchardt 1996)

B) Dissolved Phosphorous Concentration at Reference Stations



Sens Slope Estimates
Athabasca : ***s = 0.19 ug/L/yr***
Peace : *ns*
Slave : ***s = 0.40 ug/L/yr***

Phosphorous potentially limiting @ <0.005 mg/L (Bothwell 1989)

Figure 26: Dissolved Inorganic Nitrogen and Dissolved Phosphorous for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald (1989-2006).

Trophic status of a river refers to the level of productivity of the aquatic ecosystem and can range naturally from extremely low productivity (ultra-oligotrophic) to highly productive (hyper-eutrophic). These categories are described verbally (Wetzel 2001) and are often measured by the biomass of the most relevant primary producers (e.g., macrophtytes, pelagic algae or attached periphyton) (Environment Canada 2004). However, most often trophic status of ecosystems are determined by phosphorus and/or nitrogen concentrations in the water, as there is limited information on primary producer biomass. In this study, primary producer biomass was not routinely measured and therefore, we have classified these river reaches based on the concentrations of total phosphorus and nitrogen according to the suggested ranges (Table 18). From median values over the period of record in all three rivers (Table 19), using either the CCME or Dodd's trophic status ranges for total phosphorus, these river reaches are classified as Mesotrophic to Eutrophic. Not surprisingly, mean values fall into the Hyper-eutrophic CCME category due to frequent high values. The proportion of samples which would fall into this hyper-eutrophic category are; 28, 39 and 45% for the Athabasca, Peace and Slave rivers, respectively. Therefore regardless of the method of classification, these river reaches are moderate to highly productive systems in regards to total phosphorus concentrations. On the other hand, the total nitrogen concentrations (Table 19) are indicative of a low productivity (oligotrophic) ecosystem. This perhaps is not surprising given the N:P ratios and DIN concentrations discussed previously.

Table 19: Summary of Results for Nutrient Concentrations and DIN:DP Molar Ratios,

Location	**DIN:DP Molar Ratio**		**DIN (mg/L as N)**		**TN (mg/L as N)**		**DP (mg/L as P)**		**TP (mg/L as P)**	
	Mean	**Median**	**Mean**	**Median**	**Mean**	**Median**	**Mean**	**Median**	**Mean**	**Median**
Athabasca River at 27 Baseline	23.5	11.3	0.131	0.078	0.55	0.54	0.016	0.016	0.099	0.050
Peace River at Peace Point	46.3	20.5	0.092	0.077	0.56	0.34	0.010	0.007	0.168	0.056
Slave River at Fitzgerald	16.3	8.4	0.072	0.067	0.68	0.36	0.021	0.011	0.263	0.078

As naturally occurring concentrations of nutrients vary depending on the ecosystem and geographic region, the classification of these systems as highly productive is not a concern in and of itself. The concern for the functioning of an ecosystem is whether the trophic status of an aquatic ecosystem is changing through time due to the addition of point source or non-point source anthropogenic inputs. Therefore, we have examined the trends (presented earlier in Section 4.4.2) for phosphorus (dissolved and total) and dissolved inorganic nitrogen in further detail as these parameters all displayed increasing trends over the period of record.

First, we re-plotted the increasing trends in total phosphorus with the Environment Canada (2004) trophic status categories superimposed (Figure 27). The total phosphorus trend line (slope = 0.5 ug/L/yr) for the Athabasca River remains within the Eutrophic category, whereas, the trend line for the Slave River crosses from eutrophic to hyper-eutrophic in the later portion (2000-2006) of the period of record. In Section 4.2.2 we found that, although both of these trends were significant over the period of record, when the last decade was examined the trends for both total and dissolved phosphorus at these two sites were no longer significant. Clearly, the early increasing trends were enough to change the median values at the Slave River from eutrophic to hyper-eutrophic (Figure 27, open symbols with cross hairs). To extend this evaluation to the earliest recorded values we calculated and plotted the medians from the historic data (1967-1976) available for the Peace and Slave rivers. In both cases total phosphorus concentrations were even lower than the later periods and in fact, would have been classed at least one trophic level lower in the productivity scale (Figure 27, mesotrophic to meso-eutrophic). The maximum value measured in this historic time period was 0.16 mg/L TP (within the range of our current concentrations) and no values were below detection limits. Although the historic data should be viewed with some caution considering laboratory and field technique advancements and the number of samples (Peace n=12; Slave n=26), there is a clear indication of increasing trophic status for both the Athabasca and Slave rivers over the last 30 years.

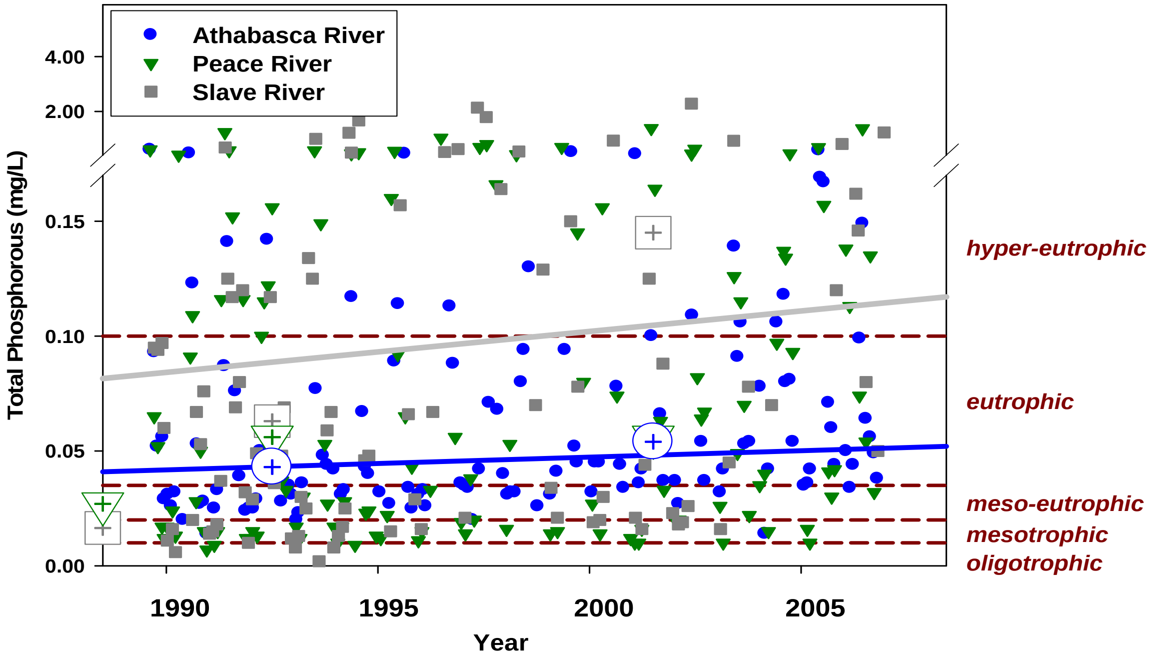


Figure 27: Total Phosphorus Trends for Athabasca River at 27 Baseline, Peace River at Peace Point, and Slave River at Fitzgerald in relation to Environment Canada (2004) Trophic Status categories. Median values are shown as large open symbols with crosshairs for three time periods; historic 1960-1967 (SR), 1967-1976 (PR); early period 1989-1996 and current decade 1997-2006.

Secondly, to augment our understanding of nutrients in these river reaches and to allow for watershed management strategies for nutrients to be effective, we examined the trends for dissolved and total phosphorus and dissolved inorganic nitrogen separately for each season (Table 20). Where trends for the complete data set were not significant, trends were not detected when we examined seasons individually (i.e., Peace River TP and DP and Slave River DIN). However, for all parameters considered here which displayed overall increasing trends when all data was used, when examining the data in each season, trends were only significant in the winter (November – April). Although somewhat higher numbers of samples were obtained in the winter due to the season length, it is unlikely a contributing factor to the significance of the results as many trends are significant with lower sample numbers. As discussed previously (Section 4.21, Table 11) peak concentrations for dissolved parameters generally occur in winter while total and particulate parameter concentrations peak in conjunction with spring/summer discharge peaks, although the dam on the Peace River has altered this typical pattern for the Peace and Slave rivers. Thus, for the dissolved parameters, concentration is increasing during the period when concentrations are already highest and is likely driving the increase in total phosphorus during winter as sediment load is low at this time. Even though winter is not the prime growing season for aquatic primary producers, the result of these trends is an overall increase in potential nutrient loadings and productivity, particularly in downstream ecosystems like the PAD, Lake

Athabasca and Great Slave Lake. In addition to considering these seasonal trends, decisions regarding watershed management will need to consider the fact that discharge has decreased in all seasons (Table 14) and that many of the trends are related to the changing discharge.

Table 20: Summary of Results for Long-term Trend Analysis for Individual Seasons.

Location	**Data Period**	**Total Dissolved Phosphorus**		**Total Phosphorus**		**Dissolved Inorganic Nitrogen**	
		Significant ($p<0.05$)	**n**	**Significant ($p<0.05$)**	**n**	**Significant ($p<0.05$)**	**n**
Athabasca River at 27 Baseline	Entire Year	↑	145	↑	146	↑	144
	Spring/Summer	↔	46	↔	47	↔	47
	Fall	↔	47	↔	45	↔	45
	Winter	↑	52	↑	54	↑	52
Peace River at Peace Point	Entire Year	↔	133	↔	136	↑	139
	Spring/Summer	↔	41	↔	39	↔	42
	Fall	↔	33	↔	35	↔	35
	Winter	↔	59	↔	62	↑	53
Slave River at Fitzgerald	Entire Year	↑	121	↑	120	↔	120
	Spring/Summer	↔	37	↔	35	↔	35
	Fall	↔	29	↔	28	↔	27
	Winter	↑	55	↑	57	↔	58

5.0 Summary and Recommendations

Long-term monitoring programs in Canada are continually re-evaluated for relevance against specific study objectives. A key step in these evaluations is a comprehensive review and interpretation of the status and trends in the data; the objective of this report. These exercises are intensive, require a long period of monitoring information, and are, thus, usually recommended every 5-10 years but are a critical component to monitoring programs. In this report we have presented and interpreted water quality data collected on the Athabasca, Peace, and Slave rivers at the boundaries of Wood Buffalo National Park between August 1989 and December 2006. We have summarized the large amount of water quality data available and provide detailed statistical summaries for the period of record as a reference for further studies (Appendix 2). Patterns in water chemistry among the three watersheds are discussed, including comparisons to upstream source waters. Parameters with national guidelines or site specific objectives for the protection of aquatic life are evaluated for excursions, including metals, major ions, and nutrients. We provide site specific regression analyses for several parameters with sediment loads. We report on the results of statistical temporal trend analyses (seasonal and yearly) conducted for 39 water quality parameters and discuss their relationship to: 1) river discharge, 2) specific time periods, and 3) season. More specific analyses were conducted to examine two issue driven concerns; changes in metal concentration in the Athabasca River, and nutrient concentrations in relation to ecosystem functioning at all stations. Finally, the monitoring program was reviewed for scientific validity, gaps and emerging issues and we forward recommendations for ongoing Parks monitoring programs. Therefore the four major purposes of the report have been addressed by:

1) reporting on status of these waters by providing statistical summaries and comparison among sites, evaluations against CCME guidelines and site specific objectives,

2) reporting trend analyses for 30 water quality parameters and determining whether the changes in chemical concentration observed are, in part, related to changes in, river discharge, a particular time period or season,

3) examination of two issue driven concerns; metals in the Athabasca River and the potential impact of increasing nutrient concentrations on ecological trophic status of these waters, and

4) providing recommendations for improvements to the monitoring program.

