

Surface Water Quality of Lower Athabasca River Tributaries

1.3
Report
Series



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Surface Water Quality of Lower Athabasca River Tributaries

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Foreword

Since February 2012, the governments of Alberta and Canada have worked in partnership to implement an environmental monitoring program for the oil sands region. In December 2017 both governments renewed their commitment to working together with Indigenous communities in the region by the signing the *Alberta-Canada Memorandum of Understanding (MOU) Respecting Environmental Monitoring in the Oil Sands Region*. The MOU establishes the foundation for an adaptive and inclusive approach to program implementation ensuring that the program is responsive to emerging priorities, information, knowledge, and input from key stakeholders and Indigenous peoples in the region.

The Oil Sands Monitoring Program is designed to enhance the understanding of the state of the environment and cumulate environmental effects as a result of oil sands development in the region through monitoring and publically reporting on the status and trends of air, water, land and biodiversity. Its vision is to integrate Indigenous knowledge and wisdom with western science to design, interpret, assess, report and govern the program.

Canada and Alberta have provided leadership to strengthen program delivery, and ensure that necessary monitoring and scientific activities meet program commitments and objectives. The oil sands industry provides funding support for the program under the Oil Sands Environmental Regulation (Alberta Regulation 226/2013). Key findings and results from the program inform regional resource management decisions and importantly, are considered as an objective source of scientific interpretation of credible environmental data.

A mandated cornerstone of the program is the public reporting of data, status and trends of environmental impacts caused by development of oil sands resources. The Oil Sands Monitoring Program *Technical Report Series* provides an objective, and timely, evaluation and interpretation of monitoring data and information collected across environmental media of the program. This includes reporting and evaluation of emission/release sources, fate, effects and transport of contaminants, landscape disturbance and responses across theme areas including atmospheric, aquatic, biotic, wetlands, and community based monitoring.

Executive Summary

In 2011, the Governments of Canada and Alberta designed a monitoring plan for surface water quality and quantity, air quality and biodiversity of the lower Athabasca River between Fort McMurray and its confluence with Lake Athabasca. The plan, known as the Joint Oil Sands Monitoring Plan (JOSM), included monitoring water quality in the main stem of the Athabasca River, its tributaries, and the deltaic and wetland ecosystems at the river mouth, April 2012 to March 2015. This report answers the following key questions identified in the JOSM regarding water quality of tributaries to the lower Athabasca River:

1. What is the current state of water quality?
2. What is the distribution of contaminants?
3. Are toxic substances increasing or decreasing and what is their rate of change?
4. Are the substances added to the rivers by natural and man-made discharges likely to cause deterioration of water quality? What is the relative importance of both inputs?

The report does not summarize or interpret all tributary water quality data collected by the JOSM but rather focuses on key water quality parameters typically associated with oil sands development: arsenic, mercury, selenium, vanadium, and polycyclic aromatic compounds.

Under the JOSM, the number of sites sampled and the frequency of sampling increased substantially. Previously, 43 tributary sites were monitored by Alberta Environment and Sustainable Development (now Alberta Environment and Parks), Environment Canada (now Environment and Climate Change Canada) or Hatfield Consultants (as part of the Regional Aquatic Monitoring Program) with, at most, monthly sample collection. Under the JOSM, 62 tributary sites were monitored: 14 tributary sites at high frequency (daily or alternate days during snow melt with decreasing frequency thereafter) and 48 sites monthly, seasonally or annually. This produced approximately 2,000 samples from tributary sites, each of which was analyzed for approximately 150 parameters.

Tributary waters throughout the lower Athabasca watershed are characterized as moderately hard to hard water because of mineral content, particularly Mg^{2+} , Ca^{2+} and bicarbonate (HCO_3^-), which originates from underlying Cretaceous deposits comprised of layers of shale, sandstone and limestone. The alkalinity, mineral content and moderately alkaline pH are indicative of moderate sensitivity to acid rain. Concentrations of nitrogen and phosphorus (indicators of nutrient status) are typically low to moderate, indicative of oligotrophic to mesotrophic conditions.

