An Assessment of Seasonal Source Water Contributions to Streamflow in the Athabasca River Basin, Utilizing a Novel Approach to Obtain a Record of Winter Streamflow From River Ice Stratigraphy

By

Jasmine Taulu

B.Sc. Nipissing University, 2016

A Thesis Submitted in Partial Fulfillment
Of the Requirements for the Degree of

MASTER OF SCIENCE

In the Department of Geography

University of Victoria

We acknowledge and respect the lək̓ʷəŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.

An Assessment of Seasonal Source Water Contributions to Streamflow in the Athabasca River Basin, Utilizing a Novel Approach to Obtain a Record of Winter Streamflow From River Ice Stratigraphy

By

Jasmine Taulu

B.Sc. Nipissing University, 2016

Supervisory Committee

Dr. David Atkinson, Supervisor
Department of Geography

Dr. John Gibson, Outside Member
Innotech Alberta

Abstract

The objective of this thesis is to quantify seasonal source water contributions to the Athabasca River in Alberta Canada. A secondary objective was to evaluate a novel method for reconstructing the isotopic composition of streamflow over the ice-on period and utilize this data to quantify source water contributions to winter streamflow. Quantifying source water contributions to streamflow is important because the Athabasca is a large, snow-dominated catchment where climate change is expected to impact the quantity and timing of source waters. The water resources in the Athabasca River Basin (ARB) are essential in supporting communities, the economy and ecosystems in the province of Alberta. This includes water needs of municipalities, oil sands operations and sensitive ecosystems, such as the Peace Athabasca Delta, an internationally recognized protected area. While the lower reaches of the Athabasca has been the subject of many studies, stable water isotope analysis has been limited in the upper portion of the ARB leaving a knowledge gap around existing snow and glacial melt water resources. This research focuses on the Upper and Middle reaches of the Athabasca and includes a subset of data for the McLeod catchment, which is nestled in the Middle Athabasca. To assess source water contributions three synoptic studies were undertaken to collect stable water isotope samples over a hydrological year from August 2016 to August 2017. This dataset was supplemented by winter streamflow data calculated using a novel method that reconstructs the isotopic composition of winter streamflow using river ice stratigraphy. The reconstruction of streamflow in the ARB produced accurate results as validated against streamflow sampling obtained over the same time period. This method also resulted ice-water fractionation values that were in alignment with the existing literature. While these results support the future use of this emerging methodology, additional studies will be required to better define the limitations to this methodology. Source water contributions to streamflow were calculated for all field samples and reconstructed values using hydrograph separation. This allowed the relative contributions of snowmelt, glacial melt, groundwater and evaporatively enriched surface waters, such as from lakes and wetlands, to be quantified. The results from this analysis have established a spatially explicit, baseline understanding of the major contributions of seasonal and annual source waters in the region. Observed patterns included an accumulation of surface water downstream in the ARB and annual source water cycling in the McLeod catchment, that aligned with results found in other studies in the Mackenzie River Basin. Trends differed in 2016 and 2017 but were linked to differences in temperature and precipitation over the two years. While this research has established baseline source water information across the Upper and Middle Athabasca, future studies to conduct a higher temporal and spatial resolution sampling of streamflow and source waters across the catchment are recommended.

Table of Contents

List of Tables

List of Figures

Acknowledgments

I would like to express my deepest appreciation to those who acted on my supervisory committee over the duration of my Masters degree; my supervisor Dr. David Atkinson, for taking me on as a student in the middle of my degree and supporting me to cross the finish line; my original co-supervisors Dr. Terry Prowse and Dr. Thomas Edwards, for their inspiration and assistance in planning, conducting and the early analysis of my field work; and my committee member Dr. John Gibson, for his continued support throughout my degree.

I'm extremely grateful to those who aided in the collection and processing of isotope samples; including field assistants Brandi Newton, Dave Barrett, Maddy Barrett and Hayley O'Neil; the University of Calgary, for processing the isotope samples that were collected from ice cores; and the Town of Whitecourt and Aspen Regional Water Services Commission, for their assistance in collecting a time-series of winter streamflow which was integral to this research.

I would also like to acknowledge that this research would not have been possible without funding from the University of Victoria and Environment and Climate Change Canada's Water & Climate Impacts Research Centre.

Most importantly, I would like to extend my sincere thanks to my support network of friends and family whose nudges forward allowed me to persevere in this endeavor; my partner Kevin Wilcox, for his unwavering patience and kindness; my dear friends Emily Barner and Lindi Anderson for helping me become excited to write once again; and to Dr. Shannon Fargey for her guidance and generous offers for additional support.

Chapter 1. Introduction

1.1 Introduction

This Chapter describes the research problem followed by an outline of the research objectives and thesis structure. Key background information and an overview of the study area provide context for why the research objectives are important. This thesis uses stable water isotopes (SWI) as a method to label source waters with the aim of quantifying the proportion of each source water in streamflow seasonally. A detailed novel analysis was undertaken over the winter months to capture the record of winter streamflow from ice cores. The Upper and Middle Athabasca River Basin was selected as the study area for this work as the snowmelt-dominated basin is sensitive to climate change, which could negatively impact key economic and environmental systems under future climate change scenarios, posing a challenge for water management. To date, there has been limited research using this methodology in the Upper or Middle Athabasca River Basin. This has resulted in a gap in our collective understanding of the seasonal impact of source waters on streamflow in the basin, requiring baseline conditions to be better understood.

1.2 Background

1.2.1 Snow-dominated catchments

Snow and glacial melt are essential water resources in the northern hemisphere and mountainous regions globally; however, due to the warming climate these resources are becoming reduced and the timing of snow and glacial melt entering streamflow is shifting. Water from snowmelt-dominated catchments directly supports 1/6th of the world's population (Center for International Earth Science Information Network [CIESIN], 2004), with many people outside of these catchments susceptible to the indirect effects of reduced water resources (Barnett *et al.,* 2005) as mountain areas contribute 32% of global discharge (Meybeck *et al.,* 2001). The Intergovernmental Panel on Climate Change (IPCC) has high confidence that global glacier extent is declining and that snowmelt is occurring sooner, affecting the seasonality of streamflow in snowmelt-dominated catchments and ultimately, the quantity of water available (IPCC, 2022). Warming trends are more pronounced in cold regions of the northern hemisphere, with the greatest warming occurring in winter months (Aygün *et al.,* 2020). While elevational warming trends are not still completely understood, warming typically occurs faster at higher elevations, creating further impacts on mountainous regions (Pepin *et al.*, 2022, Rangwala *et al.,* 2015). Between 1967 and 2012, snowmelt in the northern hemisphere decreased by 1.6 % per decade in March and April and 11.7% per decade in June, and the largest reduction of snowpack is now occurring a month sooner than in previous decades (IPCC, 2015). Climate models are projecting the ratio of rainfall to total precipitation will increase in the northern hemisphere, reducing the snowpack further (Aygün *et al.,* 2020, IPCC, 2022).

1.2.2 Water management

Climate change impacts on water resources are varied and of significant concern when assessing water management strategies. The most recent IPCC (2022) indicated high confidence that there would be reduced water resources in snowmelt-dominated catchments and that these events would have negative effects on human systems and ecosystems. This can be linked to the occurrence of earlier peak runoff caused by climate change, which is often too large to be captured and stored by reservoirs, leading to reduced availability of water resources later in the dry season (Barnett *et al.,* 2005). Climate change scenarios also predict larger, more frequent forest fires and hydro-climatic extremes, such as floods and droughts; this is expected to lead to anthropogenic changes in behavior, such as increased energy demands during extreme high and low temperatures (Eum *et al.,* 2017; IPCC 2022; Prowse *et al.,* 2006; Voutchkova & Miller, 2017). In snowmelt-dominated regions, baseline and modeled future conditions for annual snow and glacial melt are needed by water resource managers to determine strategies for water use and storage, including balancing allocations for anthropogenic uses (such as domestic use, industry, agriculture, tourism, recreation and hydropower) and water requirements for ecological processes (Prowse *et al.,* 2009; Voutchkova & Miller, 2017).

1.3 Study area

1.3.1 the Athabasca River Basin

The Athabasca River Basin is a large snowmelt-dominated basin, that provides key economic and environmental benefits. The Athabasca River Basin is the largest unregulated river in Alberta and the ARB covers approximately 24% of the province (Athabasca River Basin Research Institute, 2022). The headwaters for the Athabasca River are located in the Columbia Icefield, on the Eastern slopes of the Canadian Rocky Mountains. From the headwaters, the Athabasca River flows 1500km northeast, eventually draining into the Arctic Ocean. The ARB itself is home to approximately 170,000 residents who live in largely rural areas; the region has fourteen Indigenous reserves, one city, twelve towns and twenty-two municipalities (Athabasca River Basin Research Institute, 2022).

The Athabasca watershed is divided into three segments: the Upper, Middle and Lower Athabasca. The Upper Athabasca has mountainous terrain which is largely protected, being situated mostly within the boundaries of Jasper National Park. The Middle Athabasca begins at the forested foothills of the eastern Canadian Rocky Mountains before flowing through urban and agricultural areas. This section of the Athabasca has three main tributaries: the McLeod, Pembina and Lesser Slave Rivers. The Lower Athabasca begins at the City of Fort McMurray and contains what is referred to as the Canadian oil sands. The Athabasca River terminates at Lake Athabasca before draining into the Peace Athabasca Delta (PAD). The PAD is located within Wood Buffalo National Park, an area recognized for its global significance and designated a World Heritage Site by the United Nations Educational, Scientific and Cultural Organization. This recognition is due to the unique characteristics of the PAD: it is a large inland freshwater delta, with salt plains, many migratory bird species and free-roaming wood bison (UNESCO World Heritage Centre, 2022).

The Athabasca River is vital to economic and domestic activities in the region, including agriculture, forestry and recreation, tourism, electrical power generation and oil sands operations (Cheng *et al.,* 2017; Eum *et al.,* 2017; Prowse *et al.,* 2009; Rood *et al.,* 2015). Approximately 5% of the annual flow from the Athabasca River is allocated to water resource users, the largest of these being the oil sands operations, which received over 2% of the annual flow from the Athabasca River in 2016 (Government of Alberta, 2017). The Canadian oil sands are the third-largest crude oil reserve globally, an integral source of revenue for the province of Alberta that generates approximately 11% of Canada's greenhouse gas emissions (Canadian Association of Petroleum Producers, 2022). Water allocations for the Athabasca River have grown nine times faster than the provincial average, seeing 88% growth in an 11-year period, largely linked to oil sands operations (Environment Alberta as cited in Wolfe *et al.,* 2011). Furthermore, the oil sands water usage is expected to increase alongside increases in water usage for livestock, agriculture, commercial, municipal and habitat enhancement projects (AMEC Earth & Environmental, 2007).

1.3.2 Athabasca River Basin climate

The climate in the ARB is largely categorized as humid continental or subarctic, following the Koppen classification, with Tundra conditions over the glaciated areas of the catchment. Over the past 100 years, the temperature over the ARB has generally increased, with the greatest warming occurring downstream and during the winter months (Cheng *et al.,* 2017). The mean precipitation in the watershed is 460 mm, which has generally declined between 1958 and 2009 (Peters *et al.*, 2013). Approximately 70% of precipitation falls as rain and the precipitation maximum occurs in the summer, although water volume is net negative due to high evaporation at this time (Bawden *et al.,* 2014; Canada, 2016).

Streamflow in the ARB peaks in June or July, following peak snowmelt in late April or May and low flow conditions occur in December (Burn *et al.,* 2004). Historically, there has been a decreasing trend in mean streamflow (Bawden *et al.,* 2014; Burn *et al.,* 2004; Peters *et al.,* 2013; Schindler & Donahue, 2006; Zhang *et al.,* 2001). This has been linked to reductions in precipitation (Peters *et al.,* 2013) and reductions in snow accumulation in elevations below 2500m, which have been found to be vulnerable to loss of snowpack (Newton *et al.,* 2019). This has led to measurable changes in local flow patterns, with discharge into Lake Athabasca being reduced by 21% between 1960 and 2010 (Rasouli *et al.,* 2013). In addition, ice cover formation has also shifted from late October, now occurring in early November, with breakup typically occurring at the end of March or early April (Pietroniro *et al.,* 1998; Hutchison and Hicks, 2007; Prowse *et al.,* 2007; She *et al.,* 2009).

The projected climate changes in ARB are expected to result in changes to the hydrology of the basin. Temperature is projected to increase significantly in the ARB, resulting in warm, drought-like summers (Bonsal & Cuell., 2017; Cheng *et al.,* 2017; Lima & Wrona, 2019; Zhou *et al.,* 2018). Warming winter temperatures are expected to shift a portion of precipitation, which currently falls as snowfall, to rainfall; this would lead to an increase in snowmelt and snow ablation over the entire watershed, with the reductions being most pronounced in the high elevations of the Upper Athabasca (Dibike *et al.,* 2018b). This is projected to decrease snow cover duration by up to 50 days and reduce water storage held in the headwaters as snow (Dibike *et al.,* 2018b). Future streamflow is projected to increase by approximately 25% in the winter, resulting in an earlier, larger freshet, with decreases in the late spring and summer flows of approximately 50% (Eum *et al.,* 2017, Dibike *et al.,* 2018, Leong and Donner, 2015).

1.3.3 Athabasca River Basin water management

Climate change poses a serious threat to the stability of water resources in the ARB and increased industrialization coupled with population growth will only further pressure the system, threatening to reduce the water needed for ecosystem services. The ARB is predicted to experience more frequent hydro-climatic extremes due to climate change, such as flooding, drought and wildfires, while energy and water consumption are both expected to increase (Prowse *et al.*, 2006; Cheng *et al.,* 2017). Cumulative impacts from increasing water withdrawals for municipal and industrial use as well as municipal sewage discharge have already been raised as a concern (Lima & Wrona, 2019; Noble *et al.,* 2014). Proper water management is necessary to ensure the social, economic and environmental needs of the ARB can all be met.

Drought is of particular concern for the ARB, as snow accumulation and melt maintain summer streamflow, sustaining industrial activities and aquatic habitats (CEMA, 2006). Long-term droughts, lasting greater than six months, could impact the viability of the oil and gas industry and negatively impact aquatic ecosystems (Cheng *et al.,* 2017; Dibike *et al.,* 2018; Lima & Wrona, 2019). In assessing the future water management options for the ARB, Leong & Donner (2016) found that due to an increased frequency of drought, additional water storage will be required to maintain industrial water usage. If water storage is not expanded in the ARB future conditions are likely to result in interrupted production of oil and gas or reduced ecosystem function (Leong & Donner, 2016). The reliance on water use for natural resource production in the ARB, in combination with the sensitive ecosystem downstream in the PAD downstream, creates a complex system for the management of water resources (Milly *et al.,* 2008; Prowse *et al.,* 2006; Rood *et al.,* 2015; Wolfe *et al.,* 2008.).

Water use in Alberta is regulated under the Alberta *Water Act*. The *Water Act* regulates water through regional land use plans, water management plans, water conservation objectives and water allocation orders. When none of these regulatory instruments have been implemented, the Surface Water Allocation Directive is used (Boutillier, 2022). In the ARB, the Lower Athabasca Regional Plan and the Lesser Slave Basins Water Management Plan are both in effect; areas not covered in these plans would be managed using the Surface Water Allocation Directive, with the exception of surface water in Jasper National Park, which is regulated under the *Canada National Parks Act*. Recent stakeholder engagement on sustainable watershed management in the ARB was conducted by Marcotte *et al.* (2020), resulting in water management strategies and recommendations for policymakers, including establishing targets for streamflow needs. All stakeholders agreed that it was important to ensure that both ecosystem health and water quality were maintained or improved while providing sufficient flow for cultural activities, such as navigation and ensuring certainty for industrial development.

1.4 Stable water Isotopes

All elements have isotopes; an isotope indicates the number of neutrons present in the nucleus for a chemical element. Isotopes can be stable or radioactive, which indicates degradation over time. Water molecules are formed from largely stable isotopes (^{1}H, ^{2}H,$^{16}0$, $^{17}0$, $^{18}0$), with ^{3}H being radioactive. The most common stable water molecules are $^{1}H_2{}^{16}0$. The different numbers of neutrons isotopes have produces differing masses, which results in preferential evaporation and nucleation patterns. This property can be used to identify where water has come from and the processes that water has undergone. Due to this, isotopes can be regarded as tracers, which allow water sources to be identified and quantified in mixtures.

1.4.1 Stable water isotopes research in cold regions

For decades tracers have been commonly used to quantify water sources in cold regions (Colbeck, 1977; Obradovic & Sklash, 1986). Stable water isotopes (SWI) have been used as a tracer in a range of scales, from micro to continental, and across a variety of ecosystems, including remote areas where other methods are not feasible (Birks & Gibson 2009; Edwards *et al.,* 2004). SWI are an ideal tracer as they occur naturally and are conservative and their values change systematically through water cycle phase changes (Birks & Gibson 2009). The ability to differentiate water based on the processes it has undergone allows SWI to be used for identifying different source waters in streamflow (such as surface water, snowmelt, glacial melt and groundwater) and quantifying the proportions of each water source in a sample (Gibson *et al.,* 2005). Therefore, SWI represents a key method for researching environmental change and supports many applications, such as water resource management, including the advancement of our understanding of hydrological processes and pathways, forecasting of water availability during extreme conditions, such as floods and droughts, and exploring impacts related to climate change (Aggarwal *et al.*, 2005; Gibson *et al.,* 2021).

SWI studies in snowmelt-dominated catchments typically utilize data collected over one or two hydrologic years, allowing annual variability in streamflow to be characterized by a series of temporal "snap-shots". Sampling typically occurs in spring to capture peak snowmelt and late summer to capture peak glacial melt contributions to streamflow (Cable *et al.,* 2011; Marchina *et al.,* 2014; Sun *et al.*, 2016; Williams *et al.,* 2016). In glacially-fed headwater catchments, either glacial melt and/or snowmelt make up high contributions to streamflow in summer low-flow conditions (Cable *et al.*, 2011; Fan *et al.,* 2014; Fan *et al.,* 2016; Jeelani *et al.,* 2016; Kong & Pang, 2012; Marchina *et al.,* 2014; Penna *et al.*, 2014; Sun *et al.*, 2016; Williams *et* al., 2016). Downstream of the headwaters, streamflow often becomes more evaporatively enriched in heavy isotopes due to water sources that have been contained in reservoirs or due to the velocity of streamflow becoming reduced by plains or deltas (Marchina *et al.,* 2014; Rock & Mayer, 2007; Sun *et al.*, 2016).

1.4.2 Stable water isotope research in the Athabasca River Basin

There has been limited work done on the Upper and Middle Athabasca utilizing SWI. The isotopic signature of the meltwater from the Athabasca Glacier has been collected in two recent studies; with results showing similar values over multiple years (Arendt *et al.,* 2015; Robbins 2019). In addition, four sites within the Upper and Middle Athabasca were sampled every 1-12 months between 2013 and 2019 as part of Canada's first baseline stable isotope dataset for rivers (Gibson *et al.,* 2020). Downstream in the Lower Athabasca extensive hydrological research has been conducted, with the focus of SWI studies being groundwater and surface water pathways (Birks *et al.*, 2017; Birks *et al.*, 2019; Gibson *et al.*, 2011; Gibson *et al.*, 2016). SWI analysis is also conducted through the Joint Oil Sands Monitoring Program, which was established in 2011 by the Governments of Canada and Alberta to monitor surface water quality and quantity, air quality and biodiversity of the Lower Athabasca River between Fort McMurray and Lake Athabasca (Government of Alberta, 2022). To date neither snow or glacial melt contributions to streamflow have been explored in the Lower Athabasca.

Outside of the ARB SWI isotopes studies in the region have focused on small mountainous catchments in southern Alberta (Miller *et al.,* 2017; Rock & Mayer, 2007), and large northern basins, specifically the Mackenzie River Basin and the Liard River Basin (Gibson *et al.,* 1999; Gibson *et al.*, 2002; Hitchon & Krouse, 1972; St Amour *et al.*, 2005; Yi *et al.*, 2010; Yi *et al.,* 2012).

1.4.3 Gaps identified for stable water isotopes research

SWI have been used extensively in hydrological research, however, research has largely focused on headwater regions and small catchments. Larger catchments can provide insight into large-scale hydrological patterns but research has been previously limited due to the increased complexity of these systems. This has resulted in calls for additional research in larger catchments with less existing instrumentation (Aggarwal *et al.,* 2005; Gibson *et al.*, 2005; Hemming *et al.,* 2007). In response to this knowledge gap, Gibson *et al.*, (2020) and Gibson *et al.*, (2021) completed the first Canada-wide study and isotope data set, which is applicable to a variety of water management purposes. However, future work is still needed as many large catchments have not been studied and do not have records of baseline conditions.

In addition, there is a need to better understand the hydrological conditions during ice-on periods, the duration of time when rivers are cover in ice lasting from ice formation to break-up, as winter warming trends are leading to shifting hydrological patterns (Prowse and Beltaos, 2002). SWI research is limited during ice-on conditions, due in part to the difficulty associated with reaching remote areas in winter conditions and sampling streamflow below ice cover. River ice stratigraphy, while not extensively tested, is promising as a proxy of hydrologic conditions over the ice growth period in cold climates where the winter temperatures stay consistently below zero (Gibson & Prowse, 1999, 2002). Cold temperatures preserve a seasonal record of streamflow in the ice record and, by combining this with the ice growth rate, a timeline of the conditions when the layers of ice formed can be recreated. To date, limited studies have used SWI collected from river ice cores to reconstruct winter streamflow and no work has been done to advance this method in decades (Gibson and Prowse,1999; 2002), and only a single study has utilized the streamflow record from this method to calculate source water contributions to streamflow (St Amour *et al.,* 2005). This methodology presents a potential solution to data gaps in hydrological studies during the ice-on period and would allow source water contribution of winter streamflow to be calculated.

1.3 Research objectives

To address the gaps identified for stable water isotopes research the primary objectives of this thesis are to:

1) Assess an emerging methodology that reconstructs the isotopic composition of winter streamflow through river ice stratigraphy. This objective was met by:
    - Following the methodology set out in Gibson and Prowse (1999; 2002), ice cores were collected and the isotopic composition of winter streamflow was reconstructed;
    - The reconstruction of winter streamflow was compared to a time series of streamflow collected over the same time period; and
    - The effectiveness and limitations of this methodology was assessed.
2) Analyze the seasonal source water contributions to streamflow across a large catchment where minimal studies have taken place, exploring spatial, seasonal and annual trends. This objective was met by:
    - Conducting seasonal sampling across the Upper and Middle Athabasca Watershed and the McLeod, a sub-catchment in the Middle Athabasca, including sampling source waters; and
    - Examining the seasonal source water contributions for trends in the three catchments.

1.4 Thesis structure

This thesis consists of 4 chapters. Chapter 1 provides an introduction to this thesis, which provides context and outlines research objectives. This includes background on the importance of studying snow-dominated catchments, the value of utilizing stable water isotopes as a tool to study these regions and includes extensive background on the study area. Chapters 2 and 3 are positioned as two stand-alone manuscripts. Chapter 2 assesses an emerging methodology where river ice stratigraphy is used to reconstruct the isotopic composition of streamflow over the ice-on period. Chapter 3, pulls from the results of Chapter 2 and analyzes seasonal source water conditions in the Upper and Middle Athabasca River Basin, examining spatial, seasonal and annual trends. Due to the stand-alone nature of Chapters 2 and 3, information may be repeated materials between chapters. Chapter 4 is a summary and conclusion to this thesis that addresses how the objectives have been met and with suggestions for future research.

References

Athabasca River Basin Research Institute. (2022). About the Athabasca River Basin. Retrieved April 22, 2022, from http://arbri.athabascau.ca/About-the-Athabasca-River-basin/Index.php

Aggarwal, P. K., Gat, J., & Froehlich, K. F. (2005). *A Review of Isotope Applications in Catchment Hydrology. In Isotopes in the water cycle: Past, present and future of a developing science* (pp. 151-157). Dordrecht, the Netherlands: Springer.

AMEC Earth & Environmental. (2007). *Water for life: reliable, quality water supplies for a sustainable economy: current and future water use in Alberta* (pp. 437-474). Edmonton: Alberta Environment.

Aygün, O., Kinnard, C., & Campeau, S. (2020). Impacts of climate change on the hydrology of northern midlatitude cold regions. *Progress in Physical Geography*, 44(3), 338–375. https://doi.org/10.1177/0309133319878123

Barnett, T. P., Adam, J. C., & Lettenmaier, D. P. (2005). Potential impacts of a warming climate on water availability in snow-dominated regions. *Nature, 438*(7066), 303-309. doi:10.1038/nature04141

Birks, S., & Gibson, J. (2009). Isotope Hydrology Research in Canada, 2003-2007. *Canadian Water Resources Journal, 34*(2), 163-176. doi:10.4296/cwrj3402163

Birks, J., Fennell, J., Yi, Y., Gibson, J., & Moncur, M. (2017). Regional geochemistry study for the Southern Athabasca Oil Sands (SAOS) area. COSIA Hydrogeology Working Group: Calgary, AB, Canada.

Birks, S. J., Fennell, J. W., Gibson, J. J., Yi, Y., Moncur, M. C., & Brewster, M. (2019). Using regional datasets of isotope geochemistry to resolve complex groundwater flow and formation connectivity in northeastern Alberta, Canada. Applied Geochemistry, 101, 140-159.

Bonsal, B. R., & Cuell, C. (2017). Hydro-climatic variability and extremes over the Athabasca River basin: Historical trends and projected future occurrence. Canadian Water Resources Journal/Revue canadienne des ressources hydriques, 42(4), 315-335.

Boutillier, A. (2022). (rep.). Water Law in Alberta - A Comprehensive Guide - Chapter 2: Use and Flow of Water. Environmental Law Centre of Alberta.

Brown, R. D. (2000). Northern Hemisphere Snow Cover Variability and Change, 1915–97. *Journal of Climate, 13*(13), 2339-2355. doi:10.1175/1520-0442(2000)013<2339:nhscva>2.0.co;2

Cable, J., Ogle, K., & Williams, D. (2011). Contribution of glacier meltwater to streamflow in the Wind River Range, Wyoming, inferred via a Bayesian mixing model applied to isotopic measurements. *Hydrological Processes, 25*(14), 2228-2236. doi:10.1002/hyp.7982

Canadian Association of Petroleum Producers, 2022. What Are Greenhouse Gases | GHG Emissions & Canada's Carbon Footprint. [online] CAPP | A Unified Voice for Canada's Upstream Oil and Gas Industry. Available at: <https://www.capp.ca/explore/greenhouse-gas-emissions/> [Accessed 22 April 2022].
Center for International Earth Science Information Network (CIESIN), (2004). *Gridded Population of the World (GPW*), *v3*. Retrieved November 07, 2016, from http://beta.sedac.ciesin.columbia.edu/data/collection/gpw-v3

Cheng, G., Huang, G., Dong, C., Zhu, J., Zhou, X., & Yao, Y. (2017). High-resolution projections of 21st century climate over the Athabasca River Basin through an integrated evaluation-classification-downscaling-based climate projection framework. Journal of Geophysical Research: Atmospheres, 122(5), 2595-2615.

Colbeck, S. C. (1977). Tracer movement through snow. *IAHS-AISH Publ, 118*, 255-262.

Cooke, C. A., Schwindt, C., Davies, M., Donahue, W. F., & Azim, E. (2016). Initial environmental impacts of the Obed Mountain coal mine process water spill into the Athabasca River (Alberta, Canada). Science of the Total Environment, 557, 502-509.

Dibike, Y., Eum, H. I., & Prowse, T. (2018). Modelling the Athabasca watershed snow response to a changing climate. Journal of Hydrology: Regional Studies, 15, 134-148.

Edwards, T. W., Wolfe, B. B., Gibson, J. J., & Hammarlund, D. (2004). Use of water isotope tracers in high latitude hydrology and paleohydrology. *Developments in Paleoenvironmental Research Long-term Environmental Change in Arctic and Antarctic Lakes, 187-207*. doi:10.1007/978-1-4020-2126-8_7

Fan, Y., Chen, Y., Li, X., Li, W., & Li, Q. (2014). Characteristics of water isotopes and ice-snowmelt quantification in the Tizinafu River, north Kunlun Mountains, Central Asia. *Quaternary International, 380-381*, 116-122. doi:10.1016/j.quaint.2014.05.020

Fan, Y., Chen, Y., He, Q., Li, W., & Wang, Y. (2016). Isotopic Characterization of River Waters and Water Source Identification in an Inland River, Central Asia. *Water, 8*(7), 286. doi:10.3390/w8070286

Gibson, J. J., Edwards, T. W., Birks, S. J., Amour, N. A., Buhay, W. M., Mceachern, P., . . . Peters, D. L. (2005). Progress in isotope tracer hydrology in Canada. Hydrological *Processes, 19*(1), 303-327. doi:10.1002/hyp.5766

Gibson, J. J., & Prowse, T. D. (1999). Isotopic characteristics of ice cover in a large northern river basin. *Hydrological Processes, 13*(16), 2537-2548. doi:10.1002/(sici)1099-1085(199911)13:16<2537::aid-hyp940>3.3.co;2-1

Gibson, J. J., & Prowse, T. D. (2002). Stable isotopes in river ice: identifying primary over-winter streamflow signals and their hydrological significance. *Hydrological Processes, 16*(4), 873-890. doi:10.1002/hyp.366

Gibson, J. J., Birks, S. J., Moncur, M., Yi, Y., Tattrie, K., Jasechko, S., ... & Eby, P. (2011). Isotopic and geochemical tracers for fingerprinting process-affected waters in the oil sands industry: A pilot study. Oil Sands Research and Information Network, 1-120.

Gibson, J., Yi, Y., & Birks, S. (2016). Isotope-based partitioning of streamflow in the oil sands region, northern Alberta: Towards a monitoring strategy for assessing flow sources and water quality controls. *Journal of Hydrology: Regional Studies, 5*, 131-148. doi:10.1016/j.ejrh.2015.12.062

Gibson, J. J., Holmes, T., Stadnyk, T. A., Birks, S. J., Eby, P., & Pietroniro, A. (2020). 18O and 2H in streamflow across Canada. Journal of Hydrology: Regional Studies, 32, 100754.

Gibson, J. J., Eby, P., Stadnyk, T. A., Holmes, T., Birks, S. J., & Pietroniro, A. (2021). Dataset of 18O and 2H in streamflow across Canada: A national resource for tracing water sources, water balance and predictive modelling. Data in Brief, 34, 106723.

Government of Alberta. (2017). *Athabasca River Conditions and Use*. Retrieved March, 2017, from http://www.environment.alberta.ca/apps/OSEM/

Government of Alberta, 2022. Oil Sands Monitoring Program – Scientific papers and data. [online] Alberta.ca. Available at: <https://www.alberta.ca/oil-sands-monitoring-program-scientific-papers-and-data.aspx> [Accessed 24 April 2022].

Hemming, D., Griffiths, H., Loader, N., Marca, A., Robertson, I., Williams, D., . . . Yakir, D. (2007). The Future of Large-Scale Stable Isotope Networks [Abstract]. *Stable Isotopes as Indicators of Ecological Change Terrestrial Ecology, 361-381*. doi:10.1016/s1936-7961(07)01023-8

Hitchon, B., & Krouse, H. (1972). Hydrogeochemistry of the surface waters of the Mackenzie River drainage basin, Canada—III. *Stable isotopes of oxygen, carbon and sulphur. Geochimica et Cosmochimica Acta, 36*(12), 1337-1357. doi:10.1016/0016-7037(72)90066-x

IPCC (2015). IPCC Climate Change 2014 Synthesis Report (p. 42, Publication). Geneva, Switzerland: Intergovernmental Panel on Climate Change.

IPCC. (2022). Ar6 climate change 2021:The Physical Science Basis. Sixth Assessment Report. Retrieved April 23, 2022, from https://www.ipcc.ch/report/ar6/wg1/

Jeelani, G., Shah, R. A., Jacob, N., & Deshpande, R. D. (2016). Estimation of snow and glacier melt contribution to Liddar stream in a mountainous catchment, western Himalaya: An isotopic approach. *Isotopes in Environmental and Health Studies,53* (1) 1-18. doi:10.1080/10256016.2016.1186671

Kendall, C., & McDonnell, J. J. (1998). *Isotope tracers in catchment hydrology*. Amsterdam: Elsevier

Kong, Y., & Pang, Z. (2012). Evaluating the sensitivity of glacier rivers to climate change based on hydrograph separation of discharge. Journal of Hydrology, 434-435, 121-129. doi:10.1016/j.jhydrol.2012.02.029

Leong, D., & Donner, S. (2016). Future water supply and demand management options in the Athabasca Oil Sands. River Research and Applications, 32(9), 1853-1861.

Lima, A. C., & Wrona, F. J. (2019). Multiple threats and stressors to the Athabasca River Basin: What do we know so far?. Science of the total environment, 649, 640-651.

Marchina, C., Bianchini, G., Natali, C., Pennisi, M., Colombani, N., Tassinari, R., & Knoeller, K. (2014). The Po river water from the Alps to the Adriatic Sea (Italy): New insights from geochemical and isotopic (δ18O-δD) data*. Environmental Science and Pollution Research, 22*(7), 5184-5203. doi:10.1007/s11356-014-3750-6

Marcotte, D., MacDonald, R. J., & Nemeth, M. W. (2020). Participatory water management modelling in the Athabasca River Basin. Canadian Water Resources Journal/Revue canadienne des ressources hydriques, 45(2), 109-124.

Meybeck, M., Green, P., & Vörösmarty, C. (2001). A New Typology for Mountains and Other Relief Classes. *Mountain Research and Development, 21*(1), 34-45. doi:10.1659/0276-4741(2001)021[0034:antfma]2.0.co;2

Miller, K., & Marshall, S. (2017, December). Characterization of meltwater'ingredients' at the Haig Glacier, Canadian Rockies: the importance of glaciers to regional water resources. In AGU Fall Meeting Abstracts (Vol. 2017, pp. C11A-0888).

Newton, B., Buendia-Fores, C., & Emmerton, C. (2019). Impacts of changes to snow accumulation and melt regimes on the streamflow of regulated and unregulated rivers in the upper North Saskatchewan and Athabasca river basins. In AGU Fall Meeting Abstracts (Vol. 2019, pp. H33I-2035).

Nijssen, B., O'Donnell, G. M., Hamlet, A. F., & Lettenmaier, D. P. (2001). Hydrologic sensitivity of global rivers to climate change. *Climatic Change, 50*(1), 143-175. doi:10.1023/A:1010616428763

Obradovic, M. M., & Sklash, M. G. (1986). An isotopic and geochemical study of snowmelt runoff in a small arctic watershed*. Hydrological Processes, 1*(1), 15-30. doi:10.1002/hyp.3360010104

Penna, D., Engel, M., Mao, L., Dell'agnese, A., Bertoldi, G., & Comiti, F. (2014). Tracer-based analysis of spatial and temporal variations of water sources in a glacierized catchment. *Hydrology and Earth System Sciences, 18*(12), 5271-5288. doi:10.5194/hess-18-5271-2014

Pepin, N. C., Arnone, E., Gobiet, A., Haslinger, K., Kotlarski, S., Notarnicola, C., Palazzi, E., Seibert, P., Serafin, S., Schöner, W., Terzago, S., Thornton, J. M., Vuille, M., & Adler, C. (2022). Climate changes and their elevational patterns in the mountains of the world. Reviews of Geophysics, 60(1). https://doi.org/10.1029/2020rg000730

Peters, D. L., Atkinson, D., Monk, W. A., Tenenbaum, D. E., & Baird, D. J. (2013). A multi-scale hydroclimatic analysis of runoff generation in the Athabasca River, western Canada. Hydrological Processes, 27(13), 1915-1934.

Prowse, T. D., & Beltaos, S. (2002). Climatic control of river-ice hydrology: A review. *Hydrological Processes,* 16(4), 805-822. doi:10.1002/hyp.369

Rangwala, I., Sinsky, E., & Miller, J. R. (2015). Variability in projected elevation dependent warming in boreal midlatitude winter in CMIP5 climate models and its potential drivers. *Climate Dynamics*, 46(7-8), 2115–2122. https://doi.org/10.1007/s00382-015-2692-0

Rasouli, K., Hernández-Henríquez, M. A., & Déry, S. J. (2012). Streamflow input to Lake Athabasca, Canada. *Hydrology and Earth System Sciences Discussions, 9*(8), 9065-9093. doi:10.5194/hessd-9-9065-2012

Robbins, M. (2019). Evolution of Late Season Meltwater in Alpine and Arctic Glaciers: Sampling Strategies and Geochemical Observations (Doctoral dissertation).

Rock, L., & Mayer, B. (2007). Isotope hydrology of the Oldman River basin, southern Alberta, Canada. *Hydrological Processes, 21*(24), 3301-3315. doi:10.1002/hyp.6545 IAEA. (n.d.). *Sampling Procedures for Isotope Hydrology*. Retrieved November 11, 2016, from http://www-naweb.iaea.org/napc/ih/documents/other/Sampling booklet web.pdf

St Amour, N. A., Gibson, J. J., Edwards, T. W., Prowse, T. D., & Pietroniro, A. (2005). Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River basin, Northwest Territories, Canada. Hydrological Processes: An International Journal, 19(17), 3357-3381.

Sun, C., Li, X., Chen, Y., Li, W., Stotler, R. L., & Zhang, Y. (2016). Spatial and temporal characteristics of stable isotopes in the Tarim River Basin*. Isotopes in Environmental and Health Studies, 52*(3), 281-297. doi:10.1080/10256016.2016.1125350

UNESCO World Heritage Centre. “Wood Buffalo National Park.” UNESCO World Heritage Centre, https://whc.unesco.org/en/list/256/.

Voutchkova, D. D., & Miller, S. N. (2017, December). 50 years of change at 14 headwater snowmelt-dominated watersheds in Wyoming. In AGU Fall Meeting Abstracts (Vol. 2017, pp. H41H-1547).

Williams, M. W., Wilson, A., Tshering, D., Thapa, P., & Kayastha, R. B. (2016). Using geochemical and isotopic chemistry to evaluate glacier melt contributions to the Chamkar Chhu (river), Bhutan. Annals of Glaciology Ann. *Glaciol., 57*(71), 339-348. doi:10.3189/2016aog71a068

Yi, Y., Gibson, J. J., Hélie, J. F., & Dick, T. A. (2010). Synoptic and time-series stable isotope surveys of the Mackenzie River from Great Slave Lake to the Arctic Ocean, 2003 to 2006. Journal of Hydrology, 383(3-4), 223-232.

Yi, Y., Gibson, J. J., Cooper, L. W., Hélie, J. F., Birks, S. J., McClelland, J. W., ... & Peterson, B. J. (2012). Isotopic signals (18O, 2H, 3H) of six major rivers draining the pan-Arctic watershed. Global Biogeochemical Cycles, 26(1).

Zhou, X., Huang, G., Piwowar, J., Fan, Y., Wang, X., Li, Z., & Cheng, G. (2018). Hydrologic impacts of ensemble-RCM-projected climate changes in the Athabasca River basin, Canada. Journal of Hydrometeorology, 19(12), 1953-1971.

Chapter 2. Reconstructing the isotopic composition of winter streamflow using ice cores in the Athabasca River Basin, Alberta, Canada

Abstract

During ice growth, river ice stratigraphy is an archive that preserves the stable isotope signature of streamflow, offset by the respective ice-water fractionations. This archive makes ice cores useful for reconstructing the isotopic composition of streamflow throughout the ice-on period. A chronology of the isotopic variability of streamflow can indicate when shifts in source waters have occurred and also allows for a time-series of source water contributions to be calculated. Prior preliminary studies utilizing this method have realized accurate results when compared to those obtained by O'Neil (1968), who experimentally determined values for fractionation for the Liard–Mackenzie River Basins, though they assumed a constant value for ice-water fractionation (Gibson *et al.,* 1999; 2022). In this study, the Athabasca River, a large river in Alberta, Canada and the McLeod River, a tributary of the Athabasca River, were sampled to assess the accuracy of reconstructing the isotopic composition of streamflow using a constant value for ice-water fractionation. This allowed for site-specific changes in the isotopic composition of streamflow to be obtained which indicated shifts in source water contributions. Routine streamflow samples over the ice growth period were utilized as a means to capture the variability in fractionation. The average apparent fractionations (α^{18}0ice-water = 1.00294 and α^{2}H ice-water = 1.0181) were comparable to the existing literature (Gibson *et al.,* 1999; 2022; O'Neil, 1968) and the variation in fractionation was found to be minimal (+/- 0.48 ‰ δ^{18}0 and +/- 2.8 ‰ δ^{2}H), indicating equilibrium fractionation was occurring. During the initial ice growth period, non-equilibrium fractionation (2.34 ‰ δ^{18}0, 12.5 ‰ δ^{2}H) was recorded during the coldest conditions, which

corresponded with the most rapid ice growth. Additionally, in some cases, the oldest samples of congelation ice contained melt from snow and white ice, a factor which would not have been distinguishable from shifts in source water contributions without comparative streamflow samples, indicating the limitations of this methodology. This research suggests using a constant value for water to ice fractionations appears to be adequate, except for early during the ice archive, a topic where future research is recommended. Site-specific changes in the isotopic composition of streamflow on the McLeod River indicated that surface water contributions were reduced following freeze-up, increasing the relative contribution of groundwater. In comparison, on the Athabasca River, increased contributions of evaporated surface water occurred during periods when temperatures were above zero.

2.1 Introduction

In cold regions, during periods when temperatures are consistently below freezing, river ice forms in a systematic manner that results in a stratigraphy, which creates an archive of streamflow conditions. This archive is captured, moving down the water column as the ice grows, preserving the isotopic signature of streamflow, offset by the respective ice-water fractionations *(*Eicken *et al.,* 2005*;* Gibson & Prowse, 1999, 2002). When the ice-water fractionations are known, this methodology has the potential to be used for reconstructing the isotopic composition of streamflow for the ice-on period when other sampling methodologies may be difficult or limited (Gibson & Prowse, 1999, 2002). The use of Stable Water Isotopes (SWI) to study river ice stratigraphy has been proven to provide insight into the variability of streamflow (Gibson & Prowse, 1999), determine when shifts in source waters occurred (Gibson & Prowse, 1999, 2002) and facilitate source water calculations (St Amour *et al.*, *2005*). However, the use of this methodology has been limited requiring further research.