An additional product often over looked but derived directly from long-term monitoring programs is that much of this information is provided to many stakeholders upon request. Therefore, during any review of monitoring programs it should be recognized that the information is also frequently utilized by many partners, universities, students, provincial agencies and the public to inform specific scientific questions or studies. In the past several years alone, the water quality data from each of these three stations has been requested and provided for at least 15 individual data requests. Data for these sites continues to be available through the Prairie and Northern office of the Water Quality Monitoring and Surveillance Division, Water Science and Technology Directorate, Environment Canada.

5.1 Summary of Patterns and Trends

In general, water chemistry among the three sampling sites was similar, in that for all parameters, concentration ranges were overlapping. However, patterns between sites were apparent for many parameters. Dissolved oxygen was lowest, while total dissolved solids and most major ions were highest in the Athabasca River compared with the Peace and Slave rivers. The lower ionic content in the Slave is related to the geologic influences of the Canadian Shield, largely absent in the Athabasca River basin. Slightly elevated levels of sodium and chloride in the Slave compared to the Peace maybe due to the influence from the surrounding saline Karst area (Shaw et al., 1990). Nutrient parameters show more differences between sites and between forms (total, dissolved, and particulate). The relative concentration of the forms of nutrients between sites was;

- Carbon (total and dissolved) AR > PR ~ SR
- Nitrogen (total and dissolved) AR > PR ~ SR
- Phosphorus (total) AR < PR < SR
- Phosphorus (dissolved) AR > PR < SR

The similarity in patterns for the total and dissolved forms for carbon and nitrogen is because the majority of the total concentrations of these two nutrients were composed of the dissolved fraction (carbon 71-89 %; nitrogen 56-80 %), where as, for phosphorus the dissolved fraction was only 10-24% of the total. In fact, over 70% of the total phosphorus concentration in these waters can be explained by the suspended sediment load (TP – NFR regressions r^2 >0.72) and over 80% of the total phosphorus exceedences to the Alberta guideline (0.05mg/L) were associated with seasonal periods of high water discharge and high suspended sediment concentrations as measured by sample NFR.

Metals in the environment occur from natural sources in the soil, rocks and alluvial sediments and therefore reflect the surrounding geology and hydrologic processing. In these rivers, total metal concentrations peak in May – July corresponding to the peak discharge and sediment loading. Patterns between sites differed depending on the form. For all metals, ranges overlapped among sites, and for most, medians were similar. Where medians differed, total metal concentrations were lowest in the Athabasca, with higher concentrations in the Peace and Slave rivers. Patterns in dissolved concentrations between the AR and PR were not consistent; dissolved iron and boron were greater in the AR, while dissolved selenium and copper were greater in the SR. Exceedences of CCME total metal guidelines were frequent (e.g., iron 87%) and occurred in association with high discharge, high sediment conditions. The strong relationships between total metals and suspended sediments as measured by NFR (r^2 >0.75) and weak relationships between total and dissolved metals (r^2 <0.16) lead us to conclude that the CCME total metal guidelines are not appropriate as an indicator to assess risk to aquatic life in these waters. Excursion rates were similar among all three sites. And similar patterns have been recorded for many years at sites within the Saskatchewan River basin for sites with similar seasonal sediment loads (PPWB 2007, Glozier 2008). Therefore, development of site-specific objectives for dissolved and total metals is required.

A large component of this study focused on evaluating trends through time to assess the chemical stability of these aquatic ecosystems over the previous two decades. To allow the best management practices to be applied to aquatic ecosystems, understanding the inherent variability in water quality through seasons and years is mandatory. Seasonality analyses showed that three distinct seasons exist in which water chemistry differs due to hydrologic patterns. We defined these seasons as; spring/summer (May-July), fall (August-October) and winter (November-April). Clearly, hydrologic and chemical water quality seasons in northern rivers are neither equal in length nor related to the calendar seasons and for these analyses we choose to follow the patterns derived from data rather than force arbitrarily defined seasonal definitions. Most dissolved parameters had peak concentrations in the low flow winter period, whereas, particulate and total parameters generally peaked in the spring/summer period. These are similar to previously reported patterns for mountain headwaters (Glozier et al., 2004b). However, a key finding is that the patterns in the Peace and Slave rivers have been substantially altered from the natural patterns in unregulated rivers. A consistent change which we observed was the reversal of the seasonal timing of peak concentrations of dissolved parameters. Higher concentrations occur across the entire open water period (spring-fall), with minima in winter. Although these changes in the seasonality of water chemistry have likely been occurring since the closure of the W.A.C. Bennett dam, implications to aquatic biota is unknown and a literature review of potential effects would be useful.

Long-term trend analyses were conducted on all physical, major ion and nutrient parameters. Trend analyses included examining concentration changes through the period of record (1989-2006), in the latest decade (1997-2006) as well as the influence of changes in river discharge. In addition, for nutrients of concern (DP, TP, DIN), we examined the seasonal nature of the trends in concentration. For the physical and major ion parameters most analyses showed stability in concentration through time. Of the 50 analyses conducted over the entire period of record, only 16 showed changes in concentration and 5 of those showed no changes in the last decade. Several ions showed increasing trends at some sites (potassium AR, silica PR), while others showed decreasing trends (chloride PR, SR; sodium PR). In other locations, consistent increasing trends have been noted for most individual ions as well as total dissolved solids (Glozier et al., 2004b), clearly a trend not evident in these waters. Sulphate was the only ion which showed consistent increasing trends through time at all sites. Interestingly, this was also a universal finding at all five sites in the Mountain Parks study (Glozier et al., 2004b) which included reference sites with no point source discharges. It is recommended that these apparent regional changes in sulphate be examined with a broader regional assessment of sulphate concentrations. Two other parameters, pH and dissolved oxygen, showed increases at all three sites throughout the study period. For all rivers, the increases in the oxygen occurred throughout the year but when we examined seasons separately the trends were most significant in the winter.

Changes in nutrient concentration were dependent on site and parameter. Carbon showed few changes through time; DOC decreased in the Peace while POC increased in the Slave. Trends in nitrogen concentration were similar in the AR and PR, most dissolved forms displayed increasing concentrations, while in the Slave River, at least in the last decade, these parameters were showing decreasing trends. We detected no significant trends in phosphorus concentration in the Peace River but in both the AR and SR, dissolved and total phosphorus concentrations increased over the period of record, the majority of the increases occurred in the earlier decade.

Changes in river discharge were only evident in the Athabasca River, so flow adjusting the concentrations in the Peace and Slave rivers did not change the trend results. Because of the significant changes in flow in the Athabasca River, particularly in the last decade (spring/summer -28%; fall -23%; winter -19%), we were able to determine if changes in flow could explain changes in concentration. Our results showed that, at least in part, the concentration trends in the Athabasca River are related to the changing discharge regime. Therefore, with decreasing flows we can expect that further increases in dissolved parameters, particularly nutrients, will continue. This is a concern as increasing trends in phosphorus have changed the trophic status (based on TP concentration) of these reaches at least one and in some cases three trophic levels. When we examined the historic data (1960-1976) from the Slave River, the concentrations were within the mesotrophic (moderately productive) range; in the last decade the median TP concentration now falls within the hyper-eutrophic (very highly productive) category. Similarly the Peace River has changed form meso-eutrophic to eutrophic. No data was available from the Athabasca River for the earliest period. However, as dissolved inorganic nitrogen has increased in the Athabasca and Peace rivers, the Athabasca River appears to have the broadest changes in nutrient concentrations. All of these trends were largely driven by increases during winter months, under conditions of low flow, ice-cover, so careful consideration should be given to minimizing future nutrient inputs during this period.

Finally as concerns have been raised in recent reports (Timoney 2007, Hatch and Price 2008) regarding the potential for increasing concentration in metals due to oil sands activities in the Athabasca basin we conducted trend analyses on the three dissolved metals and six total metals for the Athabasca River sampling station which met data quality standards for trend analyses. We could not conduct detailed trend analyses on all metals due to the multiple changes in analytical technique changes and detection limits. Therefore, for the metals analyzed, it is clear that, at the sampling station in the Athabasca River ~90 km downstream of the oil sands activities, total concentrations (copper, iron, lead, nickel, vanadium, zinc) were found to be decreasing and is likely related to changes in discharge while no detectable change in the dissolved metals (arsenic, copper, zinc) was observed. The analyses for dissolved metals should be re-examined in a few years time when a 10-12 year period of record will be available.

The results from all the trend analysis should also be considered when evaluating not only conditions at the site in question but the potential for changes in loadings (i.e., the total amount of material transported) to downstream ecosystems like the PAD, Lake Athabasca and Great Slave Lake for parameters of concern. Studies of changes in river loadings are complex have not been the focus of this report. However, the transport of metals associated with sediment load into depositional environments like the PAD, and the downstream lakes is likely not an issue considering that; 1) at this point the total metal concentrations appear to be largely of natural origin, 2) concentrations are not increasing, and 3) flows (the other component to loading calculations), at least in the Athabasca River, are decreasing. On the other hand, nutrient concentrations are increasing despite the decreasing flows, so increased nutrient loading could be a concern for these downstream ecosystems, particularly as the effects of climate change scenarios are increasingly considered. We have not calculated trends in nutrient loading into the PAD as the discharge information we have for the Athabasca River is derived from the station upstream of Fort McMurray. Although we argue that this discharge information is sufficient to examine correlations between trends in concentration and flow, it is not likely appropriate for detailed loading calculations. However, a net increase in loading of total phosphorus to the PAD may be occurring if we consider that over the period of record (1989-2006), on average, flows have decreased by 12% (www.scitech.pyr.ec.gc.ca/waterweb), but predicted increases in concentration of total phosphorus could be as high as 21%, based on the slope of the trend line, (TP slope 0.0005 mg/L/yr x 17 years / 0.04 mg/L median TP 1989-1992). This would indicate a 6.5% net increase in loadings over the entire 17 years. Concern over these reaches of the Athabasca River has prompted the development of a water management framework to assess and manage Instream Flow Needs (Alberta Environment and Dept Fisheries and Oceans, 2007).