Many metals (notably vanadium, nickel, molybdenum, mercury, aluminum, antimony, arsenic, cadmium, chromium, copper, iron, lead, strontium, uranium, zinc), as well as other elements (e.g., selenium), and compounds (e.g., polycyclic aromatic compounds) have been found at higher concentrations downstream of bitumen extraction and related oil sands operations (Kelly et al. 2009, 2010). Under the JOSM, up to 43 contaminants (metals, metalloids, selenium) and 52 polycyclic aromatic compounds were analyzed in tributary water samples; 36 of these contaminants and polycyclic aromatic compounds have Guidelines for the Protection of Aquatic Life. Several elements occasionally exceeded guidelines (e.g., <5 % of all samples for total cadmium, total chromium, total silver, total zinc, total arsenic, total selenium), while a few parameters frequently exceeded guidelines (i.e., >10 % of samples for total aluminum, total copper, total iron, total lead). Concentrations of total and methyl mercury were below guidelines. For the nine polycyclic aromatic compounds with water quality guidelines, only pyrene occasionally exceeded the guideline (e.g., <5 % of all samples).

Athabasca tributaries had strong seasonal and spatial patterns in surface water quality. Concentrations of dissolved arsenic, dissolved selenium, total vanadium (2012-2014 data for the Ells, Muskeg and Steepbank rivers), total mercury (2012 data for the Firebag, Ells, Muskeg, Mackay and Steepbank rivers), and total polycyclic aromatic compounds (2012-2013 data for the Mackay,

Muskeg and Steepbank rivers) followed hydrologic discharge with concentrations typically greatest during snow melt (i.e., April-May). Patterns in methyl mercury were slightly different: concentrations increased during high flows but were greatest during mid-to-late summer months (late June to mid-August) when production via microbial pathways is highest in aquatic ecosystems. Concentrations of many parameters were greater at sites downstream of development near the mouth of the tributaries.

Due to the limited time span of the JOSM data (three years), assessment of factors determining contaminant export between upstream and downstream tributary sites will continue and will use a GIS approach to distinguish how watershed land cover (e.g., wetland types), regional geology (e.g., natural bitumen deposits), and industrial developments influence water quality. Analysis of historical water chemistry data (1972-2010) showed that concentrations and loads of total vanadium, dissolved selenium and dissolved arsenic were greater downstream of development compared to reference sites. A case study conducted on the Muskeg River (1972-2009 data) showed that concentrations and loads of the same three elements were greatest during the early land-clearing stage of mine development, with dissolved selenium remaining elevated during the subsequent expansion stage.

New water quality information on the Athabasca River tributaries obtained under the JOSM has led to these recommendations:

1. Continue monitoring water quality and discharge at the same sites, both upstream and downstream, on major tributaries;
2. Continue frequent water sampling on major tributaries during snow melt; and,
3. Ensure comparable data among analytical labs by establishing compatible methodologies for analysis of water quality samples from the oil sands region.

Ultimately, successful and continued implementation of the new monitoring program started under the JOSM will provide an integrated regional monitoring program that delivers (1) information needed for strategic decisions, (2) core results on the accumulative environmental state and relationships between system drivers and abiotic environmental response, and (3) a decision framework that sets out triggers or decision thresholds to identify when specific station numbers or monitoring intensity should be scaled back or ramped up.

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Introduction

Over the past 10 years, concerns have grown as to whether oil sands development could pollute the Athabasca River watershed and if environmental monitoring will provide all the information necessary to protect the environment. Earlier (2001-2010) assessments of contaminants and heavy metals in the Athabasca River and its tributaries attributed their presence to natural erosion of geological strata that contain bitumen (e.g., Headley et al 2001, 2005; Conly et al 2002, 2007; McMaster et al. 2006). Similarly, a 2009 study of 12 watersheds in the oil sands region plus several additional sites concluded that water quality was similar for sites downstream of development and baseline sites, and that measured parameters fell within the range of historical observations (RAMP 2009). Reviews undertaken in 2010 concluded “there has been no increase in concentrations of contaminants as oil sands development has progressed” (Government of Alberta 2010) and “that oil sands development activities are not a current threat to aquatic ecosystem viability” (Royal Society of Canada 2010). However, recent research has shown that oil sands development contributes 13 priority pollutants to the Athabasca River and its tributaries (Kelly et al. 2010). Further, chemicals associated with oil sands development may be detected at elevated levels 50 km downwind of mining and processing sites as a result of atmospheric transport and deposition (Landis et al. 2012, Kurek et al. 2013, Kirk et al. 2014).