The isotopic fractionation of water to ice in ideal conditions produces predictable isotopic values. To provide accurate results, congelation (black) ice, ice which forms moving down the water column and is often clear in nature, is the preferred archive over white ice, which has a more complex genesis and appears cloudy of "white" in colour. Sampling is targeted to areas distanced from tributary outflows, mid-river and excludes shallow rivers (Gibson & Prowse, 2002). The fractionation of water to ice is also affected by the rate of ice growth, where fractionation during slow growth in late winter is most predictable (Prowse, 1995). In comparison with experimentally determined reference values for fractionation of moving freshwater (O'Neil 1968), studies in the field have proven to return accurate results (Gibson & Prowse, 1999, 2002). These studies assumed constant values for fractionation over the ice growth period, using a single sample of streamflow per site to calculate fractionation. This suggests that the isotopic composition of winter streamflow, in particular late seasonal growth, can be reconstructed using river ice stratigraphy. This requires that the properties of ice be taken into consideration in order to improve sample selection during slow growth; in particular, avoiding samples that may have been mixed with other water sources (i.e. snow) while also ensuring that the ice can be properly dated. It is worth noting that the accuracy of assuming constant values for fractionation has yet to be rigorously tested.

To assess the use of river ice stratigraphy as a methodology to reconstruct the isotopic composition of winter streamflow, it was recommended that a complete season of isotope data from streamflow be collected, in conjunction with ice cores, to verify that the fractionations of water to ice are consistent throughout the growth period (Gibson & Prowse, 2002). In this study, that work has been performed: the Athabasca River, a large river in Alberta, Canada and the McLeod River, a tributary of the Athabasca River, were used to assess the accuracy of reconstructing the isotopic composition of streamflow from river ice stratigraphy based on constant values for fractionation. This was verified using routine streamflow samples over the ice growth period to monitor variability in fractionation.

2.2 Theory

2.2.1 Stable Water Isotopes in Ice Formation

SWI concentrations are expressed as δ^2H and $\delta^{18}O$ values in permil (‰). Due to difficulties in absolute measurement of small concentrations of rare SWI, isotopic values are expressed instead by comparing abundance ratios (R):

$$R = {}^{18}O / {}^{16}O \text{ or } {}^{2}H / {}^{1}H \qquad (2.1)$$

of the rare and common isotopic species in the sample and standard, whereby the delta value is calculated as:

$$\delta = (R_{sample} / R_{standard} - 1) \cdot 1000 \qquad (‰) \qquad (2.2)$$

The standard used for characterizing water is typically Vienna Standard Mean Ocean Water (VSMOW), such that isotopic delta values for water are typically negative (i.e., heavy isotope depleted) compared to ocean water, which is close to 0 ‰ for most continental waters.

Once an isotope becomes part of a water molecule, aggregate isotope concentrations only change through one of two main processes. One is the mixing of different water sources, where the new value is a proportionate mixture of the sources. The second process is through fractionation, which occurs when water changes state through either evaporation, condensation, freezing or in situations where it does not change state but undergoes diffusion. Fractionation is a separation of isotopic species resulting from the slight variation in mass between water molecules incorporating different isotopes: heavier molecules typically are less mobile and have higher binding energies, requiring more energy for separation, causing lighter isotopes to evaporate and heavier isotopes to condense preferentially. During fractionation, the partitioning of SWI between two states can be expressed using the fractionation factor (α)

$$\alpha_{A\text{-}B} = (1000 + \delta_A) / (1000 + \delta_B) \tag{2.3}$$

The isotopic separation or offset between water in the two states can be expressed using the fractionation constant (ε), where δ_A is the isotopic value of a sample that has changed state and δ_B is the isotopic value of the sample before its state has changed.

$$\varepsilon_{A\text{-}B} = (\alpha_{A\text{-}B} - 1) \cdot 1000 \tag{2.4}$$

In cold regions, fractionation occurs during the formation of ice cover, with heavier isotopes being preferentially incorporated into ice over lighter isotopes (Ferrick *et al.,* 2002; Gibson & Prowse, 2002). The isotopic offsets between water and ice have been found to be between 2.84 and 3.0‰ for $\delta^{18}0$ and between 17.9 and 19.5 ‰ for $\delta^{2}H$ (Gibson & Prowse, 2002; O'Neil, 1968). Four variables affect the isotopic signature of ice cover (Gibson & Prowse, 2002). The first is the base isotopic composition of the original water in the streamflow. Second is the amount of partitioning that occurs during fractionation when water changes state. This is controlled by the speed of ice growth and the conditions of the boundary layer just below the ice. Third is the reservoir effect, which is caused when water becomes trapped and freezes in isolation from flowing river water. As a result, ice in the remaining water becomes continually depleted of heavy isotopes due to Rayleigh distillation. This can be avoided by sampling ice cores in deep rivers to avoid locations where the ice has frozen to the river bottom. The fourth and final variable is post-freeze-up complexities, where conditions occur after ice has formed, such as the accumulation of snow on the ice surface or melting and refrezing of the top layer of ice. This can result in the ice being formed from a mixture of water sources, i.e. snow and ice, and often presents as white ice.

2.2.2 Ice formation and growth

The formation and growth of ice is dependent on river turbulence, water temperature, and precipitation that occurs during freezup. Ice forms first at the calm margins before expanding towards the middle of the river. In more turbulent flows, ice forms first as frazil ice that grows and accumulates, eventually bridging the river, trapping frazil from upstream to form an ice cover. This will occur faster in shallow rivers than in deep rivers, as water in shallow rivers cools at a quicker rate, allowing frazil to form and grow. Ice cover may not occur in highly turbulent areas, such as rapids, as a layer of ice cannot form on the surface. In calm conditions, transparent congelation ice will form; this is sometimes referred to as either black or blue ice. If water temperature remains consistent, the ice growth rate down the water column will slow as the ice gets thicker due to the insulating effect of ice, preventing loss of heat to the atmosphere. Similarly, snow accumulation on top of the ice adds insulation, thereby slowing growth. However, snow accumulation may also depress river ice and result in flooding, which could allow white ice to form. White ice can also form during frazil accumulation and slushing from snow melting on top of the ice. White ice is common in temperate areas where more snow accumulates over the cold period. White ice formed in this way will exhibit a mix of isotopic signatures, making it difficult to use in isotopic analysis.

Ice growth is commonly calculated using the Stefan equation (5), a simplified equation derived from Ashton (1986):

$$h_i = \gamma (D_f)^{1/2} \tag{2.5}$$

where ice thickness h_i, is calculated using the accumulated sum of freezing degree days (D_f) and the coefficient γ.

2.3 Study area

The Athabasca River is the largest unregulated river in Alberta, originating at the Columbia Glacier before flowing northeast across Alberta for 1500 km. The middle reaches of the Athabasca watershed begin at Whitecourt and end at Fort McMurray (figure 2.1). Within the study area, there were three locations chosen to be studied:

1. The McLeod River, a tributary to the Athabasca River, at the Town of Whitecourt;
2. the Athabasca River, at the Town of Athabasca; and,
3. the Athabasca River, at Fort McMurray.

The sample site at Fort McMurray is upstream from the inflows of the Horse and Clearwater Rivers and is in an area that experiences severe ice jams (Beltaos, 2019). These locations typically have average daily temperatures below freezing between the months of November and March (Environment Canada^{1}, 2018). Notable hydrologic features within the study area include wetlands that become more abundant between the Town of Athabasca and Fort McMurray, the Grand Rapids, and two large water bodies: Lesser Slave Lake and Lac La Biche.

In the Middle reaches of the Athabasca River is Lesser Slave Lake, a prominent water body that likely experiences strong evaporative effects which may lead to evaporative enrichment of SWI in the summer months. The isotopic composition of the outflow of Lesser Slave Lake has the potential to influence the isotopic value of streamflow in the Athabasca River at Athabasca, especially if the isotopic composition of the two river differs significantly. However, Lesser Slave Watershed encompasses 1,160 km^{2} and has relatively large run off volumes entering the lake from the surrounding foothills (Lesser Slave Watershed Council, 2018). This likely results in a reduced evaporatively enriched isotopic composition of Lesser Slave Lake. The numerous wetlands in the middle reaches of the Athabasca also undergo evaporative enrichment of SWI in the summer months. During cold conditions, wetlands and the pathways connecting them to the Athabasca may freeze, limiting their influence on the isotopic composition of the Athabasca River. However, during warmer conditions there is the potential that these pathways may unfreeze, allowing this source water to more easily reach streamflow. This is especially likely in areas with rapids where ice cover may not form over the winter creating a pathway where surface meltwater can easily enter streamflow.

Source waters to the Athabasca River include surface water (e.g., lakes and wetlands), snowmelt and groundwater. Due to the different hydrological processes associated with the formation of these source waters, they will each have distinctive isotopic signatures. Surface water undergoes evaporation, which removes the lighter molecules to create a more positive isotopic value with a shallower slope than the Global Meteoric Water Line (GMWL) in a plot of $\delta^{18}0$ and $\delta^{2}H$, often referred to as delta-delta space. This also results in greater proportional changes in $\delta^{2}H$ than $\delta\,^{18}0$, which is commonly measured as a “d-excess” value. Isotopically, snow is typically falls close to the slope of the GMWL and is more negative than liquid precipitation as it forms under colder conditions. Groundwater is dependent on local factors, such as topography and geology, but is often largely recharged by snowmelt or heavy precipitation, receiving water sources that have experienced only limited evaporation (Fan et al., 2014; Penna et al., 2014; Yang et al., 2011). Due to this it may appear similar isotopically to the GMWL.

2.4 Methods

2.4.1 Field collection

Between October 2016 and February 2017, SWI samples were collected from *in situ* streamflow at two of the sampling locations on a weekly to monthly basis. The water treatment centre for the Town of Whitecourt collected eighteen samples from the McLeod River, before the convergence with the Athabasca River. The Aspen Regional Water Services Commission, which conducts water testing, collected nine samples from the Athabasca River at the Town of Athabasca. At both sites, river water was collected from locations away from upstream tributaries and was pumped into the facility before being collected. Samples were collected in 30 ml HDPE bottles and were stored in the refrigerator following USGS protocols to ensure preservation of samples until isotope analysis was done in March 2017 (USGS, 2017).

From March 2nd to 4th 2017, vertical ice cores were collected from the McLeod and Athabasca Rivers at three locations. Ice cores were collected at this time to maximize the winter record. Locations for ice core samples were chosen to be near where streamflow samples had been collected and at the Athabasca River, above Fort McMurray, to analyze the impact the Grand Rapids have on the isotopic composition of streamflow. In the collection of river ice, smooth reaches were selected at least 20m from shore to maximize the likelihood that the ice was preserving the seasonal record and the water under the ice was well mixed (Gibson & Prowse 2002). When collecting an ice core at Fort McMurray there was clear evidence of ice jams that had been released from upstream. To select the best sample, a flat section of the river was sampled that appeared to be undisturbed.

Ice cores were collected using a battery-powered titanium ice auger (figure 2.2). Once collected, ice cores were quickly removed from the auger to prevent them from freezing inside the barrel. At Fort McMurray, the auger needed to be warmed briefly at room temperature to allow the ice core to be removed. To prevent contamination, ice cores were processed on a dry tarp, using dry gloves and a dry saw blade. Materials were exchanged or dried when they got wet. Between each core, the auger was also completely dried. The ice cores ranged from 71 to 85 cm long and were separated into sections 0.5 to 10 cm in length. Sections averaged 4.25 cm and were selected through natural breaks whenever possible or through manual cuts using a miter box (figure 2.2). Once separated, samples were visually classified into congelation and white ice, measured, bagged, photographed and labeled (figure 2.2). Samples were melted at room temperature (Gibson & Prowse, 2002) before 1.5 ml of each sample was pipetted into 2 ml vials for isotope analysis; this was stored in the fridge for several days until isotope analysis could take place. For quality control, a secondary core was collected at Athabasca and duplicates were collected for 11% of the samples.

2.4.2 Isotope analysis

SWI are expressed in permil (‰) relative to Vienna Standard Meteoric Waters (VSMOW). Isotope analysis was conducted in March 2017. SWI samples from streamflow were processed at the InnoTech Alberta Isotope lab at the Vancouver Island Tech Park. Here, a Thermo-Fisher Delta V Advantage IRMS with HDevice and Gasbench was used. Samples from the ice cores were processed at the Isotope Science Lab at the University of Calgary. This facility uses a Los Gatos Research (LGR) DLT-100, an instrument that employs Off-Axis Integrated-Cavity Output Spectroscopy (OA-ICOS). Both facilities have instrumental uncertainty of +/- 0.2‰ $\delta^{18}0$ and +/- 1.0 ‰ $\delta^{2}H$. In lab duplicates were conducted for the streamflow samples and had a maximum standard deviation of 0.13 ‰ $\delta^{18}0$ and 0.5 ‰ $\delta^{2}H$. Duplicates from the field had a maximum difference of 0.65‰ $\delta^{18}0$ and 1.8‰ $\delta^{2}H$. To test any difference in results between the two labs, nine samples from a synoptic survey of the Athabasca River in May 2017 were sent to both labs. This resulted in a maximum difference of 0.3 ‰ $\delta^{18}0$ and 1.2‰ $\delta^{2}H$ when comparing the samples sent to both facilities, which is reasonably comparable while it is slightly outside of the range of instrumental uncertainty.

2.4.3 Ice thickness analysis

Ice thickness over the ice growth period was calculated using the Stefan formula. Average daily temperature data were obtained from nearby meteorological stations, Athabasca AGCM and Fort McMurray A (Environment Canada[2], 2018). Hourly temperature data were not available for Whitecourt so ANUSPLINE data were used. ANUSPLINE data is interpolated, gridded climate data, generated using thin-plate smoothing splines and input into ANUSPLINE climate modeling software, a process commonly used when location-specific data are not available (McKenney *et al.*, 2011). The Stefan coefficient for snow-covered rivers ranges from 14 to 17. However, this range for the coefficient was found to under-predict ice thickness in comparison to the field measurements. This is a common concern of the Stefan formula from previous studies (Comfort & Abdelnour, 2013). To improve this measure, white ice thickness was removed from the total ice thickness measured in the field, as the Stefan formula only calculates vertical ice growth and the coefficient for snow-covered Rivers and lakes was used (17 and 21).

Utilizing the values for daily ice thickness (both loss and gain) generated by the ice growth model (averages displayed in table 2.1), the ice cores collected in the field and the corresponding isotopic data were matched to the dates when the ice was predicted to have formed. The fractionations of water to ice were calculated by comparing the isotopic values obtained from routine streamflow sampling to the ice core data on the corresponding date.

Table 2.1: Key measurements calculated from the ice growth model of the ARB. The first few days of ice growth were found to be likely exaggerated as early ice growth produced by this method can be inaccurate and were excluded from the below calculations.

Location	Average daily ice growth (cm)	Maximum daily ice growth (cm)	Accumulated ice loss (cm)
Whitecourt	5.51	17.25,	14.93
Athabasca	4.92	16.75	15.85
Fort McMurray	7.11	24.98	9.12

2.5 Results and discussion

2.5.1 Isotope analysis

When the SWI values from the streamflow and the ice cores samples are plotted in delta-delta space (figure 2.3), the water-ice fractionation relationship can be seen clearly. Streamflow samples have a linear relationship with congelation ice, where the congelation ice has a more positive isotopic signature due to fractionation. At each of the sampling locations congelation ice displayed minimal variation over the ice growth period with a range of +/- 1.00 ‰ $\delta^{18}0$ and +/- 6.0 ‰ $\delta^{2}H$.

When collecting ice core samples for Fort McMurray, all of the ice samples were initially recorded as white ice. Typically, white ice has not been used in reconstructing streamflow, however, the reliability of this ice was tested and similar results/patterns to “black ice” cores collected at Fort McMurray and ice core samples from the Athabasca River upstream of this location were found. Due to the proximity of Fort McMurray to the Grand Rapids, the dominance of white ice is attributed to having been formed in conditions with turbulent water flow. This explanation for the ice formation process was supported by the clear evidence of ice jams at Fort McMurray. The single sample that remained classified as white ice for Fort McMurray was the oldest ice sample. This sample had a distinctive difference from the rest of the ice core, suggesting that it was formed from post-freeze-up complexities such as flooding or snow incorporation. While there were no streamflow samples collected at Fort McMurray, the similarities of the ice core samples to those collected upstream at Athabasca indicate that the ice at Fort McMurray is a fairly accurate representation of streamflow for Fort McMurray. The application of this methodology, using white ice samples that have formed through distinctive processes which would capture the ice archive, offers a larger use case for this methodology than was originally set out by Gibson & Prowse (1999, 2002).

When looking at the SWI analysis, white ice exhibited two distinctive groups that form through two different processes (figure 2.3). The first group of white ice has SWI values that are situated between the streamflow and congelation ice samples. These white ice samples were all collected from the oldest ice at Athabasca and are likely formed by the accumulation of frazil ice. The sampling location at Athabasca was just upstream of a large bend in the river, which may have resulted in frazil accumulation. The Water Survey of Canada also collects ice samples at a location 500m upstream of the location selected for this study (Environment and Climate Change Canada, 2018); this potentially indicates that moving upstream would reduce the amount of frazil captured as white ice. The second group of white ice samples had a more negative SWI value when compared to streamflow and are further away from the GMWL. These white ice samples are likely formed by snow on ice that had melted and refrozen, as snow on the upper layer of ice is common (Gibson & Prowse, 2002). White ice samples were removed from the data set and not used in reconstructing the isotopic composition of streamflow. However, the white "snow" ice samples were utilized to estimate the isotopic value of the snow that formed them.

2.5.2 Ice-water fractionation

average offset between ice and water was calculated as δ^{18}0ice = 1.00294 δ^{18}0water and δ^{2}H ice = 1.0181 δ^{2}H water (figure 2.4). These differences were found to be comparable to α values obtained from the existing literature (table 2.2). Note that these offsets imply that systematic fractionation has occurred between water and ice upon freezing, whereby ice has become enriched in the heavy isotopic species compared to the formation water.

Table 2.2: Reported values for enrichment of water to ice, collected experimentally from moving fresh water and in the field from rivers in Northern Canada.

Author	Method	ε_{eff} $\delta^{18}0$ (‰)	ε_{eff} $\delta^{2}H$ (‰)	Number of samples
O'Neil, 1968	Experimental	3.0 +/- 0.1	18.7+/- 0.7	2
Gibson & Prowse, 1999	Field Study	2.94 +/- 0.33	19.5+/-1.6	14
Gibson & Prowse, 2002	Field Study	2.84+/- 0.34	17.9+/- 3.9	20
My results	Field Study	2.94+/-0.48	18.1+/- 2.8	32

The ice-water separation slopes ranged from 1.00341 to 1.00258‰ for $\delta^{18}0$ and 1.0209 to 1.0158‰ for $\delta^{2}H$. By site, the average ice-water fractionation was 1.00301 for $\delta^{18}0$ and 1.0184 for $\delta^{2}H$ for Whitecourt and 1.00287 for $\delta^{18}0$ and 1.0178 for $\delta^{2}H$ for Athabasca. The calculated ice-water offset in this study was within the range of values recorded in the literature from both experimental and field studies (table 2.2). The calculated ice-water separation for $\delta^{18}0$ was identical to the value calculated by Gibson and Prowse (1999) and $\delta^{2}H$ was similar to Gibson and Prowse (2002). The range of error for $\delta^{18}0$ (+/-0.48 ‰) was larger than the values recorded in the existing literature, while the range of error for $\delta^{2}H$ (+/- 2.8 ‰) fell within the range of error from previous studies. The range of error in the ice-water separations for this study is likely increased from natural levels because streamflow samples, which capture a moment in time, are being compared to ice samples that integrate both a range of time and conditions, while also being 'proxy' dated based on an approximate ice growth model. However, the variability in isotopic separation is roughly 2-2.5 X the analytical uncertainty of 0.2‰ $\delta^{18}0$ and 1.0‰ $\delta^{2}H$, and still provides a useful potential constraint on overwinter changes in the isotopic composition of streamflow. This finding appears to suggest consistent fractionation conditions and supports use of the methodology applied previously by Gibson and Prowse (1999, 2002) to reconstruct overwinter streamflow from limited ice core data collected in late winter.

The calculated ice-water fractionation values were applied to the SWI values of the congelation ice, to provide a reconstruction of the isotopic composition of streamflow at each site (figure 2.5).

Isotopic measurements from streamflow over the winter, as well as samples taken in August 2016, prior to freeze-up, and in May 2017, following break-up (displayed in pink), provide a guideline for the possible range of the reconstructed isotopic composition of streamflow. At Whitecourt, the reconstructed isotopic composition of streamflow from congelation ice is within the range of the winter streamflow that was sampled, with the exception of one sample. At the Town of Athabasca, the reconstructed isotopic composition of streamflow from congelation ice has less variation than Whitecourt and fits within the range of winter streamflow, with the exception of two samples. All three of the reconstructed streamflow values that did not fit within the range of winter streamflow samples fit between the range of the streamflow samples collected in August 2016 and May 2017. This indicates that these reconstructions are likely to have accurately represented the isotopic composition of streamflow and that the limited winter sampling of streamflow did not capture the entire range of values. As streamflow was only collected at Fort McMurray in May 2017, streamflow values from the Town of Athabasca are used as proxies for this location.

The calculated ice-water fractionation value for the SWI was also applied to the "snow" ice to provide a reconstruction of the isotopic composition of the snow that formed this ice (figure 2.5). Using this methodology, the snow at Whitecourt was approximated to be -22.59‰ $\delta^{18}0$ and -175.5‰ $\delta^{2}H$ and the snow at Fort McMurray was approximated at -21.43‰ $\delta^{18}0$ and -169.7‰ $\delta^{2}H$. Both of these values are relatively close to the GMWL and reflect similar values for snow as samples collected in May 2017 which can be found in Chapter 3 of this thesis.

2.5.3 Reconstructing the isotopic composition of streamflow using ice cores

By comparing the measured isotopic composition of streamflow to the reconstructed isotopic composition of streamflow over time, the accuracy of the reconstruction can be assessed (figure 2.6). Error bars are set to the instrumental uncertianty of 0.2 ‰ $\delta^{18}0$ and 1.0 ‰ $\delta^{2}H$ to highlight the potential range in instrumental error. Overall, the reconstructed isotopic composition of streamflow overlaps with the measured isotopic composition of streamflow for the majority of the samples. Athabasca only had one sample where the reconstruction did not overlap, Whitecourt has two streamflow samples for each isotope that do not overlap and Fort McMurray has two $\delta^{18}0$ and four $\delta^{2}H$ samples that do not overlap.

Of the reconstructed samples that did not overlap with the measured values for streamflow, the largest difference was +/- 0.94 ‰ $\delta^{18}0$ and +/- 4.7 ‰ $\delta^{2}H$ at Athabasca. This sample was in core 2 at Athabasca, with core 1 accurately reconstructing streamflow within the margin of instrumental error. This discrepancy in core 2 occurs at the start of the ice record and may be due to a portion of snowmelt being incorporated into the ice while it was forming. In comparison, the streamflow samples that don't overlap with the reconstructed values from Whitecourt and Fort McMurray were likely partially caused by the thickness of the ice samples, producing an average value that reduces variability in the reconstruction. This occurs when each sample is an average rather than a direct sample. This is especially evident in the late winter samples at Fort McMurray. The reconstructed streamflow at Fort McMurray has the largest percentage of samples that do not overlap with measured streamflow: 22% of $\delta^{18}0$ samples and 44% of $\delta^{2}H$ samples. As streamflow was not collected directly in Fort McMurray this result is not unexpected. However, in Fort McMurray three of the four samples that do not overlap for $\delta^{2}H$ and one of the corresponding $\delta^{18}0$ samples have more negative isotopic compositions than streamflow and occur in the second half of the ice-on period where ice cover should be established. As streamflow in Fort McMurray is expected to have a larger contribution of evaporatively enriched source waters than Athabasca, these four samples are considered to be a reliable reconstruction of streamflow. Following this assumption only the oldest streamflow sample and reconstructed ice value for Fort McMurray would not overlap. Overall, 6.25% of the total streamflow samples from Whitecourt and Athabasca do not overlap with the reconstruction, not taking into consideration the sample from core 2 at Athabasca. This suggests that using this method of streamflow reconstruction produces accurate results when streamflow samples contaminated with post freeze-up complexities have been removed. It is recommended that smaller sections of ice cores be utilized to increase the precision of the reconstruction of streamflow.

At Whitecourt, the overall trend was that the isotopic composition of streamflow became more negative early in the winter before leveling off in January (figure 2.6). There were two brief negative shifts in the reconstruction of streamflow that are not reflected in the measured isotopic composition of streamflow. The decline and leveling off of the isotopic composition of streamflow corresponds with freeze up, as surface water inputs become reduced during this time and the relative contribution of groundwater increases. The first brief negative shift in the reconstruction of streamflow occurs in the oldest congelation ice sample that was collected. This sample, while physically resembling congelation ice, isotopically appears to be a mixture containing roughly 25% of snowmelt that has melted and refrozen. The second shift occurring between December 6-9th aligns with the coldest air temperature and the fastest ice growth. Due to rapid ice growth during this time period, it is likely that fractionation was reduced from 2.94 to 2.34‰ $\delta^{18}0$ and from 18.1 to 12.5 ‰ $\delta^{2}H$. If this updated fraction value is used the reconstruction would align with streamflow. It is unlikely that this shift is caused by a change in source water contributions, an event with approximately 56 % snowmelt would need to occur. This seems unlikely due to the extremely cold temperatures at this time.

At Athabasca, the reconstructed isotopic composition of streamflow remains relatively constant over time (figure 2.6). There are two exceptions to this; the oldest samples at the start of the ice growth period in core 2 and several positive shifts in streamflow that occurred near the end of the ice growth period that were not captured in the reconstructed isotopic composition of streamflow. Examining the start of the ice growth period, the oldest samples of core 2 appear to be a mix of the white ice in the sample above and streamflow; the 2 samples have roughly 69% and 56% white ice mixed with streamflow. Examining the end of the ice growth period, the positive shifts in the measured isotopic composition of streamflow are observed in January between the 15th to 18th, 27th to 29th and February 12th to 17th. These time periods correspond with temperatures above 0°C. In response to these events, streamflow becomes more positive for both $\delta^{18}0$ and $\delta^{2}H$, with $\delta^{18}0$ remaining positive for a period of time following the event. This indicates an increased contribution of an evaporated water source during these positive shifts. However, the reconstructed isotopic composition of streamflow does not capture these positive shifts. This is potentially due to the lack of ice growth during these warm periods, which would mean the increase in surface water contribution was not captured. In addition, ice samples during this time accounted for large periods of time and additional precision would have been gained from collecting smaller ice segments.

Insight about source water contributions to the Athabasca River between Athabasca and Fort McMurray is gained from comparing the reconstruction of streamflow at Fort McMurray to the streamflow data collected from Athabasca (figure 2.6). Between Athabasca and Fort McMurray are the Grand Rapids, several tributaries including Lac La Biche, and numerous wetlands. The Grand Rapids prevent the Athabasca River from freezing up completely and create a pathway for snow and other source waters to enter the river directly. In addition, evaporatively enriched source waters accumulate as you move downstream. This may allow evaporatively enriched surface water from upstream to be incorporated into the ice cover in Fort McMurray once temperatures have dropped. This combination of the pathways for source waters to enter streamflow and the accumulation in evaporation sources likely accounts for why the reconstructed streamflow at Fort McMurray reacts more abruptly to changes in source waters in comparison to Athabasca. Following warm temperatures, the reconstruction of streamflow at Fort McMurray aligns with the streamflow samples for Athabasca. This indicated that evaporatively enriched water sources were captured in the river ice stratigraphy. This pattern was captured despite Fort McMurray having the largest ice segment samples of all three sites. If smaller segments were collected it is likely that Fort McMurray would see additional variability, which would exceed what was measured in the streamflow at Athabasca.

2.5.4 Recommendations for future work

The preliminary results from this study support the use of this methodology as a proxy for streamflow sampling when streamflow sampling is not feasible during the ice-on period. In future studies, it is recommended that thinner sections of ice be collected. This would provide greater precision in the values obtained from each ice section, and in turn result in a higher resolution for the time-series created from the reconstruction of the isotopic composition of streamflow. During the ice core extraction, it would also be beneficial to collect SWI samples from both streamflow and snow as has been done by previous studies (Gibson & Prowse, 1999, 2002). In addition, it is recommended that the oldest congelation ice samples be scrutinized as a mixture of snow and streamflow was found in several of the locations sampled.

While this methodology appears promising, several uncertainties still remain, which could be the focus of future research. This includes utilizing high-frequency streamflow sampling to better access the accuracy of this methodology at capturing high variability in winter conditions. In addition, further studies should explore the accuracy of this methodology under various ice growth conditions such as early ice growth, growth under extremely cold periods, ice growth in locations with turbulent conditions and in more temperate climates where temperature fluctuations are commonly above 0°C, resulting in a lack of ice growth and potential for ice loss.

This methodology provides an inexpensive, high-resolution solution to collecting a record of winter streamflow in comparison to traditional techniques that may require multiple visits to remote locations in undesirable weather conditions. By collecting additional source water data, this methodology could be used to calculate the contribution of each source water to streamflow over the ice growth period and the flow origins. In addition, this methodology could be used to generate multi-year streamflow records, which could provide insights for monitoring the hydrological regime of the river and allow relationships between source waters and warming temperatures to be established. To date, this methodology has only been implemented in Northern Canada. However, this methodology could be used in cold regions globally. This methodology is limited in temperate areas where temperatures frequently fluctuate above 0°C during the ice-on periods, as warm conditions lead not only to a lack of ice growth but potentially also a loss of this ice archive.

2.6 Conclusion

In conclusion, this study furthers the methodology of Gibson and Prowse (1999, 2002) by demonstrating its efficacy as a tool to reconstruct the isotopic composition of streamflow using river ice stratigraphy. The ice-water fractionation values calculated over the study period aligned with values determined by previous studies, supporting the idea that use of a single point in time calculation for ice-water fractionation could be sufficient when additional sampling is not plausible. In comparing the reconstructed isotopic composition of winter streamflow with the measured isotopic composition of streamflow, 93.75% of samples appeared to be reliable supporting the accuracy of this methodology. However, it is recommended that to capture higher precision in streamflow smaller ice segments be collected in future studies.

Site-specific changes in the middle reaches of the Athabasca watershed provided insight into the processes involved in ice formation and shifts in source water contributions. The reconstruction of streamflow at Whitecourt became progressively more depleted over time, likely due to the reduced influence of surficial waters, increasing the relative contribution of groundwater. The reconstruction of streamflow at Fort McMurray indicated that evaporatively enriched source waters were contributing to the isotopic composition of streamflow during periods when temperatures were above 0°C. This indicated that surface waters from lakes and wetlands were being captured in the ice column. In comparison, this effect did not occur in the streamflow reconstruction at Athabasca, despite the streamflow samples capturing this trend.

This methodology offers a promising solution to collecting a winter streamflow record when sampling is not feasible in cold climates, where temperatures do not frequently exceed 0°C during the winter months. Greater uptake of this methodology could allow multi-year records of winter streamflow to be easily produced, providing data sets that could assist in assessing how source water contributions to streamflow shift under warming winter conditions.

References

Ashton, G. D. (1986). *River and lake ice engineering*. Littleton, CO, U.S.A.: Water Resources Publications.

Beltaos, S. (2019). Numerical prediction of ice-jam profiles in lower Athabasca River. Canadian Journal of Civil Engineering, 46(8), 722-731.

Comfort, G., & Abdelnour, R. (2013). Ice Thickness Prediction: A Comparison of Various Practical Approaches. In *CGU HS Committee on River Ice Processes and the Environment 17th Workshop on River Ice*. Edmonton, Alberta: CRIPE.

Delavau, C. J., Stadnyk, T., & Holmes, T. (2017). Examining the impacts of precipitation isotope input (δ18Oppt) on distributed, tracer-aided hydrological modeling. *Hydrology and Earth System Sciences,* 21(5), 2595-2614. doi:10.5194/hess-21-2595-2017

Eicken, H., Dmitrenko, I., Tyshko, K., Darovskikh, A., Dierking, W., Blahak, U., . . . Kassens, H. (2005). Zonation of the Laptev Sea landfast ice cover and its importance in a frozen estuary. *Global and Planetary Change, 48*(1-3), 55-83. doi:10.1016/j.gloplacha.2004.12.005

Environment and Climate Change Canada. (2018). *Canadian River Ice Database*. Data-Donnees.ec.gc.ca. https://data-donnees.ec.gc.ca/data/water/scientificknowledge/canadian-river-ice-database/?lang=en

Ferrick, M. G., Calkins, D. J., Perron, N. M., Cragin, J. H., & Kendall, C. (2002). Diffusion model validation and interpretation of stable isotopes in river and lake ice. *Hydrological Processes, 16*(4), 851-872. doi:10.1002/hyp.374

Environment and Climate Change Canada^1. (2018). Canadian Climate Normals. Retrieved 2018, from http://climate.weather.gc.ca/climate_normals/

Environment and Climate Change Canada^2. (2018). *Historical Data*. Retrieved 2018, from http://climate.weather.gc.ca/historical_data/search_historic_data_e.html

Gibson, J. J., & Prowse, T. D. (1999). Isotopic characteristics of ice cover in a large northern river basin. *Hydrological Processes, 13*(16), 2537-2548. doi:10.1002/(sici)1099-1085(199911)13:16<2537::aid-hyp940>3.3.co;2-1

Gibson, J. J., & Prowse, T. D. (2002). Stable isotopes in river ice: identifying primary over-winter streamflow signals and their hydrological significance. *Hydrological Processes, 16*(4), 873-890. doi:10.1002/hyp.366

Government of Canada. (2018). Real-Time Hydrometric Data Graph for LESSER SLAVE RIVER AT SLAVE LAKE (07BK001) [AB]. Retrieved June 25, 2018, from https://wateroffice.ec.gc.ca/report/real_time_e.html?stn=07BK001

Lesser Slave Watershed Council. (2018, April). Lesser Slave Integrated Watershed Management Plan. Lesser Slave Watershed Council. Retrieved November 12, 2022, from https://d3n8a8pro7vhmx.cloudfront.net/lswc/pages/25/attachments/original/1548791112/Lesser_Slave_IWMP_January_2019_Final.pdf?1548791112

Mckenney, D. W., Hutchinson, M. F., Papadopol, P., Lawrence, K., Pedlar, J., Campbell, K., . . . Owen, T. (2011). Customized Spatial Climate Models for North America. *Bulletin of the American Meteorological Society*, 92(12), 1611-1622. doi:10.1175/2011bams3132.1

O'Neil, J. R. (1968). Hydrogen and oxygen isotope fractionation between ice and water. *The Journal of Physical Chemistry*, 72(10), 3683-3684. doi:10.1021/j100856a060

St. Amour, N. A., Gibson, J. J., Edwards, T. W., Prowse, T. D., & Pietroniro, A. (2005). Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River basin, Northwest Territories, Canada. *Hydrological Processes, 19*(17), 3357-3381. doi:10.1002/hyp.5975

USGS. (2017, April). *Instructions for Collecting Samples*. Retrieved April, 2017, from https://isotopes.usgs.gov/lab/instructions.html

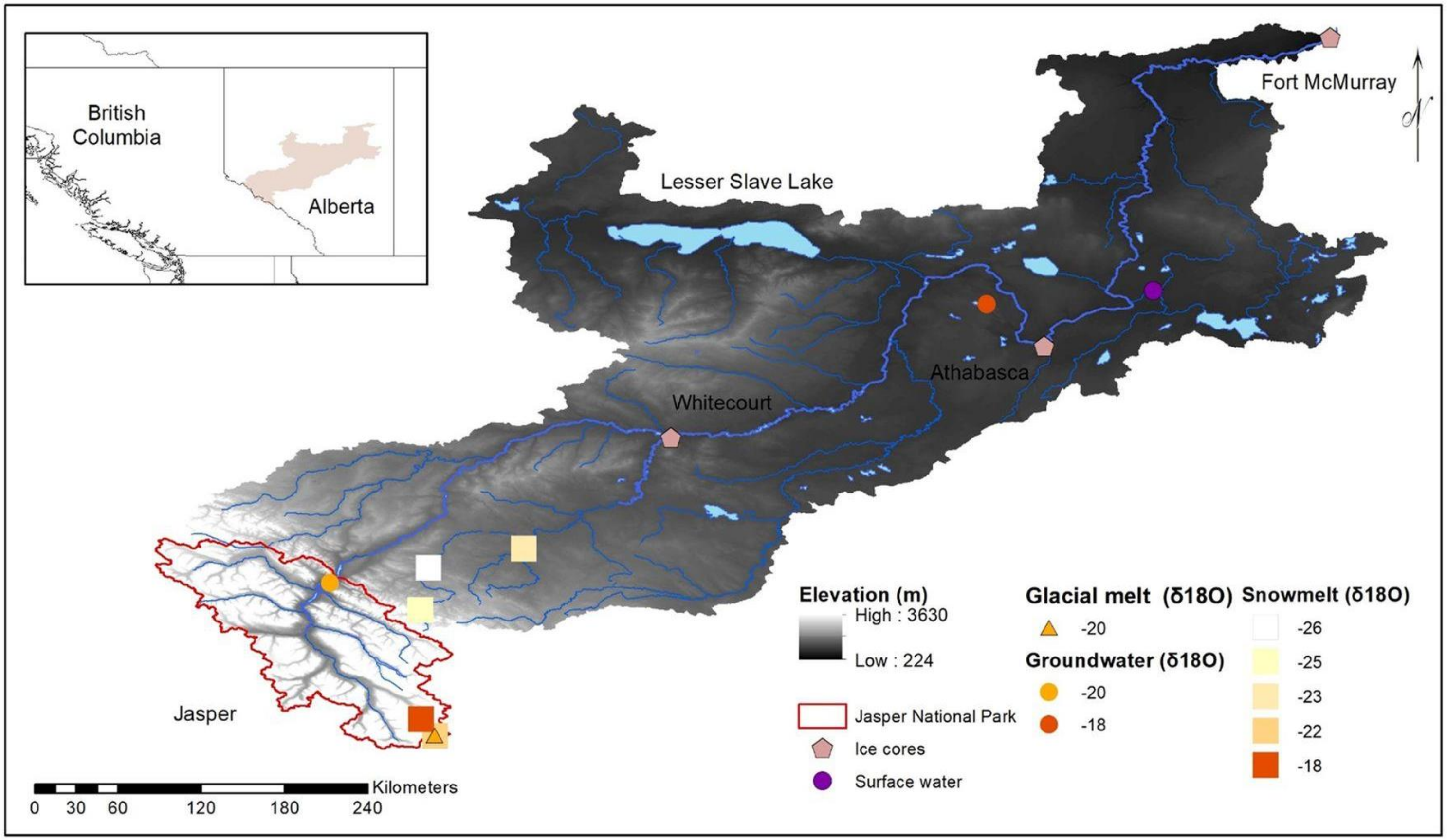


Figure 2.1: The Upper and Middle Athabasca watershed with source water locations for glacial melt, surface water, and winter sampling locations indicated. The isotopic composition of glacial melt, groundwater and snowmelt are displayed in ‰ $\delta^{18}O$.

Figure 2.2: Steps in the collection of ice core samples. A) The use of an auger to collect an ice core, B) the ice core after it had been removed, beside a metre stick for reference, C) a section of ice core separated by either a natural break or manual cut.

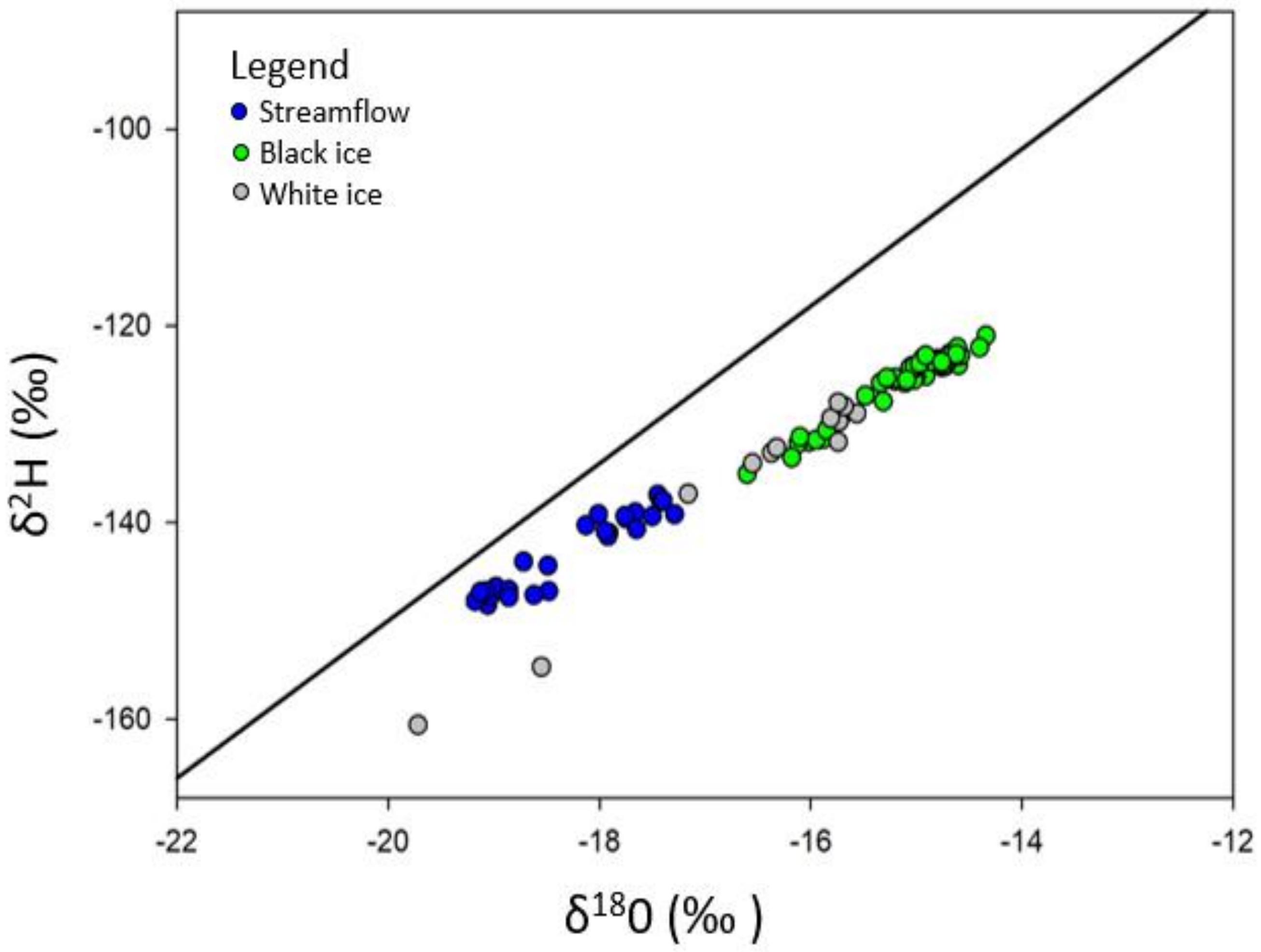


Figure 2.3: Delta-delta space displaying the isotopic values of the ice and streamflow samples collected during this study. The Global Meteoric Water Line is displayed as a solid line for reference.