In summary, the key findings and concerns raised in this study for these river reaches include;

1. A change has occurred in the seasonal patterns of dissolved parameters in the Peace and Slave rivers due to the changes in river discharge patterns related to the construction of the W.A.C. Bennett dam. Potential effects on aquatic ecosystems are unknown and could be examined further through a literature review.
2. Trends in major ion concentrations were inconsistent among sites and parameter, only 25% showed any trends, half of those increasing, half decreasing. This is different than the more universally increasing trends found in other studies (Glozier et al., 2004b). The exception was dissolved sulphate which showed increasing trends at all sites and this appears to be a broader regional change (Glozier et al., 2004b, Parker et al., 2009) which should be investigated further on a regional basis.
3. With the potential of DOC being readily available during the summer growing season as a carbon source for the base of aquatic food webs, particularly microbial components, it is recommended that the seasonal pattern for DOC (peak summer time concentrations) be examined more closely to determine if this is a natural pattern in these lower reaches
4. Oxygen concentrations increased over time largely in winter which is not a concern for the health of aquatic biota. Shorter or warmer winter periods result in shorter ice covered periods which may reduce the winter oxygen depletion documented in ice-covered northern rivers (Chambers et al., 2006).
5. Exceedences to CCME guidelines for total metal concentration were frequent but found to be directly related to the naturally high sediment loads in these rivers and probably have no negative effect on aquatic life. Therefore, the CCME guidelines for total metal concentrations should not be used to access aquatic health in these river systems. Instead, site-specific objectives for dissolved and total metals should be developed to allow a more accurate assessment.

6. Total phosphorus and nitrogen showed exceedences to the Alberta guideline but similar to total metals all were associated with periods of high sediment load and the development of site specific objectives would be best in evaluating nutrient excursions.
7. Site specific objectives for three parameters (dissolved oxygen, sulphate, total dissolved solids) developed under NREI (Donald et al., 2004) were met within the expected frequency (~ 10% of samples).
8. For the nine metal parameters for which trend analyses could be conducted on the Athabasca River, no trends of concern for aquatic ecosystems were evident.
9. Increasing nutrients along with decreasing river discharge appears to be the largest concern for the study reaches of the Athabasca and Slave rivers and those downstream. Increasing trends in phosphorus have changed the trophic status (based on TP concentration) of these reaches at least one and in some cases three trophic levels. As the hydrologic phenomena in the PAD are complex, it is difficult to predicted downstream effects. However, the dissolved phosphorus fraction appears to be transported more readily through the delta and into the Slave River system. Total phosphorus loading to the PAD over the period of study could be near to 6.5%. These changes are likely due to the many cumulative inputs including; 10 pulp mills which have been discharging effluent into these rivers since 1957, a large growth in municipal population, particularly in Grande Prairie and Fort McMurray, as well as the activities surrounding the oil sands which can also contribute to nutrient loadings in the Athabasca River.

5.2 Recommendations

The joint Environment Canada – Parks Canada – Northwest Territories – Alberta Environment monitoring program in the major rivers of Wood Buffalo National park since 1989 has provided invaluable data on water quality through time. It cannot be over emphasized that long-term monitoring programs are key to increasing our understanding of these complex systems and, most importantly, to detect changes through time. Although the current monitoring program has provided the ability to conduct the detailed statistical analyses included in this report the following recommendations will increase the value of the program:

Sample Frequency

- The program should continue. The current level of water quality monitoring should not be reduced as it is the minimum required to ensure that the Park's Strategic Goal of maintaining and restoring (where feasible) water quality and aquatic biodiversity.

- In the first 5 years of the program sampling frequency was 9-12X per year (Appendix 2). In the last decade this has been reduced to 7-8 in the AR and PR and 4-6 in the Slave. To ensure the integrity of the data and our ability to detect changes in the environment, it is highly recommended that a commitment be made by the partners to a consistent sampling frequency between sites and years. The sampling program recommended is 12X per year; once monthly. However, considering the logistical challenges with these sites as well as the yearly and seasonal variability, we recommend that a *minimum* sampling frequency of 8X per year be established with sampling distributed among the three hydrological seasons as follows:

Spring/Summer (May – July):	2
Fall (August – October):	2
Winter (November – April):	4

- Any changes to the current water quality monitoring program should not be undertaken without consideration of :

- The unique and valuable long-term nature of the current program.
- Recommended approaches for evaluating sample frequency/distribution (Vecchia 2003).
- Seasonality in parameter concentrations.
- The ability to continue to perform statistical trend analyses.
- The potential to coordinate and integrate data from provincial, national, territorially, industrial and water quality monitoring programs.

Parameter Suite Analyzed

- The parameter list analyzed at all sites should be consistent. Specifically, dissolved metals and non-filterable residue (or TSS) should be added at the Slave River suite of parameters.

- Continuation of the field instrument measurements for pH, conductivity and oxygen portion of the program is not recommended. Due to the difficulty in remote sites for accurate calibration of field instruments, the variability in the field pH and conductivity measurements compared to laboratory measurements nullified the use of the data in this study. Routine measurement of dissolved oxygen was discontinued in 2003. When considering this recommendation, it should be recognized that laboratory determination of pH on a water sample provides only an approximate measure of field pH due to the equilibrium of gases discussed earlier. Field instrumentation adds to the level of effort during sampling and if the measurements cannot be used in analyses it is recommended that continuation should be evaluated against program needs. If partners remain interested in field measurements then special attention is required for training of field personnel for equipment maintenance and calibrations.

- If dissolved oxygen becomes a concern in these river reaches, in-situ dissolved oxygen meters which log oxygen measurements through a diel period would be the recommended approach as opposed to DO field measurements at the time of sampling. In-situ meters, however, require regular visits, calibration and maintenance. Alternately, although dissolved oxygen was discontinued as a field measurement in 2003 due to the difficulty in calibration of membrane instruments, if partners re-instate the program, newer optical probes for dissolved oxygen could be considered as an alternate for DO measurements.

- Measurements of a broader range of contaminants of concern from industrial sources within the basins should be added to the suite of parameters measured in water and perhaps in sediments. Examples of potential contaminants from pulp and paper effluents include dioxins, furans and sulphur compounds and from oil and gas activities include polynuclear aromatic hydrocarbons, polycyclic aromatic hydrocarbons, napthenic acid, chlorinated phenols. The complete parameter suite should be discussed with partners and be coordinated with other monitoring or research programs operating within these aquatic ecosystems. Measurements of these contaminants are potentially time consuming and expensive and may result in many less than detection values. Currently, however, we can make no statements regarding even the presence or absence of these contaminants. To be cost-effective, the recommended sampling frequency should likely be a subset of that for routine monitoring and as concentrations and variability is documented over a 3 year period, a longer term program with a 3-5 year return frequency could be established.

Sample Locations

- It is recommended that additional sampling locations be considered for water quality and biota sampling as downstream ecosystems are a concern (specifically the PAD). This should be discussed among all partners and in conjunction with other monitoring or research programs operating within these aquatic ecosystems.

- Environment Canada and Alberta should review the feasibility of re-establishing a water *discharge* station in the main stem of the Athabasca River near the boundary of Wood Buffalo National Park (e.g., 07DD001, Athabasca at Embarras) to allow flow weighting of water quality trend analyses to be more valid and to allow accurate loading calculations. This station was discontinued in 1984. There are currently only water level stations in this area.

Data Management and Reporting

- With the completion of this intensive report, a much reduced but more regular, focused, assessment and reporting (every 5 years) should be considered. The intent would be to update the analyses presented with a focus on areas issues identified in this report. For example, nutrients and dissolved metals. A 5 year cycle would correspond to the State of the Park reporting and management planning exercises now underway for Parks Canada.
- Site-specific objectives for metals and nutrients should be established for routine (yearly) reporting. This exercise should not be onerous as the statistical summaries and results from the trend analyses in this study can be used in the approaches recommended (Environment Canada 2004, CCME 2003).
- Environment Canada should ensure that clear and accessible records be kept regarding any future changes in analytical techniques.

Biotic Components:

The current monitoring program assesses water chemistry and does not address changes or effects on biotic communities, only the potential for such effects. Although independent biotic studies have been undertaken, a consistent approach to evaluating aquatic communities and biodiversity would greatly enhance the ability to address the Parks' strategic goals of restoring water quality and aquatic biodiversity.

Specifically we recommend that;

- Biota density and community composition should be determined at sites of interest on a three year return frequency. Sites should include the established river sites as well as sensitive delta areas. Trophic levels of interest include primary producers (algae), benthic invertebrates, and zooplankton.
- Biological indicators as recommended previously by Donald et al, 1996, 2004 should be considered as an ongoing, cyclic, bio-monitoring program.
- Metal levels in fish such as goldeye and walleye, should be examined on a 3-5 year return frequency.

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Appendices

***Appendix 1**: Water quality parameter descriptive information*
***Appendix 2**: Sample frequencies and detailed statistical summaries*
***Appendix 3**: Detailed statistical results for seasonality and temporal trend analyses*

<u>Appendix 1</u>: Water quality parameter descriptive information

Turbidity in water results from the presence of suspended materials including silt, clay, and organic matter. Sources of turbidity-causing materials can be either natural or anthropogenic, and include erosion, runoff, and algal growth. Turbidity results are reported as nephelometric turbidity units (NTUs). High turbidity reduces light penetration, and can thus cause reduced growth of aquatic plants, thereby reducing the food supply available to aquatic animals.

Non-filterable residue (NFR) is a measure of the concentration of suspended materials in water, including both inorganic and organic fractions. NFR is determined by filtering a known aliquot of water through a standard filter, drying and weighing. Results are reported in mg/L.

Water colour is attributed to varying light absorption characteristics of organic and inorganic materials. High colouring agents include humic substances, tannins, lignins, iron, and manganese. Sources can be both natural (organic decomposition, rock weathering) and anthropogenic (various industrial effluents). Water colour is reported in true colour units (TCUs).

pH is the negative logarithm of the hydrogen ion concentration in water. The pH of water dictates the tendency of constituents to enter solution, and the ionic form they will take once in solution. Most sedimentary waters are buffered to within a relatively narrow pH range (pH 7.5 to 8.5) by the predominant carbonate-bicarbonate equilibrium, which provides protection from pH upsets following the addition of acidic inputs such as industrial effluents and acid rain. The pH guideline for the protection of freshwater aquatic life is pH 6.5-9.0 (CCREM 1987).