A lack of capacity to convincingly ascertain if oil sands activities pose a threat to aquatic ecosystem viability spurred recommendations to develop an integrated “state-of-the-art” monitoring program that can identify changes in environmental condition over time in Canada’s oil sands region. Although a wide range of monitoring programs and research activities are conducted in the region and have generated considerable information, integration of these efforts has not occurred, a situation identified in a number of independent science reviews or journal papers (e.g., Timoney and Lee 2009; Kelly et al. 2009, 2010; Giesy et al. 2010; Schindler 2010), as well as expert panel reviews (e.g., Royal Society of Canada 2010; Government of Canada Oil Sands Advisory Panel (2010); Alberta Water Monitoring Data Review Committee (2011)). These reviews and assessments have identified

shortcomings in past monitoring efforts, particularly a lack of rigour in statistical design (e.g., inadequate spatial coverage of sites and/or related sampling frequency), lack of clear objectives and hypothesis driven analyzes, and an inability to measure change cumulatively over space or time (Governments of Canada and Alberta 2011).

To address shortcomings identified in past monitoring efforts, the Governments of Canada and Alberta developed a monitoring plan for surface water quality and quantity for the lower Athabasca River and tributaries between Fort McMurray to Wood Buffalo National Park Boundary (Governments of Canada and Alberta 2011). As stated in the Joint Oil Sands Monitoring Plan (JOSM) Phase 1, the goal of this new monitoring program was to “obtain scientifically credible information that would allow improved description of baseline conditions and ecosystem structure and function; assessment of changes in ecosystem condition and trends; effects investigation and impact assessments; performance measurement and State of Environment (SOE) reporting; evaluation of environmental and human health risk; support and feedback for modelling, management, and policy development; and, stakeholder input” (Governments of Canada and Alberta 2011).

The purpose of this report is to describe the major findings from the JOSM with respect to surface water quality of tributaries to the lower Athabasca River. The report focuses on answering key questions identified in the JOSM:

- What is the current state of water quality of lower Athabasca River tributaries?
- What is the distribution of contaminants in surface water along tributaries to the lower Athabasca River?
- Are toxic substances, such as mercury or polycyclic aromatic compounds (PACs), increasing or decreasing and what is their rate of change?
- Are the substances added to the rivers by natural and man-made discharges likely to cause deterioration of water quality? What is the relative importance of both inputs?
- What is the relative importance of both inputs?

Wherever appropriate, a mass-balance approach was used to quantify and compare water chemistry among sites and over time, thus enabling assessment of sources, fate and loadings of contaminants in the lower Athabasca tributaries.

This report does not summarize or interpret all water quality data collected as part of the Canada-Alberta JOSM: approximately 150 water quality parameters were measured on approximately 2,000 samples, resulting in >250,000 individual water quality records over the three years (April 2012 to March 2015). The focus is on water quality parameters typically associated with oil sands development: arsenic, mercury, selenium, vanadium and polycyclic aromatic compounds. The findings presented here, and those to come from analysis of the entire JOSM water quality 2012-2015 data set, will provide (1) new information needed for strategic monitoring decisions, (2) core results on the accumulative environmental state and the relationships between system drivers and the abiotic environmental response, and (3) a decision framework that sets out triggers or decision thresholds to identify when specific station numbers or monitoring intensity should be scaled back or ramped up.

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Methods

Study design

Current water chemistry

The water quality monitoring program in the tributaries of the lower Athabasca River was guided by the Phase 1 Joint Canada/Alberta Implementation Plan for Oil Sands Monitoring (Governments of Canada and Alberta 2012). Activities included water sampling by Alberta Environment and Sustainable Resource Development (AESRD; now Alberta Environment and Parks), Hatfield Consultants, and Environment Canada (EC; now Environment and Climate Change Canada) in 10 tributaries on the west side and five tributaries on the east side of the Athabasca River, as well as the Clearwater River and several of its tributaries (Table 1, Fig. 1).