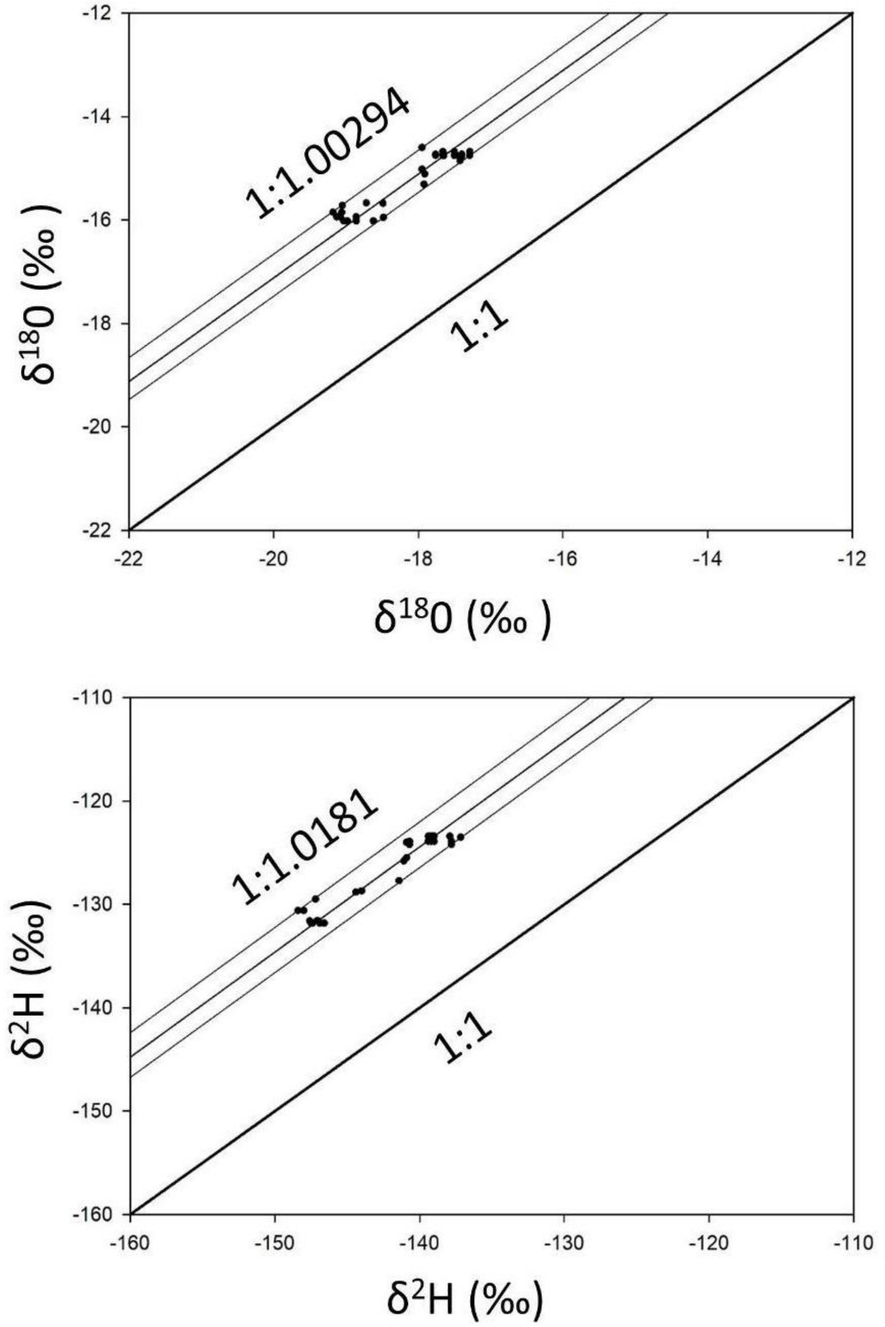


Figure 2.4: The range of fractionation found for both δ2H and δ18O calculated using the isotopic values of congelation ice and streamflow that corresponded by date. Fractionation had a range of 1.00341 to 1.00258 for δ18O and1.0209 to 1.0158 for δ2H. Lines depict minimum, maximum and average values (shown above).

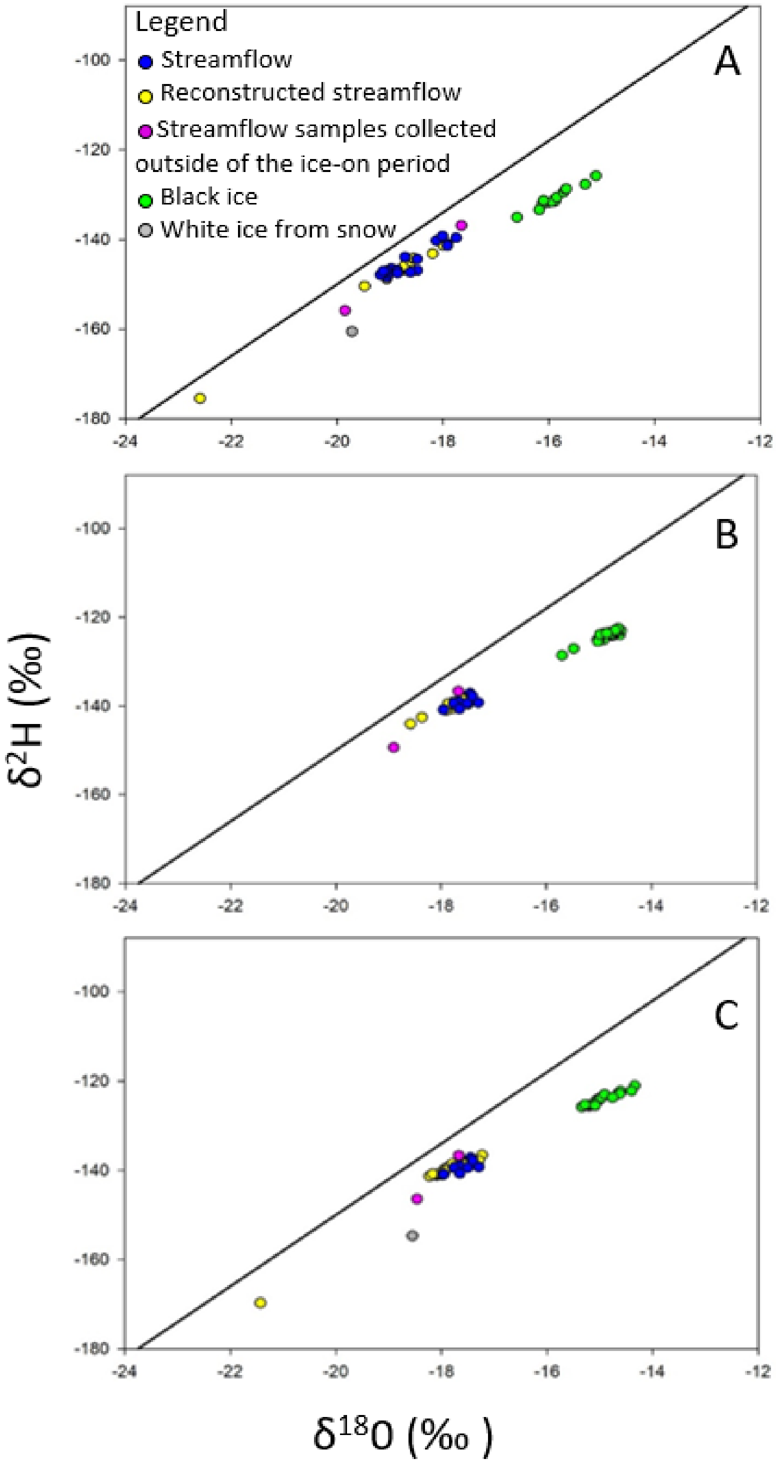


Figure 2.5: Delta-delta space for A) is Whitecourt, B) is Athabasca and C) Fort McMurray. Streamflow samples were not collected in Fort McMurray directly, with the exception of May 2017, due to this samples from Athabasca are displayed above for Fort McMurray. The GMWL is displayed as a solid line for reference.

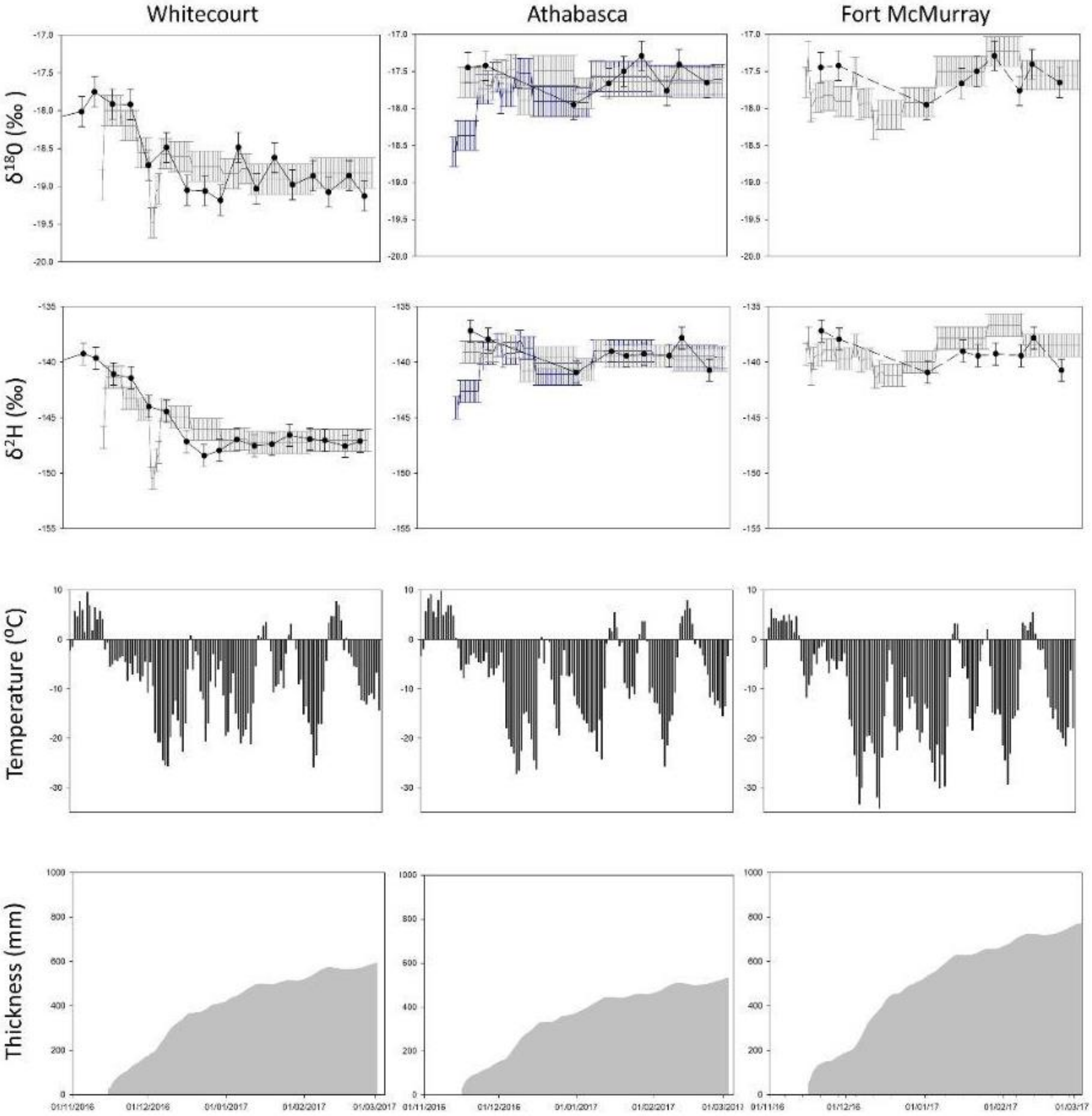


Figure 2.6: A comparison of the isotopic values of streamflow (black) and the reconstruction of streamflow (grey core 1, blue core two). Temperature and the ice growth model are also include. Error bars were determined using the values for instrumental uncertainty of 0.2 $\delta^{18}O$ and 1.0 $\delta^{2}H$. The values of streamflow for Fort McMurray are displayed as a dotted line as data from Athabasca was used.

Chapter 3. Assessing seasonal source water contributions in the Athabasca River Basin, Alberta, Canada

Abstract

The Upper and Middle reaches of the Athabasca River provide essential water resources for economic and environmental water needs in the Province of Alberta. While the Lower reaches of the Athabasca are the subject of many studies, stable water isotope analysis has been limited in the Upper and Middle Athabasca, leaving a gap in the understanding of how snow and glacial melt resources are translated into the freshwater supply. The McLeod, a sub-catchment in the Middle Athabasca was also analyzed to provide a comparison to the larger more complex Athabasca catchments. This analysis used hydrograph separation to explore source water trends in streamflow for snowmelt, glacial melt, groundwater and evaporatively enriched surface waters, such as lakes and wetlands, over a hydrological year from August 2016 to August 2017. Synoptic sampling campaigns were targeted to time periods when each source water would be at its highest contribution to streamflow. The results from this analysis provide a baseline understanding of spatial, seasonal and annual source water trends in the region. Key spatial trends included an accumulation in surface water downstream in the catchment, a result found in other studies in the region, and the identification of key inflows where snowmelt composes a high proportion of streamflow. Key seasonal trends included confirmation of dominant source waters and the importance of evaporatively enriched water sources to streamflow during low flow conditions. Analysis of annual trends identified that the source water proportions in the McLeod formed a cyclical pattern as seen in other catchments in the region. However, the Middle Athabasca did not display a cyclical pattern due to low source water variability over the year. Key differences in the source water trends in 2016 and 2017 were also noted. These differences were linked to temperature

and precipitation, where the conditions in 2016 resulted in a greater amount of glacial ablation and a shorter period when streamflow was fed by snowmelt. In comparison, the conditions in 2017 resulted in a larger snowpack which remained a key portion of streamflow in the Upper and Middle reaches of the Athabasca into the late summer. Maintaining snowpack into the late summer also reduced glacial ablation, resulting in glacial melt being a lower proportion of streamflow in 2017 in comparison to 2016. This analysis also demonstrated that the proportion of snowmelt could be traced from the headwaters of the Athabasca River to the outflow of the Middle Athabasca and that under some conditions, glacial melt proportions could also be traced into the Middle Athabasca despite the complexities of this large catchment. While this research offered a baseline into trends across the Upper and Middle Athabasca, future studies which could provide higher resolution sampling of streamflow and source waters across the catchment are recommended.

3.1 Introduction

Snow and glacial melt are essential water resources in the northern hemisphere and mountainous regions globally; however, due to the warming climate these resources are becoming reduced and the timing of snow and glacial melt entering streamflow is shifting. The Intergovernmental Panel on Climate Change (IPCC) has high confidence that global glacier extent is declining and that snowmelt is occurring sooner, affecting the seasonality of streamflow in snowmelt-dominated catchments and ultimately, the quantity of water available (IPCC, 2022). Warming trends are more pronounced in cold regions of the northern hemisphere, with the greatest warming occurring in winter months (Aygün *et al.,* 2020). While elevational warming trends are not still completely understood, warming typically occurs faster at higher elevations creating further impacts on mountainous regions (Pepin *et al.*, 2022, Rangwala *et al.,* 2015). Between 1967 and 2012 snowmelt in the northern hemisphere decreased by 1.6 % per decade in March and April and 11.7% per decade in June, and the largest reduction of snowpack is now occurring a month sooner than in previous decades (IPCC, 2015). Climate models are projecting the ratio of rainfall to total precipitation will increase in the northern hemisphere, reducing the snowpack further (Aygün *et al.,* 2020, IPCC, 2022). Due to the decreasing snow accumulation in the winter, followed by a shift to an earlier peak runoff, snowmelt-dominated regions are the areas most sensitive to warming temperatures (Barnett *et al*., 2005).

The most recent IPCC report indicated high confidence in the link between reduced water resources in snowmelt-dominated catchments and resulting negative effects on human systems and ecosystems (IPCC, 2022). This can be linked to the occurrence of earlier peak runoff caused by climate change, which is often too large to be captured and stored by reservoirs, leading to reduced availability of water resources later in the dry season (Barnett *et al.,* 2005). Climate change scenarios also predict larger, more frequent forest fires and hydro-climatic extremes, such as floods and droughts; this is expected to lead to anthropogenic changes in behavior, such as increased energy demands during extreme high and low temperatures (Eum *et al.,* 2017; IPCC 2022; Prowse *et al.,* 2006; Voutchkova & Miller, 2017). In snowmelt-dominated regions, baseline and modeled future conditions for annual snow and glacial melt are needed by water resource managers to determine strategies for water use and storage, including balancing allocations for anthropogenic uses (such as domestic use, industry, agriculture, tourism, recreation and hydropower) and water requirements for ecological processes (Prowse *et al.,* 2009; Voutchkova & Miller, 2017).

Having a baseline of the relative magnitudes of contributions from different source waters is key to making water management decisions. Stable water isotopes (SWI) have been used as a tracer in a range of scales, from micro to continental, and across a variety of ecosystems, including remote areas where other methods are not feasible (Birks & Gibson 2009; Edwards *et al.,* 2004). SWI are an ideal tracer as they occur naturally and are conservative and their values change systematically through water cycle phase changes (Birks & Gibson 2009). The ability to differentiate water based on the processes it has undergone allows SWI to be used for identifying different source waters in streamflow (such as surface water, snowmelt, glacial melt and groundwater) and quantifying the proportions of each water source in a sample (Gibson *et al.,* 2005). Therefore, SWI represents a key method for researching environmental change and supports many applications, such as water resource management, including the advancement of our understanding of hydrological processes and pathways, forecasting of water availability during extreme conditions, such as floods and droughts, and exploring impacts related to climate change (Aggarwal *et al.*, 2005; Gibson *et al.,* 2021).

SWI have been used extensively in hydrological research, however, research has largely focused on headwater regions and small catchments. Larger catchments can provide insight into large-scale hydrological patterns but research has been previously limited due to the increased complexity of these systems. This has resulted in calls for additional research in larger catchments with less existing instrumentation (Aggarwal *et al.,* 2005; Gibson *et al.*, 2005; Hemming *et al.,* 2007). In response to this knowledge gap, Gibson *et al.*, (2020) and Gibson *et al.*, (2021) completed the first Canada-wide study and isotope data set, which is applicable to a variety of water management purposes. However, future work is still needed as many large catchments have not been studied and do not have records of baseline conditions.

The objective of this study is to determine the proportions of seasonal source waters in the Upper and Middle Athabasca Watershed and explore spatial, seasonal and annual trends. This will be accomplished using stable water isotopes (SWI). This work builds on the winter streamflow dataset obtained in Chapter 2. In addition, this study will also compare trends from the Athabasca River to a smaller sub-catchment, the McLeod River. Results from this study will provide information on current seasonal source water proportions as a baseline for water resource managers.

3.2 Theory

3.2.1 Source water characteristics

In snowmelt-dominated catchments, streamflow is often dependent on source waters from headwaters, typically precipitation-derived snow and glacial melt, which mixes with groundwater and enriched surface water bodies downstream. Precipitation in liquid form is episodic, while snow and ice are stored and released continuously as snowmelt (a mixture of winter precipitation) and glacial melt (a mixture of long-term precipitation). Groundwater is typically recharged by precipitation or seasonally by snow and glacial melt, as dependent on local factors such as topography and geology, which means groundwater is composed of water sources that have undergone limited evaporation (Fan *et al.*, 2014; Penna *et al*., 2014; Yang *et al.*, 2011). Evaporation occurs in surface water bodies such as lakes and wetlands, where water has relatively long residence times (Yi *et al*., 2010).

3.2.1.1 Isotopes in precipitation

Precipitation exhibits a linear relationship between the SWI ^{18}O and ^{2}H, which has been averaged globally to form the Global Meteoric Water Line (GMWL), $\delta^2H = 8\ \delta^{18}O + 10$ (Craig, 1961). Variation in regional or local precipitation can also be expressed by local meteoric water lines (LMWL) (Kendall & McDonnell, 1998). Isotopic values for precipitation are highly variable over space and time depending on the SWI composition of the original water source and the frequency of evaporation and condensation of the precipitation (Kendall & McDonnell, 1998). Due to this, air masses originating from different locations can produce significantly different isotopic values for precipitation over the same area (Kendall & McDonnell, 1998). Fractionation of SWI is influenced by temperature, with colder temperatures resulting in an increased depletion of SWI as less evaporation occurs (Kendall & McDonnell, 1998). This can be seen seasonally with winter precipitation being more depleted than summer precipitation by approximately 0.5‰ per °C for $\delta^{18}O$ (Dansgaard, 1964; Edwards *et al.,* 2004).

Altitude effects can also be observed where the isotopic composition for precipitation becomes more depleted as altitude increases due to orographic effects at a rate of ~0.28 ‰ $\delta^{18}O$ per 100m for elevations below 5,000 m (Poage & Chamberlain, 2001). In snowmelt-dominated catchments, an altitude effect is common due to the higher elevations present in mountainous headwaters (Dalai, Bhattacharya & Krishnaswami, 2002; Jeelani *et al*., 2016; Meier *et al*., 2013; Ramish &Sarin, 1992). In addition, as air masses pass over mountain ranges they become increasingly depleted as the heavy isotopes condense first at lower elevations, leaving a higher ratio of light isotopes to precipitate out at higher elevations.

3.2.1.2 Isotope Fractionation of surface water

In surface water, fractionation occurs during evaporation or freezing. Under evaporative conditions, lighter isotopes will evaporate out of the water first, leaving a higher ratio of heavier isotopes. This creates an evaporatively enriched source water, where the isotopic composition has a shallower slope on a plot of $\delta^{18}0$ and $\delta^{2}H$, often referred to as delta-delta space when compared to precipitation. This is because ^{2}H fractionates more strongly than ^{18}O during evaporation. Regionally, water with similar inputs but differing amounts of evaporation will lie on a Local Evaporation Line (LEL), which has a linear relationship between $\delta^{18}O$ and $\delta^{2}H$ (Gibson *et al*., 2005). The LEL typically has a slope between 4 and 6 in Canada, depending on the atmospheric conditions such as humidity and temperature (Edwards *et al*., 2004). In large catchments where inputs from multiple bodies of water are present, the isotopic composition for streamflow becomes more positive as you move downstream due to the cumulative effects of evaporatively enriched water mixing with streamflow (Yi *et al.,* 2010).

3.2.1.3 Mixing of source waters

The isotopic composition of streamflow over space and time changes proportionately due to the inflows of different source waters. The proportions of inflows can be measured, where for example the change in the isotopic composition of the main channel above and below a tributary is proportional to the volume of water entering from the tributary relative to the isotopic composition of the tributary. In cold regions experiencing seasonal variability, a cyclical pattern in the isotopic composition of streamflow may occur (St. Amour *et al.*, 2005). The seasonal cycle can be simplified to the following processes which influence the isotopic composition of streamflow. During the winter, when ice cover is present, streamflow is largely composed of groundwater. When spring freshet begins, the isotopic composition of streamflow shifts to become more negative due to the influence of snowmelt. Following the freshet, warm temperatures evaporatively enrich the signature of surface water bodies, which mix with streamflow and create a more positive isotopic composition. Finally, streamflow returns to being largely composed of groundwater during the winter when ice cover reduces the influence of evaporative sources to streamflow and the cycle begins again.

3.2.2 Seasonal collection of stable water isotopes

SWI studies in snowmelt-dominated catchments often report on one to two hydrologic years, where annual variability in streamflow is captured in "snap-shots". Due to the importance of snowmelt contributions to streamflow during the spring melt, and glacial melt during late summer, the times commonly studied are spring and late summer (Cable *et al*., 2011; Marchina *et al*., 2014; Sun *et al*., 2016; Williams *et al*., 2016). In glacially-fed headwater catchments, either glacial melt and/or snowmelt typically make up high contributions to streamflow in summer low-flow conditions (Cable *et al*., 2011; Fan *et al*., 2014; Fan *et al*., 2016; Jeelani *et al*., 2016; Kong & Pang, 2012; Marchina *et al*., 2014; Penna *et al*., 2014; Sun *et al*., 2016; Williams *et al*., 2016). Downstream of the headwaters, streamflow can include evaporatively enriched water sources when water was held in reservoirs, or the velocity was slowed by plains or deltas (Marchina *et al*., 2014; Rock & Mayer, 2007; Sun *et al*., 2016).

Hydrological research during ice-on periods is underrepresented in the literature. A better understanding of this time period is becoming increasingly imperative as winter warming trends are leading to shifting hydrological patterns (Prowse and Beltaos, 2002). The limited research available during ice-on conditions is in part due to the difficulty associated with reaching remote areas in winter conditions and sampling streamflow below ice cover. River ice stratigraphy, while not extensively tested, is promising as a proxy of hydrologic conditions over the ice growth period in cold climates where the winter temperatures stay consistently below zero (Gibson & Prowse, 1999, 2002). Cold temperatures preserve a seasonal record in the ice and, by combining this with the ice growth rate, a timeline of the conditions when the layers of ice formed can be reconstructed. To date, SWI collected from river ice cores have been used with success when compared to experimental results (Gibson and Prowse,1999; 2002). In Chaper 2 of this thesis, this methodology is further tested with the results supporting this methodology as a potential solution to data gaps in hydrological studies during the ice-on period. Further work would allow source water contributions of winter streamflow to be calculated.

3.2.3 Hydrograph separation

In order to partition a streamflow sample into the various source waters it is composed of hydrograph separation is a methodology that is frequently used. SWI are the most used tracers in hydrograph separation (Birks & Gibson 2009), as source waters are naturally isotopically labeled. This is due to the systematic fractionation source waters have undergone during the hydrologic processes they underwent to reach their current location, which results in source waters typically differing isotopically from one another (Gibson *et al.*, 2016). Using multiple tracers allows for the use of more source waters to be included in the analysis as well as more complex hydrograph separation techniques (Klaus & Mcdonnell, 2013). Electrical conductivity is commonly used in combination with stable water isotopes (Jeelani *et al*., 2016; Lambs 2000; Penna *et al*., 2014).

Hydrograph separations utilizing stable water isotopes have been widely used in a variety of environments and catchment sizes to improve our understanding of hydrologic systems (Gibson *et al.,* 2005). In snow and glacialmelt-dominated catchments, the majority of analyses to partition sources to streamflow is done using both a two and three-component hydrograph separation (Fan *et al.*, 2014; Jeelani *et al.*, 2016; Kong & Pang, 2012; Williams *et al*., 2016). Studies of larger catchments rarely quantify sources to streamflow, instead opting to simplify this process by looking at trends and comparing the value of streamflow to the value of source waters (Lambs *et al.*, 2012; Marchina *et al.,* 2014; Meier *et al*., 2013), or to provide overall general values for the river or region (Fan *et al.*, 2014; Fan *et al.*, 2016; Sun *et al.*, 2016). This is because large catchments are complex, reflecting the cumulative influence of a variety of hydrological processes (Gibson *et al*., 2005).

3.3 Study area

The Athabasca River Basin (ARB) is a large snowmelt-dominated basin, that provides key economic and environmental benefits. The Athabasca River is the largest unregulated river in Alberta, with the ARB covering approximately 24% of the province (Athabasca River Basin Research Institute, 2022). The headwaters for the Athabasca River are located in the Columbia Icefield, on the Eastern slopes of the Canadian Rocky Mountains. From the headwaters, the Athabasca River flows 1500km northeast, eventually draining into the Arctic Ocean. The ARB itself is home to approximately 170,000 residents who live in largely rural areas; the region has fourteen Indigenous reserves, one city, twelve towns and twenty-two municipalities (Athabasca River Basin Research Institute, 2022).

The Athabasca watershed is divided into three segments: the Upper, Middle and Lower Athabasca. This study will focus on the Upper and Middle reaches of the ARB (figure 3.1). The Upper Athabasca has mountainous terrain, including alpine glaciers and is largely protected within the boundaries of Jasper National Park terminating at the Town of Whitecourt. The Middle Athabasca begins with forested foothills, many of which contain coal, before flowing through urban and agricultural areas. This section of the Athabasca has three main tributaries: the McLeod, Pembina and Lesser Slave, two large water bodies: Lesser Slave Lake and Lac La Biche and many wetlands which become more numerous as you move downstream. There are also several moderately sized urban centers (population 8,000-10,000) in the Middle Athabasca, these include Hinton, Edson and Whitecourt. Overall, the study area is composed largely of forested areas (37%) and wetlands (32%), with developed areas accounting for less than 1% of the area.

The Lower Athabasca, which is excluded from this study, begins at the City of Fort McMurray and contains the Canadian oil sands. The Athabasca River terminates at Lake Athabasca before draining into the Peace Athabasca Delta (PAD). The PAD is located within Wood Buffalo National Park, an area recognized for its global significance through a World Heritage Site designation bestowed by the United Nations Educational, Scientific and Cultural Organization (UNESCO). This recognition is due to the unique characteristics of the PAD, as it contains a large inland freshwater delta, salt plains, many migratory bird species and free-roaming wood bison (UNESCO World Heritage Centre, 2022).

The Athabasca River is vital to economic and domestic activities in the region including agriculture, forestry and recreation, tourism, electrical power generation and oil sands operations (Cheng *et al*. 2017; Eum *et al*. 2017; Prowse *et al*., 2009; Rood *et al*. 2015). Approximately 5% of the annual flow from the Athabasca River is allocated to water resource users (Government of Alberta, 2017). Water needs are expected to increase for industry, agriculture, commercial, municipal and habitat enhancement projects (AMEC Earth & Environmental, 2007). However, Climate change poses a serious threat to the stability of water resources in the ARB and increased industrialization coupled with population growth will only further pressure the system, threatening to reduce the water needed for ecosystem services.

Over the past 100 years, the temperature over the ARB has generally increased, with the greatest warming occurring downstream and during the winter months (Cheng *et al*., 2017). Temperature is projected to increase significantly in the ARB, resulting in warm, drought-like summers (Bonsal & Cuell., 2017; Cheng *et al*., 2017; Lima & Wrona, 2019; Zhou *et al*., 2018). Warming winter temperatures are expected to shift a portion of precipitation, which currently falls as snowfall, to rainfall; this would lead to an increase in snowmelt and snow ablation over the entire watershed, with the reductions being most pronounced in the high elevations of the Upper Athabasca (Dibike *et al*. 2018b). This is projected to decrease snow cover duration by up to 50 days and reduce water storage held in the headwaters as snow (Dibike *et al*. 2018b). In addition, ice cover formation has also shifted from late October, now occurring in early November, with breakup typically occurring at the end of March or early April (Hutchison and Hicks, 2007; Pietroniro *et al*., 1998; Prowse *et al*., 2007; She *et al*., 2009).

Streamflow in the ARB peaks in June or July, following peak snowmelt in late April or May and low flow conditions occur in December (Burn *et al*., 2004). Historically, there has been a decreasing trend in mean streamflow (Bawden *et al*., 2014; Burn *et al*., 2004; Peters *et al*., 2013; Schindler & Donahue, 2006; Zhang *et al*., 2001). This has been linked to reductions in precipitation (Peters *et al*., 2013) and reductions in snow accumulation in elevations below 2500m, which have been found to be vulnerable to loss of snowpack (Newton *et al*., 2019). This has led to measurable changes in local flow patterns, with discharge into Lake Athabasca being reduced by 21% between 1960 and 2010 (Rasouli *et al*., 2013). Future streamflow is projected to increase by approximately 25% in the winter, resulting in an earlier, larger freshet, with decreases in the late spring and summer flows of approximately 50% (Eum *et al*., 2017, Dibike *et al*. 2018, Leong and Donner, 2016).

The ARB is predicted to experience more frequent hydro-climatic extremes due to climate change, such as flooding, drought and wildfires (Prowse *et al*., 2006; Cheng *et al*. 2017). Drought is of particular concern for the ARB, as snow accumulation and melt maintain summer streamflow, sustaining industrial activities and aquatic habitats (CEMA, 2006). Large-scale droughts could impact the viability of the oil and gas industry and negatively impact aquatic ecosystems (Cheng *et al*., 2017; Dibike *et al*., 2018; Lima & Wrona, 2019). In assessing the future water management options for the ARB, Leong & Donner (2016) found that additional water storage will be required to maintain industrial water usage, as future conditions are likely to result in interrupted production of oil and gas or reduced ecosystem function.

To date there has been limited work done on the Upper and Middle Athabasca utilizing SWI. The isotopic signature of the meltwater from the Athabasca Glacier has been collected in two recent studies; with results showing similar values over multiple years (Arendt *et al.,* 2015; Robbins 2019). In addition, four sites within the Upper and Middle Athabasca were sampled every 1-12 months between 2013 and 2019 as part of Canada's first baseline stable isotope dataset for rivers (Gibson *et al.,* 2020). Downstream in the Lower Athabasca extensive hydrological research has been conducted, with the focus of SWI studies being groundwater and surface water pathways, but to date neither snow or glacial melt contributions to streamflow have been explored in the Lower Athabasca (Birks *et al.*, 2017; Birks *et al.*, 2019; Gibson *et al.*, 2011; Gibson *et al.*, 2016).

3.4 Methodology

3.4.1- Field collection

Synoptic SWI sampling campaigns, each occurring over three days and covering up to forty-three study sites were conducted in and around the Athabasca watershed in August 2016, May 2017 and August 2017. Sampling in May 2017 and August 2017 expanded sampling from August 2016 to include Lac La Biche and the Athabasca River at Fort McMurray. Sampling was done to target the main channels and major tributaries of the Athabasca and McLeod Rivers. Sampling was timed to capture seasonal highs of snowmelt in May and glacial melt in August, which were identified in the headwaters of the Athabasca River by Arendt *et al.* (2015).

Time-series of SWI samples were collected from streamflow at two locations between October 2016 and February 2017. The water treatment centre for the Town of Whitecourt collected eighteen samples from the McLeod River, before the convergence with the Athabasca River. The Aspen Regional Water Services Commission collected nine samples from the Athabasca River, at the Town of Athabasca. In March 2017 ice cores were collected at Whitecourt, the Town of Athabasca and Fort McMurry (figure 3.1). Utilizing a novel methodology presented by Gibson and Prowse (1999, 2002), a reconstruction of the isotopic composition of the winter streamflow was generated from the ice cores using the calculated ice-water fraction value. More details on the collection of this data and associated analysis can be found in Chapter 2 of this thesis.

All samples of river water were collected in 30 ml Scintillation Vials following the USGS (2017) and IAEA (2017) sampling procedures. Sampling locations with fast-moving water and away from convergences of tributaries were selected to ensure the samples would be fully mixed and representative of streamflow. In the winter, river water was collected after it had been pumped into testing facilities. Following USGS recommendations, samples were stored at ambient temperature in the summer as they were processed within one week of collection. Samples were stored in the refrigerator for up to five months in the winter before processing (USGS, 2017). In May and August of 2017, a YSI probe was used to provide electrical conductivity (EC) measurements as a secondary tracer, in conjunction with the SWI sampling. However, EC was not found to have distinctive values for each of the source waters and was therefore not included in this analysis.

Previous studies determined that the source water types in the region were glacial melt, snowmelt, groundwater and surface water (Arendt *et al.* 2015; Birks *et al*., 2017; Birks *et al.*, 2019;

Gibson *et al*., 2011; Gibson *et al*., 2016; Robbins 2019). SWI were not collected for glacial melt from the terminus of the Athabasca glacier as these values were recently reported over multiple years by Arendt *et al.* (2015) and Robbins (2019). In May 2017, six snow samples were collected in the study area (figure 3.1). One of these samples, which was collected near Athabasca Falls, was removed from this analysis as isotope analysis indicated river water had contaminated the sample. During the SWI analysis, one of the samples collected in May 2017 at the Athabasca Glacier was also classified as 100% snowmelt. Snow samples were collected in tightly sealed bags and allowed to melt at an ambient temperature before SWI samples were collected and electrical conductivity was measured. In August 2017, three groundwater SWI samples were collected in the Upper and Middle Athabasca from wells (figure 3.1). One of these samples, collected from the McLeod River Provincial Recreation Area, was removed from the analysis as there were concerns that this sample was contaminated by river water. This was supported by isotopic analysis and a water drinking ban enforced on the water from this well. In the collection of groundwater samples, wells were purged until a stable reading for temperature and electrical conductivity was reached. Surface water was not directly collected, but tributaries from large water bodies were sampled, such as Lesser Slave River and Lac La Biche River. SWI analysis confirmed that evaporation had occurred at both of these locations. Aside from snowmelt, other forms of precipitation were not included as source waters in this study. To ensure other forms of precipitation were not key source waters, sampling was conducted following periods with little to no precipitation.

3.4.2 Isotope analysis

Stable isotopes are expressed in permil (‰) relative to Vienna Standard Mean Ocean Waters (VSMOW). Stable water isotope samples collected from streamflow, groundwater and snowmelt were processed at the InnoTech Alberta Isotope lab at the Vancouver Island Institute of Technology, using a Thermo-Fisher Delta V Advantage IRMS with HDevice and Gasbench. Instrumental uncertainty was reported as +/- 0.2‰ ^{18}O and +/- 1.0 ‰ ^{2}H. In lab duplicates from streamflow, samples had a maximum Standard deviation of 0.1‰ ^{18}O and 0.6‰ ^{2}H. Duplicates from the field accounted for 13% of total samples and had a maximum difference of 0.20 ‰ ^{18}O and 0.43 ‰ ^{2}H. Additional information on the isotope analysis for the ice can be found in Chapter 2 of this thesis.

3.4.3 Partitioning of source waters

The Athabasca is a large, complex watershed with seasonal variation. Due to this complexity, when partitioning streamflow into source waters a combination of both two and three-component hydrograph separations were used based on the identification of source waters for each site. Hydrograph separations were conducted for each synoptic survey and the winter period. For each synoptic survey, the study area was broken up into the Upper Athabasca, Middle Athabasca and McLeod. The following equations conceptualize hydrograph separation in the Athabasca River:

$$Q_T = Q_1 + Q_2 + Q_3 \ldots Q_n \quad \text{Where } Q_T = 1 \qquad (3.1)$$

$$1 = Q_M + Q_S + Q_G + Q_L \qquad (3.2)$$

where total streamflow (QT) is the sum of all the proportion of each of the source waters and equal is to 1 (equation 1). This can be rearranged to include the source waters from this study, glacial melt (M), snowmelt (S), groundwater (G) and surficial water (L), where the total streamflow is equal to 1 (equation 2). For this study, of the ARB glacial melt and surface water values were static across the analysis, while the values for snowmelt and groundwater varied regionally based on the locations of the samples collected in the field.

Two-component separations utilized a single tracer, ^{18}O (O), where the two-component separation is similar to equation 1 but the proportion (Q) is replaced with a tracer (O) (equation 3). By rearranging equation 3 the proportions of both of the source waters can be calculated (equations 4 & 5).

$$O_t = O_1 + O_2 \quad (3.3)$$

$$\frac{O_1}{O_T} = \frac{O_{T-}O_2}{O_1 - O_2} \quad (3.4)$$

$$\frac{O_2}{O_T} = \frac{O_{T-}O_1}{O_2 - O_1} \quad (3.5)$$

Three-component separations require two tracers and utilized ^{18}O (O) and ^{2}H (H) as the tracers. Three-component separations are similar to equation 1, where the proportions (Q) are replaced with both tracers (O & H) (equations 6,7,8). By rearranging and substituting the equations the proportion of each source water can be calculated (equations 9,10,11) (Jelinii 2016).

$$O_T = Q_1 O_1 + Q_2 O_2 + Q_3 O_3 \quad (3.6)$$

$$H_T = Q_1 H_1 + Q_2 H_2 + Q_3 H_3 \quad (3.7)$$

$$O_T H_T = Q_1 O_1 H_1 + Q_2 O_2 H_2 + Q_3 O_3 H_3 \quad (3.8)$$

$$Q_1 = \frac{O_T H_2 - O_T H_3 + O_2 H_3 - O_2 H_T + O_3 H_T - O_3 H_2}{O_1 H_2 - O_1 H_3 + O_2 H_3 - O_2 H_1 + O_3 H_1 - O_3 H_2} \quad (3.9)$$

$$Q_2 = \frac{O_T H_3 - O_T H_1 + O_1 H_T - O_1 H_3 + O_3 H_1 - O_3 H_T}{O_1 H_2 - O_1 H_3 + O_2 H_3 - O_2 H_1 + O_3 H_1 - O_3 H_2} \quad (3.10)$$

$$Q_3 = \frac{O_T H_1 - O_T H_2 + O_1 H_1 - O_1 H_T + O_2 H_T - O_2 H_1}{O_1 H_2 - O_1 H_3 + O_2 H_3 - O_2 H_1 + O_3 H_1 - O_3 H_2} \quad (3.11)$$

In utilizing hydrograph separation to quantify each source water several assumptions are made: 1) the source waters are significantly different from one another, 2) the values for source waters are constant over space and time and 3) contributions from other sources are negligible (Klaus & Mcdonnell, 2013). These assumptions cause some limitations on the data being generated as they cannot always be fully met. Despite this, hydrograph separation has been proved to provide highly valuable results globally in a variety of environments (Gibson *et al.,* 2005).

3.4.4 Source water identification

In determining which source waters were likely to be present at each site the study area was broken down into the Upper Athabasca, Middle Athabasca, the McLeod and tributaries of these three catchments. In the Upper Athabasca, the main channel had the potential to be composed of glacial melt, snowmelt and groundwater. In the tributaries of the Upper Athabasca, the same three source waters were used, however, some tributaries did not come from glaciated areas and was therefore removed as a source water for these locations. The Middle Athabasca had the same potential source waters as the Upper Athabasca, with the addition of surface water. Glacial melt was removed as a source water for the Middle Athtbasca for August 2016 and winter 2016-2017. This was due to higher than possible proportions of streamflow at these locations, that increased in proportion moving downstream away from a glacial source. These values could not be explained by the local hydrology and were removed as errors that were likely caused by low spatial data for the source waters. The tributaries in the Middle Athabasca, the McLeod and the tributaries of the McLeod had the potential to be composed of snowmelt, groundwater and surface water.

In determining the SWI composition for source waters for hydrograph separation, the following procedure was used. The SWI composition of glacial melt used the value reported by Arendt *et al.* (2015). Two groundwater samples were used in calculating the SWI composition for groundwater. The sample collected in the Upper Athabasca was used as the SWI composition of groundwater in the Upper Athabasca tributaries in the Upper Athabasca and for the upper three samples in the McLeod River. The sample from the Middle Athabasca was used for the SWI composition of groundwater for tributaries of the Middle Athabasca and the Mcleod. Finally, an average of the two groundwater samples was used for samples of the Athabasca River in the Middle Athabasca and the lower portion of the McLeod River. The value for surface water was selected from Lac La Biche in 2017 as this was the most evaporatively enriched sample in the study.