Specific conductance is a measure of the electrical conductivity of water, which is dependent on the concentration of dissolved ions and water temperature. Specific conductance provides an estimate of the total dissolved solids (TDS) in water (and is reported in microsiemens/centimeter (µS/cm). The TDS-specific conductance relationship is approximated by TDS = 0.6 X specific conductance. Typical freshwater ranges for specific conductance are between 50 and 1500 µS/cm.

Total dissolved solids (TDS) is a measure of the concentration of ions dissolved in water, and is calculated by summing the analyzed concentrations of individual ions. Results are reported in mg/L. The solution of ions into water occurs naturally, with the degree of solution influenced by a number of geological and physical characteristics. TDS tends to be highly seasonal, lowest during periods of high discharge, and highest during winter, when groundwater, which tends to be relatively highly mineralized, becomes a major component of discharge. Many human activities can increase the TDS of surface waters, including point and non-point source activities.

Dissolved oxygen concentrations are dependent on a number of physical (temperature, salinity, altitude, turbulence, degree of ice cover) and biological (photosynthesis, organic decomposition, inorganic oxidation) factors. Concentrations are primarily controlled by the balance between the rates of biological depletion, biological replenishment, and physical re-aeration. Dissolved oxygen concentrations can fluctuate diurnally due to photosynthetic schedules and seasonally, due to changes in water temperature. High biological and/or chemical oxygen demand can deplete dissolved oxygen concentrations to near zero. Saturated dissolved oxygen concentrations range from approximately 15 mg/L at 0º C to 8 mg/L at 25 º C. For protection of salmonid spawning habitat, the dissolved oxygen minimum concentration should be 9.5 mg/L from spawning until 30 days after hatch (CCREM 1987).

Alkalinity is the capacity of water to buffer acid. In sedimentary waters, this capacity is primarily due to the presence of bicarbonate (total alkalinity) and carbonate ions (phenolphthalein alkalinity). Other ions which add to alkalinity include hydroxide, silicates, phosphates, and some organic bases. Alkalinity is expressed in mg/L equivalents of calcium carbonate. Alkalinity values in the range of 30-500 mg/L are acceptable for most uses.

Total hardness is inversely proportional to the capacity of water to produce a lather from soap. Water with low concentration of total hardness (<80 mg/L as $CaCO_3$) is termed soft water. The major source of hardness in water is the presence of calcium and magnesium ions. A number of metals can add small amounts of hardness as well. Total hardness in excess of 500 mg/L is generally undesirable for industrial and domestic uses.

Major cations: the predominant cations (positively charged ions) in most Park waters include, in relative order of abundance, calcium, magnesium, sodium, and potassium. Cationic and anionic concentrations are determined by a number of factors, including basin geology and ion solubilities. Calcium is soluble in water in the presence of CO_2, but can precipitate as $CaCO_3$ if the pH increases significantly. Magnesium is more soluble than calcium, remaining in solution after calcium has precipitated. A major magnesium source is the solution of dolomite. Sodium and potassium have similar chemical properties, but differ in their resistance to weathering. Potassium is present in very low concentration in many rocks. Rocks with larger concentrations of potassium tend to be resistant to weathering (feldspars, micas, clay minerals). Sodium leaches freely from rocks and soils and tends to remain in aqueous solution once dissolved.

Major anions: in relative order of abundance, the major anions (negatively charged ions) include bicarbonate-carbonate, sulphate, silicate, chloride, and fluoride. Bicarbonate and carbonate ions, and to a lesser degree dissolved carbon dioxide or carbonic acid, are the major inorganic carbon sources for aquatic plant photosynthesis. At normal surface water pH (near 8.0), inorganic carbon in water is nearly 100% bicarbonate. Sources of sulphate include weathering of sedimentary rock, with major sulphate minerals including gypsum and anhydrite. Oxidation of organic materials can also contribute sulphate to surface waters. Silica is the second most abundant element in the earth's crust, but concentrations in surface waters are limited by sillica's low solubility in water. It usually appears in water in the colloidal state, with concentrations usually below 5 mg/L. Chloride is highly soluble, but can be precipitated by divalent cations (calcium, magnesium). Chloride is present in calcareous and sulphatic deposits, and is released by weathering and leaching. Fluoride is released from weathering of igneous and sedimentary rock, especially shale. Principal fluoride bearing minerals include fluorspar, fluorapatite, and cryolite. Chloride concentrations in surface waters generally exceed fluoride concentrations by >10:1.

Nutrients: Phosphorous, nitrogen, and carbon are the major elements required for the growth of both aquatic and terrestrial plants. Of the three elements, phosphorous is usually present at the lowest concentrations, and can be the limiting factor for aquatic plant growth. All three major elemental nutrients undergo cycles of reduction to complex organic forms, and oxidation to simpler inorganic forms. Nutrient sources are diverse, and can be combinations of natural (weathering), anthropogenic (sewage disposal, etc.), and internal (i.e. regeneration from sediments) mechanisms. A number of nutrient fractions are analyzed, including dissolved, particulate, and total fractions. Dissolved nutrients are largely available for biological use, while the particulate fractions are mostly unavailable. Nitrogen analyses have historically included nitrate-nitrite nitrogen and ammonia, which is present in water mainly as ammonium ion (NH_4OH). Unionized ammonia (NH_3) is highly toxic to fish, but is present at extremely low concentrations in most surface waters.

Bacteriological parameters: a number of bacterial tests are available to provide a measure of the degree of enteric waste pollution, and thus an indication of the probability of the presence of pathogenic organisms. These tests include total coliform (gram-negative, non spore-forming, rod-shaping bacteria associated with the feces of warm-blooded animals and soil), fecal coliform (similar to total coliform, but restricted to warm-blooded animal sources), and fecal streptococci. The fecal streptococci are more resistant than coliforms to treatment processes, and thus may provide some information regarding the viral concentrations in water. The three bacterial indicator tests are done by membrane filtration, followed by specific incubation and manual counting of colonies.

***Appendix 2**: Sample frequencies and detailed statistical summaries*

Sample Frequency for Period of Record 1989-2006

	Number of Water Quality Sampling Events		
Sampling Year	Athabasca River at 27 Baseline	Peace River at Peace Point	Slave River at Fitzgerald
1989	5	5	5
1990	11	12	11
1991	9	10	12
1992	10	9	11
1993	8	10	11
1994	8	9	8
1995	9	8	5
1996	9	6	6
1997	10	8	6
1998	7	3	6
1999	6	6	6
2000	9	7	6
2001	7	7	7
2002	7	7	6
2003	7	7	5
2004	8	8	4
2005	9	9	4
2006	9	8	6
Total	148	139	125
Yearly Average	8.2	7.7	6.9
Yearly Average last decade	7.9	7.0	5.6

Physicals & Major Ions

Parameter	*units*	n	Mean	Median	Maximum	Minimum	Std. Dev.	90th Percentile
Athabasca River								
Physicals								
COLOUR TRUE	**rel units**	133	37	25	125	3	24	70
OXYGEN DISSOLVED	**mg/L**	105	10.26	10.20	16.00	7.20	1.91	12.77
pH Lab	**units**	126	7.83	7.87	8.22	7.17	0.20	8.06
RESIDUE NONFILTRABLE	**mg/L**	146	93	31	774	2	147	267
SPECIFIC CONDUCTANCE Lab	**usie/cm**	123	340.55	294.00	778.00	186.00	111.44	490.60
TURBIDITY	**ntu**	148	51.54	17.20	452.00	2.70	79.70	133.10
Major Ions								
ALKALINITY TOTAL CACO3	**mg/L**	138	115.65	105.50	232.00	71.50	28.24	153.00
BICARBONATE (CALCD.)	**mg/L**	134	139.80	127.40	282.81	87.20	33.52	183.72
CALCIUM DISSOLVED/FILTERED	**mg/L**	139	35.39	32.60	71.20	21.30	7.98	45.64
CHLORIDE DISSOLVED	**mg/L**	139	17.97	12.10	78.10	0.95	14.01	36.76
FLUORIDE DISSOLVED	**mg/L**	138	0.11	0.11	0.20	0.05	0.02	0.14
HARDNESS TOTAL (CALCD.) CACO3	**mg/L**	135	126.19	117.00	266.30	75.20	29.30	162.58
MAGNESIUM DISSOLVED/FILTERED	**mg/L**	139	9.45	8.56	21.50	5.34	2.52	12.80
POTASSIUM DISSOLVED/FILTERED	**mg/L**	139	1.26	1.20	3.05	0.53	0.41	1.77
SILICA	**mg/L**	138	6.32	5.41	18.00	2.44	2.44	9.62
SODIUM DISSOLVED/FILTERED	**mg/L**	138	19.71	14.15	72.90	2.80	12.46	36.45
SULPHATE DISSOLVED	**mg/L**	138	26.14	23.40	69.50	7.10	9.91	38.62
TOTAL DISSOLVED SOLIDS (CALCD.)	**mg/L**	133	182.60	153.00	476.01	105.00	62.31	269.36
Peace River								
Physicals								
COLOUR TRUE	**rel units**	124	32	23	195	3	34	90
OXYGEN DISSOLVED	**mg/L**	95	11.44	11.90	17.70	7.40	2.26	14.12
pH Lab	**units**	125	7.87	7.89	8.21	7.20	0.17	8.06
RESIDUE NONFILTRABLE	**mg/L**	138	194	58	2120	2	329	614
SPECIFIC CONDUCTANCE Lab	**usie/cm**	127	238.94	235.00	431.00	152.00	26.77	265.00
TURBIDITY	**ntu**	139	156.79	32.60	1840.00	3.40	292.69	454.00
Major Ions								
ALKALINITY TOTAL CACO3	**mg/L**	137	97.41	95.60	190.00	60.30	11.66	106.40
BICARBONATE (CALCD.)	**mg/L**	133	118.80	116.50	224.05	73.51	13.90	130.16
CALCIUM DISSOLVED/FILTERED	**mg/L**	137	33.34	33.00	63.00	20.10	3.58	36.20
CHLORIDE DISSOLVED	**mg/L**	137	2.50	1.93	32.30	0.80	3.32	2.95
FLUORIDE DISSOLVED	**mg/L**	136	0.08	0.07	0.25	0.04	0.03	0.11
HARDNESS TOTAL (CALCD.) CACO3	**mg/L**	133	115.02	113.30	226.89	91.93	12.82	125.99
MAGNESIUM DISSOLVED/FILTERED	**mg/L**	137	7.61	7.51	16.90	4.77	1.12	8.44
POTASSIUM DISSOLVED/FILTERED	**mg/L**	136	0.82	0.70	3.16	0.40	0.43	1.24
SILICA	**mg/L**	106	3.98	4.04	5.28	0.54	0.64	4.68
SODIUM DISSOLVED/FILTERED	**mg/L**	137	4.67	4.17	33.40	2.19	3.11	6.03
SULPHATE DISSOLVED	**mg/L**	137	22.06	20.70	45.20	12.40	5.58	29.94
TOTAL DISSOLVED SOLIDS (CALCD.)	**mg/L**	132	134.12	132.80	263.20	112.00	19.23	148.89
Slave River								
Physicals								
COLOUR TRUE	**rel units**	122	45	30	330	3	62	90
OXYGEN DISSOLVED	**mg/L**	105	11.16	11.70	16.60	0.90	2.39	13.60
pH Lab	**units**	115	7.90	7.92	8.22	7.29	0.19	8.10
RESIDUE NONFILTRABLE	**mg/L**	41	158	45	2320	6	390	239
SPECIFIC CONDUCTANCE Lab	**usie/cm**	115	226.33	219.00	1200.00	57.60	94.88	242.20
TURBIDITY	**ntu**	120	242.27	55.00	6400.00	2.50	697.84	596.90
Major Ions								
ALKALINITY TOTAL CACO3	**mg/L**	118	83.74	84.20	121.00	23.00	11.01	94.23
BICARBONATE (CALCD.)	**mg/L**							
CALCIUM DISSOLVED/FILTERED	**mg/L**	124	28.13	28.10	41.20	6.87	3.69	31.10
CHLORIDE DISSOLVED	**mg/L**	120	5.21	5.04	9.01	1.47	1.41	7.10
FLUORIDE DISSOLVED	**mg/L**	120	0.08	0.08	0.20	0.05	0.02	0.10
HARDNESS TOTAL (CALCD.) CACO3	**mg/L**	59	95.11	96.60	122.60	23.25	13.24	106.37
MAGNESIUM DISSOLVED/FILTERED	**mg/L**	124	6.58	6.58	9.55	1.48	0.83	7.42
POTASSIUM DISSOLVED/FILTERED	**mg/L**	124	1.03	0.86	3.63	0.17	0.51	1.63
SILICA	**mg/L**							
SODIUM DISSOLVED/FILTERED	**mg/L**	124	6.44	6.24	9.64	1.45	1.29	8.18
SULPHATE DISSOLVED	**mg/L**	120	18.81	18.05	37.20	4.71	4.73	25.14
TOTAL DISSOLVED SOLIDS (CALCD.)	**mg/L**	120	134.07	126.50	360.00	31.29	39.22	173.00