A three-year (April 2012 - March 2015) intensive program of grab water sampling was conducted by EC at 14 sites (Table 1) that entailed daily or alternate-day sampling during snow melt (April-May) followed by weekly (June), biweekly (July-August), and monthly sampling (September-November) and then occasional under-ice sampling (approximately three times/winter). All EC grab samples were analyzed for a suite of 163 parameters that included 41 metals and metalloids (total and dissolved); selenium (total and dissolved); mercury (both total mercury (THg), which includes all forms of Hg in a sample, and methyl mercury (MeHg), the toxic form of mercury that bioaccumulates and biomagnifies through food webs); major anions and cations; nutrients (nitrogen, phosphorus and carbon forms); and conventional parameters (Table 2). Select grab samples (typically one sample per site every 1-5 days during snow melt and every 1-2 weeks throughout summer and fall from three tributaries, Mackay, Muskeg and Steepbank) were analyzed for 52 polycyclic aromatic compounds (PACs), including unsubstituted-PACs (unPACs), alkylated-PACs (aPACs) and dibenzothiophenes (DBTs). (Not all water samples were analyzed for PACs because of cost and lack of laboratory capacity; samples were selected to best represent the range in concentrations likely to be observed.) All water samples were collected following standard operating protocols and preserved on-site if required. Samples for metals, major ions and

nutrients were analyzed at EC's National Laboratory for Environmental Testing (NLET) facility using nationally recognized analytical standards and procedures. Samples for determining THg and MeHg were analyzed at EC's Low-level Mercury Analytical Laboratory using standard protocols and detection by cold vapour atomic fluorescence spectrophotometry. Samples for PAC determination were extracted (unfiltered) with dichloromethane using standard protocols at NLET and then analyzed at EC's Air Quality Research Division (AQRD) laboratory in Ottawa, Ontario, where they were fractionated using silica gel solid phase columns with hexane followed by benzene. The benzene fraction was then analyzed by GC-MS, following AQRD protocol 3.03/5.1/M and targeting 52 PACs: 25 unsubstituted PACs (unPACs), 22 alkylated PACs (aPACs) and five dibenzothiophenes (DBTs).

Alberta (AESRD) and Hatfield Consultants collected grab samples at a total of 50 sites on a monthly, quarterly or fall only schedule (Table 1). All AESRD/Hatfield Consultants grab samples were analyzed for a suite of 149 parameters that included 30 metals and metalloids (total and dissolved, including mercury), selenium (total and dissolved), major anions and cations, nutrients (nitrogen and phosphorus forms), 43 PACs, and conventional parameters (Table 2). All samples were collected following standard operating protocols and analyzed using nationally recognized analytical standards and procedures. Grab samples collected by AESRD for anions, cations, nutrients, and conventional parameters were analyzed either at Maxxam Analytics (Edmonton, AB) or Alberta Innovates Technology Futures (AITF) in Vegreville, Alberta. Grab samples collected by Hatfield Consultants (for the same suite of parameters) were analyzed at ALS Environmental Ltd. (Edmonton, Alberta). All samples collected by AESRD and Hatfield Consultants for total and dissolved metals (including ultra-trace mercury), acid-extractable organics (naphthenic acids), and PAHs were analyzed by AITF. In addition to the parameter groups identified above (namely metals and metalloids, major ions, nutrients, PACs, conventional parameters), limited sampling of naphthenic acids (NAs) was conducted under JOSM. At the start of JOSM, consensus regarding a universal analytical method for NAs could not be achieved with current techniques each having advantages and limitations. NAs are not

Table 1. Sites where grab water samples were collected by Environment Canada (EC) or Alberta Environment and Sustainable Resource Development (AESRD) / Hatfield Consultants as part of JOSM (April 2012 – March 2015). * identifies sites where automated sondes were also deployed. EC sites were sampled daily or every second day during snowmelt (April-May), followed by weekly (June), biweekly (July-August), or monthly sampling (Sept-Nov) and then occasional under-ice sampling (~ 3 times/winter). AESRD / Hatfield Consultants sites were sampled: a monthly; b quarterly; c fall only. Site names in brackets are Regional Aquatic Monitoring Program (RAMP) site names.