The SWI composition of snowmelt across the ARB was highly variable when compared to the other source waters. In the Upper Athabasca there were two potential values for snowmelt. The most commonly used value came from a sample of meltwater collected at the Athabasca Glacier in May 2017. The value of this sample was 0.59‰ δ18O, which was more depleted than a snowmelt sample collected in the Upper Athabasca further downstream at Beauty falls. The sample of meltwater was selected as one of the source water values for snow as it came from a higher elevation and was more depleted, which provided a more diverse range of values for source waters, which is preferential for hydrograph separation. For select samples in the Upper Athabasca, a secondary snowmelt value was used where snowmelt was likely present but the hydrograph separation was not capturing this. This secondary snowmelt value was also collected at the Athabasca Glacier but was not as isotopically depleted as the other snowmelt sample had a difference of +3.95‰ δ18O. In the McLeod, three snowmelt samples were collected and were averaged for the source water value. This averaged value was also used for the tributaries in the Middle Athabasca. For the main channel of the Middle Athabasca, the source water value from snowmelt was calculated by averaging the snowmelt value for the McLeod with the more common snowmelt value from the Upper Athabasca.

3.4.5 Limitations in source water values

This methodology has several limitations linked to the low resolution of source water data collected. Source water samples were assumed to be consistent across multiple seasons and large areas. In addition, limited source water sampling occurred over time and a low density of source water samples were collected, reducing the accuracy of SWI values for source waters. This is especially true for snowmelt, where the limited samples that were collected showed a high degree of variability, even for samples collected at similar elevations. Due to the large size of the ARB and the low density of source water sampling, the calculated proportions of source waters in streamflow should be viewed as approximations and not true values. Smaller-scale analysis of the ARB would require high-resolution sampling to have a more accurate calculation for source water contributions to streamflow.

3.5 Results and Discussion

3.5.1 Key trends

During the three synoptic surveys, a key trend that emerged was that in general the isotopic composition of streamflow became more positive downstream in both the Athabasca and McLeod Rivers, where distance is measured along the flow path (figure 3.2). This is caused by the mixing of tributaries entering the main channel, as the tributaries to the Athabasca and McLeod often have a more positive isotopic composition than the main channels. This is supported by a study of the Mackenzie River that indicated similar patterns (Yi *et al.*, 2010). The exception to this occurs in the headwaters of the Athabasca and McLeod Rivers, where samples were taken from the main channel do not always have a more negative isotopic concentration than the samples downstream of them and tributaries do not always have a more positive signature. This likely occurred due to the high presence of snowmelt in the headwaters, which has a high degree of variation, the lack of isotopically enriched surface water sources, and the lower volume of water in the main channel which allows the mixing of inputs to more easily affect the overall signature. For example, in August 2017, the first samples in the Athabasca River are more positive than the following samples. These samples were taken from above and below Sunwapta Lake, which is located in front of the Athabasca Glacier and potentially had a higher percentage of glacier melt giving them a more positive isotopic composition than the following downstream samples, which are likely derived from a larger percentage of snowmelt. Similarly, in the headwaters of the McLeod River in August 2016 and May 2017, the most upstream sample has a more positive signature than those directly downstream. Samples from neighbouring catchments to the headwaters of the ARB had similar SWI values. This indicated that neighbouring headwater basins source waters have undergone similar processes.

3.5.2 Trends in the Upper Athabasca, Middle Athabasca and McLeod

Displaying the isotopic composition from each of the three synoptic surveys on a map and using delta-delta space plots allowed spatial and seasonal trends to be observed (figures 3.3- 3.5). During all three surveys, streamflow samples in the delta-delta plots appear to be mostly contained between the source waters glacial melt, snowmelt, groundwater and evaporatively enriched surface water. Groundwater appears central in all of the plots and therefore likely contributed a large component of the water samples collected. Of the three synoptic surveys, May had the most negative isotopic composition, which appears to be due to the prevalence of snowmelt at this time.

The Upper Athabasca had several samples of interest that require discussion (figure 3.4). In May, two of the streamflow samples were more negative than the snow samples collected. These samples likely had high concentrations of snowmelt, resulting in more negative SWI values due to the limited sampling and high variation present in snowmelt. Only two snowmelt samples were collected from Upper Athabasca, which varied by +/-1.56‰ $\delta^{18}0$ and +/-4.95‰ $\delta^{2}H$, demonstrating the high variability of snowmelt in the region. This is especially evident as the two samples collected had similar elevations and snowmelt from different elevations would demonstrate even greater variation due to orographic effects (Poage & Chamberlain, 2001). This also explains why the streamflow in the Upper Athabasca had higher variability in May than in August of 2016 and 2017. In August 2016 and 2017, some of the samples in the Upper Athabasca are above the GMWL, indicating the presence of glacial melt. The samples from the Upper Athabasca in August 2016 and 2017 had the least variation of any of the regions or time periods sampled; this is likely due to the limited input of source waters at this time, including a lack of highly evaporated source water and limited snowmelt.

Reviewing the spatial and seasonal trends for the Middle Athabasca, there was a more positive isotopic composition for the tributaries than the Athabasca River (figure 3.4). This is linked to the presence of large water bodies and wetlands and is supported by the lower slopes these samples have in the delta-delta plots indicating evaporation has occurred. In August 2016 and 2017, all of the tributaries indicate evaporation, however, in May 2017, the only site which appears to exhibit traits of evaporation is Lac la Biche. This indicated that Lac la Biche may be supplied by evaporative source waters maintaining a high isotopic concentration over the winter months. Further multi-year sampling from this location would be required to confirm this.

Reviewing the spatial and seasonal trends for the McLeod indicated that streamflow in May appears to be largely composed of groundwater and is shifted down the GMWL due to the presence of snowmelt (figure 3.5). In comparison, streamflow in August 2016 and 2017 appears to be largely composed of groundwater and is shifted towards the evaporative water source. Samples in 2017 have a shallower slope in comparison to 2016, indicating evaporation was likely more prevalent at this time.

3.5.3 Source water contributions

Source water contributions to the Upper Athabasca, Middle Athabasca and the McLeod were calculated for each of the three synoptic sampling surveys and are displayed both as ternary plots and as how source waters change moving downstream from the headwaters of the rivers (figure 3.6-3.8). Overall, in each of the three regions, groundwater made up the largest portion of streamflow, contributing over 50% of groundwater at 79% of the sites sampled. General seasonal and spatial trends can also be observed for each of the source waters. Glacial melt in the Athabasca is the highest in

August in the headwaters and became a smaller contributor to streamflow downstream. Snowmelt is the highest in May. Surface water is the highest in August and became a larger contributor to streamflow as you move downstream.

3.5.3.1 Upper Athabasca

The Upper Athabasca was composed of the source waters groundwater, snowmelt and glacial melt (figure 3.6). Snowmelt was present in every sample in the Upper Athabasca for all three surveys. In May 2017, the headwaters had the highest percentage of snowmelt, which decreased moving downstream in the Athabasca to less than 1% at Athabasca after Jasper, where the percentage of snowmelt began to increase again into the Middle Athabasca. This is linked to the high proportion of snowmelt in the tributaries downstream of Jasper. In August 2016, the proportion of snowmelt generally decreased moving downstream with the exception of the samples at the Athabasca Icefield and at Athabasca falls. In comparison, in August 2017 snowmelt follows a similar pattern to May 2017, with the contribution of snowmelt increasing after Jasper.

Glacial melt in the Upper Athabasca was present in 29% of the samples in May (figure 3.6). At this time, the maximum proportion of glacial melt is 13% of streamflow at the Athabasca Glacier Icefield. Downstream of the icefield, the proportion of glacial melt generally decreased until it is zero percent at Athabasca after Jasper. In August 2016 and 2017, glacial melt contributed to all of the samples in the Upper Athabasca except for the two tributaries that were determined not to be fed by glacial melt prior to the analysis. Glacial melt contributions to the Athabasca River in the Upper Athabasca averaged from 23% for August 2016 and 19% for August 2017. Glacial melt contributions in tributaries were generally lower than the main channel at similar distances downstream. This resulted in a general decreasing trend in glacial melt moving downstream on the Athabasca River.

3.5.3.2 Middle Athabasca

The Middle Athabasca was composed of groundwater and a combination of snowmelt, glacial melt and surface water (figure 3.7). In the Middle Athabasca, snowmelt was present in all the May 2017 and August 2017 sites, except for the three most downstream tributaries in August 2017. In May 2017, snowmelt in the Athabasca River ranged from 15-37% and generally increased until Athabasca at Blue Ridge and then decreased moving as you move downstream. This increase may be due to the inflows from the McLeod tributary and inflows from the Sakwatemau River, which was not sampled. The following decreasing trend occurred due to tributaries downstream of Blue Ridge having a lower proportion of snowmelt than the Athabasca River. In August 2017, snowmelt peaked at 17% at the Athabasca River just upstream of the McLeod and then decreased to a low of 7% at Athabasca at the town of Athabasca before it increased to 13% at Fort McMurray. This increase in Fort McMurray seems unlikely and may be due to a lack of resolution in source water data in this location.

In the Middle Athabasca, glacial melt was present in the most upstream sites on the Athabasca River in August 2017 and decreased moving downstream. At this time glacial melt peaked at 11% on the Athabasca before the McLeod River. This is an increase of 1% from Athabasca at Hinton from the Upper Athabasca and likely occurred due to the shifting of source water values for the calculations between the Upper and Middle Athabasca. This minor increase in glacial melt moving downstream should be interpreted as the Athabasca maintaining a similar glacial melt contribution between these two locations. Downstream of the Athabasca at McLeod the contribution of glacial melt is reduced to 4% and 2% at the sites on the Athabasca River upstream of the Town of Athabasca. This shows that, while the proportion of glacial melt can be monitored in the Middle Athabasca, it made up a minor contribution of streamflow at this time. Glacial melt was removed as a source water for August 2016 due to inaccuracies around this analysis as outlined in the methodology.

Surface water in the Athabasca River was present in all samples from all three sampling periods, except for the three most upstream samples in August 2017. Surface water peaked at 22% in August 2016, 21% in May 2017 and 35% in August 2017. Samples from the Athabasca River had an increasing proportion of surface water moving downstream. This is due to an increasing proportion of surface water in tributaries as you move downstream, which is higher than the proportion of surface water in the comparable sites on the Athabasca River. While August 2016 and 2017 are not directly comparable as sampling was extended further downstream in August 2017, a comparison of the two time periods shows all the sites from August 2017 had a higher proportion of surface water than August 2016, when surface water was present. A comparison of May 2017 and August 2017 also found that August 2017 had a higher proportion of surface water than May 2017 in all sites where surface water was present. In May 2017, Athabasca at Blue Ridge also had a slight increase in surface water which may be linked to inflows from the Sakwatemau River. The Sakwatemau River includes an outflow from Carson Lake but was not sampled. In August 2017, there is a proportion of surface water in all sites on the Athabasca River. However, these are not being identified in the hydrograph separation due to the complexity of streamflow at this time with both snowmelt and glacial melt being present in samples in the Middle Athabasca. One tributary, Lac La Biche, maintains a high proportion of surface water in May, indicating that this site remains isotopically enriched over the entire year. This is supported by the SWI composition of this site. However, the proportion of surface water is exaggerated as the source water value for surface water is based on the sample collected at Lac La Biche in August 2017.

3.5.3.1 McLeod

The McLeod was composed of groundwater, snowmelt and surface water (figure 3.8). In May 2017, the proportion of snowmelt on the McLeod River ranged from 27-48%. Snowmelt peaked in the middle of the catchment prior to the inflow of larger tributaries. The proportion of snowmelt decreased moving downstream from this location as the tributaries in the McLeod had a lower proportion of snowmelt than the McLeod River. August 2016 and August 2017 differed from one another. In August 2016, snowmelt is not present in any of the samples collected. By comparison in August 2017, snowmelt is present in eight of the nine samples collected. At this time, the proportion of snowmelt on the McLeod River ranged from 0-27%. Snowmelt in the upper portions of the McLeod River were fairly limited (<5%), but generally increased moving downstream. This is not supported by mixing with tributaries on the McLeod as tributaries in the lower portion of the catchment has a lower proportion of snowmelt than the McLeod River. This may indicate that additional source waters were not being captured. However, this trend follows a similar pattern in the Upper Athabasca where snowmelt was higher in August 2017 than in 2016 and is likely not an error.

Surface water was present in streamflow for all sites during all three of the sampling periods in the McLeod. The average contribution of snowmelt was 14% in August 2016, 9% in May 2017 and 20% in August 2017. In August 2016 and August 2017, the proportion of surface water increased downstream. In May 2017, surface water generally increased moving downstream but stayed at a consistent value for most of the catchment. In August 2016, the proportion of surface water in the tributaries increased moving downstream. The inverse to this occurred in August 2017, with the most upstream tributaries having the highest proportion of surface water. However, in August 2017, surface water made up a larger proportion of the streamflow in the McLeod River than in August 2016. This may indicate that wetlands or other inflows are adding enriched water sources to streamflow.

3.5.4 Winter source water trends

SWI data from the 2016-2017 winter on the Athabasca River at the Town of Athabasca and Fort McMurray, and Whitecourt on the McLeod River provided additional source water information (figure 3.9). Delta-delta plots and ternary plots were used to display the source water composition of streamflow at these three sites. Source waters were determined to be groundwater, snowmelt and surface water. Groundwater made up a large portion of streamflow for all of the samples. In comparison, snowmelt was not a common component of winter streamflow and was only present in three samples, one for Athabasca and two for McLeod. These samples came from the direct streamflow sampling and not the reconstruction of winter streamflow. This indicated that snowmelt entered streamflow during warmer periods when ice was not forming.

Surface water was present in all of the samples from all three locations. This indicated that an evaporative signature persisted in streamflow throughout the winter. Looking at the two locations on the Athabasca, evaporation became greater moving downstream in the catchment, with more evaporation at Fort McMurray than at the Town of Athabasca. This is supported by the delta-delta plots which have progressively lower slopes than the GMWL as you move downstream from Whitecourt to Fort McMurray, indicating increased evaporation has occurred. In Chapter 2, which analyzed the winter record, changes in the SWI composition in water were also tied to warming events at both Athabasca and Fort McMurray. These warming events created a more evaporation signature in streamflow.

Variability in source water contributions was higher for the McLeod River than the sites on the Athabasca River. This is likely due to the larger volume of streamflow in the Athabasca River than in the McLeod. In comparison, the McLeod is considerably smaller and may have variations in flow if tributaries freeze or unfreeze shifting the water sources downstream.

3.5.5 Source water contributions compared to weather conditions in the ARB

SWI analysis in August 2016 and August 2017 showed both years had key differences in the proportions of source waters. Using historic climate data from Environment and Climate Change Canada (2022), temperature and precipitation data were compared for 2016 and 2017 in the ARB. In the Upper Athabasca, temperature was generally higher than average between December 2015 to April 2016, and in the Middle Athabasca between October 2015-August 2016 and April 2017 to September 2017. In comparison, in the Upper Athabasca, temperatures were generally lower than average between November 2016 to May 2017, and in the Middle Athabasca between December 2016 to April 2017. In the Upper Athabasca, precipitation was generally greater in 2016 than in 2017 during the months of May, July, August and December. In the Middle Athabasca, precipitation was generally greater in 2016 than in 2017 between November to March, May and August. In 2017, precipitation in the Middle Athabasca was greater than in 2016 between January to March.

The weather in the ARB can be summarized as follows: the winter and spring freshest of 2015-2016 were warmer than average and less precipitation was observed than in 2017; this was followed by a wetter summer than in 2017. In comparison, the winter and spring freshest of 2016-2017 were colder than average and more precipitation was observed than in 2016, which was followed by a dryer summer in the Upper Athabasca than in 2016. This would likely result in more ablation of glacial ice in the summer of 2016 than in 2017, as the snowpack would be depleted faster and additional summer precipitation would lead to further melt. In comparison, 2017 should have received a larger snowpack which would have reduced glacial melt and lasted longer into the summer. The wetter summer of 2016 would have also dampened the isotopic composition of surface water making it less evaporatively enriched. All three of these trends were reflected in the analysis of source water contributions.

3.5.6 Annual source water trends

Annual patterns in the SWI composition and source water contributions to streamflow were examined for both the Athabasca River at the Town of Athabasca (figure 3.10) and the McLeod River at Whitecourt (figure 3.11). This data set included the synoptic sampling in August 2016, May 2017 and August 2017, as well as streamflow from winter 2016-2017. In the Liard, a large river also in the Mackenzie River Basin, St Amour *et al.*, (2005), found that seasonal changes in source waters resulted in a cyclical pattern. Looking at the delta-delta plot, the SWI composition of streamflow for the Athabasca in the winter and August samples are clustered together. This suggests that there is very little variation in late summer and winter streamflow at this site. However, in May the isotopic composition of streamflow is more isotopically depleted due to the presence of snowmelt. In the ternary plot of Figure 3.10 this is confirmed. May 2017 has the highest proportion of snowmelt for all samples and August 2016 has very similar source water proportions to the average of winter 2016-2017 samples. In comparison, August 2017 does not resemble average winter streamflow but there are some similarities. At this time, there is a slightly higher proportion of snowmelt than in the single winter sample where snowmelt was present. However, surface water was not the highest at this time, as a sample from winter streamflow has a higher proportion. It was expected that the Athabasca would show cyclical patterns. However, the low variation at Athabasca and key differences between the August 2016 and August 2017 streamflow prevented a pattern from forming after this single hydrological year. Longer-term research would be required to test if cyclical patterns exist at this location or for the Athabasca River more broadly.

The McLeod displayed a more cyclical pattern in delta-delta space (figure 3.11). Due to the damped SWI signal in 2016, the proportion of surface water is lower than 2017, however, a cyclical pattern can still be observed. Over winter, contributions from surface water and snowmelt were decreased, increasing the proportional contribution of groundwater in streamflow. There is some variation over the winter period as warm conditions allow snowmelt and surface water to enter streamflow. In May 2017, snowmelt entered streamflow, depleting the isotopic signature to its lowest annual contribution. In August 2017, lakes and wetlands became more evaporatively enriched and contributed a larger portion of streamflow. This cycle is expected to repeat for each hydrologic year but further studies would be required to confirm this.

3.6 Conclusion

This study explored spatial, seasonal and annual trends in source waters across the Upper and Middle sections of the ARB, a large snowmelt-dominated catchment in Alberta, Canada, over one hydrological year. Additional analyses were undertaken to explore trends from the larger regions of the ARB to one of the sub-catchments, the McLeod. The source waters identified in the ARB included groundwater, glacial melt, snowmelt and evaporatively enriched surface waters, such as lakes and wetlands. The proportions of these source waters in streamflow were calculated using hydrograph separation so trends could be analyzed.

Spatial, seasonal and annual trends in the source waters of the ARB were observed. Spatial trends included increasing surface water contributions to streamflow downstream for both the McLeod and Athabasca Rivers, due to the accumulation and increased density of water bodies and wetlands downstream. In addition, there was a decreasing glacial melt downstream due to a larger distance from the glaciated headwaters. Snowmelt did not have a consistent trend, but inflows that contributed high proportions of snowmelt were identified on the Athabasca downstream of Jasper and upstream of Blue Ridge.

Seasonal trends in source water contributions allowed confirmation that the proportion of glacial melt in streamflow was the highest in August, the proportion of snowmelt in streamflow was the highest in May and the proportion of surface water was highest in August. In addition, during the winter, surface water continued to be an integral source water to streamflow. Annual source waters trends were analyzed and it was found that the source waters in the McLeod follow a cyclical pattern where streamflow is depleted in May due to snowmelt, enriched in August due to the influence of surface water and generally resembles groundwater over the ice on-period. The Athabasca had limited variability over the hydrologic year so no cyclical patterns were observed.

Differences between August 2016 and 2017 were also linked to temperature and precipitation. The 2015/2016 winter was warmer and dryer leading to a reduced snowpack, which was followed by a wet summer. This led to a larger proportion of glacial melt in streamflow, reduced snowmelt in streamflow and dampened surface water inputs. In comparison, the winter of 2016/2017 was colder and wetter with a dryer summer, which would allow a larger snowpack to form and be maintained into the summer. This resulted in a larger proportion of snowmelt in 2017, a reduced proportion of glacial melt and surface water becoming more evaporatively enriched. This also demonstrated that under some conditions, glacial melt proportions could be traced to the Middle Athabasca.

While this analysis provided insight into how water sources change spatially, seasonally and annually across the region, and provides evidence of the efficacy of the methodology, the low density of sampling sites and limited scope of the source water sampling program limits the claims that can be made prior to follow up investigations being conducted. In particular, further reconnaissance surveys and research are needed to assess source water isotopic signatures and their variability in greater detail.

References

Aggarwal, P. K., Gat, J., & Froehlich, K. F. (2005). *A Review of Isotope Applications in Catchment Hydrology. In Isotopes in the water cycle: Past, present and future of a developing science* (pp. 151-157). Dordrecht, the Netherlands: Springer.

AMEC Earth & Environmental. (2007). *Water for life: reliable, quality water supplies for a sustainable economy: current and future water use in Alberta* (pp. 437-474). Edmonton: Alberta Environment.

Athabasca River Basin Research Institute. (2022). About the Athabasca River Basin. Retrieved April 22, 2022, from http://arbri.athabascau.ca/About-the-Athabasca-River-basin/Index.php

Arendt, C. A., Aciego, S. M., & Hetland, E. A. (2015). An open source Bayesian Monte Carlo isotope mixing model with applications in Earth surface processes. Geochemistry, Geophysics, Geosystems, 16(5), 1274-1292.

Barnett, T. P., Adam, J. C., & Lettenmaier, D. P. (2005). Potential impacts of a warming climate on water availability in snow-dominated regions. *Nature, 438*(7066), 303-309. doi:10.1038/nature04141

Bawden, A. J., Linton, H. C., Burn, D. H., & Prowse, T. D. (2014). A spatiotemporal analysis of hydrological trends and variability in the Athabasca River region, Canada. *Journal of Hydrology*, *509*, 333-342.

Birks, S., & Gibson, J. (2009). Isotope Hydrology Research in Canada, 2003-2007. *Canadian Water Resources Journal, 34*(2), 163-176. doi:10.4296/cwrj3402163

Birks, J., Fennell, J., Yi, Y., Gibson, J., & Moncur, M. (2017). Regional geochemistry study for the Southern Athabasca Oil Sands (SAOS) area. COSIA Hydrogeology Working Group: Calgary, AB, Canada.

Birks, S. J., Fennell, J. W., Gibson, J. J., Yi, Y., Moncur, M. C., & Brewster, M. (2019). Using regional datasets of isotope geochemistry to resolve complex groundwater flow and formation connectivity in northeastern Alberta, Canada. Applied Geochemistry, 101, 140-159.

Bonsal, B. R., & Cuell, C. (2017). Hydro-climatic variability and extremes over the Athabasca River basin: Historical trends and projected future occurrence. Canadian Water Resources Journal/Revue canadienne des ressources hydriques, 42(4), 315-335.

Brown, R. D. (2000). Northern Hemisphere Snow Cover Variability and Change, 1915–97. *Journal of Climate, 13*(13), 2339-2355. doi:10.1175/1520-0442(2000)013<2339:nhscva>2.0.co;2

Burn, D. H., Abdul Aziz, O. I., & Pietroniro, A. (2004). A comparison of trends in hydrological variables for two watersheds in the Mackenzie River Basin. *Canadian Water Resources Journal/Revue canadienne des ressources hydriques*, *29*(4), 283-298.

Cable, J., Ogle, K., & Williams, D. (2011). Contribution of glacier meltwater to streamflow in the Wind River Range, Wyoming, inferred via a Bayesian mixing model applied to isotopic measurements. *Hydrological Processes, 25*(14), 2228-2236. doi:10.1002/hyp.7982

Center for International Earth Science Information Network (CIESIN), (2004). *Gridded Population of the World (GPW*), *v3*. Retrieved November 07, 2016, from http://beta.sedac.ciesin.columbia.edu/data/collection/gpw-v3

Cheng, G., Huang, G., Dong, C., Zhu, J., Zhou, X., & Yao, Y. (2017). High-resolution projections of 21st century climate over the Athabasca River Basin through an integrated evaluation-classification-downscaling-based climate projection framework. Journal of Geophysical Research: Atmospheres, 122(5), 2595-2615.

Craig, H. (1961). Isotopic variations in meteoric waters. Science, 133(3465), 1702-1703.

Dalai, T. K., Bhattacharya, S. K., & Krishnaswami, S. (2002). Stable isotopes in the source waters of the Yamuna and its tributaries: Seasonal and altitudinal variations and relation to major cations. Hydrological Processes, 16(17), 3345-3364. doi:10.1002/hyp.1104
Dansgaard, W. (1964). Stable isotopes in precipitation. tellus, 16(4), 436-468.

Dibike, Y., Eum, H. I., & Prowse, T. (2018). Modelling the Athabasca watershed snow response to a changing climate. Journal of Hydrology: Regional Studies, 15, 134-148.

Dibike, Y., Shakibaeinia, A., Eum, H. I., Prowse, T., & Droppo, I. (2018b). Effects of projected climate on the hydrodynamic and sediment transport regime of the lower Athabasca River in Alberta, Canada. *River Research and Applications*, *34*(5), 417-429.

Edwards, T. W., Wolfe, B. B., Gibson, J. J., & Hammarlund, D. (2004). Use of water isotope tracers in high latitude hydrology and paleohydrology. *Developments in Paleoenvironmental Research Long-term Environmental Change in Arctic and Antarctic Lakes, 187-207*. doi:10.1007/978-1-4020-2126-8_7

Environment and Climate Change Canada (2022). Historical Climate Data, Government of Canada , 2 Mar. 2022, https://climate.weather.gc.ca/historical_data/search_historic_data_e.html.

Erler, A. R., & Peltier, W. R. (2017). Projected hydroclimatic changes in two major river basins at the Canadian west coast based on high-resolution regional climate simulations. Journal of Climate, 30(20), 8081-8105.

Eum, H. I., Dibike, Y., & Prowse, T. (2017). Climate-induced alteration of hydrologic indicators in the Athabasca River Basin, Alberta, Canada. *Journal of hydrology*, *544*, 327-342.

Fan, Y., Chen, Y., Li, X., Li, W., & Li, Q. (2014). Characteristics of water isotopes and ice-snowmelt quantification in the Tizinafu River, north Kunlun Mountains, Central Asia. *Quaternary International, 380-381*, 116-122. doi:10.1016/j.quaint.2014.05.020

Fan, Y., Chen, Y., He, Q., Li, W., & Wang, Y. (2016). Isotopic Characterization of River Waters and Water Source Identification in an Inland River, Central Asia. *Water, 8*(7), 286. doi:10.3390/w8070286

Gibson, J. J., Edwards, T. W., Birks, S. J., Amour, N. A., Buhay, W. M., Mceachern, P., . . . Peters, D. L. (2005). Progress in isotope tracer hydrology in Canada. Hydrological *Processes, 19*(1), 303-327. doi:10.1002/hyp.5766

Gibson, J. J., & Prowse, T. D. (1999). Isotopic characteristics of ice cover in a large northern river basin. *Hydrological Processes, 13*(16), 2537-2548. doi:10.1002/(sici)1099-1085(199911)13:16<2537::aid-hyp940>3.3.co;2-1

Gibson, J. J., & Prowse, T. D. (2002). Stable isotopes in river ice: identifying primary over-winter streamflow signals and their hydrological significance. *Hydrological Processes, 16*(4), 873-890. doi:10.1002/hyp.366

Gibson, J. J., Birks, S. J., Moncur, M., Yi, Y., Tattrie, K., Jasechko, S., ... & Eby, P. (2011). Isotopic and geochemical tracers for fingerprinting process-affected waters in the oil sands industry: A pilot study. Oil Sands Research and Information Network, 1-120.

Gibson, J., Yi, Y., & Birks, S. (2016). Isotope-based partitioning of streamflow in the oil sands region, northern Alberta: Towards a monitoring strategy for assessing flow sources and water quality controls. *Journal of Hydrology: Regional Studies, 5*, 131-148. doi:10.1016/j.ejrh.2015.12.062

Gibson, J. J., Holmes, T., Stadnyk, T. A., Birks, S. J., Eby, P., & Pietroniro, A. (2020). 18O and 2H in streamflow across Canada. Journal of Hydrology: Regional Studies, 32, 100754.

Gibson, J. J., Eby, P., Stadnyk, T. A., Holmes, T., Birks, S. J., & Pietroniro, A. (2021). Dataset of 18O and 2H in streamflow across Canada: A national resource for tracing water sources, water balance and predictive modelling. Data in Brief, 34, 106723.

Government of Alberta. (2017). *Athabasca River Conditions and Use*. Retrieved March, 2017, from http://www.environment.alberta.ca/apps/OSEM

Hemming, D., Griffiths, H., Loader, N., Marca, A., Robertson, I., Williams, D., . . . Yakir, D. (2007). The Future of Large-Scale Stable Isotope Networks [Abstract]. *Stable Isotopes as Indicators of Ecological Change Terrestrial Ecology, 361-381*. doi:10.1016/s1936-7961(07)01023-8

Hutchison, T. K., & Hicks, F. E. (2007). Observations of ice jam release waves on the Athabasca River near Fort McMurray, Alberta. *Canadian Journal of Civil Engineering*, *34*(4), 473-484.

IPCC (2015). IPCC Climate Change 2014 Synthesis Report (p. 42, Publication). Geneva, Switzerland: Intergovernmental Panel on Climate Change.

IPCC. (2022). Ar6 climate change 2021:The Physical Science Basis. Sixth Assessment Report. Retrieved April 23, 2022, from https://www.ipcc.ch/report/ar6/wg1/

Jeelani, G., Shah, R. A., Jacob, N., & Deshpande, R. D. (2016). Estimation of snow and glacier melt contribution to Liddar stream in a mountainous catchment, western Himalaya: An isotopic approach. *Isotopes in Environmental and Health Studies*,*53* (1) 1-18. doi:10.1080/10256016.2016.1186671

Kendall, C., & McDonnell, J. J. (1998). *Isotope tracers in catchment hydrology*. Amsterdam: Elsevier

Klaus, J., & Mcdonnell, J. (2013). Hydrograph separation using stable isotopes: Review and evaluation. Journal of Hydrology, 505, 47-64. doi:10.1016/j.jhydrol.2013.09.006

Kong, Y., & Pang, Z. (2012). Evaluating the sensitivity of glacier rivers to climate change based on hydrograph separation of discharge. *Journal of Hydrology*, 434-435, 121-129. doi:10.1016/j.jhydrol.2012.02.029

Lambs, L. (2000). Correlation of conductivity and stable isotope 18O for the assessment of water origin in river system. Chemical Geology, 164(1-2), 161-170. doi:10.1016/s0009-2541(99)00140-0

Lambs, L., Horwath, A., Otto, T., Julien, F., & Antoine, P. (2012). Isotopic values of the Amazon headwaters in Peru: Comparison of the wet upper Río Madre de Dios watershed with the dry Urubamba-Apurimac river system. Rapid Communications in Mass Spectrometry, 26(7), 775-784. doi:10.1002/rcm.6157

Leong, D., & Donner, S. (2016). Future water supply and demand management options in the Athabasca Oil Sands. River Research and Applications, 32(9), 1853-1861.

Lima, A. C., & Wrona, F. J. (2019). Multiple threats and stressors to the Athabasca River Basin: What do we know so far?. Science of the total environment, 649, 640-651.

Marchina, C., Bianchini, G., Natali, C., Pennisi, M., Colombani, N., Tassinari, R., & Knoeller, K. (2014). The Po river water from the Alps to the Adriatic Sea (Italy): New insights from geochemical and isotopic (δ18O-δD) data. Environmental Science and Pollution Research, 22(7), 5184-5203. doi:10.1007/s11356-014-3750-6

Meier, C., Knoche, M., Merz, R., & Weise, S. M. (2013). Stable isotopes in river waters in the Tajik Pamirs: Regional and temporal characteristics. Isotopes in Environmental and Health Studies, 49(4), 542-554. doi:10.1080/10256016.2013.835809

Newton, B., Buendia-Fores, C., & Emmerton, C. (2019). Impacts of changes to snow accumulation and melt regimes on the streamflow of regulated and unregulated rivers in the upper North Saskatchewan and Athabasca river basins. In AGU Fall Meeting Abstracts (Vol. 2019, pp. H33I-2035).

Nijssen, B., O'Donnell, G. M., Hamlet, A. F., & Lettenmaier, D. P. (2001). Hydrologic sensitivity of global rivers to climate change. *Climatic Change, 50*(1), 143-175. doi:10.1023/A:1010616428763

Penna, D., Engel, M., Mao, L., Dell'agnese, A., Bertoldi, G., & Comiti, F. (2014). Tracer-based analysis of spatial and temporal variations of water sources in a glacierized catchment. *Hydrology and Earth System Sciences, 18*(12), 5271-5288. doi:10.5194/hess-18-5271-2014

Peters, D. L., Atkinson, D., Monk, W. A., Tenenbaum, D. E., & Baird, D. J. (2013). A multi-scale hydroclimatic analysis of runoff generation in the Athabasca River, western Canada. Hydrological Processes, 27(13), 1915-1934.

Pietroniro, A., Chambers, P. A., & Ferguson, M. E. (1998). Application of a dissolved oxygen model to an ice-covered river. *Canadian Water Resources Journal*, *23*(4), 351-368.

Poage, M. A., & Chamberlain, C. P. (2001). Empirical relationships between elevation and the stable isotope composition of precipitation and surface waters: considerations for studies of paleoelevation change. American Journal of Science, 301(1), 1-15.

Prowse, T. D., & Beltaos, S. (2002). Climatic control of river-ice hydrology: A review. *Hydrological Processes,* 16(4), 805-822. doi:10.1002/hyp.369

Prowse, T. D., Beltaos, S., Gardner, J. T., Gibson, J. J., Granger, R. J., Leconte, R., ... & Toth, B. (2006). Climate change, flow regulation and land-use effects on the hydrology of the Peace-Athabasca-Slave system; Findings from the Northern Rivers Ecosystem Initiative. *Environmental Monitoring and Assessment*, *113*(1), 167-197.

Prowse, T. D., Bonsal, B. R., Duguay, C. R., & Lacroix, M. P. (2007). River-ice break-up/freeze-up: a review of climatic drivers, historical trends and future predictions. *Annals of Glaciology*, *46*, 443-451.

Prowse, T. D., Furgal, C., Chouinard, R., Melling, H., Milburn, D., & Smith, S. L. (2009). Implications of climate change for economic development in northern Canada: Energy, resource, and transportation sectors. *Ambio*, 272-281.

Ramesh, R., & Sarin, M. M. (1992). Stable isotope study of the Ganga (Ganges) river system. Journal of Hydrology, 139(1-4), 49-62.

Rasouli, K., Hernández-Henríquez, M. A., & Déry, S. J. (2012). Streamflow input to Lake Athabasca, Canada. *Hydrology and Earth System Sciences Discussions, 9*(8), 9065-9093. doi:10.5194/hessd-9-9065-2012

Robbins, M. (2019). Evolution of Late Season Meltwater in Alpine and Arctic Glaciers: Sampling Strategies and Geochemical Observations (Doctoral dissertation).

Rock, L., & Mayer, B. (2007). Isotope hydrology of the Oldman River basin, southern Alberta, Canada. *Hydrological Processes, 21*(24), 3301-3315. doi:10.1002/hyp.6545 IAEA. (n.d.). *Sampling Procedures for Isotope Hydrology*. Retrieved November 11, 2016, from http://www-naweb.iaea.org/napc/ih/documents/other/Sampling booklet web.pdf

Rood, S. B., Stupple, G. W., & Gill, K. M. (2015). Century-long records reveal slight, ecoregion-localized changes in Athabasca River flows. *Hydrological Processes*, *29*(5), 805-816.

Schindler, D. W., & Donahue, W. F. (2006). An impending water crisis in Canada's western prairie provinces. *Proceedings of the National Academy of Sciences*, *103*(19), 7210-7216.

She, Y., Andrishak, R., Hicks, F., Morse, B., Stander, E., Krath, C., ... & Mahabir, C. (2009). Athabasca River ice jam formation and release events in 2006 and 2007. *Cold regions science and technology*, *55*(2), 249-261.

St Amour, N. A., Gibson, J. J., Edwards, T. W., Prowse, T. D., & Pietroniro, A. (2005). Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River basin, Northwest Territories, Canada. Hydrological Processes: An International Journal, 19(17), 3357-3381.

Sun, C., Li, X., Chen, Y., Li, W., Stotler, R. L., & Zhang, Y. (2016). Spatial and temporal characteristics of stable isotopes in the Tarim River Basin*. Isotopes in Environmental and Health Studies, 52*(3), 281-297. doi:10.1080/10256016.2016.1125350

UNESCO World Heritage Centre. “Wood Buffalo National Park.” UNESCO World Heritage Centre, https://whc.unesco.org/en/list/256/.

USGS. (2017, April). Instructions for Collecting Samples. Retrieved April, 2017, from https://isotopes.usgs.gov/lab/instructions.html

Voutchkova, D. D., & Miller, S. N. (2017, December). 50 years of change at 14 headwater snowmelt-dominated watersheds in Wyoming. In AGU Fall Meeting Abstracts (Vol. 2017, pp. H41H-1547).

Williams, M. W., Wilson, A., Tshering, D., Thapa, P., & Kayastha, R. B. (2016). Using geochemical and isotopic chemistry to evaluate glacier melt contributions to the Chamkar Chhu (river), Bhutan. Annals of Glaciology Ann. *Glaciol., 57*(71), 339-348. doi:10.3189/2016aog71a068

Yang, Y., Xiao, H., Wei, Y., Zhao, L., Zou, S., Yang, Q., & Yin, Z. (2011). Hydrological processes in the different landscape zones of alpine cold regions in the wet season, combining isotopic and hydrochemical tracers. Hydrological Processes, 26(10), 1457-1466. doi:10.1002/hyp.827

Yi, Y., Gibson, J. J., Hélie, J. F., & Dick, T. A. (2010). Synoptic and time-series stable isotope surveys of the Mackenzie River from Great Slave Lake to the Arctic Ocean, 2003 to 2006. Journal of Hydrology, 383(3-4), 223-232.

Zhang, X., Harvey, K. D., Hogg, W. D., & Yuzyk, T. R. (2001). Trends in Canadian streamflow. *Water Resources Research*, *37*(4), 987-998.

Zhou, X., Huang, G., Piwowar, J., Fan, Y., Wang, X., Li, Z., & Cheng, G. (2018). Hydrologic impacts of ensemble-RCM-projected climate changes in the Athabasca River basin, Canada. Journal of Hydrometeorology, 19(12), 1953-1971.

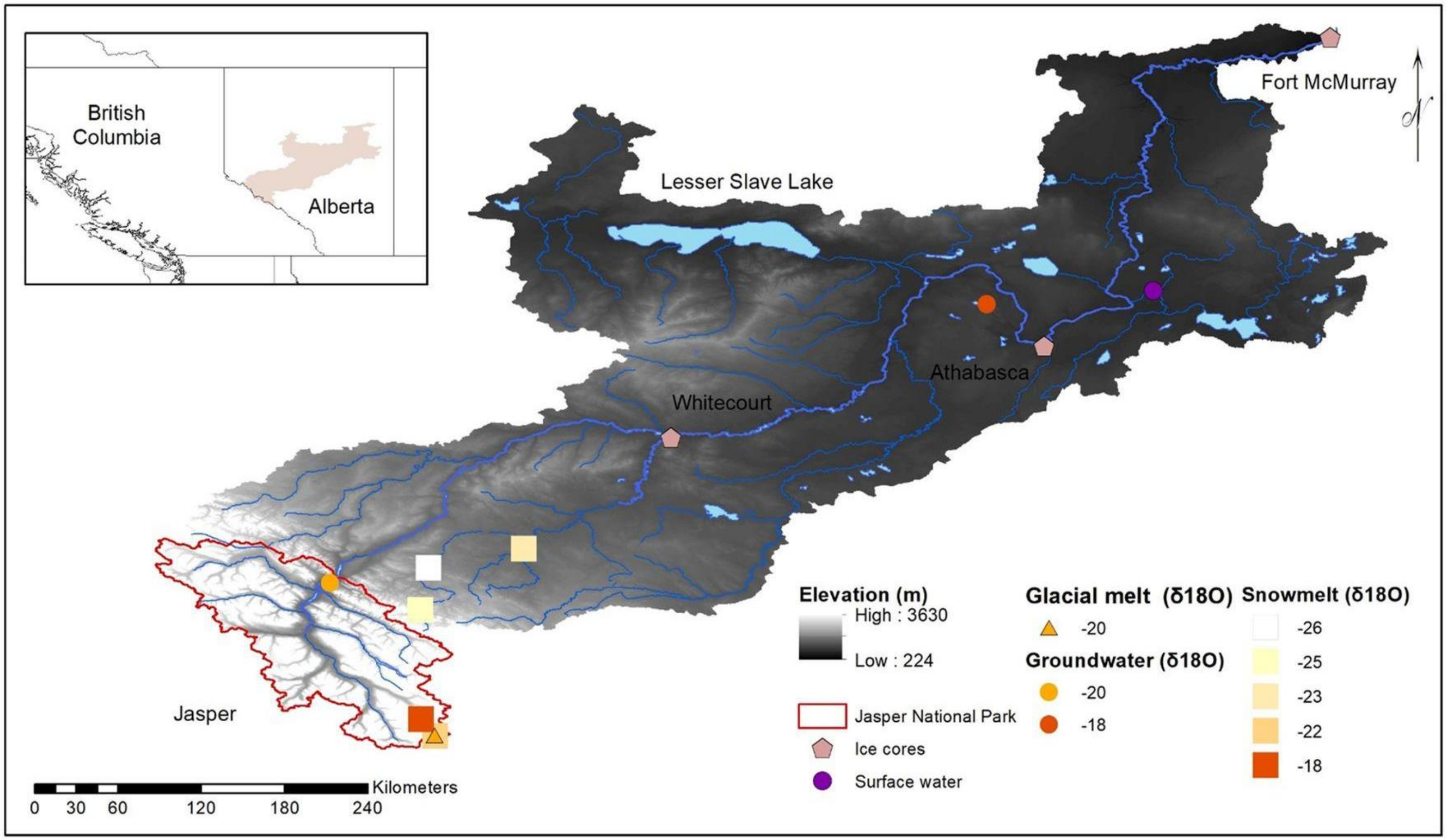


Figure 3.1: The Upper and Middle Athabasca watershed with source water locations for glacial melt, surface water, and winter sampling locations indicated. The isotopic composition of glacial melt, groundwater and snowmelt are displayed as $\delta^{18}O$ values as units permil.