Nutrients (parameters with > 30% censored data are highlighted)

Parameter	*units*	Analytical Detection Limit (DL)	% <DL	n	Mean	Median	Maximum	Minimum	Std. Dev.	90th Percentile
Athabasca River										
CARBON DISSOLVED ORGANIC	**mg/L**	0.1	0	147	8.9	8.6	19.6	2.4	3.2	13.1
CARBON PARTICULATE ORGANIC	**mg/L**	0.1	0	145	2.2	1.2	16.9	0.2	2.9	5.3
CARBON TOTAL ORGANIC (Calc)	**mg/L**	0.1	0	144	11.1	9.7	29.5	2.6	5.2	18.3
AMMONIA DISSOLVED	**mg/L**	0.005	6	139	0.053	0.034	0.630	0.003	0.065	0.107
NITROGEN DISSOLVED NO3 & NO2	**mg/L**	0.01	36	145	0.08	0.04	0.53	0.01	0.09	0.21
NITROGEN DISSOLVED INORGANIC (Calc)	**mg/L**	0.01	0	145	0.13	0.08	0.85	0.01	0.13	0.30
NITROGEN TOTAL DISSOLVED	**mg/L**	0.01	0	147	0.36	0.36	1.01	0.06	0.16	0.55
NITROGEN PARTICULATE	**mg/L**	0.01	0	146	0.19	0.11	1.34	0.01	0.22	0.40
NITROGEN TOTAL (Calc.)	**mg/L**	0.01	0	145	0.55	0.54	1.70	0.15	0.28	0.85
PHOSPHOROUS TOTAL DISSOLVED	**mg/L**	0.002	1	147	0.016	0.016	0.038	0.001	0.006	0.024
PHOSPHOROUS PARTICULATE (Calc.)	**mg/L**	0.002	1	148	0.083	0.038	0.589	0.004	0.113	0.211
PHOSPHOROUS TOTAL	**mg/L**	0.002	0	148	0.099	0.050	0.600	0.014	0.112	0.227
Peace River										
CARBON DISSOLVED ORGANIC	**mg/L**	0.1	0	137	6.0	5.2	14.7	2.1	3.2	10.7
CARBON PARTICULATE ORGANIC	**mg/L**	0.1	0	136	3.5	1.1	32.6	0.1	5.5	10.7
CARBON TOTAL ORGANIC (Calc)	**mg/L**	0.1	0	136	9.4	6.9	43.2	2.5	7.7	20.9
AMMONIA DISSOLVED	**mg/L**	0.005	12	138	0.027	0.013	0.695	0.003	0.062	0.043
NITROGEN DISSOLVED NO3 & NO2	**mg/L**	0.01	21	136	0.07	0.06	0.39	0.00	0.06	0.11
NITROGEN DISSOLVED INORGANIC (Calc)	**mg/L**	0.01	1	139	0.09	0.08	0.78	0.01	0.09	0.15
NITROGEN TOTAL DISSOLVED	**mg/L**	0.01	0	137	0.23	0.19	0.75	0.08	0.12	0.43
NITROGEN PARTICULATE	**mg/L**	0.01	1	136	0.33	0.11	3.51	0.00	0.52	0.98
NITROGEN TOTAL (Calc.)	**mg/L**	0.01	0	136	0.56	0.34	4.04	0.12	0.58	1.29
PHOSPHOROUS TOTAL DISSOLVED	**mg/L**	0.002	12	136	0.010	0.007	0.060	0.001	0.010	0.020
PHOSPHOROUS PARTICULATE (Calc.)	**mg/L**	0.002	0	136	0.161	0.047	1.359	0.004	0.257	0.463
PHOSPHOROUS TOTAL	**mg/L**	0.002	0	139	0.168	0.056	1.380	0.007	0.259	0.464
Slave River										
CARBON DISSOLVED ORGANIC	**mg/L**	0.1	0	119	6.8	5.4	40.4	1.6	5.3	11.3
CARBON PARTICULATE ORGANIC	**mg/L**	0.1	0	117	4.4	1.7	68.5	0.1	8.2	12.1
CARBON TOTAL ORGANIC (Calc)	**mg/L**	0.1	0	114	11.3	7.6	77.7	0.0	10.7	25.3
AMMONIA DISSOLVED	**mg/L**	0.005	9	81	0.029	0.016	0.205	0.001	0.038	0.067
NITROGEN DISSOLVED NO3 & NO2	**mg/L**	0.01	15	109	0.06	0.05	0.22	0.00	0.04	0.11
NITROGEN DISSOLVED INORGANIC (Calc)	**mg/L**	0.01	1	121	0.07	0.07	0.32	0.00	0.06	0.13
NITROGEN TOTAL DISSOLVED	**mg/L**	0.01	0	118	0.24	0.20	1.04	0.05	0.16	0.43
NITROGEN PARTICULATE	**mg/L**	0.01	0	116	0.44	0.16	6.67	0.01	0.83	1.10
NITROGEN TOTAL (Calc.)	**mg/L**	0.01	0	114	0.68	0.36	7.01	0.07	0.90	1.45
PHOSPHOROUS TOTAL DISSOLVED	**mg/L**	0.002	6	122	0.021	0.011	0.343	0.001	0.039	0.035
PHOSPHOROUS PARTICULATE (Calc.)	**mg/L**	0.002	0	120	0.248	0.070	4.648	0.006	0.566	0.615
PHOSPHOROUS TOTAL	**mg/L**	0.002	0	121	0.263	0.078	4.670	0.002	0.571	0.625

Metals (parameters with > 30% censored data are highlighted)