Streams	Original Sites (Prior to JOSM)	JOSM recommendation ¹	Sampled under JOSM	
			EC	AESRD / Hatfield
Athabasca River – western tributaries				
Unnamed (Big Creek)		UN1		UN1 (BIC-1) ^{a or c}
Calumet		CA1, CA2		CA1 (CAR-1) ^c , CAR-2 ^c
Tar		TA1		TA1 ^c , TAR-2 ^c
Ells	EL1	EL1, EL2	EL1*, ELLS RIFF2*, ELLS RIFF5*	EL1 ^c , EL2 (ELR-2) ^c , ELR-3 ^b
Dover		DO1		
Mackay		MA1, MA2	MA1* (A,B,D), MA2*	MA2 (MAR-1) ^c , MAR-2A ^c , MAR-2 ^a
Poplar		PO1		POC-1 ^a
Beaver				BER-2 ^c , BER-1 ^c
Pierre				PIR-1 ^c
Eymundson				EYC-1 ^c
Red Clay				RCC-1 ^c
Athabasca River – eastern tributaries				
Mills				MIC-1 ^c
Firebag	FI1	FI1, FI2	FI1*, FIR WSC*	FI2 (FIR-2) ^c , FI1 ^{*a} , FIR-1 ^c
Muskeg	MU1, MU2, MU3, MU4, MU5, MU6, MU7, JA1, NM1	MU1, MU2, MU3, MU4, MU5, MU6, MU7, JA1, NM1, JA2, KL1, PE1, WA1	MU1* (A,B), MU6*, MU7*	M7 ^a , M6 ^a , M4.5 ^{*a} , M4 ^a , M3 ^{*a} , M2 ^{*a} , MU0 (MUR-1) ^a , JA1 (JAC-1) ^a , JA2 (JAC-2) ^a , NM1 (MUC-1) ^c , STC-1 ^c , IYC-1 ^c , WAC-1 ^c
Steepbank	ST1	ST1, ST2	ST1*, STB WSC*, STB RIFF7*, STB RIFF10*	ST2 (STR-3) ^c , STR-2 ^a , ST1 (STR-1) ^a , NSR-1 ^c
McLean				MCC-1 ^c
Athabasca River – southern tributaries				
Clearwater		CL1, CL2, CL3		CL3 (CLR-2) ^a , CL2 (CLR-1) ^c
Horse		HO1		
Hangingstone		HA1		HAR-1 ^c , HAR-1A ^c
Christina		CH1		CHR-4 ^b , CHR-3 ^b , CHR-2 ^a , CH1 (CHR-1) ^a
High Hills			HIH1*	HIH1 ^b