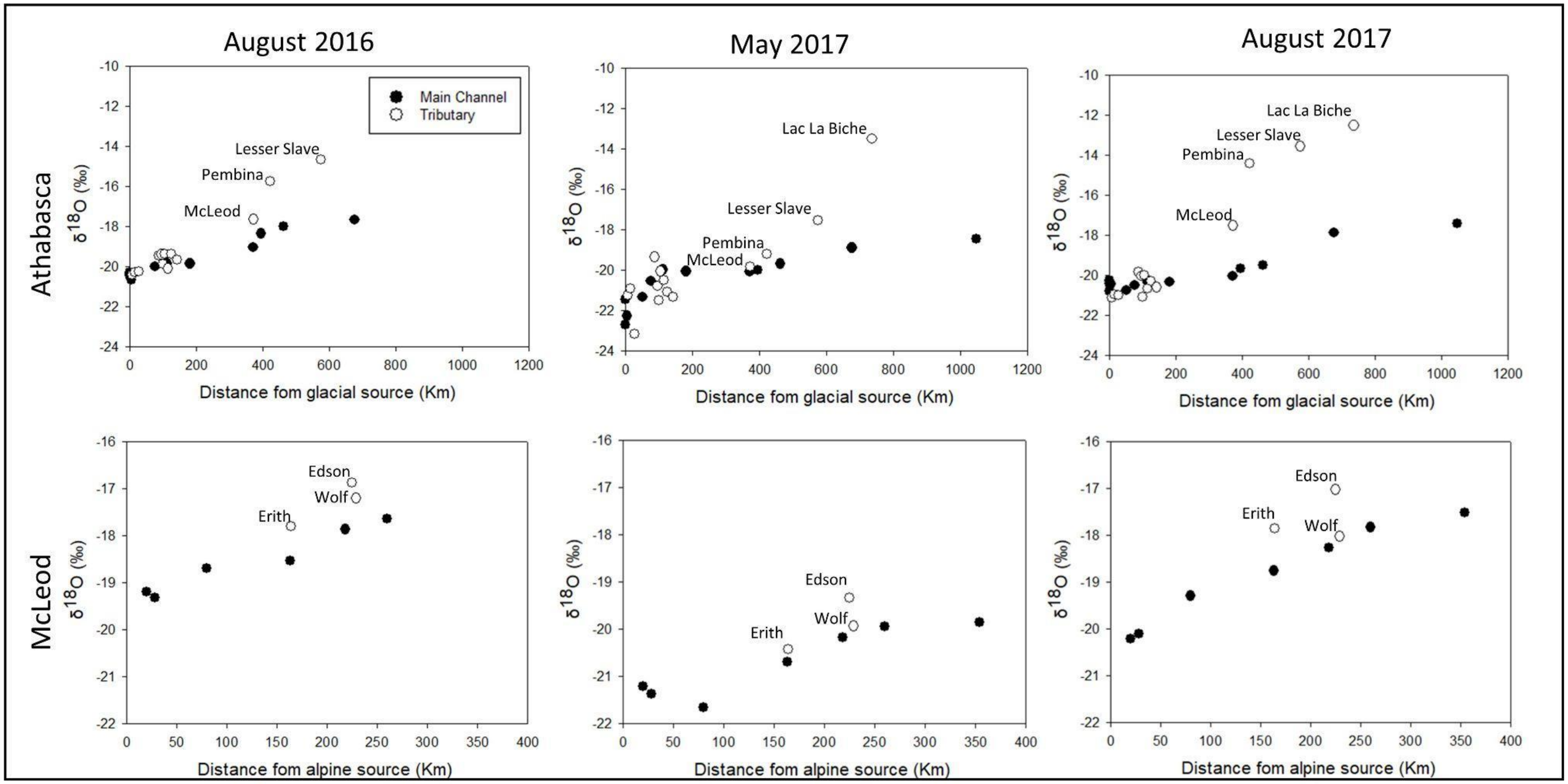


Figure 3.2: A snapshot of each of the synoptic surveys on both the Athabasca River and McLeod River, where the isotopic composition in δ18O values of streamflow is displayed over space moving from the headwaters (left) downstream. Tributaries from the Middle Athabasca and the McLeod are labeled to provide a spatial reference.

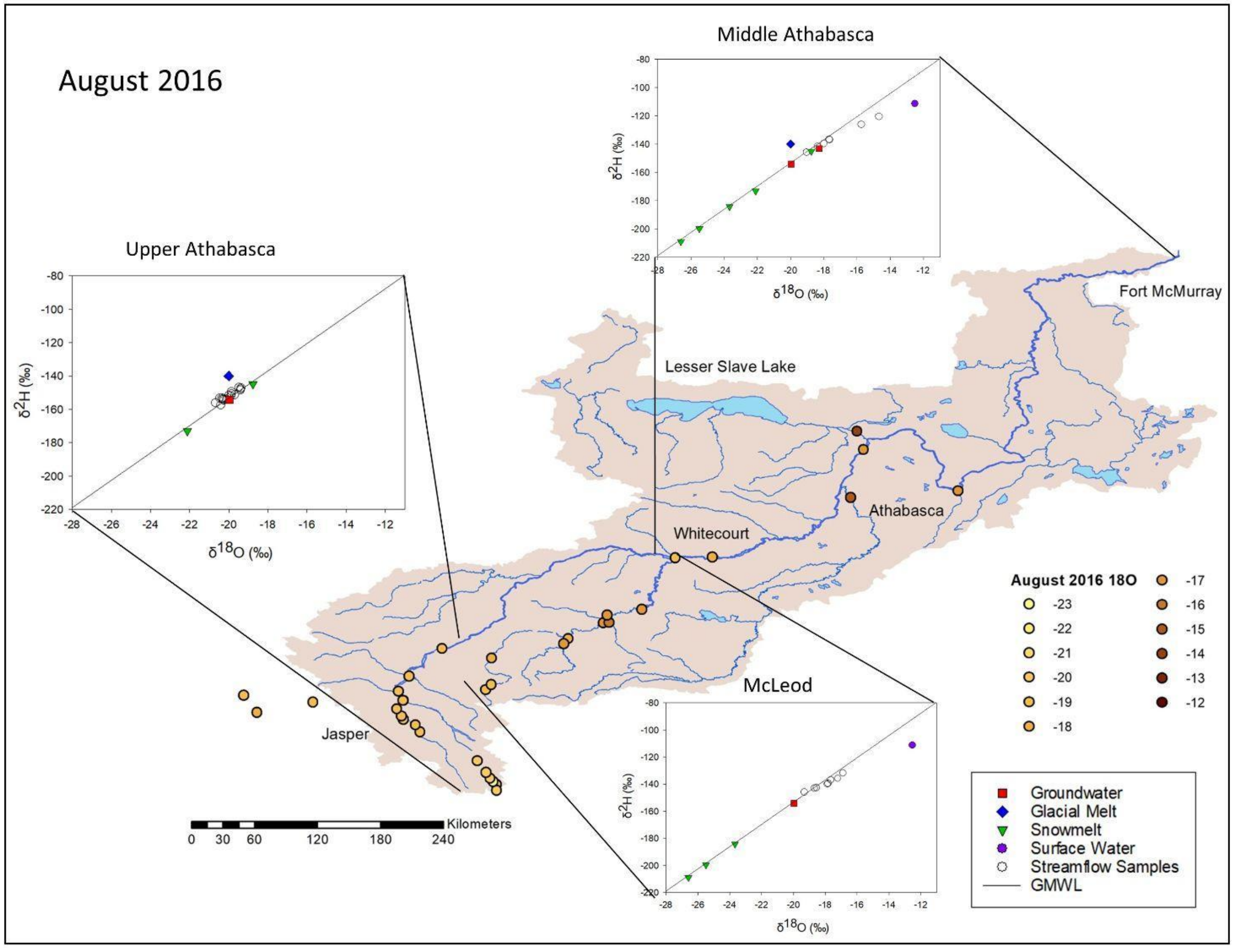


Figure 3.3: A study area-wide view of the δ18O and δ2H values of streamflow in August 2016. Delta-delta plots display the isotopic composition of streamflow and the source water samples which could be impacting each of the three catchments.

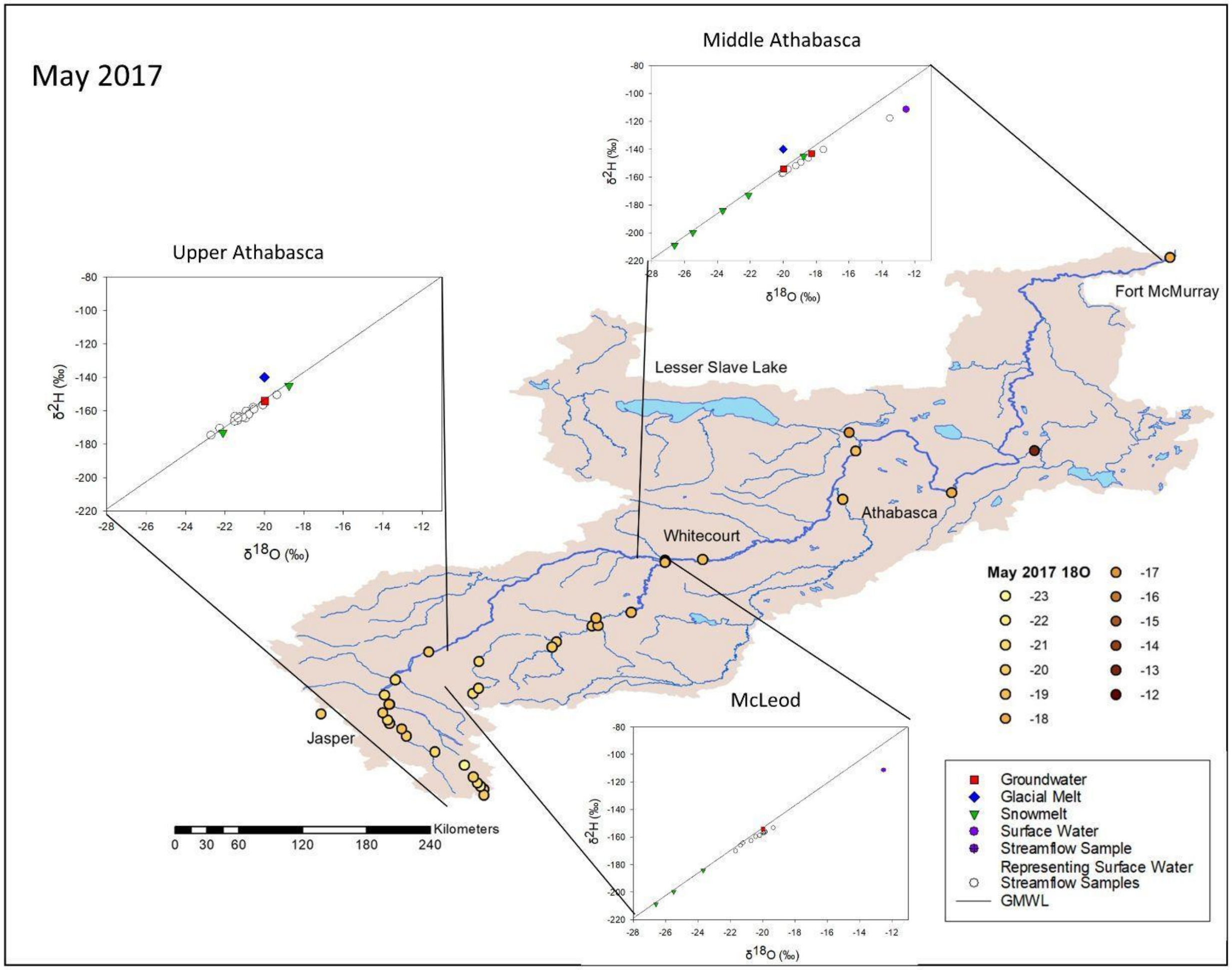


Figure 3.4: A study area-wide view of δ18O and δ2H values of streamflow in May 2017. Delta-delta plots display the isotopic composition of streamflow and the source water samples which could be impacting each of the three catchments.

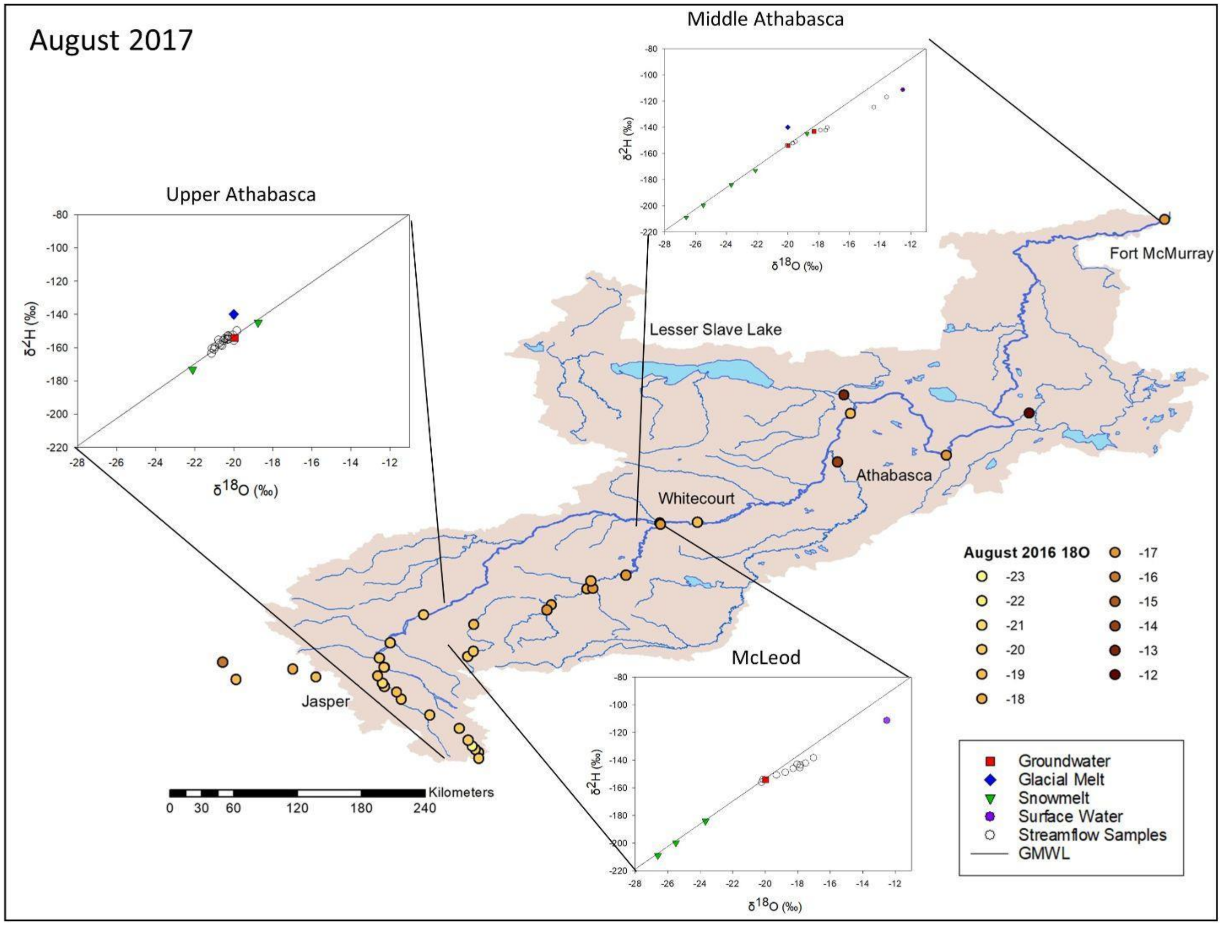


Figure 3.5: A study area-wide view of δ^{18}O and δ^{2}H values of streamflow in August 2017. Delta-delta plots display the isotopic composition of streamflow and the source water samples which could be impacting each of the three catchments.

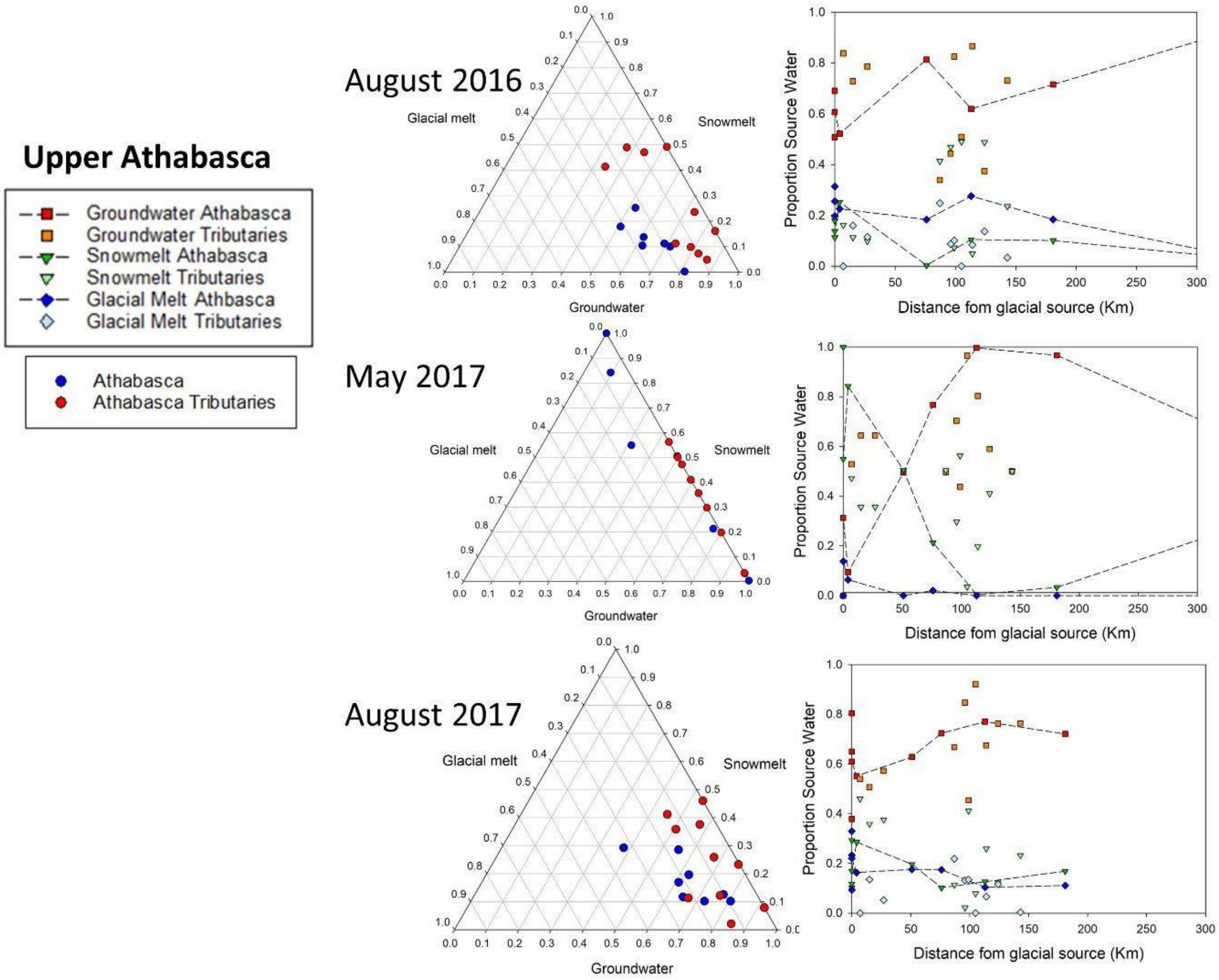


Figure 3.6: The proportion of source waters in each of the samples collected in the Upper Athabasca. This analysis is shown as a ternary plot, where the contribution of all three source waters is indicated. In addition, the proportion of source waters are shown over space moving downstream from the headwaters. Dashed lines extending to the right of the graphs indicate the progression of a source water into the Middle Athabasca

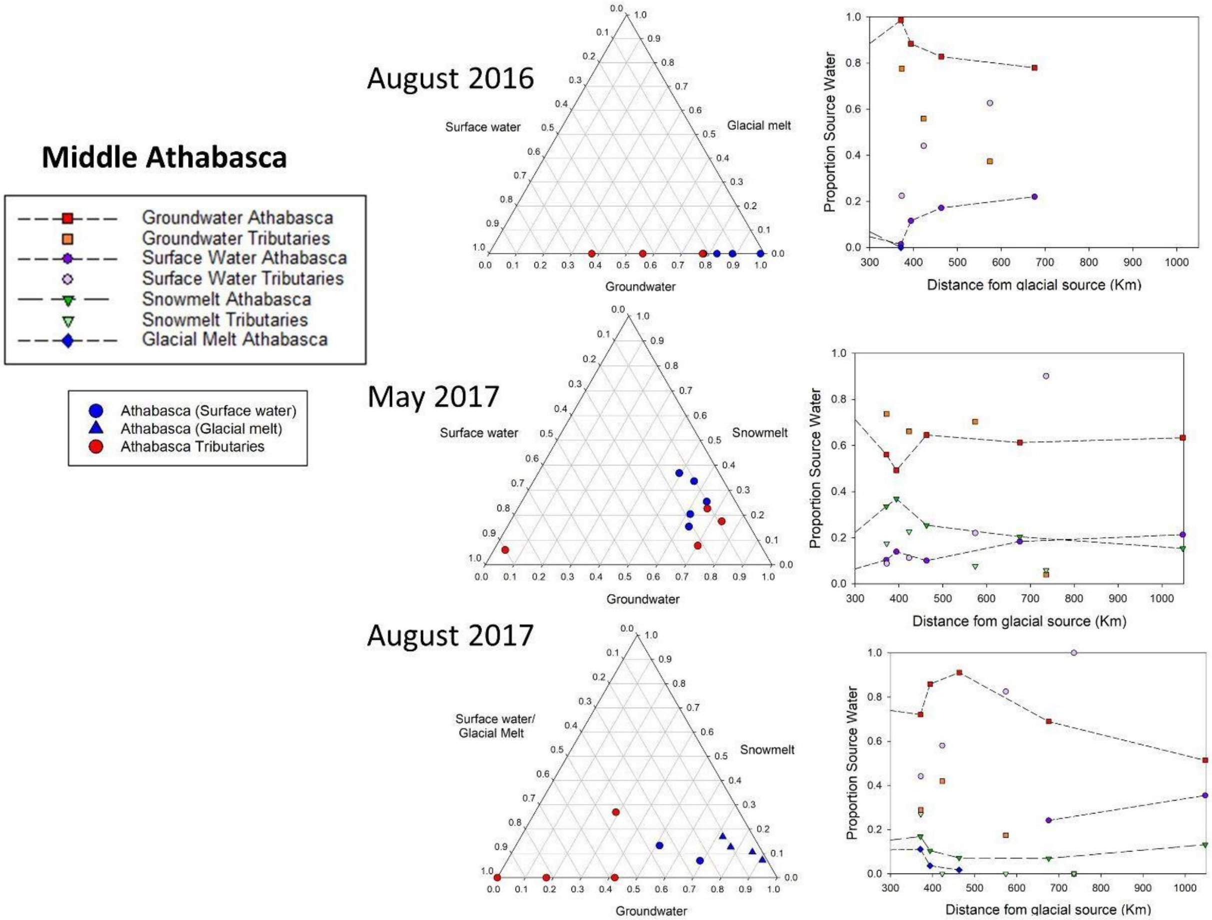


Figure 3.7: The proportion of source waters in each of the samples collected in the Middle Athabasca. This analysis is shown as a ternary plot, where the contribution of all three source waters is indicated. In addition, the proportion of source waters are shown over space moving downstream from the headwaters.

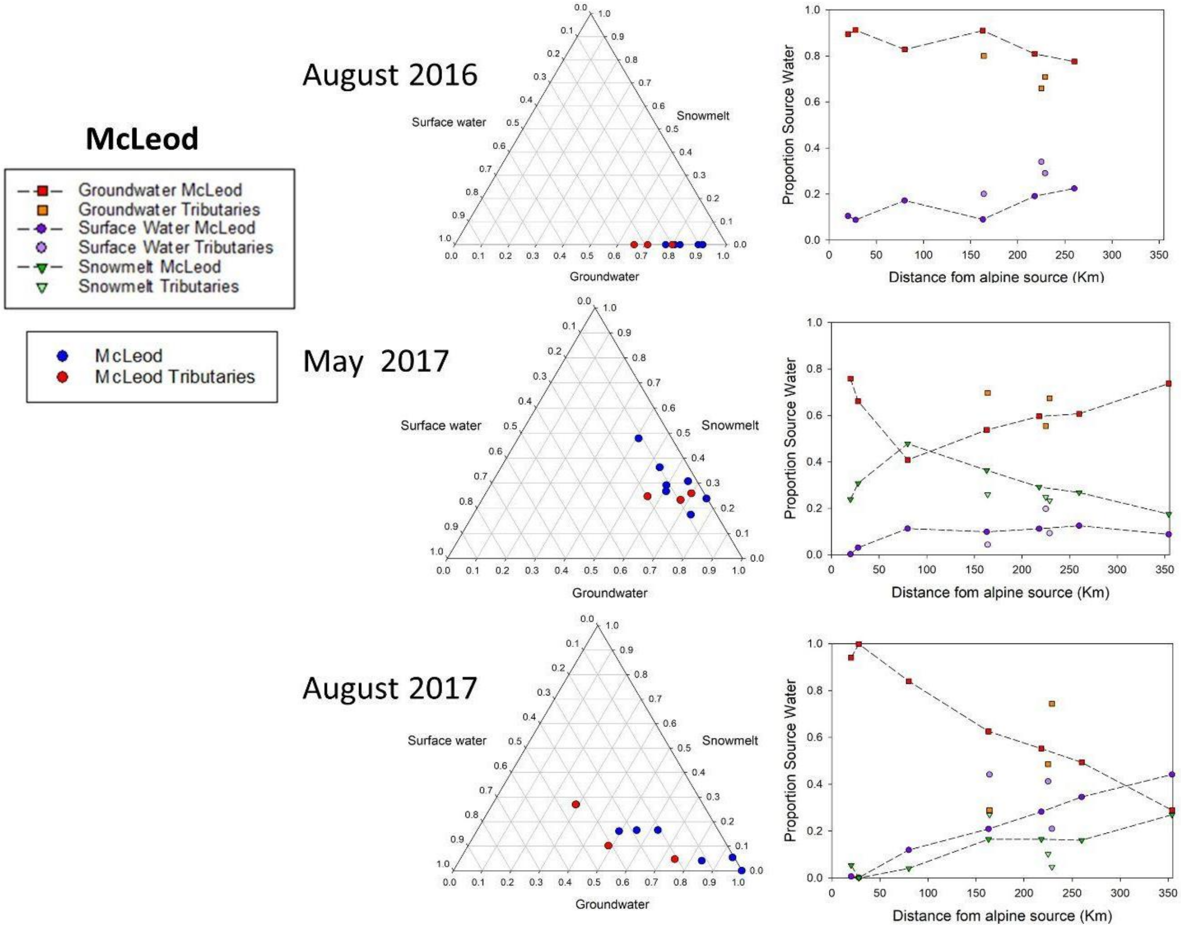


Figure 3.8: The proportion of source waters in each of the samples collected in the McLeod. This analysis is shown as a ternary plot, where the contribution of all three source waters is indicated. In addition, the proportion of source waters are shown over space moving downstream from the headwaters.

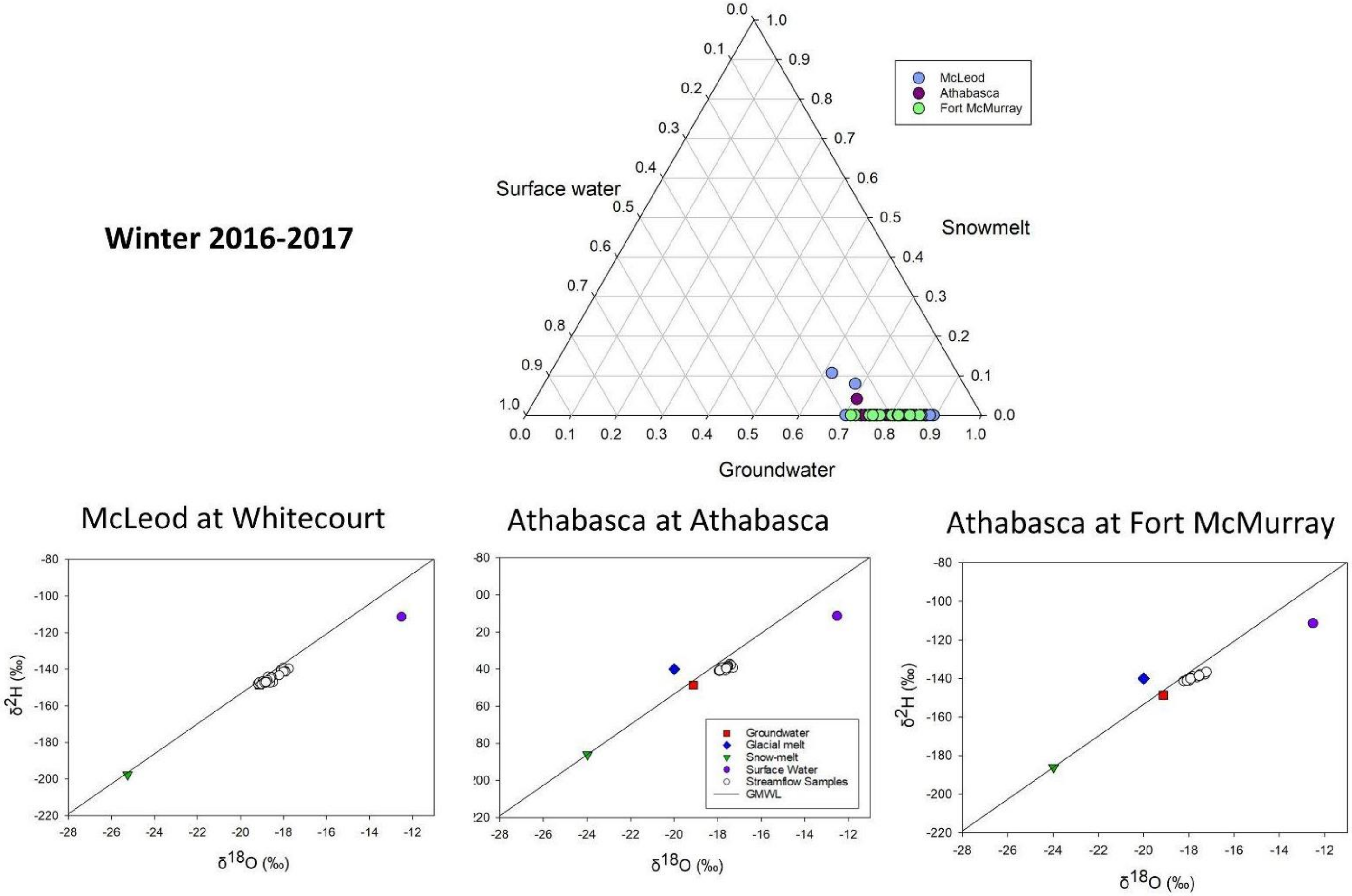


Figure 3.9: The samples collected over the winter of 2015-2016 are shown as a ternary plot, where the contribution of all three source waters is indicated. In addition, delta-delta plots for each of the three sampling site provide an overview of the isotopic composition of the samples compared to the isotopic composition of the source waters at each site.

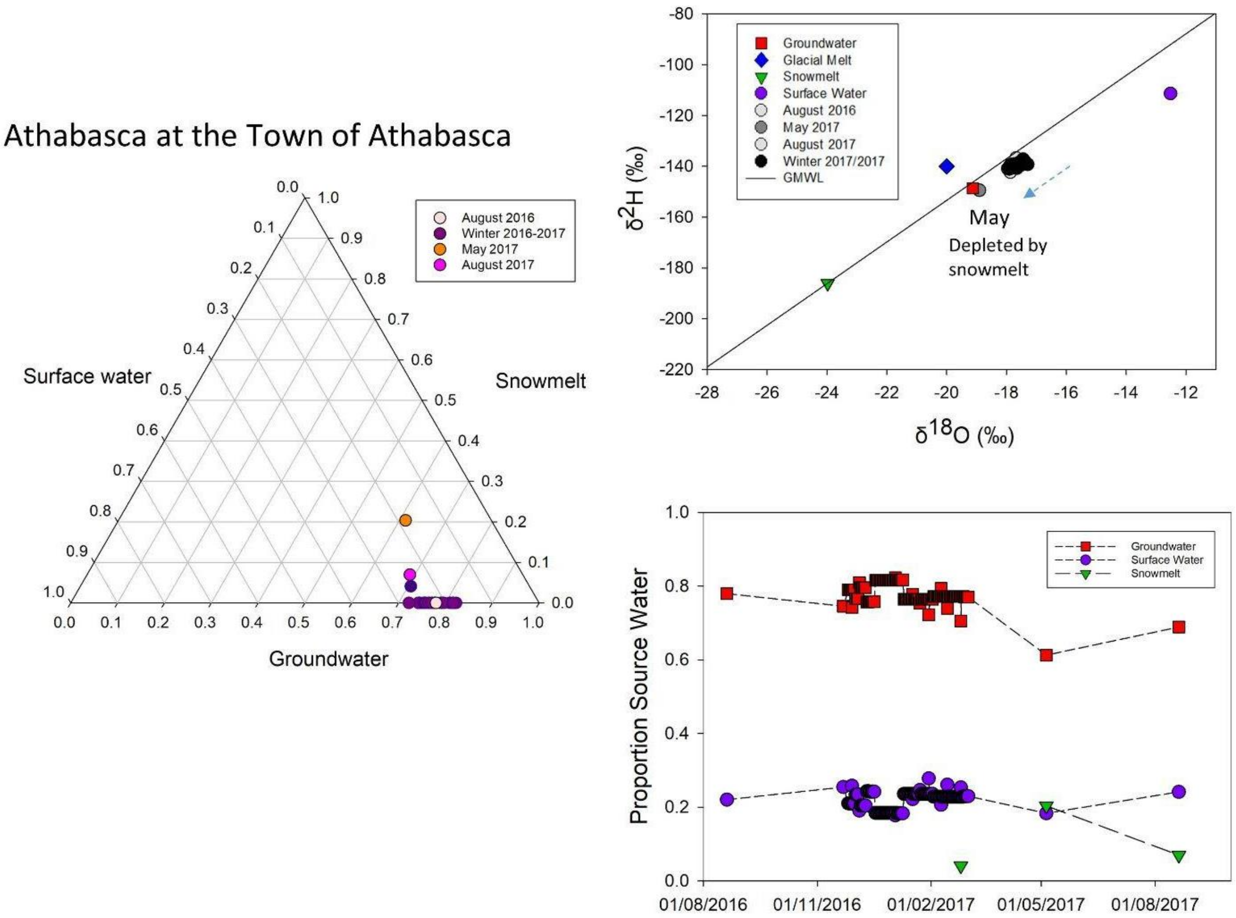


Figure 3.10: Annual patterns for streamflow of the Athabasca River at the Town of Athabasca are shown. The data in delta-delta space provides an overview of the isotopic composition of the samples compared to the isotopic composition of the source waters at each site. The ternary plot identifies the source water contribution of all of the samples at various times of the year. Trends over time are identified in a time series of source water contributions.

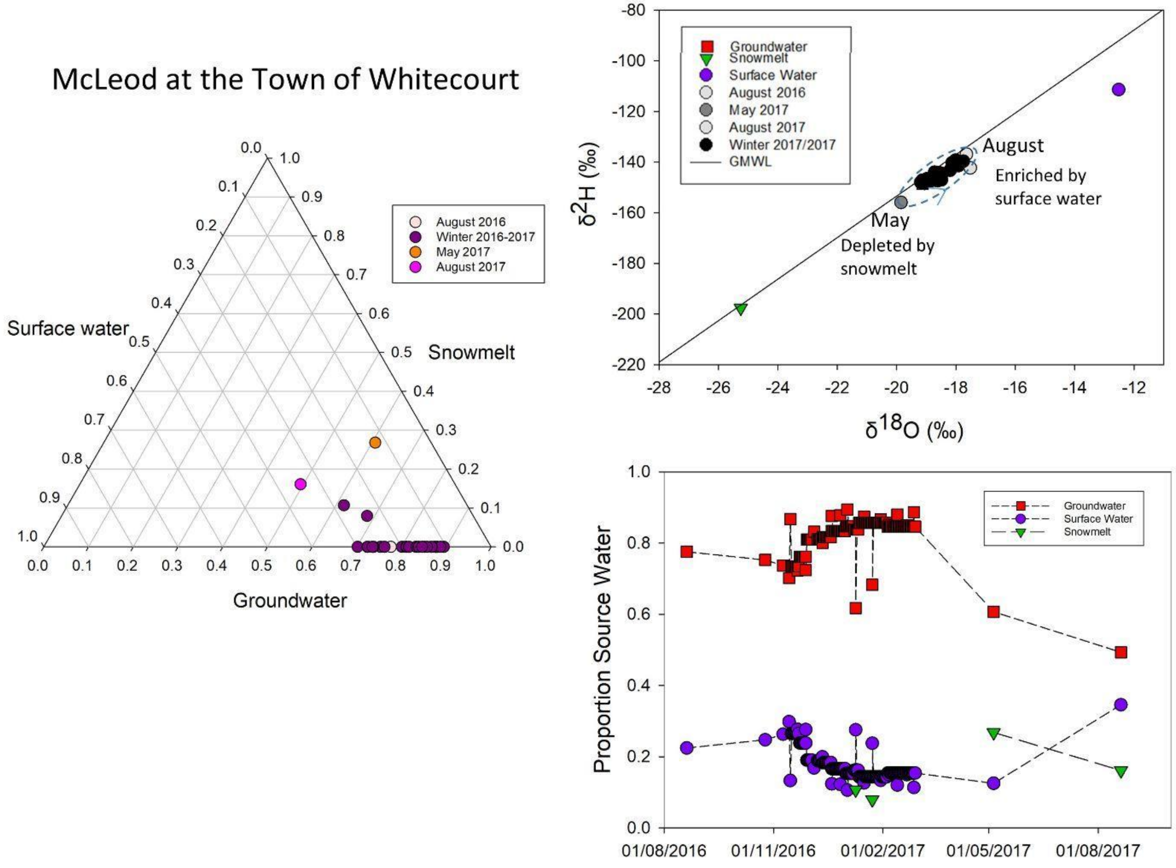


Figure 3.11: Annual patterns for streamflow of the McLeod River at the Town of Whitecourt are shown. The data in delta-delta space provides an overview of the isotopic composition of the samples compared to the isotopic composition of the source waters at each site. The ternary plot identifies the source water contribution of all of the samples at various times of the year. Trends over time are identified in a time series of source water contributions.

Chapter 4. Conclusions and recommendations for future research

4.1 Summary of thesis objectives

This thesis aimed to provide more knowledge on the source water contributions to streamflow in the Athabasca River Basin (ARB), a large snowmelt-dominated catchment with key ecological and economical value, where stable water isotope (SWI) studies have been limited. A key piece of analysis to meet this aim was the novel utilization of ice cores as a record that could allow a reconstruction of the isotopic composition of winter streamflow following the method described by Gibson and Prowse (1999; 2002). This was included with other seasonal (spring and late summer) synoptic surveys across the Upper and Middle ARB and provided insight into trends for source water contributions spatially, seasonally and annually across the basin. This data set and the trends that were analyzed could have applications for local water resource managers; however, future work is still required.

The primary objectives of this thesis were to:

1) Assess an emerging methodology that reconstructs the isotopic composition of winter streamflow through river ice stratigraphy.

2) Analyze the seasonal source water conditions across a large catchment where minimal studies have taken place, exploring spatial, seasonal and annual trends.

The aim of Chapter 2 of this thesis was to meet objective one. Building on the methodology laid out by Gibson and Prowse (1999; 2002), the isotopic composition of streamflow was successfully reconstructed at three locations in the ARB. The ice-water fractionation calculated was in alignment with experimental values and values collected in the field (Gibson & Prowse, 199; 2002; O’Neil, 1968), and results supported that a single streamflow would be sufficient to use this methodology. A comparison of the isotopic reconstructions of streamflow to the time-series of winter streamflow demonstrated close alignment between the two data sets when congelation ice had formed at all three locations. The occurrences for when this methodology had lower accuracy were (1) during extremely cold temperatures early on in the ice growth record, as temperature impacts water-ice fractionation rates; and (2) in the oldest samples at the surface of the ice which visually appeared to be congelation ice but isotope analysis indicated these samples were a mixture of streamflow and snowmelt or frazil ice. Overall, this methodology performed well, indicating there would be value in researching this methodology further in a variety of conditions and environments.

The aim of Chapter 3 of this thesis aims was to meet objective two. Spatial, seasonal and annual trends were explored using the synoptic datasets collected in the ARB alongside the record of winter streamflow produced in Chapter 2 providing new insights into the hydrology of the ARB. Spatial trends included an increase in the proportion of surface water as you move downstream as seen in other studies in the region (Yi *et al*., 2010). Seasonal trends confirmed that in general snowmelt peaks in spring, glacial melt peaks in late summer and groundwater was dominant over the winter. Annual trends indicated that the source waters in the McLeod follow a cyclical pattern, which was similar to the annual cycling of source waters on the nearby Liard River reported by St Amou*r et al.,* (2005). The Athabasca was not found to have a clear annual pattern due to the low variability of the samples over the course of the year. In addition, an analysis of August 2016 and August 2017 was completed which identified key differences in source water contributions that were linked to differences in weather conditions across these two years. Longer-term research over various locations on the Athabasca would be required to determine patterns for the annual cycling of source waters. Further insight into the catchment could likely be obtained if a higher spatial resolution of source waters, specifically snowmelt and groundwater, was collected and if further data to better understand the complexity of the region was available. For example, one of the goals of this assessment was to calculate snow and glacial melt contributions throughout the Upper and Middle Athabasca as this had not been included in previous SWI studies in the region (Birks *et al.,* 2017; Birks *et al*., 2019; Gibson *et al*., 2011; Gibson *et al.*, 2016). However, glacial melt contributions could not be calculated for all the sites and time periods studied due to the complexity of this catchment.

4.2 Recommendations for future studies

In assessing Gibson and Prowse's methodology for reconstructing winter streamflow using river ice stratigraphy (1999; 2002), it was found that the reconstruction was largely accurate. However, several variables would benefit from being studied further. These include studying how effective this methodology is when using thinner sections of ice cores as a higher resolution data set for winter streamflow when compared to a high-frequency time-series of streamflow samples. Future research could also explore how effective this methodology is under various ice growth conditions, such as early ice growth, growth under extremely cold periods and ice growth in locations with turbulent conditions. In addition, future studies should extend this methodology to catchments outside of the Mackenzie River Basin, where all of the existing studies have taken place.

The analysis of the source water contributions to the Upper Athabasca, Middle Athabasca and the McLeod identified key trends but future work is needed. A key area for future research could be collecting a higher resolution data set of source water values in the catchment over space and time. This study had limited source water samples collected which limited the scope and accuracy of the analysis that was conducted. This is especially needed in determining the value for snowmelt due to the high variability of snowmelt and large elevation changes in this catchment. A higher resolution data set may allow future studies to more accurately capture snow and glacial melt contributions to the Middle Athabasca and further downstream. Future studies should also take a multi-year approach. This could allow the seasonal cycling in the Athabasca to be better understood and could capture long-term trends such as decreasing source waters over time which would be valuable information for water resource managers.