Parameter	units	Analytical Detection Limits (DL)			n	Mean	Median	Maximum	Minimum	Std. Dev.	90th Percentile
		Tot 1989-2006; Diss 1999-2006	Apr 2003-2006	% <DL							
Athabasca River											
ALUMINUM DISSOLVED	mg/L	0.02	0.0002	46	57	0.01	0.01	0.05	0.00	0.01	0.01
ALUMINUM TOTAL	mg/L	0.0002	---	0	99	1.02	0.39	7.14	0.00	1.50	2.75
ARSENIC DISSOLVED	mg/L	0.00001	---	0	141	0.0004	0.0003	0.0015	0.0001	0.0002	0.0005
BARIUM DISSOLVED	mg/L	0.00005	---	0	57	0.05	0.05	0.09	0.04	0.01	0.07
BARIUM TOTAL	mg/L	0.08	0.00005	14	138	0.07	0.06	0.20	0.03	0.03	0.11
BERYLLIUM DISSOLVED	mg/L	0.5	0.001	53	57	0.000121	0.000008	0.000250	0.000001	0.000124	0.000250
BERYLLIUM TOTAL	mg/L	0.05	0.000001	40	97	0.000074	0.000025	0.000510	0.000001	0.000096	0.000184
BORON DISSOLVED	mg/L	0.01	0.002	2	139	0.033	0.024	0.232	0.001	0.035	0.044
CADMIUM DISSOLVED	mg/L	0.001	---	44	57	0.0003	0.0002	0.0010	0.0000	0.0003	0.0005
CADMIUM TOTAL	mg/L	0.0001	0.000001	24	138	0.0002	0.0001	0.0016	0.0000	0.0002	0.0005
CHROMIUM DISSOLVED	mg/L	0.001	---	46	57	0.0003	0.0001	0.0040	0.0000	0.0005	0.0005
CHROMIUM TOTAL	mg/L	0.0002	---	3	99	0.002	0.001	0.021	0.000	0.003	0.005
COBALT DISSOLVED	mg/L	0.001	0.000002	44	57	0.0003	0.0001	0.0010	0.0000	0.0003	0.0005
COBALT TOTAL	mg/L	0.0005	0.000002	17	138	0.0010	0.0004	0.0069	0.0000	0.0013	0.0023
COPPER DISSOLVED	mg/L	0.001	0.00002	7	57	0.001	0.001	0.003	0.001	0.001	0.002
COPPER TOTAL	mg/L	0.00002	---	0	138	0.003	0.002	0.019	0.000	0.003	0.007
IRON DISSOLVED	mg/L	0.0005	---	0	57	0.11	0.11	0.28	0.01	0.07	0.19
IRON EXTRACTABLE	mg/L	0.04	---	0							
IRON TOTAL	mg/L	0.0005	---	0	97	2.2	0.9	13.9	0.0	2.8	5.7
LEAD DISSOLVED	mg/L	0.002	0.000005	39	57	0.0008	0.0003	0.0100	0.0000	0.0014	0.0010
LEAD TOTAL	mg/L	0.0007	0.0002	27	138	0.002	0.001	0.086	0.000	0.007	0.004
LITHIUM DISSOLVED	mg/L	0.0002	---	0	57	0.006	0.006	0.017	0.002	0.003	0.010
LITHIUM TOTAL	mg/L	0.0002	---	0	97	0.011	0.010	0.025	0.002	0.005	0.017
MANGANESE DISSOLVED	mg/L	0.001	0.00005	9	57	0.004	0.001	0.060	0.000	0.010	0.012
MANGANESE EXTRACTABLE	mg/L	0.002	---	0							
MANGANESE TOTAL	mg/L	0.00005	---	0	97	0.079	0.054	0.449	0.000	0.084	0.143
MERCURY TOTAL*	mg/L	0.01	0.005	50	100	0.000009	0.000005	0.000051	0.000003	0.000010	0.000020
MOLYBDENUM DISSOLVED	mg/L	0.001	0.000005	5	57	0.001	0.001	0.003	0.000	0.000	0.001
MOLYBDENUM TOTAL	mg/L	0.0001	0.000005	2	97	0.001	0.001	0.005	0.000	0.001	0.001
NICKEL DISSOLVED	mg/L	0.002		28	57	0.001	0.001	0.005	0.001	0.001	0.002
NICKEL TOTAL	mg/L	0.002	0.00002	1	138	0.004	0.002	0.027	0.000	0.004	0.007
SELENIUM DISSOLVED	mg/L	0.0001	0.00005	11	141	0.0001	0.0001	0.0005	0.0001	0.0001	0.0003
SILVER TOTAL	mg/L	0.0001	0.000001	43	54	0.00012	0.00003	0.00340	0.00000	0.00048	0.00011
STRONTIUM DISSOLVED	mg/L	0.00005	---	0	57	0.22	0.19	0.47	0.12	0.08	0.32
STRONTIUM TOTAL	mg/L	0.00005	---	0	97	0.23	0.21	0.52	0.12	0.07	0.31
VANADIUM DISSOLVED	mg/L	0.001	---	35	57	0.0005	0.0005	0.0050	0.0001	0.0006	0.0010
VANADIUM TOTAL	mg/L	0.0005	---	7	138	0.003	0.001	0.019	0.000	0.004	0.007
ZINC DISSOLVED	mg/L	0.002	0.00005	39	57	0.001	0.001	0.006	0.000	0.001	0.003
ZINC TOTAL	mg/L	0.00005	---	0	138	0.008	0.005	0.054	0.001	0.010	0.019

* Total mercury was removed from the analytical request list in 2002 as the results were found to be suspect because of inadequate field techniques; statistical summary provided for completeness but should be interpreted with caution

Metals (parameters with > 30% censored data is highlighted) (con't)

Parameter	units	Analytical Detection Limits (DL)			n	Mean	Median	Maximum	Minimum	Std. Dev.	90th Percentile
		Tot 1989-2006; Diss 1999-2006	Apr 2003-2006	% <DL							
Peace River											
ALUMINUM DISSOLVED	**mg/L**	**0.02**	**0.0002**	**42**	55	0.01	0.01	0.04	0.00	0.01	0.01
ALUMINUM TOTAL	**mg/L**	**0.0002**	**---**	**0**	101	2.64	0.55	68.70	0.00	7.23	6.77
ARSENIC DISSOLVED	**mg/L**	**0.00001**	**---**	**0**	55	0.0003	0.0003	0.0008	0.0001	0.0002	0.0005
BARIUM DISSOLVED	**mg/L**	**0.00005**	**---**	**0**	55	0.05	0.05	0.08	0.03	0.01	0.06
BARIUM TOTAL	**mg/L**	**0.08**	**0.00005**	**12**	139	0.11	0.07	0.41	0.04	0.08	0.22
BERYLLIUM DISSOLVED	**mg/L**	**0.5**	**0.001**	**53**	55	0.0000001	0.000008	0.000250	0.000001	0.000124	0.000250
BERYLLIUM TOTAL	**mg/L**	**0.05**	**0.000001**	**38**	100	0.000161	0.000025	0.002240	0.000001	0.000281	0.000475
BORON DISSOLVED	**mg/L**	**0.01**	**0.002**	**18**	131	0.016	0.009	0.172	0.001	0.025	0.024
CADMIUM DISSOLVED	**mg/L**	**0.001**	**---**	**45**	55	0.0003	0.0002	0.0005	0.0000	0.0002	0.0005
CADMIUM TOTAL	**mg/L**	**0.0001**	**0.000001**	**17**	139	0.0004	0.0001	0.0063	0.0000	0.0008	0.0013
CHROMIUM DISSOLVED	**mg/L**	**0.001**	**---**	**36**	55	0.0003	0.0001	0.0010	0.0001	0.0003	0.0005
CHROMIUM TOTAL	**mg/L**	**0.0002**	**---**	**4**	101	0.004	0.001	0.077	0.000	0.009	0.010
COBALT DISSOLVED	**mg/L**	**0.001**	**0.000002**	**35**	55	0.0003	0.0001	0.0010	0.0000	0.0003	0.0008
COBALT TOTAL	**mg/L**	**0.0005**	**0.000002**	**11**	139	0.0019	0.0006	0.0189	0.0000	0.0028	0.0056
COPPER DISSOLVED	**mg/L**	**0.001**	**0.00002**	**0**	55	0.002	0.001	0.005	0.001	0.001	0.003
COPPER TOTAL	**mg/L**	**0.00002**	**---**	**0**	139	0.006	0.003	0.056	0.001	0.008	0.016
IRON DISSOLVED	**mg/L**	**0.0005**	**---**	**0**	55	0.05	0.04	0.30	0.00	0.06	0.12
IRON EXTRACTABLE	**mg/L**	**0.04**	**---**	**0**	38	2.0	0.8	19.1	0.1	3.7	3.4
IRON TOTAL	**mg/L**	**0.0005**	**---**	**0**	100	5.0	1.1	61.7	0.0	8.6	15.3
LEAD DISSOLVED	**mg/L**	**0.002**	**0.000005**	**35**	55	0.0008	0.0003	0.0050	0.0000	0.0011	0.0020
LEAD TOTAL	**mg/L**	**0.0007**	**0.0002**	**14**	139	0.003	0.001	0.046	0.000	0.005	0.009
LITHIUM DISSOLVED	**mg/L**	**0.0002**	**---**	**0**	55	0.004	0.004	0.010	0.001	0.002	0.006
LITHIUM TOTAL	**mg/L**	**0.0002**	**---**	**0**	100	0.009	0.006	0.115	0.002	0.012	0.017
MANGANESE DISSOLVED	**mg/L**	**0.001**	**0.00005**	**20**	55	0.001	0.001	0.015	0.000	0.002	0.002
MANGANESE EXTRACTABLE	**mg/L**	**0.002**	**---**	**0**	39	0.066	0.032	0.587	0.000	0.113	0.157
MANGANESE TOTAL	**mg/L**	**0.00005**	**---**	**0**	100	0.092	0.034	0.679	0.000	0.125	0.307
MERCURY TOTAL*	**mg/L**	**0.01**	**0.005**	**56**	102	0.000011	0.000005	0.000130	0.000000	0.000020	0.000021
MOLYBDENUM DISSOLVED	**mg/L**	**0.001**	**0.000005**	**7**	55	0.001	0.001	0.002	0.001	0.000	0.002
MOLYBDENUM TOTAL	**mg/L**	**0.0001**	**0.000005**	**3**	100	0.001	0.001	0.005	0.000	0.000	0.001
NICKEL DISSOLVED	**mg/L**	**0.002**	**---**	**25**	55	0.002	0.001	0.055	0.000	0.007	0.002
NICKEL TOTAL	**mg/L**	**0.002**	**0.00002**	**1**	139	0.007	0.003	0.064	0.000	0.009	0.017
SELENIUM DISSOLVED	**mg/L**	**0.0001**	**0.00005**	**2**	131	0.0003	0.0003	0.0008	0.0001	0.0001	0.0004
SILVER TOTAL	**mg/L**	**0.0001**	**0.000001**	**47**	58	0.00012	0.00005	0.00390	0.00000	0.00051	0.00011
STRONTIUM DISSOLVED	**mg/L**	**0.00005**	**---**	**0**	55	0.15	0.13	0.35	0.11	0.04	0.17
STRONTIUM TOTAL	**mg/L**	**0.00005**	**---**	**0**	100	0.16	0.14	0.35	0.12	0.04	0.19
VANADIUM DISSOLVED	**mg/L**	**0.001**	**---**	**35**	55	0.0004	0.0004	0.0010	0.0002	0.0002	0.0008
VANADIUM TOTAL	**mg/L**	**0.0005**	**---**	**10**	139	0.007	0.001	0.201	0.000	0.018	0.016
ZINC DISSOLVED	**mg/L**	**0.002**	**0.00005**	**33**	55	0.003	0.001	0.047	0.000	0.008	0.004
ZINC TOTAL	**mg/L**	**0.00005**	**---**	**0**	139	0.022	0.007	0.279	0.000	0.036	0.059

* Total mercury was removed from the analytical request list in 2002 as the results were found to be suspect because of inadequate field techniques; statistical summary provided for completeness but should be interpreted with caution

Metals (parameters with > 30% censored data is highlighted) (con't)