¹ Governments of Canada and Alberta 2012

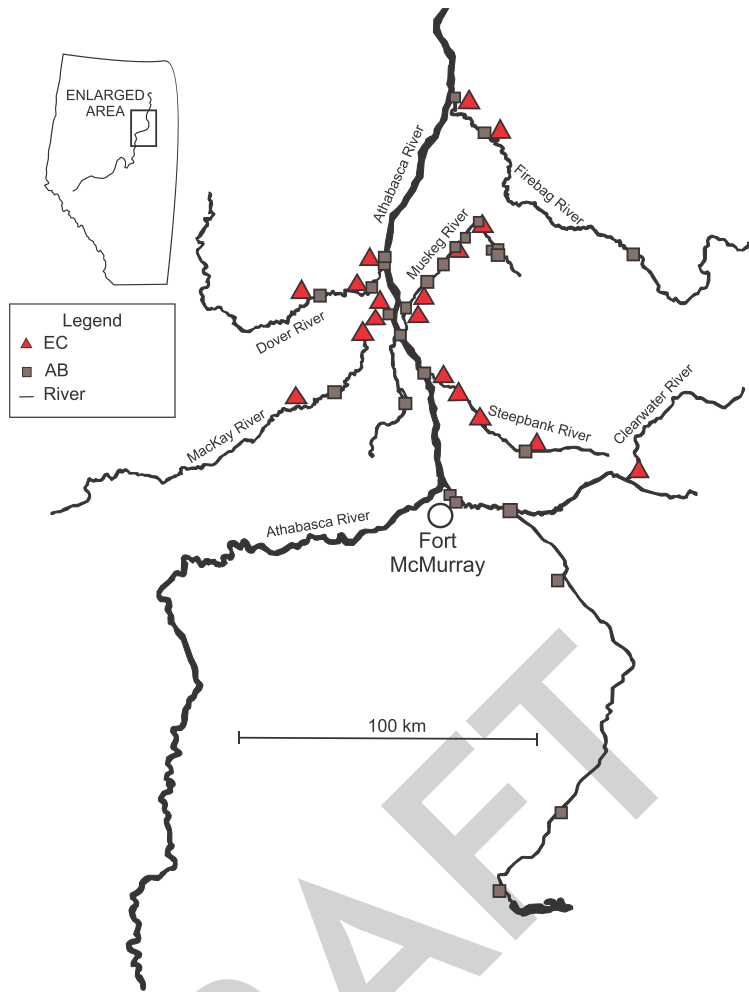


Figure 1. Athabasca River tributary sites sampled by Alberta Environment and Sustainable Resources Development or Hatfield Consultants (solid squares) and Environment Canada (red triangles). The study area spanned $55^{\circ} 52' 36''$ N x $110^{\circ} 48' 46.8''$ W and $59^{\circ} 52' 9''$ N x $111^{\circ} 35' 8''$ W, or approximately 30,000 km² centred on Fort McMurray, AB, Canada.

discussed in this report; results are available at <http://www.ramp-alberta.org/data/Water/waterquality/water.aspx>.

In addition to grab sampling, automated sondes were deployed year-round at 15 EC and three AESRD tributary sites to automatically record dissolved oxygen, pH, temperature, conductivity and water level every 30 minutes.

EC and Alberta chemistry data were combined for parameters with comparable sampling and analytical methods. In this report, combined data are presented for mercury and parameters sampled using sondes (pH, conductivity, temperature). Concentrations of metals, metalloids and selenium measured as part of the EC and

Alberta/Hatfield Consultants programs were not combined because laboratories used extraction techniques that were not identical; future efforts will be directed at evaluating techniques to determine which parameters can be merged.

Historical water chemistry

Two analyzes of long-term data were undertaken:

- a. dissolved selenium (diss Se), dissolved arsenic (diss As) and total vanadium (total V) over a period of 38 years 1972-2010);
- b. pH during snow melt over a period of 25 years (1989-2014).

Table 2. Parameter list, and associated analytical labs, for water chemistry samples collected from Athabasca River tributaries by AESRD / Hatfield Consultants or Environment Canada (EC) as part of the JOSM, April 2012 to March 2015. ALS Environmental Ltd. In Fort McMurray and Edmonton, Alberta; Alberta Innovates Technology Futures (AITF) in Vegreville, Alberta; AXYS Analytical Services Ltd. in Sidney, British Columbia; Maxxam Analytics (MA) in Edmonton, Alberta; EC National Laboratory for Environmental Testing in Burlington, Ontario (NLET-Burl), Saskatoon, Saskatchewan (NLET-SK) and Vancouver, British Columbia (NLET-PY); EC Air Quality Research Division (AQRD) in Ottawa, Ontario.