References

Arendt, C. A., Aciego, S. M., & Hetland, E. A. (2015). An open source Bayesian Monte Carlo isotope mixing model with applications in Earth surface processes. Geochemistry, Geophysics, Geosystems, 16(5), 1274-1292.

Birks, J., Fennell, J., Yi, Y., Gibson, J., & Moncur, M. (2017). Regional geochemistry study for the Southern Athabasca Oil Sands (SAOS) area. COSIA Hydrogeology Working Group: Calgary, AB, Canada.

Birks, S. J., Fennell, J. W., Gibson, J. J., Yi, Y., Moncur, M. C., & Brewster, M. (2019). Using regional datasets of isotope geochemistry to resolve complex groundwater flow and formation connectivity in northeastern Alberta, Canada. Applied Geochemistry, 101, 140-159.

Gibson, J. J., & Prowse, T. D. (1999). Isotopic characteristics of ice cover in a large northern river basin. *Hydrological Processes, 13*(16), 2537-2548. doi:10.1002/(sici)1099-1085(199911)13:16<2537::aid-hyp940>3.3.co;2-1

Gibson, J. J., & Prowse, T. D. (2002). Stable isotopes in river ice: identifying primary over-winter streamflow signals and their hydrological significance. *Hydrological Processes, 16*(4), 873-890. doi:10.1002/hyp.366

Gibson, J. J., Birks, S. J., Moncur, M., Yi, Y., Tattrie, K., Jasechko, S., ... & Eby, P. (2011). Isotopic and geochemical tracers for fingerprinting process-affected waters in the oil sands industry: A pilot study. Oil Sands Research and Information Network, 1-120.

Gibson, J., Yi, Y., & Birks, S. (2016). Isotope-based partitioning of streamflow in the oil sands region, northern Alberta: Towards a monitoring strategy for assessing flow sources and water quality controls. *Journal of Hydrology: Regional Studies, 5*, 131-148. doi:10.1016/j.ejrh.2015.12.062

O'Neil, J. R. (1968). Hydrogen and oxygen isotope fractionation between ice and water. *The Journal of Physical Chemistry*, 72(10), 3683-3684. doi:10.1021/j100856a060=

St Amour, N. A., Gibson, J. J., Edwards, T. W., Prowse, T. D., & Pietroniro, A. (2005). Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River basin, Northwest Territories, Canada. Hydrological Processes: An International Journal, 19(17), 3357-3381.

Yi, Y., Gibson, J. J., Hélie, J. F., & Dick, T. A. (2010). Synoptic and time-series stable isotope surveys of the Mackenzie River from Great Slave Lake to the Arctic Ocean, 2003 to 2006. Journal of Hydrology, 383(3-4), 223-232.

Appendices

Appendix A: Field notes and isotopic results

A.1 Chapter 2

Table 1: Field notes and isotopic results for the ice core collected from the McLeod River in Whitecourt (54^{o}08’20.9” N 115^{o}41’56.3” W), on March 2nd. Isotope analysis was conducted at the Isotope Science Lab at the University of Calgary.

Label	Thickness from Bottom (cm)	Break type (N-Natural, M-Manual)	Ice Type (B-Black, W-White, S-Snow ice)	Length of segment (cm)	δ ^{18}0 (‰)	δ ^{2}H (‰)	D-excess
WC000	0-5	M	B	5	-15.94	-131.6	-4.08
WC005	5-10	N	B	5	-16.02	-131.8	-3.64
WC010	10-12.5	N	B	2.5	-15.88	-131.5	-4.46
WC012.5	12.5-17.7	M	B	5	-15.95	-131.6	-4.00
WC017.5	17.5-22.5	N	B	5	-15.85	-130.6	-3.80
WC022.5	22.5-27	M	B	4.5	-15.72	-129.5	-3.74
WC027	27-31.5	N	B	4.5	-15.68	-128.8	-3.36
WC031.5	31.5-32.5	N	B	1	-16.12	-132.0	-3.04
WC032.5	32.5-35	N	B	2.5	-16.18	-133.4	-3.96
WC035	35-39	N	B	4	-16.60	-135.1	-2.30
WC039	39-43	N	B	4	-15.67	-128.7	-3.34
WC043	43-48	N	B	5	-15.31	-127.7	-5.22
WC048	48-55	N	B	7	-15.11	-125.8	-4.92
WC055	55-56.25	N	B	1.25	-16.10	-131.3	-2.50
WC056.25	56.25-62.25	N	S	6	-19.72	-160.6	-2.84

Table 2. Field notes and isotopic results for the two ice cores (approximately 1 meter apart), collected from the Athabasca River, in Athabasca (54^{o} 43’.4” N, 113^{o}17’02.4 W), on March 3rd. Isotope analysis was conducted at the Isotope Science Lab at the University of Calgary.

Label	Thickness from Bottom (cm)	Break type (N-Natural, M-Manual)	Ice Type (B-Black, W-White)	Length of segment (cm)	$\delta\ ^{18}0$ (‰)	$\delta\ ^{2}H$ (‰)	D-excess
1AT000	0-2.7	N	B	2.7	-14.76	-124.2	-6.12
1AT002.7	2.7-8.7	M	B	6	-14.75	-123.9	-5.90
1AT08.7	8.7-10.7	N	B	2	-14.66	-123.4	-6.12
1AT010.7	10.7-15.2	N	B	4.5	-14.91	-125.1	-5.82
1AT015.2	15.2-20.7	M	B	5.5	-14.60	-124.0	-7.20
1AT020.7	20.7-27.1	N	B	6.4	-15.00	-125.2	-5.20
1AT027.1	27.1-33.1	N	B	6	-14.58	-123.0	-6.36
1AT033.1	33.1-35.1	N	B	2	-14.66	-123.0	-5.72
1AT035.1	35.1-38.1	N	B	3	-14.65	-122.8	-5.60
1AT038.1	38.1-40.6	N	B	2.5	-14.80	-123.4	-5.00
1AT040.6	40.6-41.6	N	B	1	-14.73	-124.1	-6.26
1AT041.6	41.6-46.6	N	B	5	-14.76	-123.5	-5.42
1AT046.6	46.6-52.8	N	W	6.2	-15.56	-128.9	-4.42
1AT052.8	52.8-53.8	N	W	1	-15.75	-129.4	-3.40
1AT053.8	53.8-60	N	W	6.2	-16.37	-132.9	-1.94
1AT060	60-68	M	W	8	-15.73	-129.7	-3.86
1AT068	68-76	N	W	8	-15.74	-131.8	-5.88
2AT000	0-1.5	N	B	1.5	-14.72	-124.0	-6.24
2AT001.5	1.5-6.5	M	B	5	-14.73	-123.9	-6.06
2AT006.5	6.5-11.5	M	B	5	-14.68	-123.4	-5.96
2AT011.5	11.5-14.7	N	B	3.2	-15.03	-125.1	-4.86
2AT014.7	14.7-21.1	N	B	6.4	-15.02	-125.5	-5.34
2AT021.1	21.1-25.9	N	B	4.8	-14.64	-123.1	-5.98
2AT025.9	25.9-28.7	N	B	2.8	-14.63	-122.5	-5.46

2AT028.7	28.7-35.2	N	B	6.5	-14.89	-123.6	-4.48
2AT035.2	35.2-37.2	N	B	2	-14.98	-123.9	-4.06
2AT037.2	37.2-38.7	N	B	1.5	-14.69	-122.9	-5.38
2AT038.7	38.7-42.2	N	B	3.5	-14.85	-123.6	-4.80
2AT042.2	42.2-29.2	N	B	7	-15.48	-127.1	-3.26
2AT049.2	49.2-53.2	N	B	4	-15.70	-128.6	-3.00
2AT053.2	53.2-55.2	N	W	2	-16.32	-132.4	-1.84
2AT055.2	55.2-57	N	W	1.8	-17.16	-137.1	0.180
2AT057	57-57.5	N	W	0.5	-16.55	-134.0	-1.60
2AT057.5	57.5-59	N	W	1.5	-15.81	-129.4	-2.92
2AT059	59-63.7	M	W	4.7	-15.68	-128.2	-2.76
2AT063.7	63.7-69.2	N	W	5.5	-15.74	-127.8	-1.88

Table 3. Field notes and isotopic results for the ice core collected from the Athabasca River, above Fort McMurray (56°43'10.5" N, 111°24'34.0 W), on March 4th. Isotopic analysis was conducted at the Isotope Science Lab at the University of Calgary. Note the core was frozen in ice core barrel and briefly warmed up in the vehicle to remove it.

Label	Thickness from Bottom (cm)	Break type (N-Natural, M-Manual)	Ice Type (W-White, S-Snow ice)	Length of segment (cm)	$\delta^{18}0$ (‰)	$\delta^{2}H$ (‰)	D-excess
FM000	0-6	M	W	6	-14.66	-122.9	-5.62
FM006	6-12	N	W	6	-14.34	-121.0	-6.28
FM012	12-22	M	W	10	-14.61	-122.2	-5.32
FM022	22-30	N	W	8	-15.03	-124.4	-4.16
FM030	30-38	N	W	8	-15.20	-125.6	-4.00
FM038	38-40.5	N	W	2.5	-15.20	-125.3	-3.70
FM040.5	40.5-42.5	N	W	2	-15.34	-125.8	-3.08
FM042.5	42.5-50.3	N	W	7.8	-15.04	-124.1	-3.78
FM050.3	50.3055	N	W	4.7	-15.06	-124.3	-3.82
FM055	55-57.3	N	W	2.3	-14.62	-122.9	-5.94
FM057.3	57.3-60.9	N	W	3.6	-15.02	-124.1	-3.94
FM60.9	60.9-63.7	N	W	2.8	-14.94	-123.3	-3.78
FM063.7	63.7-67.5	N	W	3.8	-14.97	-123.8	-4.04
FM067.5	67.5-68.5	N	W	1	-15.28	-125.3	-3.06
FM068.5	68.5-70.1	N	W	1.6	-14.91	-123.0	-3.72
FM070.1	70.1-72.1	N	W	2	-15.09	-125.5	-4.78
FM072.1	72.1-76.6	N	W	4.5	-14.40	-122.2	-7.00
FM076.6	76.6-78.7	N	W	2.1	-14.76	-123.7	-5.62
FM078.7	78.7-82.3	N	S	3.6	-18.55	-154.7	-6.30

Table 4. Winter streamflow samples collected from the McLeod River in Whitecourt (54^o 07' 59.11' N, 115^o 42' 15.28' W), by the Town of Whitecourt. Isotope analysis was conducted at the InnoTech Alberta Isotope lab at the Vancouver Island Tech Park.

Sample ID	δ ^{2}H (‰)	δ ^{18}0 (‰)	D-excess	δ^{2}H stdev	δ ^{18}0 stdev
Mcleod River 10/25/16	-140.3	-18.13	4.77		
Nov.9, 2016 Mcleod River	-139.2	-18.01	4.86		
14 Nov 2016 10:40 Mcleod River	-139.6	-17.75	2.37		
Mcleod River Nov 21/16 11:30	-141.1	-17.91	2.23		
Mcleod River Nov. 28/16	-141.4	-17.92	1.90		
dec.5, 2016 Mcleod River	-144.0	-18.72	5.77		
dec. 12, 2016 Mcleod River	-144.4	-18.49	3.45	0.2	
Mcleod River Dec. 20/16 5:15	-147.2	-19.05	5.25		
Dec 27th, 16 Mcleod River 8:20	-148.4	-19.06	4.08		
Jan 2, 2017 Mcleod River	-148.0	-19.18	5.52		
Jan 9, 2017 Mcleod River	-147.0	-18.48	0.91		
Jan 16, 2017 Mcleod River	-147.5	-19.03	4.73		
Jan 23, 2017 Mcleod River	-147.4	-18.62	1.58		0.13
Mcleod River Jan. 30, 2017	-146.6	-18.98	5.26	0.0	
Feb. 6, 2017 Mcleod River	-146.9	-18.86	3.97		
Mcleod River Feb 13 2017	-147.0	-19.08	5.57		
Feb. 21, 2017 Mcleod river	-147.6	-18.86	3.32	0.2	
Mcleod River Feb 27, 2017	-147.1	-19.13	5.90	0.3	

Table 5. Winter streamflow samples collected from Athabasca River in Athabasca (54° 43.412’ N, 113° 17.247’ W), by the Aspen Regional Water Services Commission. Isotope analysis was conducted at the InnoTech Alberta Isotope lab at the Vancouver Island Tech Park.

Sample ID	δ ^{2}H (‰)	δ ^{18}0 (‰)	D-excess	δ^{2}H stdev	δ ^{18}0 stdev
ARWSC Nov 22,2016 1:55 PM	-137.2	-17.45	2.40	0.5	
ARWSC Nov 29,2016 11:30 AM	-137.9	-17.42	1.46		
01/03/17 ARWSC 1245 PM	-140.9	-17.95	2.71		
ARWSC Jan 17, 2017 8:45 AM	-139.0	-17.66	2.27		
ARWSC Jan 23, 2017 10:00 AM	-139.4	-17.50	0.58		
ARWSC Jan 30, 2017 10:00 AM	-139.2	-17.29	-0.92		
ARWSC Athabasca Feb 9, 2017	-139.4	-17.76	2.68	0.2	0.09
ARWSC Feb 14, 2017 10:00 AM	-137.8	-17.40	1.43		
ARWSC Feb 25, 2017 10:10 AM	-140.7	-17.65	0.49		

A.2 Chapter 3

Table 6. Site locations and field notes for the stable water isotope surveys of the Athabasca River Basin in August 2016, May 2017 and August 2017. Coordinates were taken from the vehicle and not directly at the sampling location.

Site ID	Coordinates		Location	Notes
	N	W		
JT-01	52°50.0	116°17.0	Swift River at Valemont	Headwaters to the Fraser
JT-02	52°59.7	119°23.8	Robson River	Headwaters to the Fraser
JT-03	52°55.2	118°42.2	Moose River	Headwaters to the Fraser
JT-45	52°51.1	118°36.3	Fraser River	Headwaters to the Fraser
JT-04	52°12.8	117°13.9	Glacial melt stream	Athabasca icefield
JT-05	52°12.8	117°13.9	Sunwapta Lake	Athabasca icefield
JT-06	52°12.8	117°13.9	Inflow to Sunwapta Lake	Athabasca icefield
JT-53	52°12.7	117°14.1	Inflow Sunwapta Lake under bridge	Athabasca icefield
JT-07	52°10.3	117°04.4	Saskatchewan River	Headwaters to the Saskatchewa River, JT-54 Duplicate
JT-08	52°14.7	117°15.7	Sunwapta River	Headwaters to the Athabasca
JT-09	52°16.0	117°17.3	Tangle Creek	No glacial melt
JT-10	52°19.7	117°19.9	Beauty Creek	JT-44 Duplicate

JT-11	52^{o}25.0	117^{o}23.8	Jonas Creek	
JT-12	52^{o}28.6	117^{o}30.2	Sunwapta Falls	
JT-14	52^{o}40.0	117^{o}53.0	Athabasca Falls	
JT-15	52^{o}43.5	117^{o}55.6	Whirlpool River	
JT-16	52^{o}46.5	118^{o}01.9	Astoria River	
JT-17	52^{o}48.0	118^{o}02.8	Portal Creek	
JT-18	52^{o}51.7	118^{o}05.1	Miette River	No glacial melt
JT-19	52^{o}56.7	118^{o}01.8	Malgine River	
JT-20	52^{o}55.9	118^{o}02.0	Athabasca After Jasper	
JT-21	53^{o}00.9	118^{o}04.7	Snarring River	JT-55 Duplicate
JT-22	53^{o}08.5	117^{o}58.7	Rocky River	
JT-23	53^{o}22.6	117^{o}42.0	Athabasca before Hinton	JT-24 Duplicate
JT-25	53^{o}01.3	117^{o}19.7	White Horse River	Headwaters to the McLeod, JT-46 Duplicate
JT-26	53^{o}04.3	117^{o}16.7	McLeod River	
JT-27	53^{o}18.0	117^{o}16.7	McLeod at North Camp	
JT-28	53^{o}27.7	116^{o}37.1	McLeod before Areth	
JT-29	53^{o}25.1	116^{o}18.4	Erith River	also referred to as the Embarrass river on some maps

JT-30	53°35.8	116°18.9	McLeod At Edson	JT-47 Duplicate
JT-31	53°35.9	116°16.2	Wolfe Creek	
JT-32	53°39.8	116°17.3	Edson River	JT-56 Duplicate
JT-33	53°42.6	115°59.5	McLeod at Riverside Park	
JT-34	54°09.0	115°42.1	Athabasca before McLeod	
JT-35	54°08.4	115°41.9	McLeod aver agri ditch	New location in May 2017
JT-36	54°08.0	115°42.2	McLeod before Athabasca	
JT-37	54°09.5	115°23.4	Athabasca after McLeod	
JT-38	54°43.3	113°17.1	Athabasca in Athabasca	JT-39 Duplicate
JT-40	55°13.8	114°08.9	Lesser Slave River	JT-48 Duplicate
JT-41	55°04.5	114°05.8	Athabasca at Hondo	
JT-42	55°40.0	114°12.2	Pembina River	JT-43 Duplicate
JT-49	55°04.8	112°35.0	La Biche River	JT 50 Duplicate
JT-51	56°43.3	111°24.5	Athabasca at Fort McMurray	JT-52 Duplicate

Table 7. Tracer results for the stable water isotope surveys of the Athabasca River Basin in August 2016, May 2017 and August 2017. Tracers include δ^{2}H (‰), δ^{18}O (‰), temperature (^{o}C) and electrical conductivity (µS/cm). Bad sample quality is indicated by *. Isotopic data collected over the winter of 2016-2017 can be found in appendix 2.

Site ID	August 2016		May 2017				August 2017			
	δ^{2}H (‰)	δ^{18}O (‰)	δ^{2}H (‰)	δ^{18}O (‰)	EC (µS/cm)	Temp (^{o}C)	δ^{2}H (‰)	δ^{18}O (‰)	EC (µS/cm)	Temp (^{o}C)
JT-01	-143.54	-18.99					-154.09	-19.97		
JT-02	-147.91	-19.41					-141.11	-16.99		
JT-03	-146.01	-19.28					-143.18	-18.28		
JT-04	-153.36	-20.47					-153.22	-20.30	0.06	1.41
JT-05	-153.62	-20.28	-174.69	-22.70	0.12	9.27	-154.87	-20.25	0.18	8.00
JT-06	-153.32	-20.35	-163.46	-21.47	0.27	10.12	-155.47	-20.78	0.12	7.62
JT-07	-151.69	-20.16	-160.28	-20.98	0.16	5.36	-152.93	-20.26	0.07	1.73
JT-08	-156.10	-20.67	-170.54	-22.27	0.21	1.59	-154.47	-20.44	0.09	4.61
JT-09	-157.28	-20.41	-163.72	-21.26	0.41	6.33	-163.57	-21.13	0.39	7.84
JT-10	-154.16	-20.28	-160.37	-20.92	0.29	9.26	-159.57	-20.95	0.24	11.38
JT-11	-154.50	-20.24	-179.25	-23.16	0.14	2.68	-161.09	-21.00	0.11	10.82
JT-12	*	*	-165.91	-21.35	0.21	7.01	-157.67	-20.76	0.16	7.31
JT-14	-151.57	-19.99	-158.19	-20.55	0.20	12.24	-155.66	-20.51	0.15	10.41
JT-15	-146.82	-19.48	-150.55	-19.36	0.18	10.28	-149.97	-19.84	0.13	10.99
JT-16	-148.57	-19.40	-162.12	-20.78	0.15	1.88	-152.68	-20.03	0.11	12.33
JT-17	-151.99	-19.89	-166.50	-21.51	0.26	2.50	-160.67	-21.10	0.24	11.43
JT-18	-147.06	-19.37	-156.45	-20.07	0.25	10.71	-155.72	-19.99	0.25	12.46
JT-19	-153.92	-20.11	-159.13	-20.51	0.27	6.53	-158.48	-20.68	0.24	12.10
JT-20	-149.25	-19.85	-155.47	-19.98	0.20	7.75	-153.73	-20.26	0.16	12.72
JT-21	-147.70	-19.38	-163.94	-21.09	0.24	4.42	-154.96	-20.31	0.22	12.71
JT-22	-151.46	-19.69	-164.44	-21.34	0.33	3.82	-158.83	-20.61	0.43	13.98
JT-23	-150.58	-19.85	-156.59	-20.06	0.40	10.45	-155.23	-20.32	0.23	16.99
JT-24	-150.46	-19.66								
JT-25	-147.61	-19.19	-164.36	-21.21	0.38	4.02	-156.17	-20.21	0.53	6.97
JT-26	-145.85	-19.32	-166.18	-21.37	0.45	3.38	-154.05	-20.11	0.63	8.16
JT-27	-142.95	-18.69	-170.10	-21.66	0.18	1.86	-150.74	-19.30	0.47	11.90
JT-28	-142.73	-18.54	-162.76	-20.70	0.21	6.12	-148.93	-18.76	0.44	16.82
JT-29	-139.46	-17.80	-159.72	-20.43	0.15	4.89	-145.37	-17.86	0.38	15.11
JT-30	-139.97	-17.87	-158.76	-20.18	0.19	8.70	-146.17	-18.27	0.41	17.27
JT-31	-131.74	-16.88	-153.39	-19.34	0.14	8.04	-138.24	-17.03	0.38	16.25

JT-32	-135.77	-17.21	-156.59	-19.94	0.21	7.00	-143.09	-18.03	0.40	16.37
JT-33	-136.86	-17.65	-157.09	-19.94	0.19	8.50	-143.62	-17.83	0.42	18.83
JT-34	-145.86	-19.03	-157.38	-20.07	0.25	10.33	-153.99	-20.04	0.28	16.59
JT-35	*	*	-155.89	-19.85	0.21	9.61	-142.27	-17.52	0.51	18.61
JT-36	*	*	-156.75	-19.86	0.19	10.32				
JT-37	-141.63	-18.36	-157.26	-19.99	0.22	8.41	-152.25	-19.67	0.30	17.01
JT-38	-136.73	-17.67	-149.43	-18.90	0.23	13.11	-142.24	-17.87	0.30	18.44
JT-39	*	*								
JT-40	-120.49	-14.67	-140.34	-17.55	0.10	8.62	-116.90	-13.56	0.20	18.10
JT-41	-139.70	-17.99	-154.40	-19.69	0.21	11.28	-151.18	-19.49	0.29	19.03
JT-42	-126.18	-15.74	-151.91	-19.21	0.23	12.89	-124.68	-14.40	0.37	20.17
JT-43	-126.05	-15.67								
JT-44			-160.10	-20.85			-159.18	-20.95		
JT-45			-154.18	-20.10	0.14	6.55	-150.87	-19.78	0.12	10.32
JT-46			-164.08	-21.31						
JT-47			-158.54	-20.13						
JT-48			-140.26	-17.71						
JT-49			-117.71	-13.50	0.24	14.54	-111.32	-12.52	0.27	16.58
JT-50			-117.28	-13.44			-111.30	-12.61		
JT-51			-146.44	-18.46	0.22	12.27	-140.35	-17.42	0.31	18.15
JT-52			-146.55	-18.59			-140.43	-17.43		
JT-53							-155.53	-20.41	0.30	13.83
JT-54							-152.73	-20.06		
JT-55							-154.72	-20.26		
JT-56							-142.84	-18.01		

Table 8. Source water site locations, and tracer results from the Athabasca River Basin. Tracers include δ²H (‰), δ¹⁸O (‰), temperature (ºC) and electrical conductivity (µS/cm). Snowmelt was collected in May 2017 and groundwater was collected in August 2017.

Source water type	Site ID	Coordinates		Location	δ²H	δ¹⁸O	EC	Temp	Notes
		N	W		(‰)	(‰)	(µS/cm)	(ºC)	
Snowmelt	JT-80	52.665	-117.886	Athtbasca Falls	-137.37	-16.96	0.035	18.9	Sampled contaminated by streamflow
Snowmelt	JT-82	52.322	-117.324	Beauty Falls	-144.95	-18.75	0.015	20.07	

Appendix B: Duplicates and errors values

B.1 Chapter 2

Table 9. Error values for ice core and winter streamflow samples. Where VITP denotes the InnoTech Alberta Isotope lab at the Vancouver Island Tech Park and U Calgary denotes the Isotope Science Lab at the University of Calgary.

Errors	δ ^{18}0 (‰)	δ ^{2}H (‰)
Precision and Accuracy	0.2	1
VITP max standard deviation	0.13	0.5
Difference between VITP and U Calgary	0.3	1.2
Ice core field duplicates	0.65	1.8

Table 10. Comparison of isotope samples that underwent analysis at both the InnoTech Alberta Isotope lab at the Vancouver Island Tech Park and at the Isotope Science Lab at the University of Calgary. Samples were collected May 2017.

Sample ID	VITP		U of Calgary		Difference	
	δ ^{18}0 (‰)	δ ^{2}H (‰)	δ ^{18}0 (‰)	δ ^{2}H (‰)	δ ^{18}0 (‰)	δ ^{2}H (‰)
JT-10	-20.92	-160.37	-20.66	-159.99	-0.26	-0.38
JT-11	-23.16	-179.25	-20.94	-164.43	-2.22	-14.82
JT-19	-20.51	-159.13	-20.30	-157.94	-0.21	-1.19
JT-20	-19.98	-155.47	-19.81	-155.03	-0.17	-0.44
JT-90	-16.96	-137.37	-16.93	-138.41	-0.03	1.04
JT-91	-22.11	-173.10	-21.93	-172.50	-0.18	-0.60
JT-92	-18.75	-144.95	-18.54	-144.57	-0.21	-0.38
JT-93	-25.49	-199.75	-25.50	-199.36	0.01	-0.39
JT-94	-26.60	-208.96	-26.62	-208.26	0.02	-0.70
JT-95	-23.67	-184.11	-23.53	-183.17	-0.14	-0.94

Table 11. Comparison of field duplicates accounting for 16% of total ice core samples and 11% of all ice core and winter streamflow samples combined. Isotope analysis was conducted at the University of Calgary. Note all duplicates were taken from Fort Murray core in random order.

Sample ID	Original core		Duplicates		Difference	
	δ ^{18}0 (‰)	δ ^{2}H (‰)	δ ^{18}0 (‰)	δ ^{2}H (‰)	δ ^{18}0 (‰)	δ ^{2}H (‰)
FM006	-14.34	-121	-14.24	-121.1	-0.1	0.1
FM012	-14.61	-122.2	-14.42	-122	-0.19	-0.2
FM022	-15.03	-124.4	-14.93	-124	-0.1	-0.4
FM030	-15.2	-125.6	-15.16	-125.2	-0.04	-0.4
FM050.3	-15.06	-124.3	-14.83	-123.1	-0.23	-1.2
FM055	-14.62	-122.9	-15.18	-123.9	0.56	1
FM060.9	-14.94	-123.3	-15.07	-122.9	0.13	-0.4
FM063.7	-14.97	-123.8	-15.23	-123.7	0.26	-0.1
FM067.5	-15.28	-125.3	-15.28	-126	0	0.7
FM072.1	-14.4	-122.2	-15.05	-124	0.65	1.8
FM078.7	-18.55	-154.7	-18.88	-155.3	0.33	0.6

B.2 Chapter 3

Table 12. Stable water isotope field duplicates collected across over the Athabasca River Basin in August 2016, May 2017 and August 2018. Instrumental uncertainty was reported as +/- 0.2‰ ^{18}O and +/- 1.0 ‰ ^{2}H. In lab duplicates from streamflow, samples had a maximum Stdev of 0.1‰ ^{18}O and 0.6‰ ^{2}H. Duplicates from the field accounted for 13% of total samples and had a maximum difference of 0.20 ‰ ^{18}O and 0.43 ‰ ^{2}H. Bad sample quality is indicated by *.

Site ID	Sampling campaign	Difference		Notes
		δ^2H (‰)	δ^{18}O (‰)	
JT–07	August 2017	0.19	0.20	
JT-10	May 2017	0.27	0.07	
JT-10	August 2017	0.19	0.20	
JT-21	August 2017	0.25	0.04	
JT-23	August 2016	0.12	0.19	
JT-25	May 2017	0.27	-0.10	
JT-30	May 2017	0.22	0.05	
JT-32	August 2017	0.25	0.02	
JT-38	August 2016	*	*	Poor sampling methodology
JT-40	May 2017	0.08	-0.16	
JT-42	August 2016	0.13	0.06	
JT-49	May 2017	0.43	0.06	
JT-49	August 2017	0.02	-0.09	
JT-51	May 2017	-0.11	-0.13	
JT-51	August 2017	-0.07	0.00	

Appendix C: Calculations

C.1 Chapter 2

Table 13. Calculations for the isotopic fractionation of the streamflow(water) to ice, where the ice was dated using an ice growth model.

Date	Location	Ice δ ^{18}0 (‰)	Water δ ^{18}0 (‰)	Apparent fractionation	Ice δ ^{2}H (‰)	Water δ ^{2}H (‰)	Apparent fractionation
11/21/2016	WC	-15.11	-17.91	1.00285	-125.8	-141.1	1.0178
11/28/2016	WC	-15.31	-17.92	1.00265	-127.7	-141.4	1.0160
12/05/2016	WC	-15.67	-18.72	1.00311	-128.7	-144.0	1.0179
12/12/2016	WC	-15.68	-18.49	1.00286	-128.8	-144.4	1.0183
12/20/2016	WC	-15.72	-19.05	1.00339	-129.5	-147.2	1.0207
12/27/2016	WC	-15.85	-19.06	1.00327	-130.6	-148.4	1.0209
01/02/2017	WC	-15.85	-19.18	1.00340	-130.6	-148.0	1.0204
01/09/2017	WC	-15.95	-18.48	1.00258	-131.6	-147.0	1.0180
01/16/2017	WC	-16.02	-19.03	1.00307	-131.8	-147.5	1.0185
01/23/2017	WC	-16.02	-18.62	1.00265	-131.8	-147.4	1.0183
01/30/2017	WC	-16.02	-18.98	1.00302	-131.8	-146.6	1.0173
02/06/2017	WC	-16.02	-18.86	1.00290	-131.8	-146.9	1.0177
02/13/2017	WC	-15.94	-19.08	1.00320	-131.6	-147.0	1.0181
02/21/2017	WC	-15.94	-18.86	1.00298	-131.6	-147.6	1.0187

02/27/2017	WC	-15.94	-19.13	1.00325	-131.6	-147.1	1.0182
11/29/2016	ATHA	-14.85	-17.42	1.00262	-123.6	-137.9	1.0166
01/03/2017	ATHA	-15.02	-17.95	1.00299	-125.5	-140.9	1.0179
01/17/2017	ATHA	-14.68	-17.66	1.00303	-123.4	-139.0	1.0181
01/23/2017	ATHA	-14.68	-17.50	1.00287	-123.4	-139.4	1.0186
01/30/2017	ATHA	-14.68	-17.29	1.00266	-123.4	-139.2	1.0184
02/09/2017	ATHA	-14.73	-17.76	1.00309	-123.9	-139.4	1.0180
02/14/2017	ATHA	-14.73	-17.40	1.00272	-123.9	-137.8	1.0161
02/25/2017	ATHA	-14.73	-17.65	1.00297	-123.9	-140.7	1.0196
11/22/2016	ATHA	-14.76	-17.45	1.00273	-123.5	-137.2	1.0158
11/29/2016	ATHA	-14.80	-17.42	1.00267	-123.4	-137.9	1.0168
01/03/2017	ATHA	-14.60	-17.95	1.00341	-124.0	-140.9	1.0197
01/17/2017	ATHA	-14.75	-17.66	1.00296	-123.9	-139.0	1.0176
01/23/2017	ATHA	-14.75	-17.50	1.00280	-123.9	-139.4	1.0180
01/30/2017	ATHA	-14.75	-17.29	1.00258	-123.9	-139.2	1.0178
02/09/2017	ATHA	-14.75	-17.76	1.00307	-123.9	-139.4	1.0180
02/14/2017	ATHA	-14.76	-17.40	1.00269	-124.2	-137.8	1.0158
02/25/2017	ATHA	-14.76	-17.65	1.00294	-124.2	-140.7	1.0192

Table 14. Summary statistics from the calculated isotopic fractionation of water to ice for each site

	δ ^{18}0 apparent fractionation			δ ^{2}H apparent fractionation		
	average	max	min	average	max	min
All	1.00294	1.00341	1.00258	1.0181	1.0209	1.0158
Whitecourt	1.00301	1.00340	1.00258	1.0184	1.0209	1.0160
Athabasca	1.00287	1.00341	1.00258	1.0178	1.0197	1.0158
Fort McMurray	1.00292	1.00348	1.00245	1.0190	1.0214	1.0155

Table 15. Using the average isotopic fractionation the isotopic composition of streamflow was calculated for each ice core section sampled.

Site	Ice δ ^{18}0 (‰)	New value δ ^{18}0 (‰)	Ice δ ^{2}H (‰)	New value δ ^{2}H (‰)
WC	-15.94	-18.82	-131.6	-147.0
WC	-16.02	-18.90	-131.8	-147.2
WC	-15.88	-18.76	-131.5	-146.9
WC	-15.95	-18.83	-131.6	-147.0
WC	-15.85	-18.73	-130.6	-146.1
WC	-15.72	-18.61	-129.5	-145.0
WC	-15.68	-18.57	-128.8	-144.3
WC	-16.12	-19.00	-132	-147.4
WC	-16.18	-19.06	-133.4	-148.8
WC	-16.6	-19.48	-135.1	-150.5
WC	-15.67	-18.56	-128.7	-144.2
WC	-15.31	-18.20	-127.7	-143.2
WC	-15.11	-18.00	-125.8	-141.3
WC	-16.1	-18.98	-131.3	-146.7
ATHA	-14.76	-17.65	-124.2	-139.8
ATHA	-14.75	-17.64	-123.9	-139.5
ATHA	-14.66	-17.55	-123.4	-139.0
ATHA	-14.91	-17.80	-125.1	-140.7
ATHA	-14.6	-17.49	-124	-139.6
ATHA	-15	-17.89	-125.2	-140.8
ATHA	-14.58	-17.47	-123	-138.6

ATHA	-14.66	-17.55	-123	-138.6
ATHA	-14.65	-17.54	-122.8	-138.4
ATHA	-14.8	-17.69	-123.4	-139.0
ATHA	-14.73	-17.62	-124.1	-139.7
ATHA	-14.76	-17.65	-123.5	-139.1
ATHA	-14.72	-17.61	-124	-139.6
ATHA	-14.73	-17.62	-123.9	-139.5
ATHA	-14.68	-17.57	-123.4	-139.0
ATHA	-15.03	-17.92	-125.1	-140.7
ATHA	-15.02	-17.91	-125.5	-141.0
ATHA	-14.64	-17.53	-123.1	-138.7
ATHA	-14.63	-17.52	-122.5	-138.1
ATHA	-14.89	-17.78	-123.6	-139.2
ATHA	-14.98	-17.87	-123.9	-139.5
ATHA	-14.69	-17.58	-122.9	-138.5
ATHA	-14.85	-17.74	-123.6	-139.2
ATHA	-15.48	-18.37	-127.1	-142.6
ATHA	-15.7	-18.59	-128.6	-144.1
FM	-14.66	-17.55	-122.9	-138.5
FM	-14.34	-17.23	-121	-136.6
FM	-14.61	-17.50	-122.2	-137.8
FM	-15.03	-17.92	-124.4	-140.0
FM	-15.2	-18.09	-125.6	-141.1
FM	-15.2	-18.09	-125.3	-140.9
FM	-15.34	-18.23	-125.8	-141.3
FM	-15.04	-17.93	-124.1	-139.7
FM	-15.06	-17.95	-124.3	-139.9
FM	-14.62	-17.51	-122.9	-138.5
FM	-15.02	-17.91	-124.1	-139.7
FM	-14.94	-17.83	-123.3	-138.9
FM	-14.97	-17.86	-123.8	-139.4
FM	-15.28	-18.17	-125.3	-140.9
FM	-14.91	-17.80	-123	-138.6
FM	-15.09	-17.98	-125.5	-141.0
FM	-14.4	-17.29	-122.2	-137.8
FM	-14.76	-17.65	-123.7	-139.3

Table 16. Using the average isotopic fractionation a potential isotopic composition of snow was calculated for the white ice sample

Location	Ice δ ^{18}0 (‰)	New value δ ^{18}0 (‰)	Ice δ ^{2}H (‰)	New value δ ^{2}H (‰)
WC	-19.72	-22.59	-160.6	-175.5
FM	-18.55	-21.43	-154.7	-169.7

Table 17. Using a comparison of the ice core and streamflow samples at Whitecourt non-equilibrium fractionations were calculated.

Sample	Ice δ ^{18}0 (‰)	streamflow δ ^{18}0 (‰)	Fractionation	Ice δ ^{2}H (‰)	streamflow δ ^{2}H (‰)	Fractionation
31.5	-16.12	-18.57	1.00250	-132	-144.3	1.01437
32.5	-16.18	-18.59	1.00246	-133.4	-144.3	1.01274
035	-16.6	-18.64	1.00208	-135.1	-144.1	1.01052

Table 18. The percent of new (snow or white ice) and old water (streamflow) in the uppermost congelation ice samples was calculated when samples did not isotopically resemble the streamflow samples that were collected at this time.

Site	Sample		New water		Old water	Mixing (%)	
	ID	δ ^{18}0 (‰)	source	δ ^{18}0 (‰)	(‰)	New water δ ^{18}0 (‰)	Old water δ ^{18}0 (‰)
WC	055	-18.98	Snow	-22.59	-17.75	25.49	74.51
ATHA	42.2	-18.59	White ice	-19.09	-17.45	69.15	30.85
ATHA	49.2	-18.37	White ice	-19.09	-17.42	56.44	43.56

Appendix D: Additional figures

D.1 Chapter 2

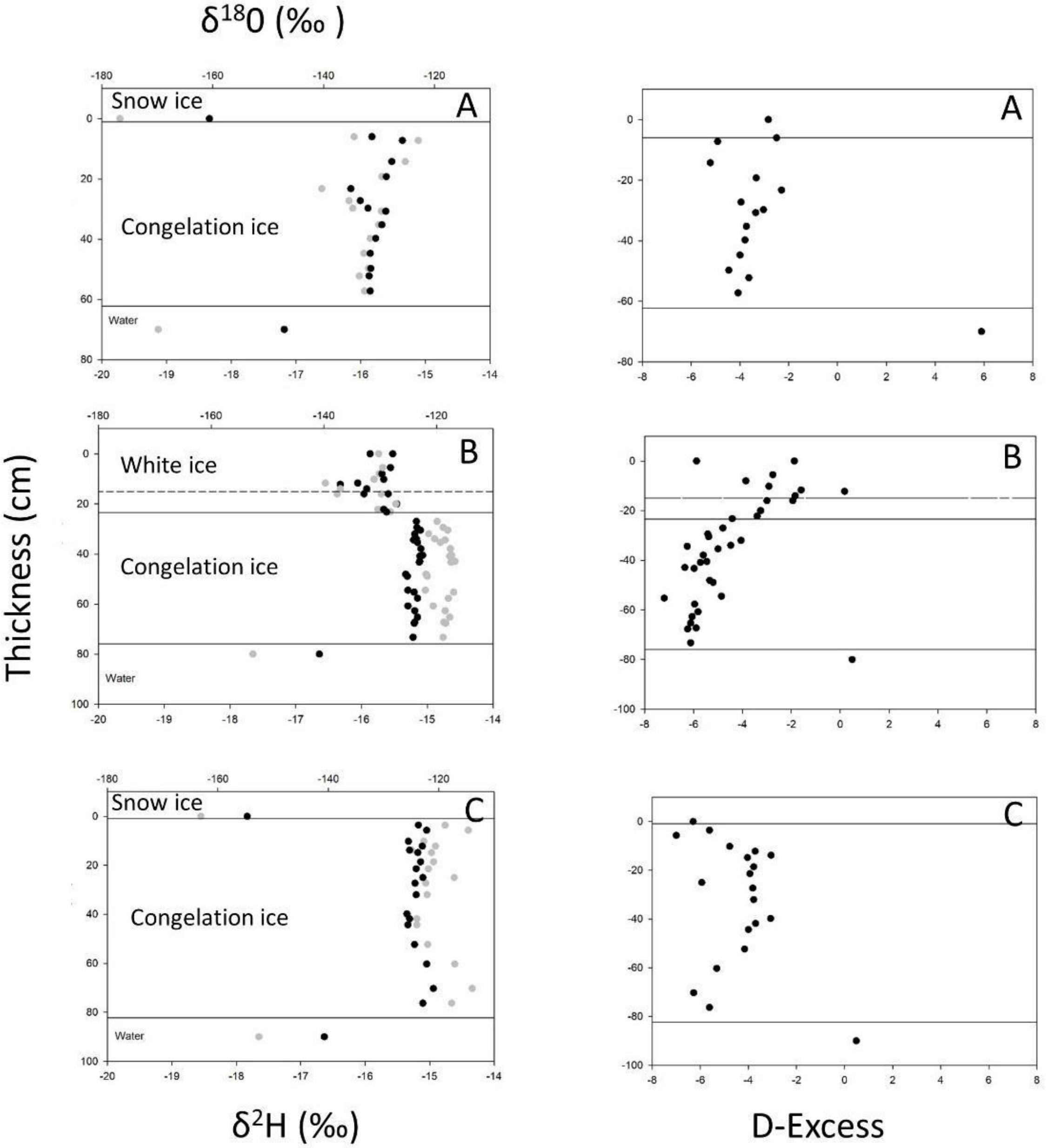


Figure 1. The isotopic composition and D-exess of the ice cores and streamflow are displayed vertically to highlight trends over the thickness of the core, where A) is Whitecourt, B) is Athabasca and C) is Fort McMurray. The dotted line at Athabasca displays a difference between where the white ice ends between the two cores. Note the water samples displayed at Fort McMurray was collected upstream at Athabasca.