Parameter	units	Analytical Detection Limits (DL)			n	Mean	Median	Maximum	Minimum	Std. Dev.	90th Percentile
		Tot 1989-2006; Diss 1999-2006	Apr 2003-2006	% <DL							
Slave River											
ALUMINUM DISSOLVED	**mg/L**	**0.02**	**0.0002**								
ALUMINUM TOTAL	**mg/L**	**0.0002**	**---**	**0**	75	3.18	1.33	48.70	0.08	6.52	6.85
ARSENIC DISSOLVED	**mg/L**	**0.00001**	**---**	**0**	108	0.0006	0.0003	0.0170	0.0001	0.0018	0.0007
BARIUM DISSOLVED	**mg/L**	**0.00005**	**---**								
BARIUM TOTAL	**mg/L**	**0.08**	**0.00005**	**20**	117	0.13	0.07	1.73	0.02	0.19	0.27
BERYLLIUM DISSOLVED	**mg/L**	**0.5**	**0.001**								
BERYLLIUM TOTAL	**mg/L**	**0.05**	**0.000001**	**28**	76	0.000182	0.000043	0.002190	0.000000	0.000365	0.000500
BORON DISSOLVED	**mg/L**	**0.01**	**0.002**	**0**	22	2.356	0.015	18.700	0.003	5.335	10.280
CADMIUM DISSOLVED	**mg/L**	**0.001**	**---**								
CADMIUM TOTAL	**mg/L**	**0.0001**	**0.000001**	**25**	118	0.0008	0.0002	0.0150	0.0000	0.0019	0.0017
CHROMIUM DISSOLVED	**mg/L**	**0.001**	**---**								
CHROMIUM TOTAL	**mg/L**	**0.0002**	**---**	**5**	76	0.005	0.002	0.050	0.000	0.008	0.012
COBALT DISSOLVED	**mg/L**	**0.001**	**0.000002**								
COBALT TOTAL	**mg/L**	**0.0005**	**0.000002**	**13**	116	0.0024	0.0011	0.0303	0.0001	0.0042	0.0063
COPPER DISSOLVED	**mg/L**	**0.001**	**0.00002**								
COPPER TOTAL	**mg/L**	**0.00002**	**---**	**0**	118	0.008	0.004	0.097	0.000	0.013	0.018
IRON DISSOLVED	**mg/L**	**0.0005**	**---**								
IRON EXTRACTABLE	**mg/L**	**0.04**	**---**	**0**	97	3.3	1.5	35.0	0.1	5.9	9.1
IRON TOTAL	**mg/L**	**0.0005**	**---**	**0**	76	8.2	2.8	128.0	0.2	18.3	16.1
LEAD DISSOLVED	**mg/L**	**0.002**	**0.000005**								
LEAD TOTAL	**mg/L**	**0.0007**	**0.0002**	**17**	118	0.004	0.002	0.051	0.000	0.007	0.010
LITHIUM DISSOLVED	**mg/L**	**0.0002**	**---**								
LITHIUM TOTAL	**mg/L**	**0.0002**	**---**	**0**	76	0.010	0.007	0.057	0.001	0.011	0.017
MANGANESE DISSOLVED	**mg/L**	**0.001**	**0.00005**								
MANGANESE EXTRACTABLE	**mg/L**	**0.002**	**---**	**0**	96	0.111	0.048	1.080	0.005	0.193	0.277
MANGANESE TOTAL	**mg/L**	**0.00005**	**---**	**0**	76	0.145	0.060	1.980	0.007	0.278	0.356
MERCURY TOTAL*	**mg/L**	**0.01**	**0.005**								
MOLYBDENUM DISSOLVED	**mg/L**	**0.001**	**0.000005**	**1**	76	0.001	0.001	0.003	0.000	0.000	0.001
MOLYBDENUM TOTAL	**mg/L**	**0.0001**	**0.000005**								
NICKEL DISSOLVED	**mg/L**	**0.002**	**---**								
NICKEL TOTAL	**mg/L**	**0.002**	**0.00002**	**1**	118	0.008	0.004	0.093	0.000	0.013	0.019
SELENIUM DISSOLVED	**mg/L**	**0.0001**	**0.00005**		103	0.0003	0.0002	0.0040	0.0001	0.0004	0.0004
SILVER TOTAL	**mg/L**	**0.0001**	**0.000001**	**43**	58	0.00689	0.00005	0.29000	0.00000	0.03866	0.00215
STRONTIUM DISSOLVED	**mg/L**	**0.00005**	**---**								
STRONTIUM TOTAL	**mg/L**	**0.00005**	**---**	**0**	76	0.14	0.14	0.29	0.04	0.03	0.17
VANADIUM DISSOLVED	**mg/L**	**0.001**	**---**								
VANADIUM TOTAL	**mg/L**	**0.0005**	**---**	**9**	116	0.007	0.003	0.085	0.000	0.012	0.018
ZINC DISSOLVED	**mg/L**	**0.002**	**0.00005**								
ZINC TOTAL	**mg/L**	**0.00005**	**---**	**0**	118	0.029	0.011	0.561	0.001	0.063	0.064

* Total mercury was removed from the analytical request list in 2002 as the results were found to be suspect because of inadequate field techniques; statistical summary provided for completeness but should be interpreted with caution

***Appendix 3**: Detailed statistical results for seasonality and temporal trend analyses*

Seasonality Statistical Results

Parameter	*Athabasca River at 27 Baseline*			*Peace River at Peace Point*			*Slave River at Fitzgerald*		
	KW critical = 5.991								
	KW Calc.	***p<0.05**	**Peak Season**	**KW Calc.**	***p<0.05**	**Peak Season**	**KW Calc.**	***p<0.05**	**Peak Season**
Physical Parameters									
Specific Conductance (L) (usie/cm)	94.07	*	W	12.41	*	S/F	6.60	ns	none
pH-L (pH units)	7.32	ns	none	2.17	ns	none	5.62	ns	none
Residue NF (mg/L)	115.80	*	S	66.10	*	S	21.75	*	S
Turbidity-L (NTU)	116.70	*	S	63.49	*	S	44.31	*	S
Colour-T (Rel Unit)	40.70	*	S	65.71	*	S	47.87	*	S
Oxygen Dissolved (mg/L)	35.02	*	W	42.31	*	W	53.34	*	W
Major Ions									
Total Dissolved Solids (mg/L) Calc.	94.89	*	W	15.11	*	S/F	9.55	*	S
Alkalinity-T (mg/L)	100.24	*	W	6.78	*	S/F	4.38	ns	none
Bicarbonate (mg/L)	96.75	*	W	8.55	*	S/F			
Calcium (mg/L)	98.02	*	W	10.77	*	S/F	10.55	*	S
Chloride (mg/L)	97.23	*	W	9.59	*	W	22.53	*	F/W
Fluoride (mg/L)	64.92	*	W	37.44	*	S	16.67	*	S
Hardness Total (mg/L) Calc.	95.76	*	W	17.25	*	S/F	1.60	ns	none
Magnesium (mg/L)	98.92	*	W	20.63	*	S/F	5.50	ns	none
Potassium (mg/L)	64.71	*	W	48.55	*	S	41.70	*	S
Silica (mg/L)	91.80	*	W	30.56	*	W			
Sodium (mg/L)	92.72	*	W	34.94	*	S	7.97	*	F
Sulphate (mg/L)	75.49	*	W	26.76	*	S	22.94	*	S
Nutrients									
Carbon Dissolved Organic (mg/L)	20.10	*	S	76.52	*	S	51.92	*	S
Carbon Particulate Organic (mg/L)	113.40	*	S	64.14	*	S	34.00	*	S
Carbon Total Organic (mg/L) Calc.	53.60	*	S	74.76	*	S	39.42	*	S
Ammonia-D (mg/L)	80.20	*	W	10.61	*	S	2.53	ns	none
Nitrogen Dissolved (mg/L)	27.40	*	W	23.36	*	S	6.29	*	S/W
Nitrogen NO23 (mg/L)	101.90	*	W	76.23	*	S/W	44.62	*	S/W
Nitrogen Diss Inorganic (mg/L) Calc.*	100.20	*	W	56.27	*	S/W	32.66	*	S/W
Nitrogen Particulate (mg/L)	115.50	*	S	66.08	*	S	39.25	*	S
Nitrogen Total (mg/L) Calc.	30.50	*	S	49.18	*	S	24.67	*	S
Phosphorous Dissolved (mg/L)	18.50	*	W	26.61	*	S	23.23	*	S
Phosphorous Particulate (mg/L) Calc.	93.20	*	S	60.41	*	S	46.94	*	S
Phosphorous Total (mg/L)	85.40	*	S	61.62	*	S	46.79	*	S

S = significant seasonality ($p<0.05$) with high concentrations during spring-summer
W = significant seasonality ($p<0.05$) with high concentrations during winter
S/W = significant seasonality ($p<0.05$) with high concentrations during spring-summer/winter
F/W = significant seasonality ($p<0.05$) with high concentrations during fall/winter
none = no significant seasonality ($p>0.05$)

Temporal Trend Statistical Results

Parameter	**Athabasca River at 27 Baseline**				**Athabasca River at 27 Baseline**			
	Z Critical = 1.960				**Z Critical = 1.960**			
	n	**Z Calc**	*** p<0.05**	**Slope units/yr**	**n**	**Z Calc**	*** p<0.05**	**Slope units/yr**
	Period of Record				**Last Decade**			
Physical Parameters								
Colour-T (RelUnit)	133	-1.710	ns		64	-2.740	*	-1.4400
Oxygen Dissolved (mg/L) 89-03	105	1.962	*	0.0500				
pH-L (pHunits)	126	4.260	*	0.0140	59	3.250	*	0.0220
Residue NF (mg/L)	146	-0.680	ns		77	-1.630	ns	
Specific Conductance (L) (usie/cm)	123	0.726	ns		56	0.510	ns	
Turbidity-L (NTU)	148	-1.210	ns		79	-2.260	*	-0.3200
Major Ions								
Alkalinity-T (mg/L)	138	-0.330	ns		71	0.520	ns	
Bicarbonate (mg/L)	134	-0.470	ns		68	0.540	ns	
Calcium (mg/L)	139	0.210	ns		72	-0.040	ns	
Chloride (mg/L)	139	0.960	ns		72	1.698	ns	
Fluoride (mg/L)	136	2.290	*	0.0010	72	3.204	*	0.0020
Hardness Total (mg/L) Calc.	135	0.017	ns		69	0.121	ns	
Magnesium (mg/L)	139	-0.210	ns		72	-0.040	ns	
Potassium (mg/L)	139	3.512	*	0.0140	72	0.040	ns	
Silica (mg/L)	138	0.200	ns		72	0.890	ns	
Sodium (mg/L)	138	1.490	ns		71	1.950	ns	
Sulphate (mg/L)	138	2.922	*	0.2520	71	0.406	ns	
Total Dissolved Solids (mg/L) Calc.	133	1.590	ns		67	1.110	ns	
Nutrients								
Carbon Dissolved Organic (mg/L)	147	-0.100	ns		78	-0.700	ns	
Carbon Particulate Organic (mg/L)	145	0.170	ns		77	-1.060	ns	
Carbon Total Organic (mg/L) Calc.	144	-0.310	ns		76	-0.960	ns	
Ammonia-D (mg/L)	138	2.120	*	0.0006	71	-3.470	*	-0.0020
Nitrogen NO23 (mg/L)	145	2.012	*	0.0015	76	-0.420	ns	
Nitrogen Diss Inorganic (mg/L) Calc.*	144	2.940	*	0.0010	76	-1.060	ns	
Nitrogen Dissolved Oct 93 - 2006	106	-0.920	ns		78	-0.940	ns	
Nitrogen Particulate (mg/L)	146	1.178	ns		78	-0.780	ns	
Nitrogen Total Oct 93 - 2006	104	1.048	ns		77	-1.400	ns	
Phosphorous Dissolved (mg/L)	145	2.017	*	0.0002	76	-0.820	ns	
Phosphorous Particulate (mg/L) Calc.	146	1.480	ns		77	1.210	ns	
Phosphorous Total (mg/L)	146	2.130	*	0.0005	77	1.060	ns	

ns = not significant at p>0.05; slopes not reported

Temporal Trend Statistical Results (con't)