Group	Water Quality Variable	AESRD / Hatfield	EC
Conventional variables			
	Conductivity	ALS, MA or AITF	NLET-Burl
	Dissolved Organic Carbon	ALS, MA or AITF	NLET-PY
	Hardness (as CaCO ₃)	ALS, MA or AITF	
	pH	ALS, MA or AITF	NLET-Burl
	Total alkalinity	ALS, MA or AITF	NLET-Burl
	Total Dissolved Solids	ALS, MA or AITF	NLET-PY
	Total Organic Carbon	ALS, MA or AITF	
	Total Suspended Solids	ALS, MA or AITF	NLET-PY
	True Colour	ALS, MA or AITF	NLET-PY
	Turbidity	ALS, MA or AITF	NLET-PY
General Organics			
	Benzene	ALS, MA or AITF	
	CCME Fraction 1 (BTEX)	ALS, MA or AITF	
	CCME Fraction 1 (C6-C10)	ALS, MA or AITF	
	CCME Fraction 2 (C10-C16)	ALS, MA or AITF	
	CCME Fraction 3 (C16-C34)	ALS, MA or AITF	
	CCME Fraction 4 (C34-C50)	ALS, MA or AITF	
	Ethylbenzene	ALS, MA or AITF	
	m+p-Xylene	ALS, MA or AITF	
	Naphthenic acids	ALS, MA or AITF	
	Oilsands extractable	ALS, MA or AITF	
	o-Xylene	ALS, MA or AITF	
	Toluene	ALS, MA or AITF	
	Total phenolics mg/L	ALS, MA or AITF	
	Total recoverable hydrocarbons	ALS, MA or AITF	
	Xylenes	ALS, MA or AITF	
Major Ions			
	Bicarbonate (HCO ₃)	ALS, MA or AITF	
	Calcium (Ca)	ALS, MA or AITF	NLET-Burl
	Carbonate (CO ₃)	ALS, MA or AITF	
	Chloride (Cl)	ALS, MA or AITF	NLET-Burl
	Fluoride (F)		NLET-Burl
	Hydroxide (OH)	ALS, MA or AITF	
	Magnesium (Mg)	ALS, MA or AITF	NLET-Burl
	Potassium (K)	ALS, MA or AITF	NLET-Burl
	Silica (SiO ₂)		NLET-Burl
	Sodium (Na)	ALS, MA or AITF	NLET-Burl
	Sulphate (SO ₄)	ALS, MA or AITF	NLET-Burl
	Sulphide	ALS, MA or AITF	

Table 2. Continued

Nutrients and BOD

Ammonia-N	ALS, MA or AITF	NLET- SK
Biochemical Oxygen Demand	ALS, MA or AITF	
Nitrate	ALS, MA or AITF	
Nitrite	ALS, MA or AITF	
Nitrate+Nitrite	calculated	NLET- SK
Phosphorus, dissolved	ALS, MA or AITF	NLET- SK
Phosphorus, total	ALS, MA or AITF	NLET- SK
Total Kjeldahl Nitrogen	ALS, MA or AITF	
Total nitrogen	calculated	calculated
Nitrogen, total dissolved		NLET- SK
Nitrogen, particulate organic		NLET- SK
Carbon, particulate organic		NLET- SK
Carbon, dissolved organic		NLET-PY

Metals (Total and Dissolved)

Aluminum	AITF	NLET-Burl
Antimony	AITF	NLET-Burl
Arsenic	AITF	NLET-Burl
Barium	AITF	NLET-Burl
Beryllium	AITF	NLET-Burl
Bismuth	AITF	NLET-Burl
Boron	AITF	NLET-Burl
Cadmium	AITF	NLET-Burl
Cerium		NLET-Burl
Cesium		NLET-Burl
Chlorine	AITF	
Chromium	AITF	NLET-Burl
Cobalt	AITF	NLET-Burl
Copper	AITF	NLET-Burl
Gallium		NLET-Burl
Germanium		NLET-Burl
Indium		NLET-Burl
Iron	AITF	NLET-Burl
Lanthanum		NLET-Burl
Lead	AITF	NLET-Burl
Lithium	AITF	NLET-Burl
Manganese	AITF	NLET-Burl
Mercury	AITF	
Mercury, ultra -trace	AITF	EC-LMAL
Methyl Mercury		EC-LMAL
Molybdenum	AITF	NLET-Burl
Nickel	AITF	NLET-Burl
Niobium		NLET-Burl
Palladium		NLET-Burl