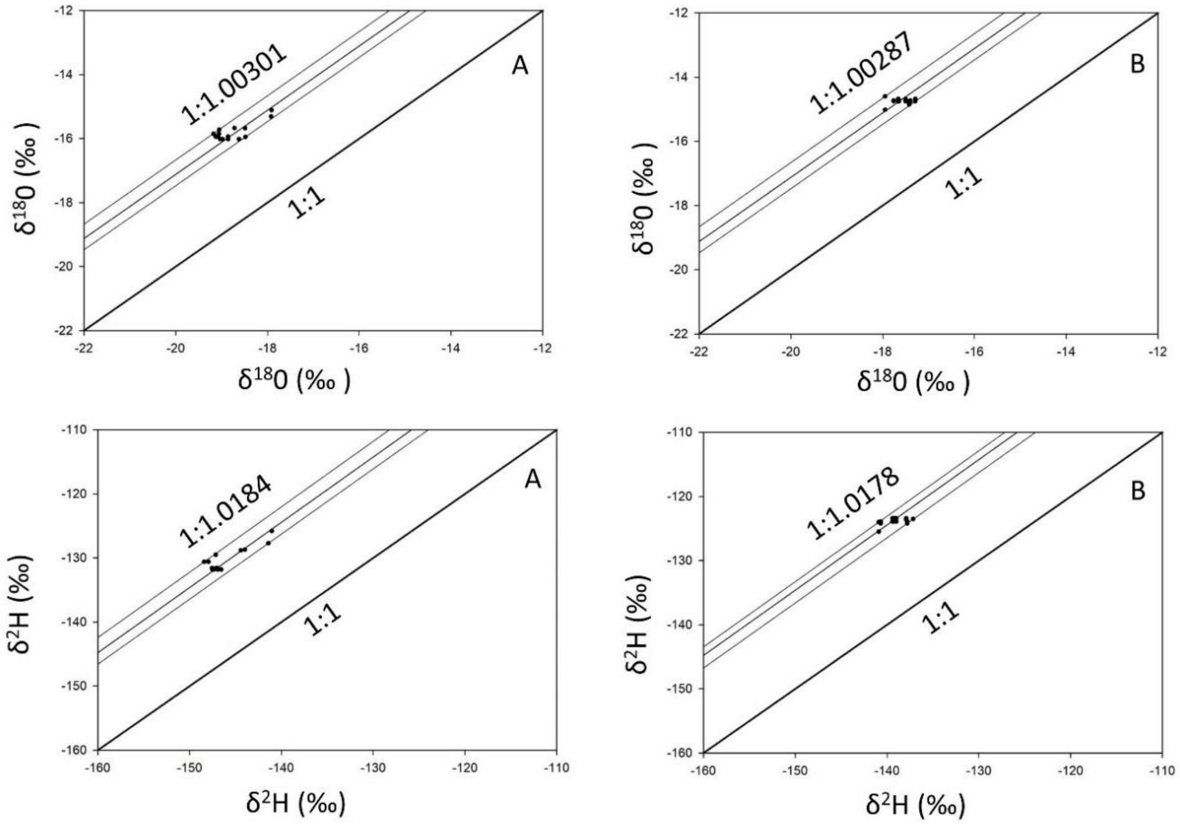


Figure 2. The site-specific range of fractionations found for both δ^2H and δ^{18}O for A) Whitecourt and B) Athabasca. Calculated using the isotopic values of congelation ice and streamflow that corresponded by date.

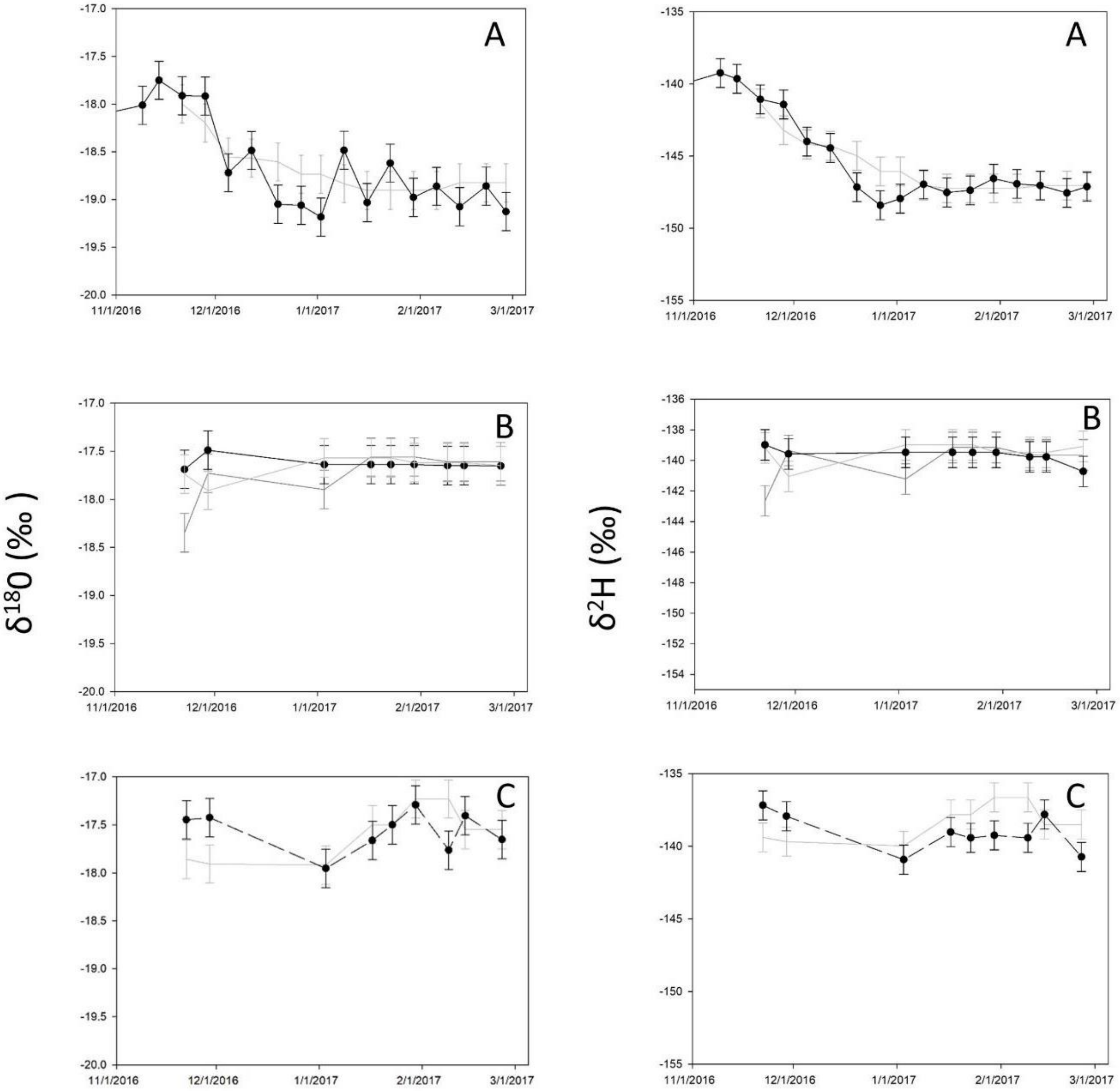


Figure 3. A comparison of the isotopic values of streamflow (black) and the reconstructed isotopic composition of streamflow (grey) displaying only the dates when streamflow was directly collected for A) Whitecourt, B) Athabasca, and C) Fort McMurray. Error bars were determined using the values for instrumental uncertainty of 0.2 $\delta^{18}O$ and 1.0 $\delta^{2}H$. The values of streamflow for Fort McMurray are displayed as a dotted line as data from Athabasca was used.

A.2 Chapter 3

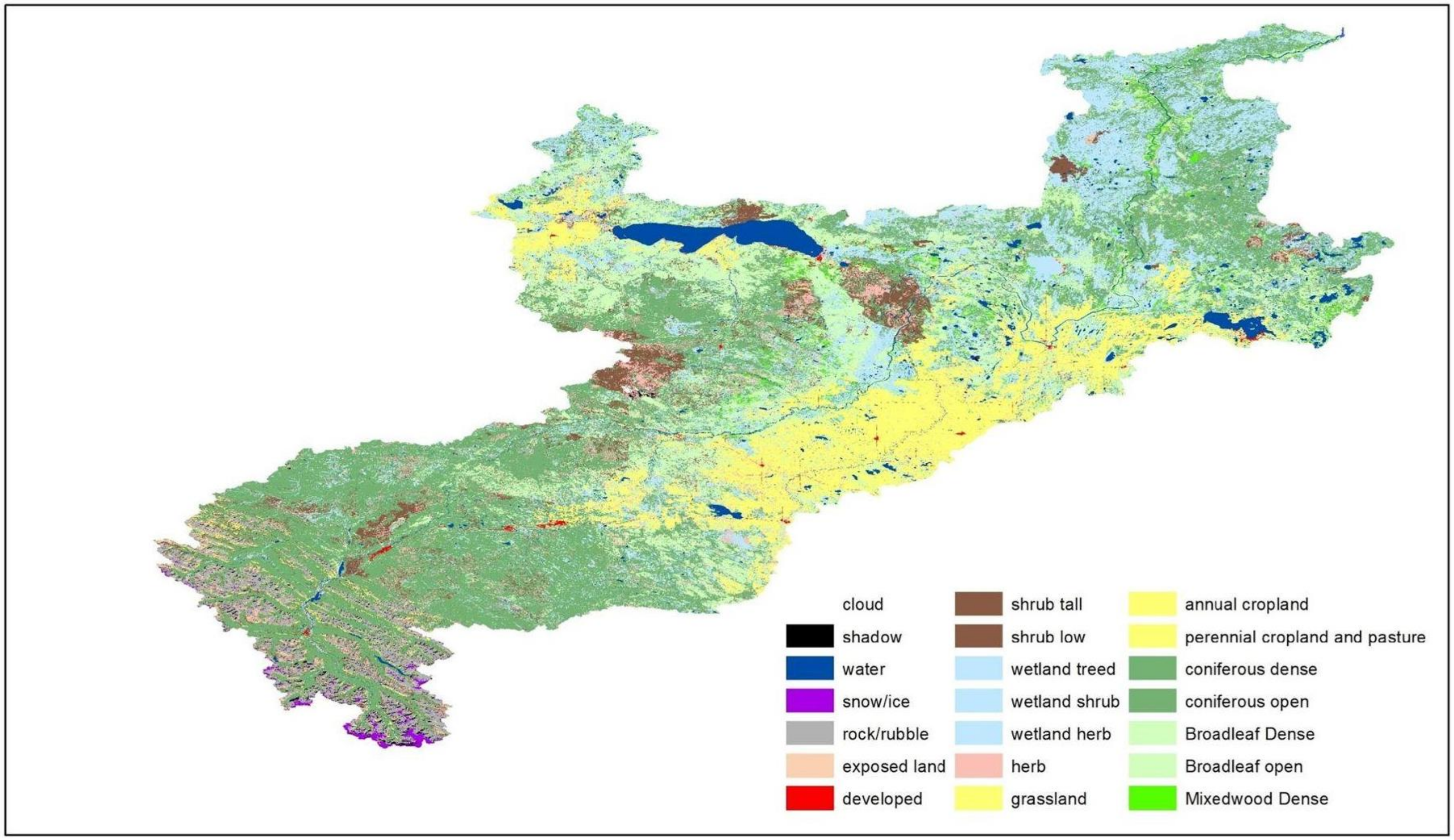


Figure 4. Distribution of landcover classifications[1] over the Athabasca watershed. Similar landcover classifications have been displayed in the same colour to identify areas where wetlands, agriculture and forests are located.

---

[1] Natural Resources Canada. (2006, January 1). *Land cover*. Open Government Portal. Retrieved September 2017, from https://open.canada.ca/data/en/dataset/4f46b49e-7852-5f05-9328-a67ec67f52cb

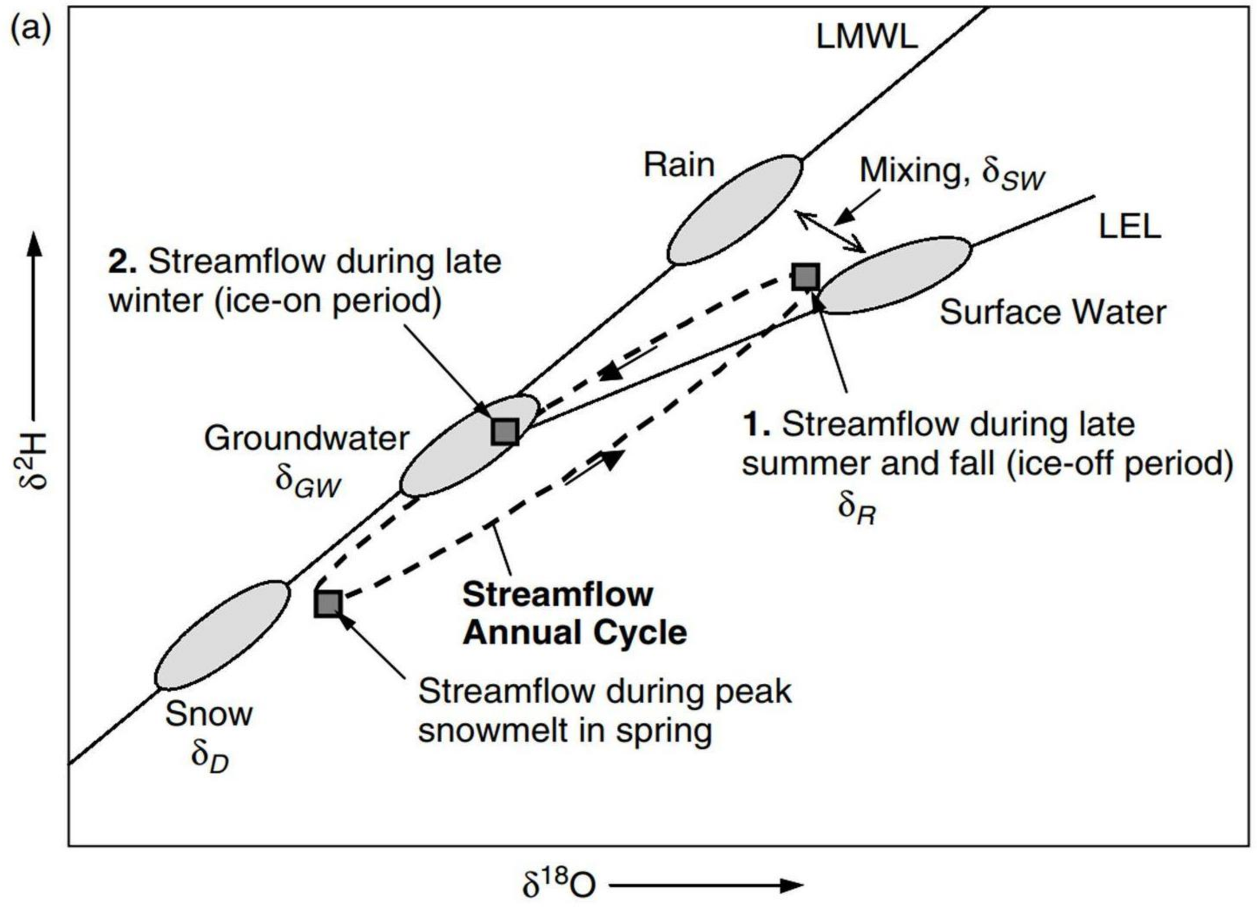


Figure 5. St. Amour et al., 2005[2] conception of the cyclical nature of the annual isotopic composition of streamflow in the neighbouring Liard Watershedue, due to seasonal source water contributions to streamflow.

---

[2] St. Amour, N. A., Gibson, J. J., Edwards, T. W., Prowse, T. D., & Pietroniro, A. (2005). Isotopic time-series partitioning of streamflow components in wetland-dominated catchments, lower Liard River basin, Northwest Territories, Canada. *Hydrological Processes, 19*(17), 3357-3381. doi:10.1002/hyp.5975

Appendix E: Photographs

E.1 Chapter 2

Figure 6. The sampling location on the Mcleod River at Whitecourt (54^{o} 08.4’ N, 115^{o} 41.8’ W).

Figure 7. The sampling location on the Athabasca River at Athabasca (54^{o} 43.3’N, 113^{o} 17.1’W).

Figure 8. The sampling location on the Athabasca River at Fort McMurray (56^{o} 43.3’N, 111^{o} 24.5’W).

Figure 9. Safety Equipment utilized including: A) floater suit, B) Ice rescue bag.

Figure 10. Ice cores were collected using an ice auger to drill into the ice.

Figure 11. Ice samples were processed in the field by A) dividing samples using a miter box, followed by B) dividing sampled into individual bags and photographing them for later analysis.

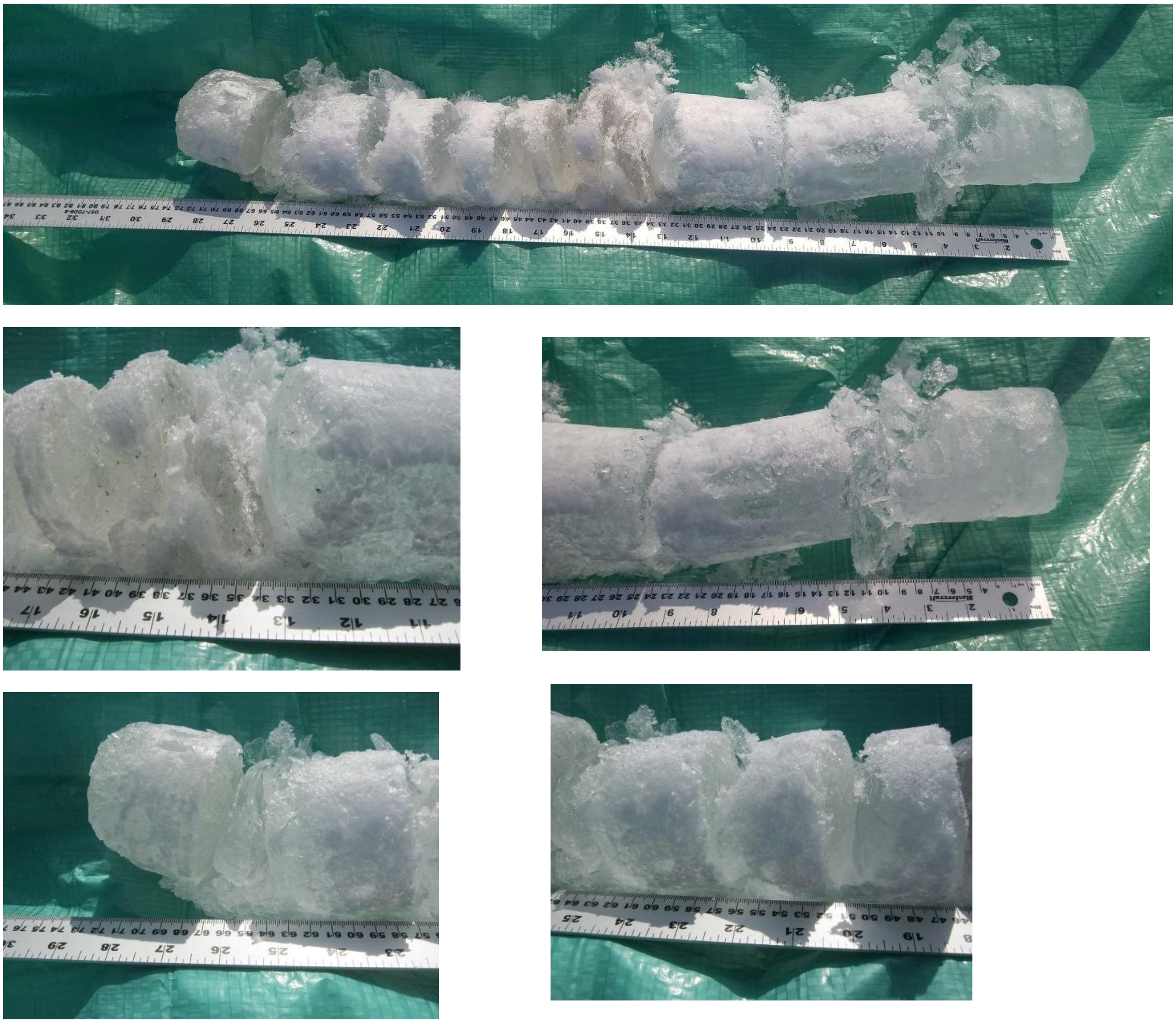


Figure 12. Horizontal profile of the Whitecourt ice core after it was removed from the ice auger.

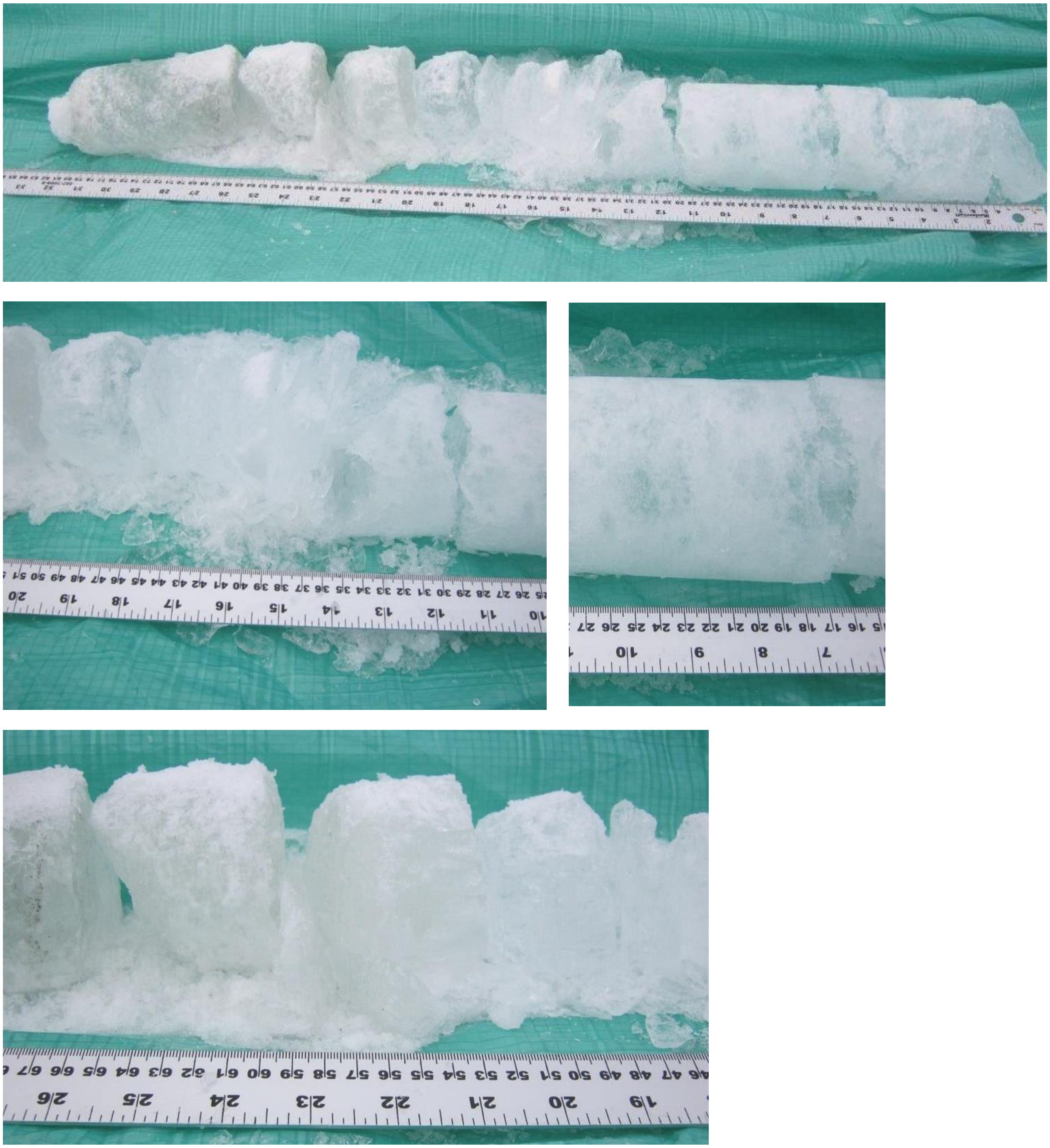
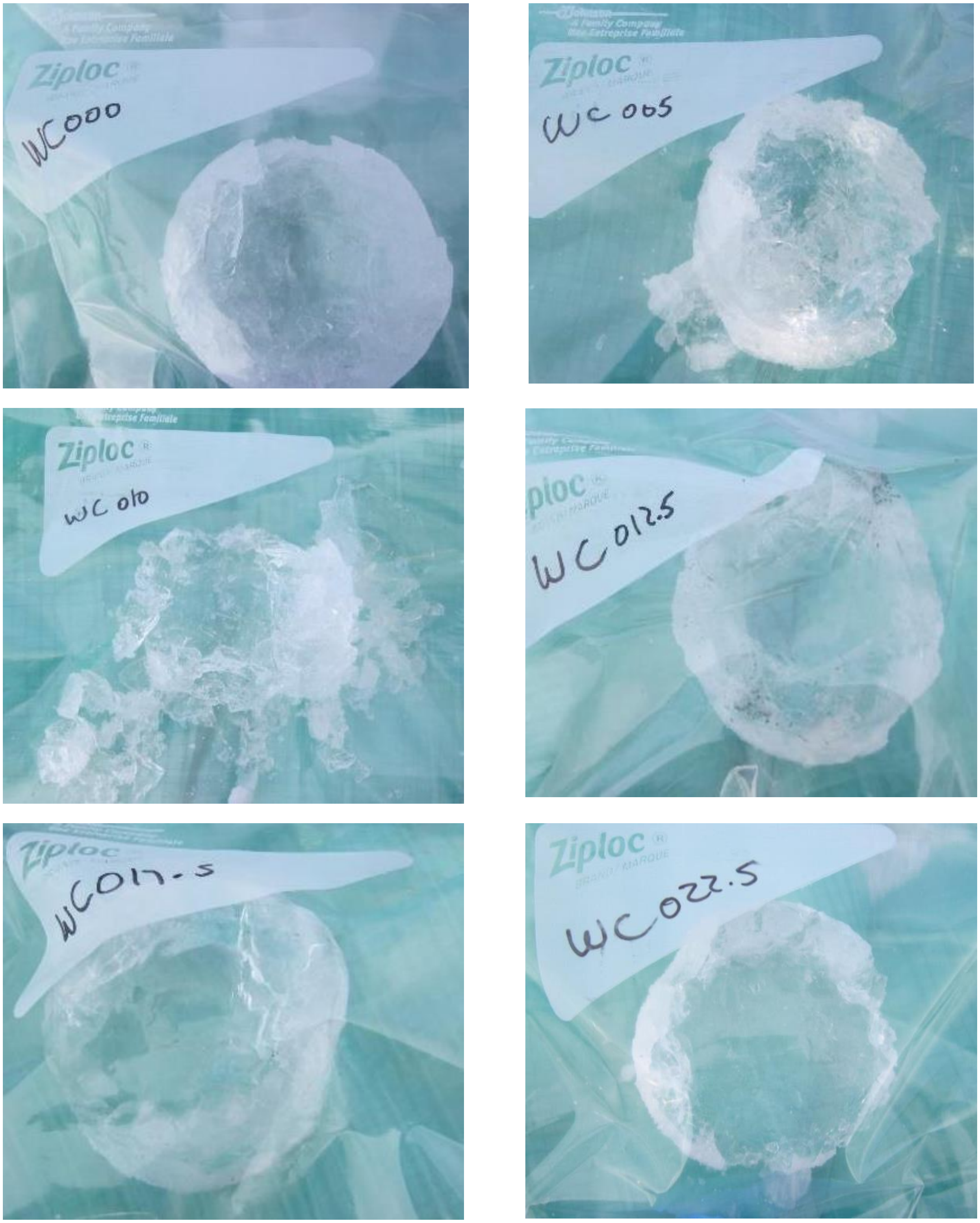


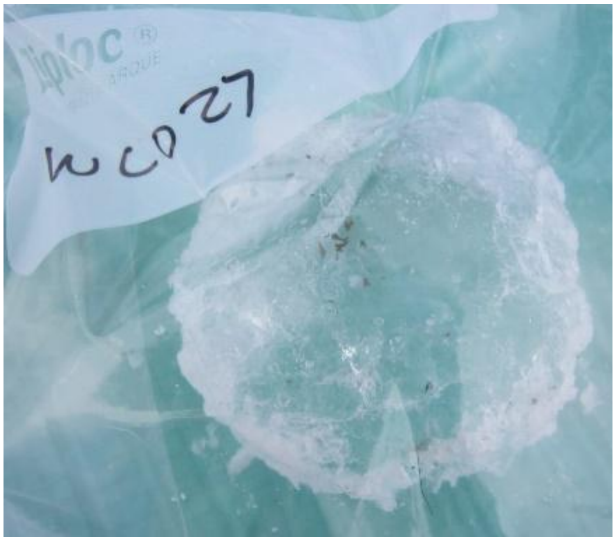
Figure 13. Horizontal profile of the first Athabasca ice core after it was removed from the ice auger.

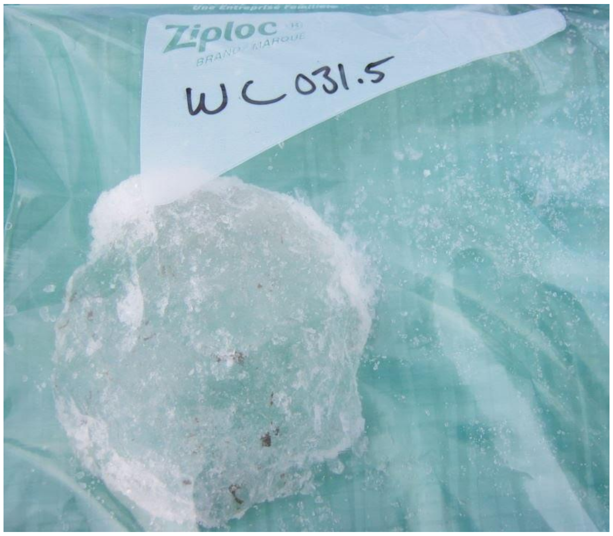
Figure 14. Horizontal profile of the second Athabasca ice core after it was removed from the ice auger.

Figure 15. Horizontal profile of the Fort McMurray ice core after it was removed from the ice auger.

Table 19. Ice core sections from Whitecourt beginning at the base (streamflow) and moving towards the service of the ice with measurements in cm.



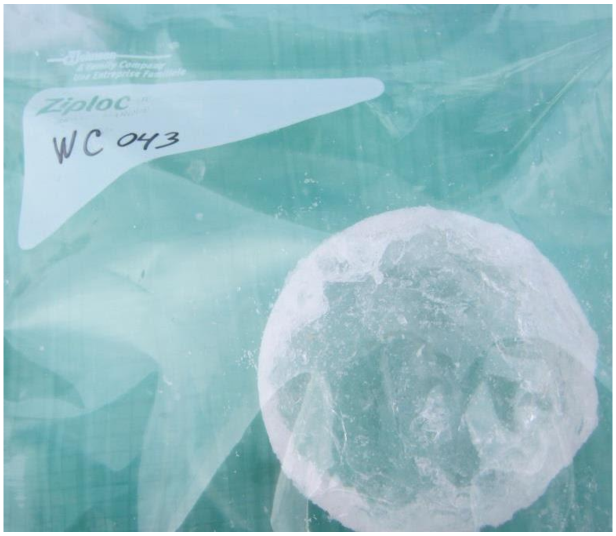

Ziploc
WC027

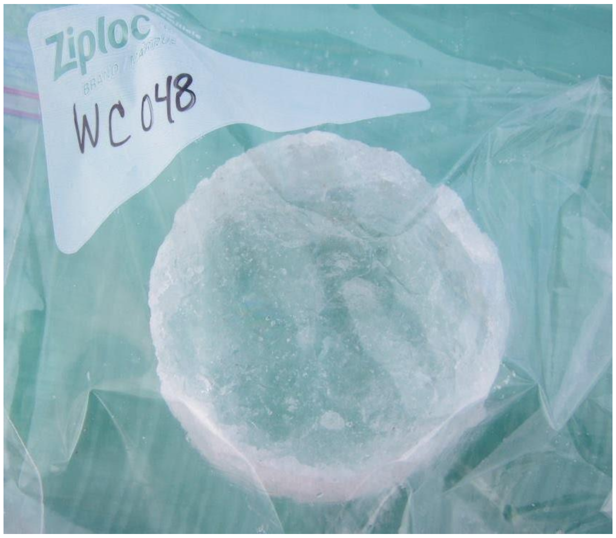

Ziploc
WC031.5

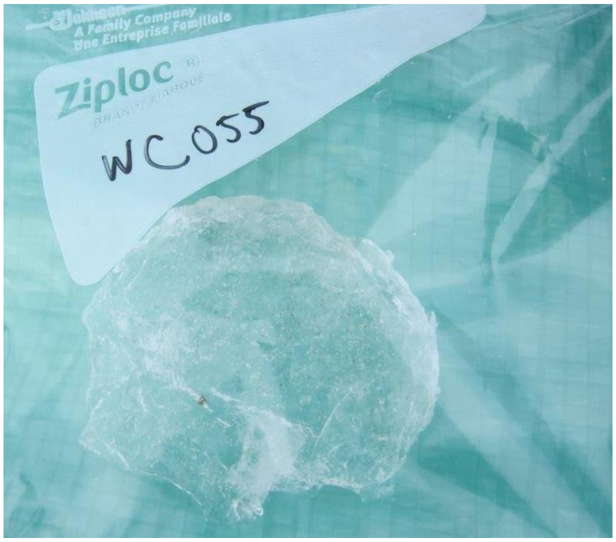

WC032.5


WC035


Ziploc
WC039


Ziploc
WC043


Ziploc
WC048


Johnson
A Family Company
Une Entreprise Familiale
Ziploc
WC055

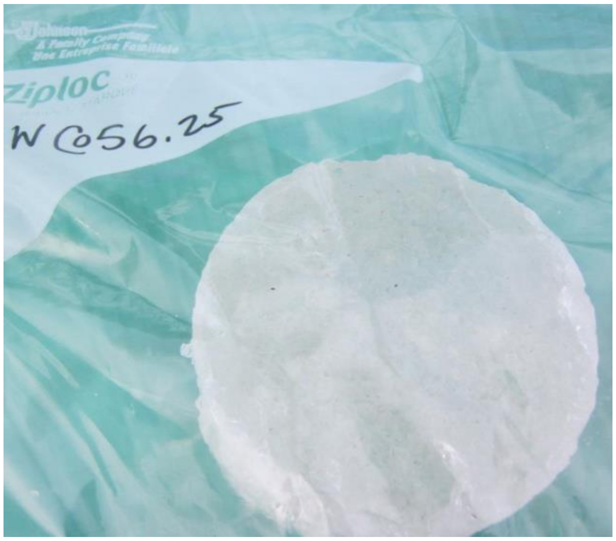
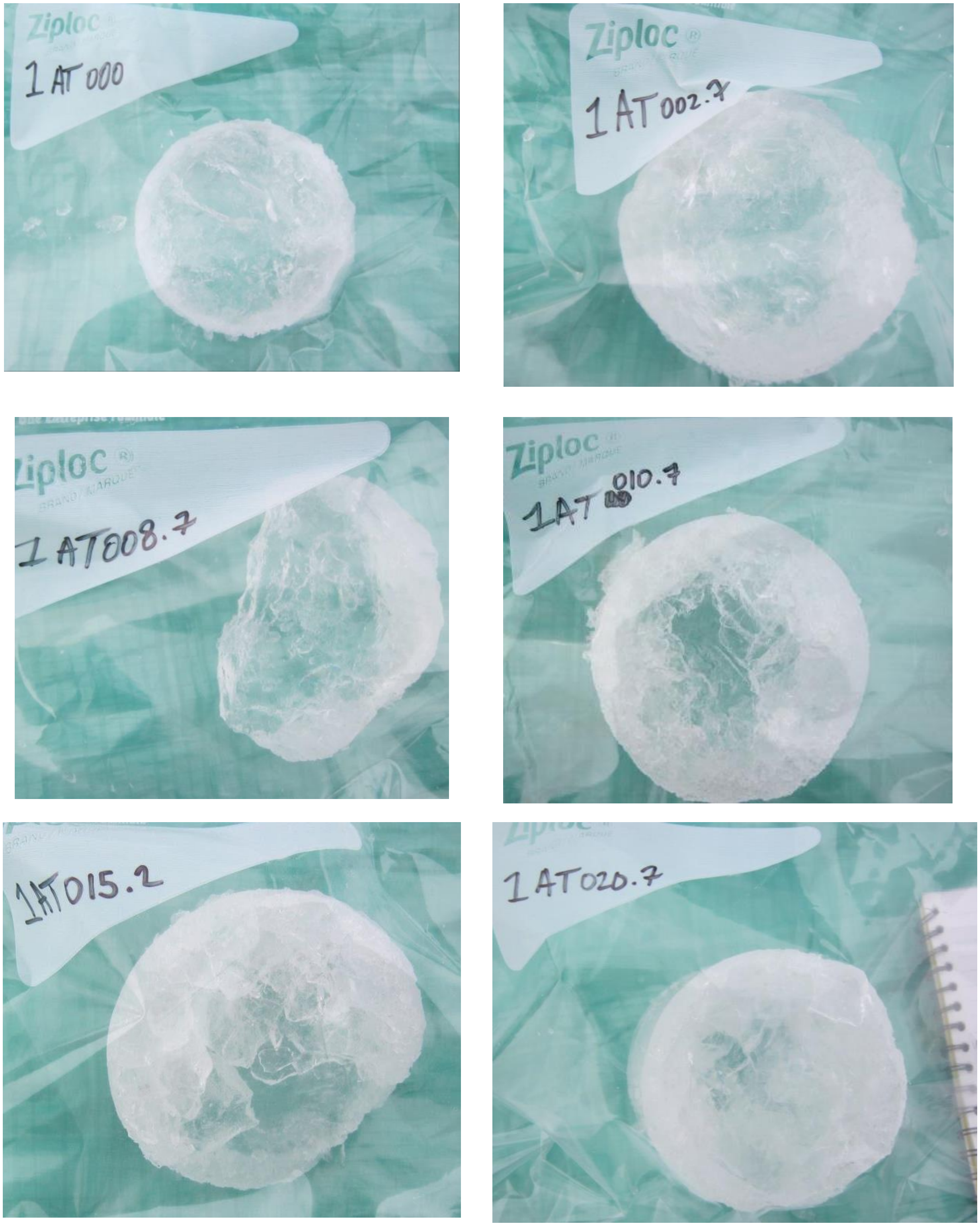
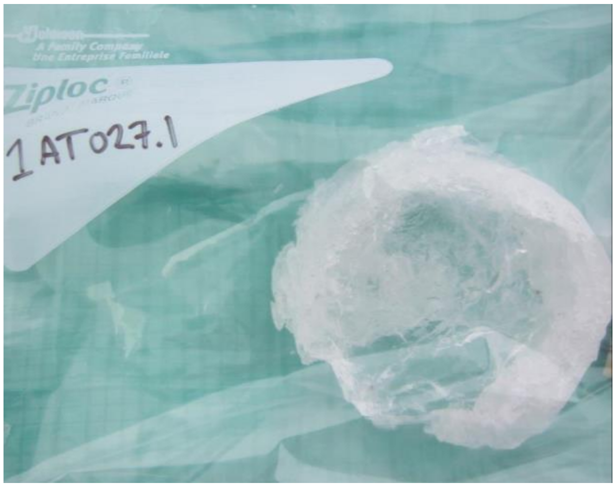
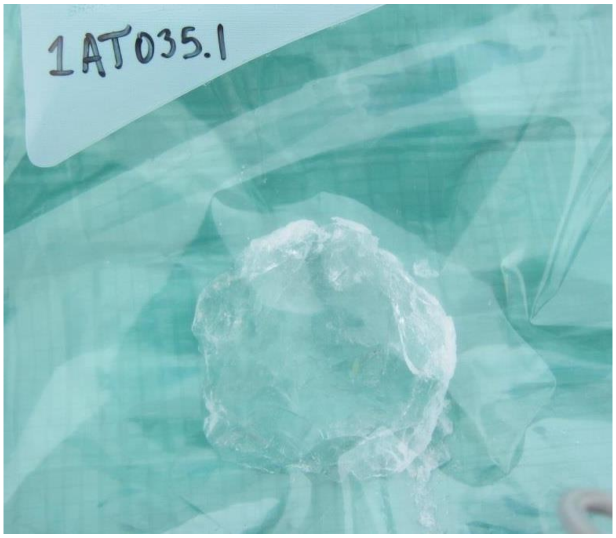

Johnson
A Family Company
Une Entreprise Familiale
Ziploc
WC056.25

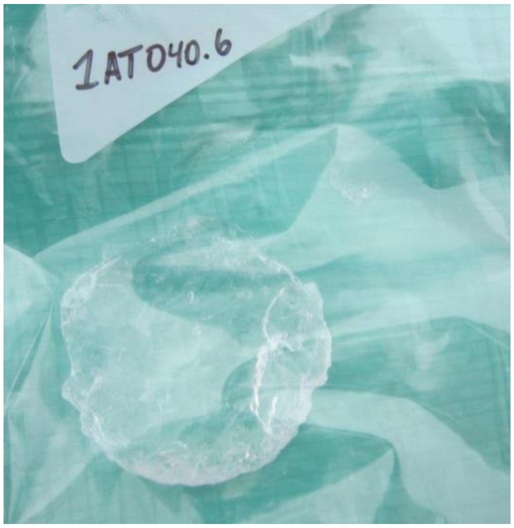
Table 16. Ice core sections from Athabasca (core 1) beginning at the base (streamflow) and moving towards the service of the ice with measurements in cm.