	Peace River at Peace Point					Peace River at Peace Point			
	Z Critical = 1.960					Z Critical = 1.960			
Parameter	**n**	**Z Calc**	*** p<0.05**	**Slope units/yr**		**n**	**Z Calc**	*** p<0.05**	**Slope units/yr**
	Period of Record					**Last Decade**			
Physical Parameters									
Colour-T (RelUnit)	121	-1.160	ns			57	-0.320	ns	
Oxygen Dissolved (mg/L) 89-03	93	1.965	*	0.0730		35	-1.750	ns	
pH-L (pHunits)	121	4.770	*	0.0140		57	4.010	*	0.0250
Residue NF (mg/L)	135	0.510	ns			71	-1.480	ns	
Specific Conductance (L) (usie/cm)	123	-1.460	ns			59	0.270	ns	
Turbidity-L (NTU)	136	-0.610	ns			72	-1.400	ns	
Major Ions									
Alkalinity-T (mg/L)	133	0.910	ns			69	1.360	ns	
Bicarbonate (mg/L)	129	0.890	ns			65	1.520	ns	
Calcium (mg/L)	133	1.400	ns			69	1.580	ns	
Chloride (mg/L)	133	-5.370	*	-0.0520		69	-3.880	*	-0.0820
Fluoride (mg/L)	132	-0.780	ns			69	0.630	ns	
Hardness Total (mg/L) Calc.	129	1.420	ns			65	0.990	ns	
Magnesium (mg/L)	133	0.770	ns			69	0.660	ns	
Potassium (mg/L)	132	0.540	ns			69	-0.820	ns	
Silica (mg/L)	102	2.370	*	0.0310		38	-0.420	ns	
Sodium (mg/L)	133	-2.220	*	-0.0300		69	-1.520	ns	
Sulphate (mg/L)	133	3.960	*	0.3000		69	1.490	ns	
Total Dissolved Solids (mg/L) Calc.	130	1.830	ns			62	0.490	ns	
Nutrients									
Carbon Dissolved Organic (mg/L)	134	-3.990	*	-0.0690		70	-1.390	ns	
Carbon Particulate Organic (mg/L)	133	0.940	ns			70	-0.540	ns	
Carbon Total Organic (mg/L) Calc.	133	-1.640	ns			70	-0.590	ns	
Ammonia-D (mg/L)	134	1.854	ns			70	1.820	ns	
Nitrogen NO23 (mg/L)	133	2.640	*	0.0006		69	-0.820	ns	
Nitrogen Diss Inorganic (mg/L) Calc.*	136	2.817	*	0.0010		71	0.530	ns	
Nitrogen Dissolved Oct 93 - 2006	97	0.190	ns			70	-1.310	ns	
Nitrogen Particulate (mg/L)	133	0.630	ns			70	-0.330	ns	
Nitrogen Total Oct 93 - 2006	96	0.520	ns			70	-0.810	ns	
Phosphorous Dissolved (mg/L)	133	-1.020	ns			69	-1.580	ns	
Phosphorous Particulate (mg/L) Calc.	133	0.434	ns			69	-0.790	ns	
Phosphorous Total (mg/L)	136	0.790	ns			70	-1.000	ns	

ns = not significant at p>0.05; slopes not reported

Temporal Trend Statistical Results (con't)

	Slave River at Fitzgerald				**Slave River at Fitzgerald**			
	Z Critical = 1.960				**Z Critical = 1.960**			
Parameter	**n**	**Z Calc**	*** p<0.05**	**Slope units/yr**	**n**	**Z Calc**	*** p<0.05**	**Slope units/yr**
	Period of Record				**Last Decade**			
Physical Parameters								
Colour-T (RelUnit)	121	2.120	*	0.2780	53	0.46	ns	
Oxygen Dissolved (mg/L) 89-03	103	2.920	*	0.0720	39	2.72	*	0.2400
pH-L (pHunits)	114	2.750	*	0.0099	45	-0.67	ns	
Residue NF (mg/L)	41	-2.370	*	-9.2000				
Specific Conductance (L) (usie/cm)	112	-1.930	ns		45	-2.21	*	-3.6700
Turbidity-L (NTU)	119	0.640	ns		55	-0.22	ns	
Major Ions								
Alkalinity-T (mg/L)	117	0.520	ns		52	-0.98	ns	
Bicarbonate (mg/L)								
Calcium (mg/L)	123	0.390	ns		54	-0.62	ns	
Chloride (mg/L)	119	-2.000	*	-0.0400	54	-0.36	ns	
Fluoride (mg/L)	119	-0.110	ns		54	1.00	ns	
Hardness Total (mg/L) Calc.								
Magnesium (mg/L)	123	0.000	ns		54	-1.14	ns	
Potassium (mg/L)	123	0.190	ns		54	-0.34	ns	
Silica (mg/L)								
Sodium (mg/L)	123	-0.750	ns		54	-0.70	ns	
Sulphate (mg/L)	119	2.700	*	0.1880	54	-1.59	ns	
Total Dissolved Solids (mg/L) Calc.	119	1.856	ns		51	-2.35	*	-2.2700
Nutrients								
Carbon Dissolved Organic (mg/L)	118	-0.730	ns		55	-0.43	ns	
Carbon Particulate Organic (mg/L)	116	2.340	*	0.0360	53	0.01	ns	
Carbon Total Organic (mg/L) Calc.	112	0.570	ns		53	-0.17	ns	
Ammonia-D (mg/L)	80	-0.070	ns		55	-0.52	ns	
Nitrogen NO23 (mg/L)	108	0.640	ns		43	-1.45	ns	
Nitrogen Diss Inorganic (mg/L) Calc.*	120	0.598	ns		55	-3.35	*	-0.0070
Nitrogen Dissolved Aug 93 - Sep 02	73	-2.400	*	-0.0110	52	-2.13	*	-0.0150
Nitrogen Particulate (mg/L)	115	1.650	ns		52	-0.51	ns	
Nitrogen Total Aug 93 - Sep 02	71	-2.190	*	-0.0160	52	-2.19	*	-0.0330
Phosphorous Dissolved (mg/L)	121	3.240	*	0.0004	53	-1.55	ns	
Phosphorous Particulate (mg/L) Calc.	119	1.710	ns		51	-0.18	ns	
Phosphorous Total (mg/L)	120	2.680	*	0.0016	52	-0.099	ns	

ns = not significant at p>0.05; slopes not reported

Seasonality and Trend Results for Limited Metals Analysis

Parameter	***Athabasca River at 27 Baseline***			***Peace River at Peace Point***		
	KW critical = 5.991					
	KW Calc.	***p<0.05**	**Peak Season**	**KW Calc.**	***p<0.05**	**Peak Season**
Metals						
ARSENIC DISSOLVED (mg/L)	24.3	*	S	15.2		S
COPPER DISSOLVED (mg/L)	12.1	*	S	13.2		S
COPPER TOTAL (mg/L)	55.9	*	S	16.3		S
IRON DISSOLVED (mg/L)	6.0	*	W	21.4		S
IRON TOTAL (mg/L)	50.3	*	S	15.2		S
LEAD TOTAL (mg/L)	67.4	*	S	15.7		S
NICKEL TOTAL (mg/L)	58.6	*	S	17.2		S
VANADIUM TOTAL (mg/L)	71.1	*	S	15.6		S
ZINC TOTAL (mg/L)	52.3	*	S	10.9		S

S = significant seasonality (p<0.05) with highest concentrations during spring-summer

W = significant seasonality (p<0.05) with highest concentrations during winter

Parameter	**Valid Period of Record**	***Athabasca River at 27 Baseline***				***Athabasca River at 27 Baseline***				***Peace River at Peace Pt***			
		Z Critical = 1.960				**Z Critical = 1.960**				**Z Critical = 1.960**			
		n	**Z Calc**	*** p<0.05**	**Slope units/yr**	**n**	**Z Calc**	*** p<0.05**	**Slope units/yr**	**n**	**Z Calc**	*** p<0.05**	**Slope units/yr**
			Period of Record			**Flow Weighted**				**Period of Record**			
METALS													
ARSENIC DISSOLVED (mg/L)	89-2002	106	-1.81	ns	---	106	-0.79	ns	---				
COPPER DISSOLVED (mg/L)	99-2006	57	-1.20	ns	---	57	-1.07	ns	---	55	-1.17	*	0.000017
COPPER TOTAL (mg/L)	89-2006	136	-2.24	*	0.000023	136	-1.07	ns	---	139	-0.09	ns	---
IRON DISSOLVED (mg/L)	99-2006	57	0.42	ns	---	57	0.06	ns	---	55	-2.10	*	0.002
IRON TOTAL (mg/L)	93-2006	96	-2.52	*	-0.023	96	-1.02	ns	---	100	-1.29	ns	---
LEAD TOTAL (mg/L)	89-2006	134	-4.36	*	-0.0002	134	-2.98	*	-0.000024	139	-2.11	*	-0.00002
NICKEL TOTAL (mg/L)	89-2006	136	-3.31	*	-0.000043	136	-1.87	ns	---	139	-0.84	ns	---
VANADIUM TOTAL (mg/L)	89-2006	136	-1.02	ns	---	136	1.87	ns	---	138	1.83	*	-0.000022
ZINC TOTAL (mg/L)	89-2006	136	-2.23	*	-0.0007	136	-0.07	ns	---	138	-0.39	ns	---

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