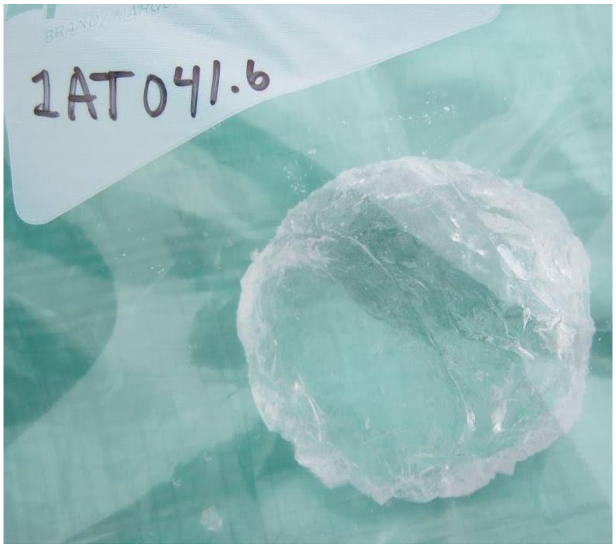


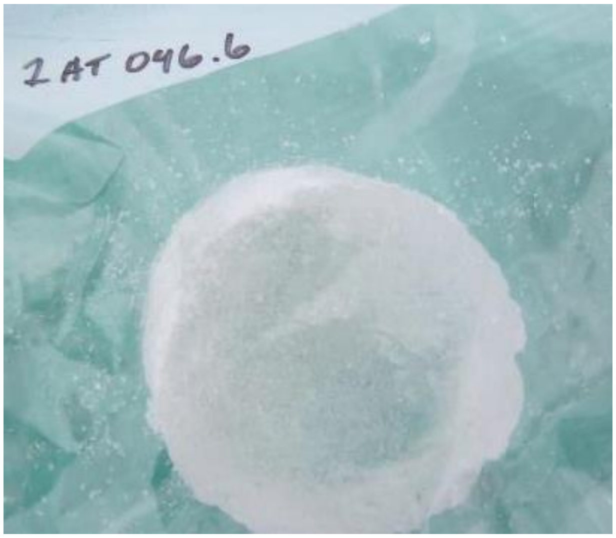

Ziploc
1AT027.1

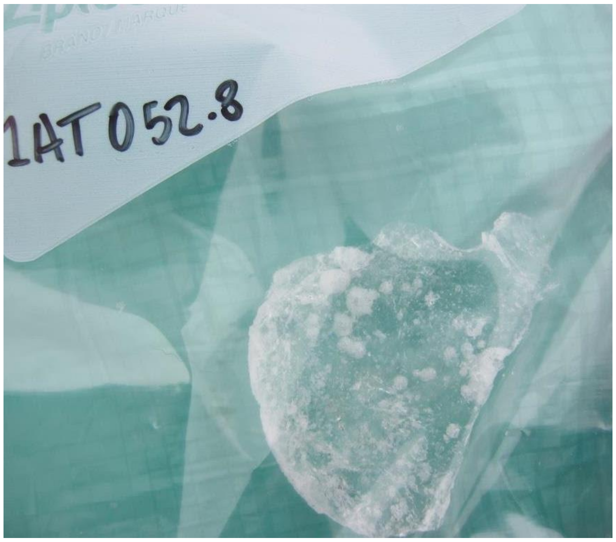

1AT035.1

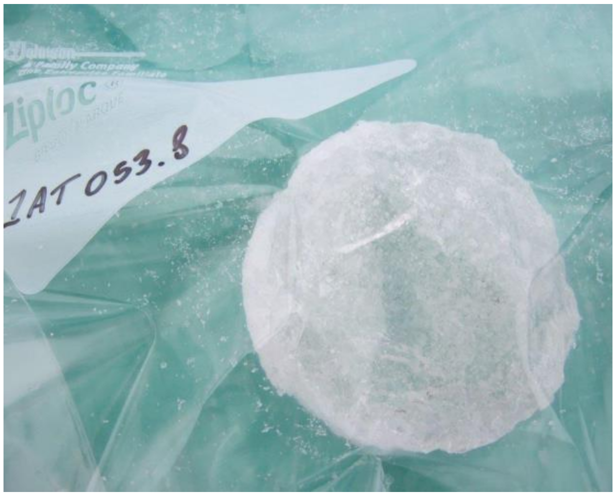

1AT038.1


1AT040.6


1AT041.6


1AT046.6


1AT052.8


1AT053.8


1AT060

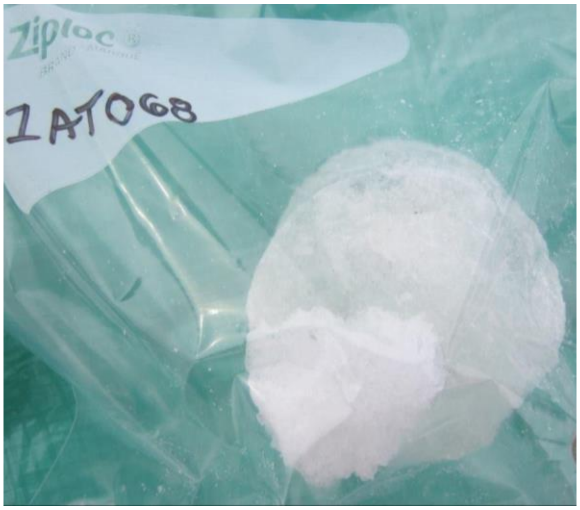
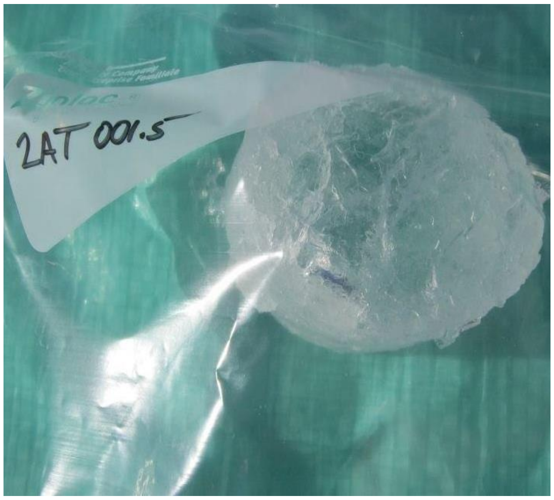
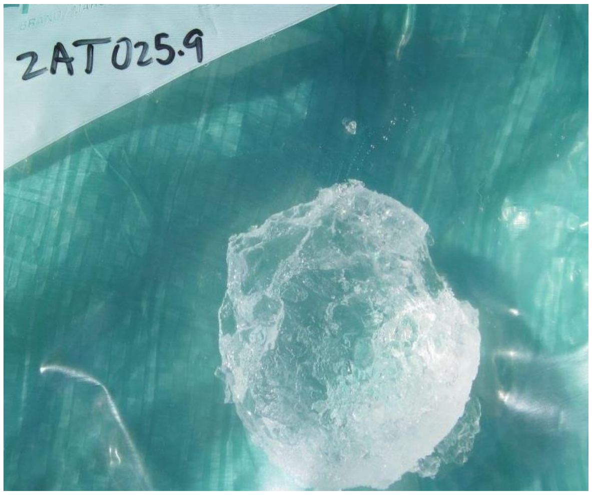

1AT068

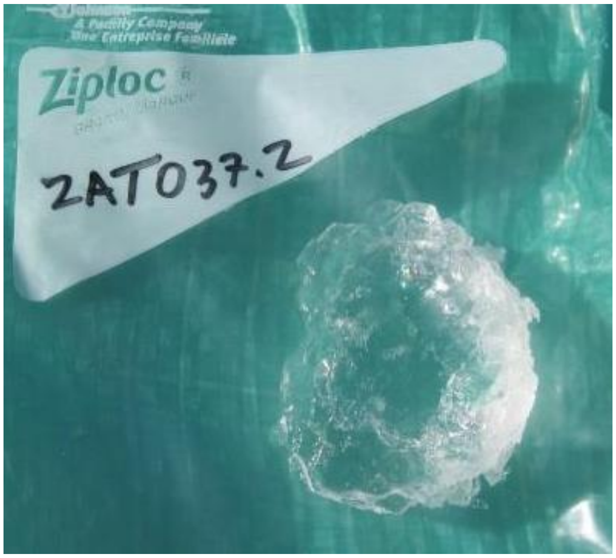
Table 20. Ice core sections from Athabasca (core 2) beginning at the base (streamflow) and moving towards the service of the ice with measurements in cm.

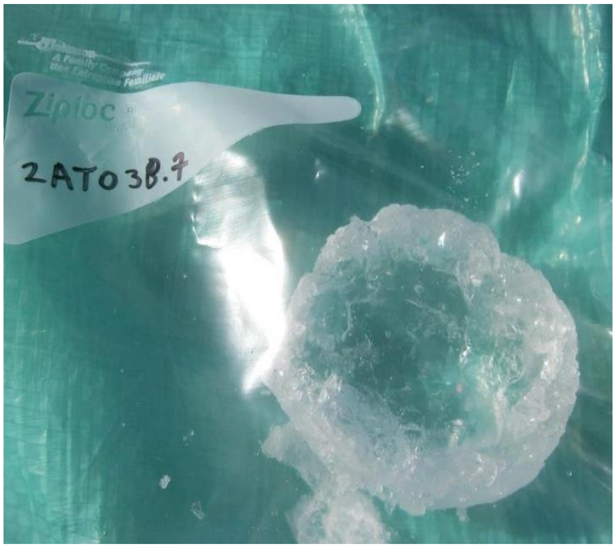


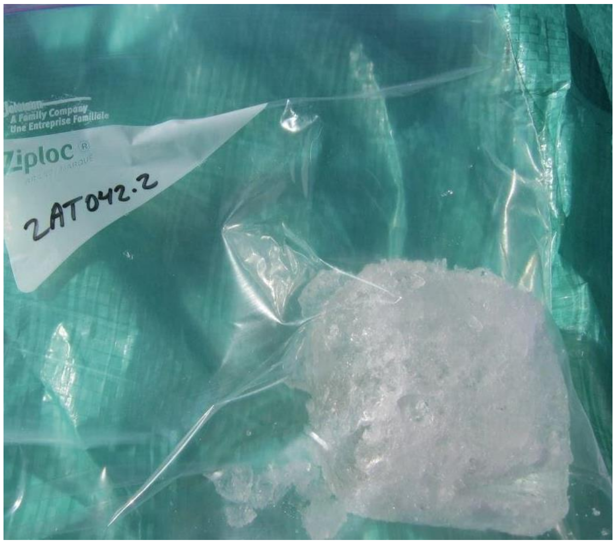

2AT025.9


2AT028.7


2AT035.2


2AT037.2

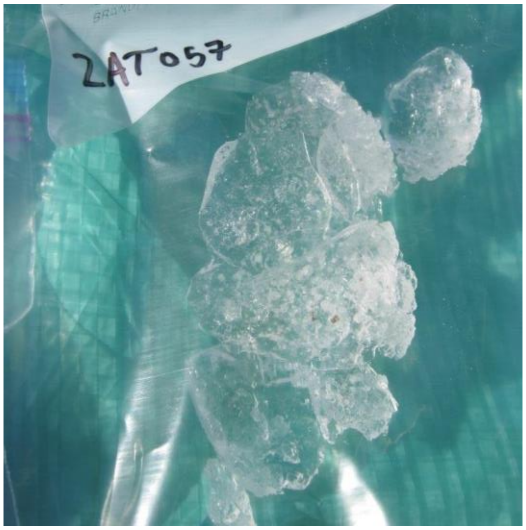

2AT038.7

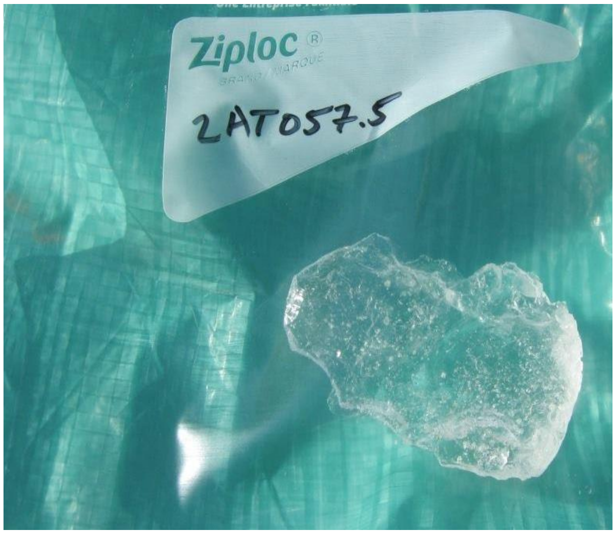

2AT042.2


Ziploc
2AT049.2


Ziploc
2AT053.2


2AT055.2


2AT057


Ziploc
2AT057.5


Ziploc
2AT059

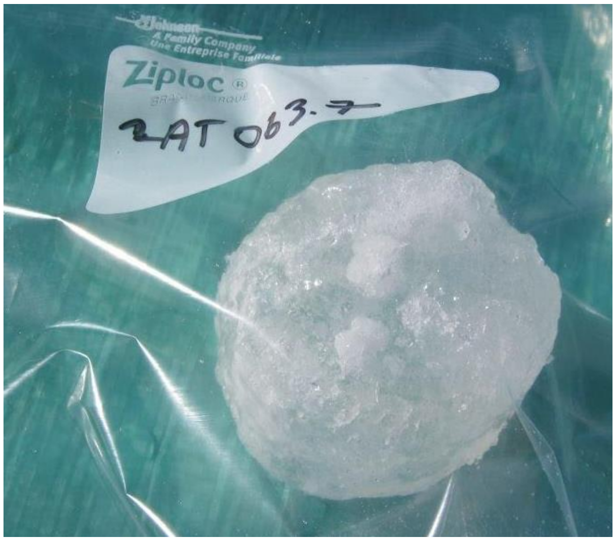
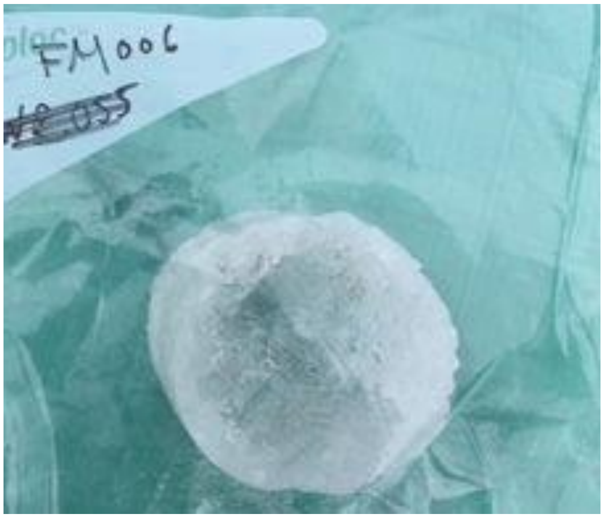
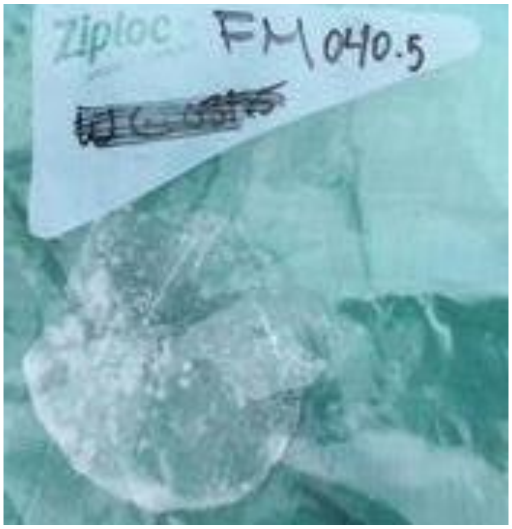

Ziploc
2AT 063.7

Table 18. Ice core sections from FortMcMurray beginning at the base (streamflow) and moving towards the service of the ice with measurements in cm.




Ziploc
FM030


Ziploc
FM038

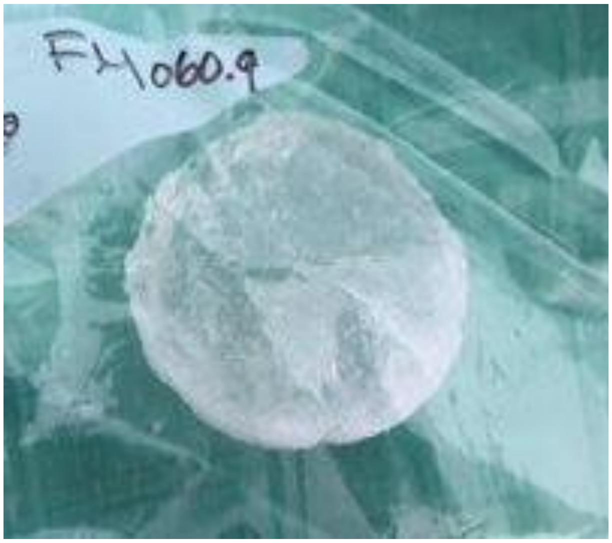

Ziploc
FM040.5


Ziploc
FM042.5


Ziploc
FM050.3


Ziploc
FM 055


Ziploc
FM057.3
[redacted]


FM060.9


Ziploc
FM063.7
[redacted]


FM067.5


Ziploc
FM068.5


FM 070.1

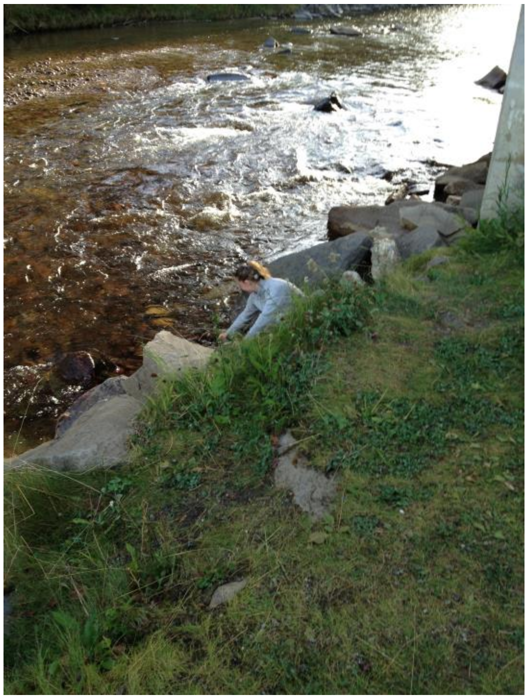
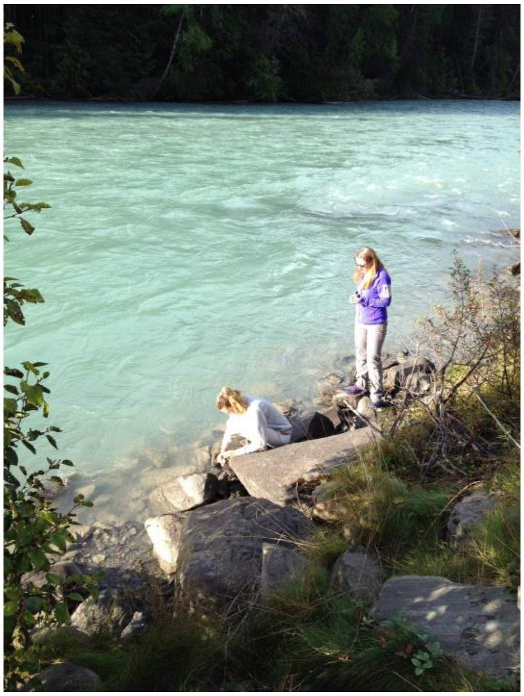

Ziploc
FM072.1


FM096.6


FM 078.7

E.2 Chapter 3

Table 21. Sampling locations across the Athabasca River Basin in August 2016 and August 2017*.

Site ID	Photograph
JT-1	
JT-2	

JT-3

JT-5

JT-6

JT-53*

JT-7

JT-8

JT-9

JT-11

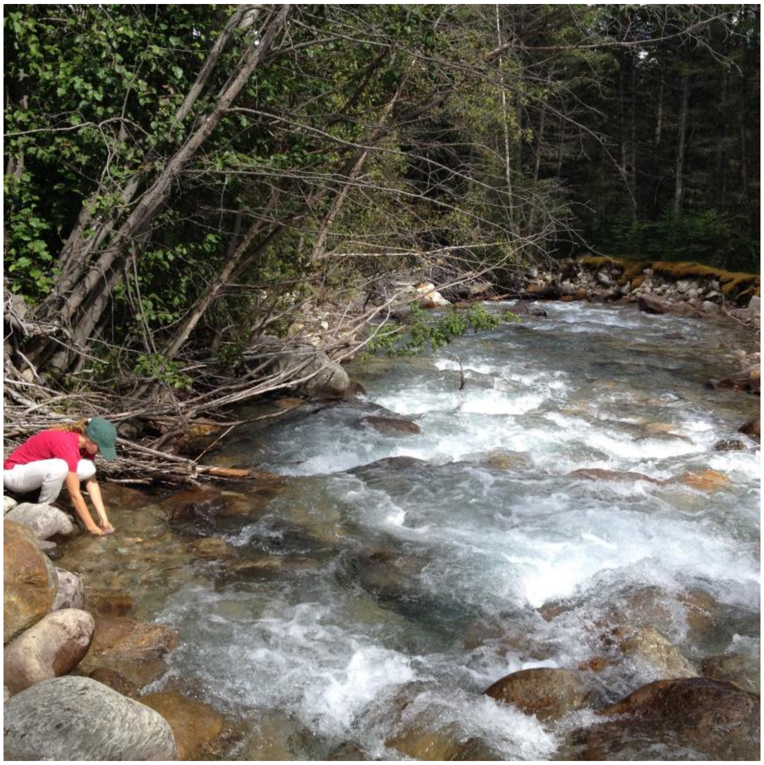
JT-12

JT-14

JT-15

JT-16

JT-17



JT-18

JT-19

JT-20

JT-21

JT-22

JT-23

JT-25

JT-26

JT-27

JT-28

JT-29

JT-30

JT-31

JT-32

JT-33

JT-34

JT-35

JT-36

JT-37

JT-38

JT-40

JT-41

JT-42

JT-49*

Table 6. Sampling locations across the Athabasca River Basin in May 2017

Site ID	Photograph
JT-5	
JT-27	

JT-51

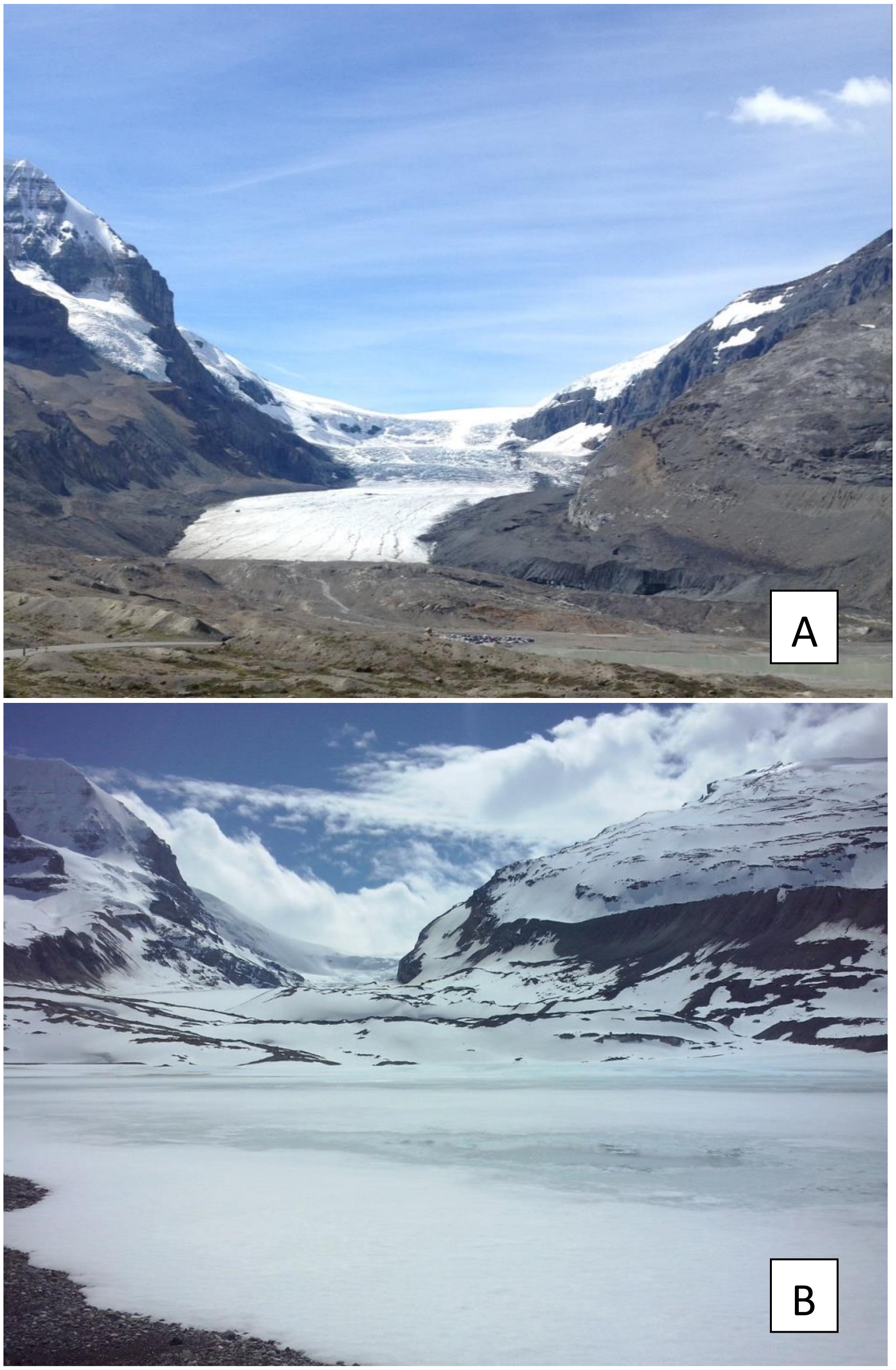


Figure 16. Columbia Icefield in August 2016 (A) and May 2017 (B).

Figure 17. Reduced visibility at Site JT-7 due to the wildfire smoke in August 2017

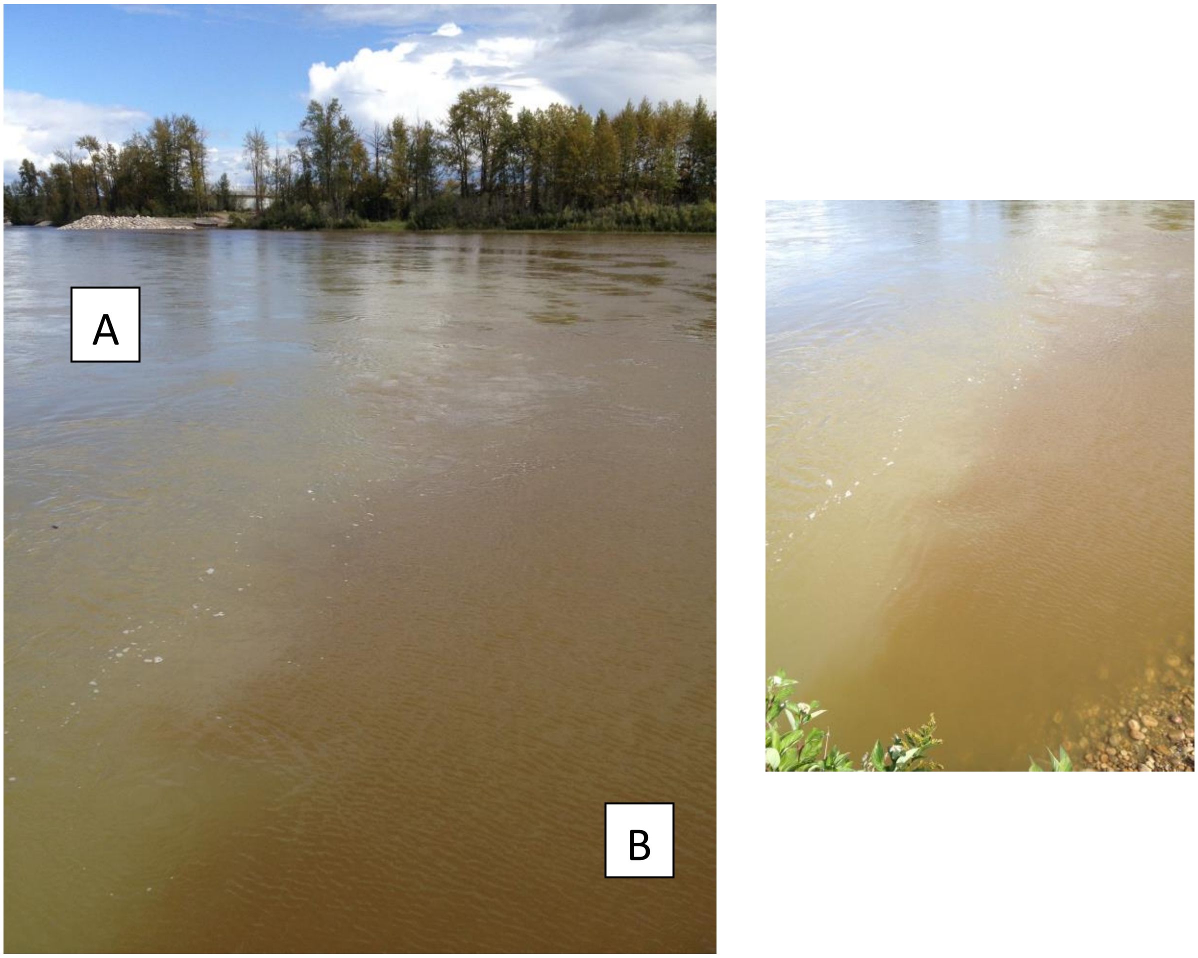
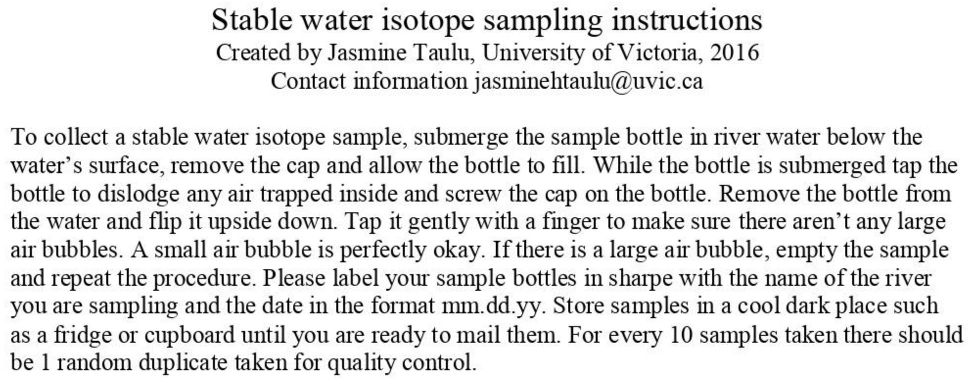


Figure 18. The convergence of the Athabasca (A) and McLeod (B) Rivers.

Figure 19. Sampling was made possible due to field assistants Brandi Newton August 2016 (A), Dave and Maddy Barrett March 2017 (B), Dave Barrett May 2017 (C) and Hayley O’Neil August 2017 (D).

Appendix F: Sampling instructions sent to partners

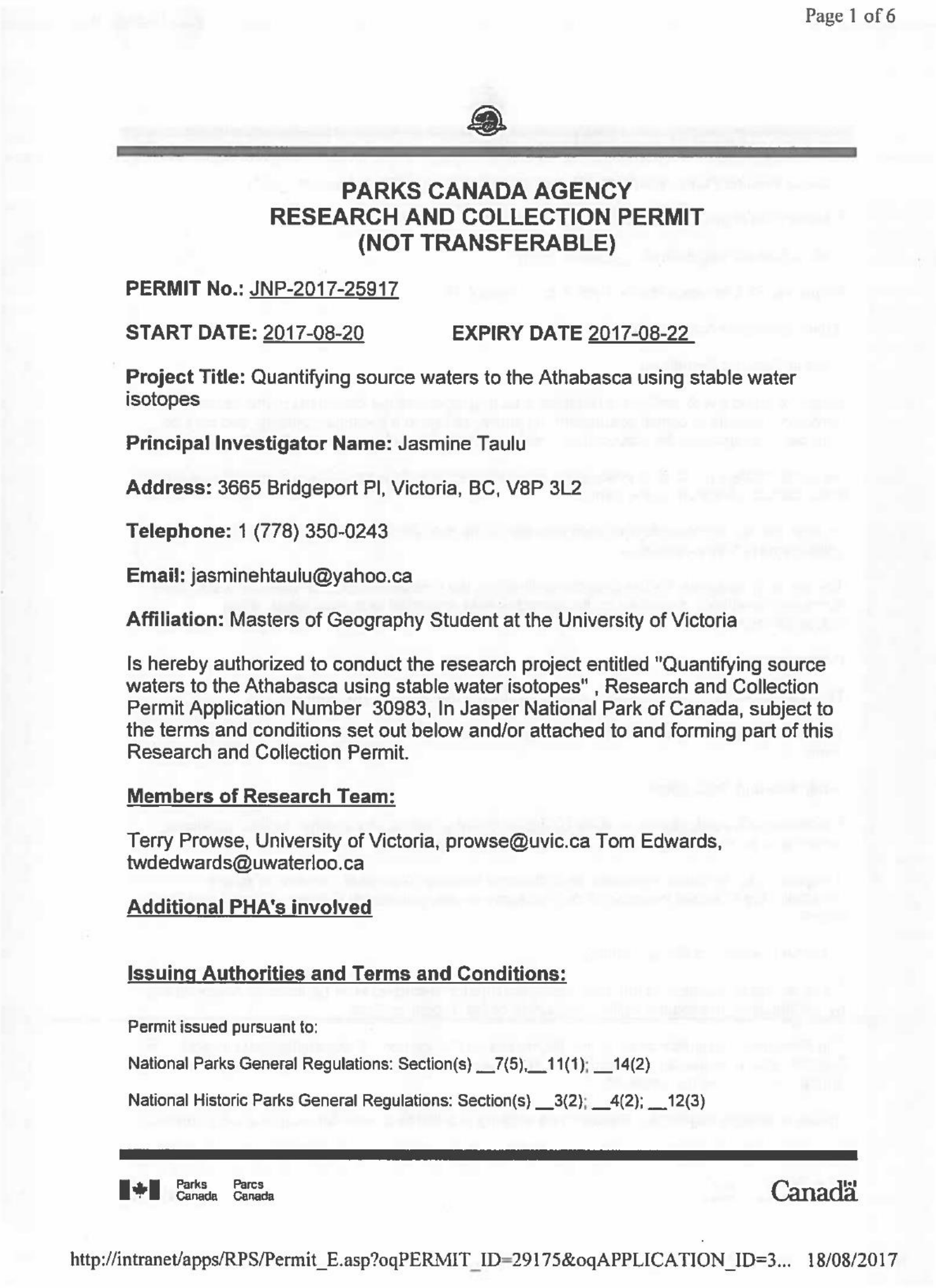


Stable water isotope sampling instructions
Created by Jasmine Taulu, University of Victoria, 2016
Contact information jasminehtaulu@uvic.ca

To collect a stable water isotope sample, submerge the sample bottle in river water below the water's surface, remove the cap and allow the bottle to fill. While the bottle is submerged tap the bottle to dislodge any air trapped inside and screw the cap on the bottle. Remove the bottle from the water and flip it upside down. Tap it gently with a finger to make sure there aren't any large air bubbles. A small air bubble is perfectly okay. If there is a large air bubble, empty the sample and repeat the procedure. Please label your sample bottles in sharpe with the name of the river you are sampling and the date in the format mm.dd.yy. Store samples in a cool dark place such as a fridge or cupboard until you are ready to mail them. For every 10 samples taken there should be 1 random duplicate taken for quality control.

Figure 20. Sampling instructions sent to the Whitecourt Water Treatment Centre and the Aspen Regional Water Services Commission, for their collection of weekly isotope samples over the winter of 2016/2017.

Appendix G: Parks Canada Sampling Permit



Page 1 of 6

PARKS CANADA AGENCY
RESEARCH AND COLLECTION PERMIT
(NOT TRANSFERABLE)

PERMIT No.: JNP-2017-25917

START DATE: 2017-08-20 **EXPIRY DATE** 2017-08-22

Project Title: Quantifying source waters to the Athabasca using stable water isotopes

Principal Investigator Name: Jasmine Taulu

Address: 3665 Bridgeport Pl, Victoria, BC, V8P 3L2

Telephone: 1 (778) 350-0243

Email: jasminehtaulu@yahoo.ca

Affiliation: Masters of Geography Student at the University of Victoria

Is hereby authorized to conduct the research project entitled "Quantifying source waters to the Athabasca using stable water isotopes" , Research and Collection Permit Application Number 30983, In Jasper National Park of Canada, subject to the terms and conditions set out below and/or attached to and forming part of this Research and Collection Permit.

Members of Research Team:

Terry Prowse, University of Victoria, prowse@uvic.ca Tom Edwards, twdedwards@uwaterloo.ca

Additional PHA's involved

Issuing Authorities and Terms and Conditions:

Permit issued pursuant to:

National Parks General Regulations: Section(s) __7(5),__11(1); __14(2)

National Historic Parks General Regulations: Section(s) __3(2); __4(2); __12(3)

Parks Canada Parcs Canada

Canadä

http://intranet/apps/RPS/Permit_E.asp?oqPERMIT_ID=29175&oqAPPLICATION_ID=3... 18/08/2017

National Parks Wildlife Regulations: Section __15(1)(a)

National Historic Parks Wildlife and Domestic Animals Regulations: Section __5(1)

Federal Real Property Regulations: __Section 4(2)

Historic Canals Regulations: __Section 11(3)

Saguenay-St. Lawrence Marine Park Act: __Section 10

(Other applicable Act(s) or Regulations)

National General Conditions:

Failure to comply with applicable Heritage Area regulations or the conditions of the permit may constitute grounds to cancel or suspend the permit, refuse to issue future permits, and may be considered as grounds for prosecution under the applicable Act(s) or Regulation(s).

All permit holders must be in possession of a valid permit before the fieldwork commences and at other periods as stated on the permit.

Permits are not transferable and each member of the field work team must have a copy of the valid permit in their possession.

The permit is valid only for the geographic location, the time period, the activities, and under the terms and conditions described on the permit, unless amended and revalidated by the Superintendent.

Restrictions:

The Superintendent may suspend, cancel, or restrict the scope of the permit.

The permit shall cease to be valid if the fieldwork is not started within six months of the date of issue.

Other Acts and Regulations:

The Principal Investigator must abide by applicable regulations and all other federal, provincial, territorial or municipal regulations applying to the Heritage Area.

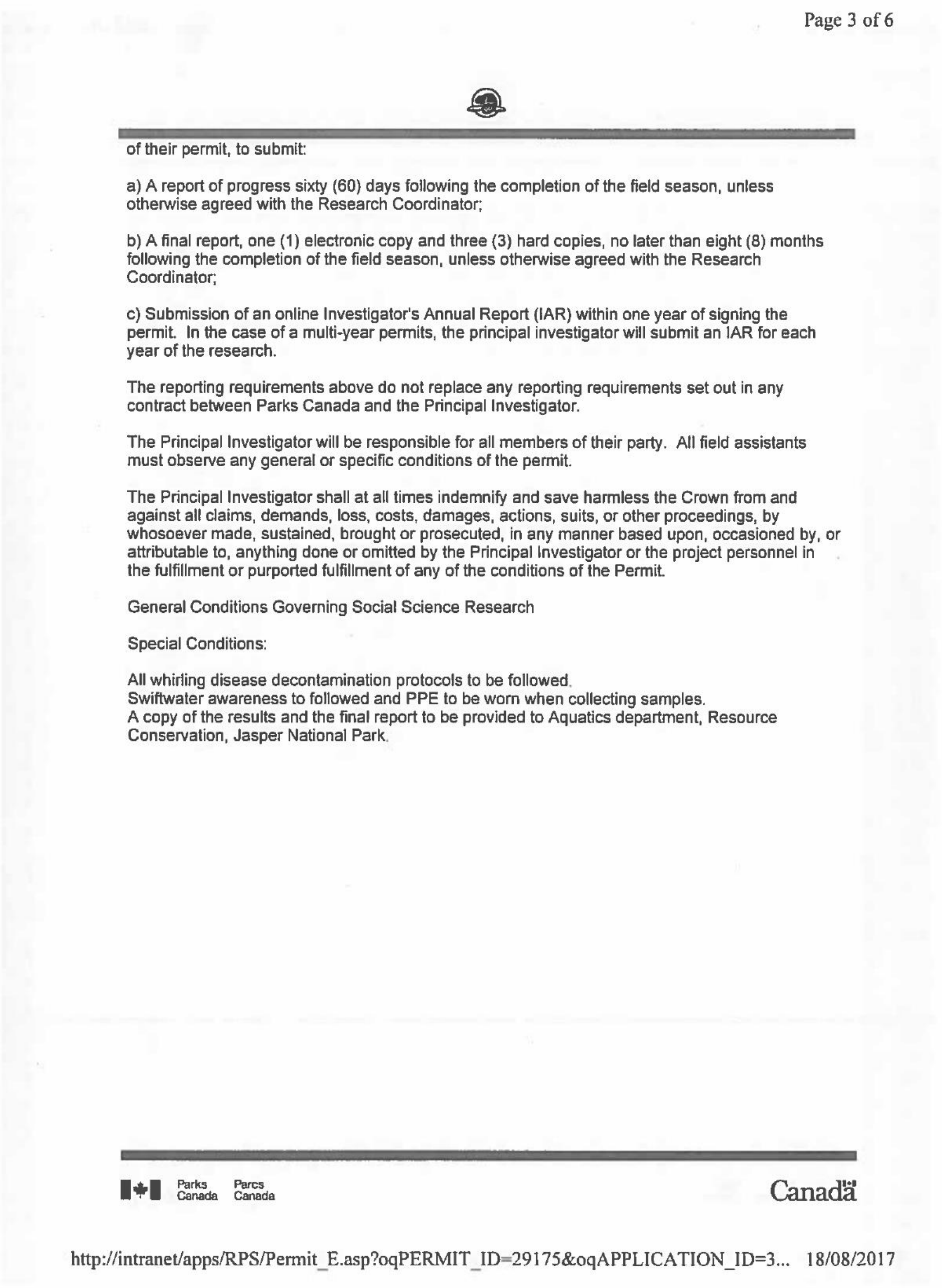
If requested by the Superintendent, an authorized Heritage Area staff member, or police constable, the Principal Investigator or any team member will identify themselves and show the permit.

Principal Investigator Responsibilities :

A site, or site component(s) that has been excavated or disturbed shall be restored or conserved by the Principal Investigator to the satisfaction of the Superintendent.

The Principal Investigator must advise the Research Coordinator of any adjustments in work location, research plan and methodology, implementation schedule, or main personnel, etc., during the course of the research.

Unless otherwise negotiated, Researchers working in a Heritage Area are required, as a condition



of their permit, to submit:

a) A report of progress sixty (60) days following the completion of the field season, unless otherwise agreed with the Research Coordinator;

b) A final report, one (1) electronic copy and three (3) hard copies, no later than eight (8) months following the completion of the field season, unless otherwise agreed with the Research Coordinator;

c) Submission of an online Investigator's Annual Report (IAR) within one year of signing the permit. In the case of a multi-year permits, the principal investigator will submit an IAR for each year of the research.

The reporting requirements above do not replace any reporting requirements set out in any contract between Parks Canada and the Principal Investigator.

The Principal Investigator will be responsible for all members of their party. All field assistants must observe any general or specific conditions of the permit.

The Principal Investigator shall at all times indemnify and save harmless the Crown from and against all claims, demands, loss, costs, damages, actions, suits, or other proceedings, by whosoever made, sustained, brought or prosecuted, in any manner based upon, occasioned by, or attributable to, anything done or omitted by the Principal Investigator or the project personnel in the fulfillment or purported fulfillment of any of the conditions of the Permit.

General Conditions Governing Social Science Research

Special Conditions:

All whirling disease decontamination protocols to be followed.
Swiftwater awareness to followed and PPE to be worn when collecting samples.
A copy of the results and the final report to be provided to Aquatics department, Resource Conservation, Jasper National Park.