Table 2. Continued

Platinum		NLET-Burl
Rubidium		NLET-Burl
Scandium		NLET-Burl
Selenium	AITF	NLET-Burl
Silver	AITF	NLET-Burl
Strontium	AITF	NLET-Burl
Sulphur	AITF	
Tellurium		NLET-Burl
Thallium	AITF	NLET-Burl
Thorium	AITF	
Tin	AITF	NLET-Burl
Titanium	AITF	NLET-Burl
Tungsten		NLET-Burl
Uranium	AITF	NLET-Burl
Vanadium	AITF	NLET-Burl
Yttrium		NLET-Burl
Zinc	AITF	NLET-Burl
Zirconium		NLET-Burl
PAH variables		
Biphenyl	AXYS	AQRD
C1-Biphenyls	AXYS	AQRD
C2-Biphenyls	AXYS	AQRD
Naphthalene	AXYS	AQRD
C1-Naphthalenes	AXYS	AQRD
C2-Naphthalenes	AXYS	AQRD
C3-Naphthalenes	AXYS	AQRD
C4-Naphthalenes	AXYS	AQRD
Acenaphthylene	AXYS	AQRD
Acenaphthene	AXYS	AQRD
C1-Acenaphthenes	AXYS	AQRD
Fluorene	AXYS	AQRD
C1-Fluorenes	AXYS	AQRD
C2-Fluorenes	AXYS	AQRD
C3-Fluorenes	AXYS	AQRD
C4-Fluorenes		AQRD
Phenanthrene	AXYS	AQRD
Anthracene	AXYS	AQRD
C1-Phenanthrenes/Anthracenes	AXYS	AQRD
C2-Phenanthrenes/Anthracenes	AXYS	AQRD

Table 2. Continued

C3-Phenanthrenes/Anthracenes	AXYS	AQRD
C4-Phenanthrenes/Anthracenes	AXYS	AQRD
Retene	AXYS	AQRD
Dibenzothiophene	AXYS	AQRD
C1-Dibenzothiophenes	AXYS	AQRD
C2-Dibenzothiophenes	AXYS	AQRD
C3-Dibenzothiophenes	AXYS	AQRD
C4-Dibenzothiophenes	AXYS	AQRD
Fluoranthene	AXYS	AQRD
Pyrene	AXYS	AQRD
C1-Fluoranthenes/Pyrenes	AXYS	AQRD
C2-Fluoranthenes/Pyrenes	AXYS	AQRD
C3-Fluoranthenes/Pyrenes	AXYS	AQRD
C4-Fluoranthenes/Pyrenes	AXYS	AQRD
Benz[a]anthracene	AXYS	AQRD
Chrysene	AXYS	AQRD
C1-Benzo[a]anthracenes/Chrysenes	AXYS	AQRD
C2-Benzo[a]anthracenes/Chrysenes	AXYS	AQRD
C3-Benzo[a]anthracenes/Chrysenes	AXYS	AQRD
C4-Benzo[a]anthracenes/Chrysenes	AXYS	AQRD
Benzo[b,j,k]fluoranthene	AXYS	AQRD
Benzo[a]pyrene	AXYS	AQRD
C1-Benzofluoranthenes/Benzopyrenes	AXYS	AQRD
C2-Benzofluoranthenes/Benzopyrenes	AXYS	AQRD
C3-Benzofluoranthenes/Benzopyrenes	AXYS	AQRD
C4-Benzofluoranthenes/Benzopyrenes	AXYS	AQRD
Indeno[1,2,3-c,d]-pyrene	AXYS	AQRD
Dibenz[a,h]anthracene	AXYS	AQRD
Benzo[g,h,i]perylene	AXYS	AQRD
Perylene	AXYS	AQRD
Anthanthrene	AXYS	AQRD
Triphenylene	AXYS	AQRD

Using data sets obtained from AESRD and the Regional Aquatic Monitoring Plan (RAMP), we compiled a database of diss Se, diss As and total V measurements collected during active flow seasons (2 March to 1 November) from 1972 to 2010. Winter sampling events (2 November to 1 March) were excluded because not all programs, sites and years included winter sampling. Entries at or below analytical detection limits were entered as half the value of the detection limit. Sites along the same river were aggregated if locations were <10 km apart and in the same geological formation (QGIS v2.6.1 – Brighton, <http://qgis.org/en/site/>).

As well as the historical data set for diss Se, diss As and total V, a database of automated (“sonde”) water quality measurements (pH and temperature) during snow melt (2 March to 14 June) was compiled from records obtained from AESRD and EC. The final data set contained snowmelt data from 18 sites on five rivers: Firebag, Muskeg, Steepbank, Mackay and High Hills. Each of these rivers had daily data that spanned the entire snowmelt period for three years (2012-2014): Firebag and High Hills with one site each; Muskeg and Mackay with two sites each; and Steepbank with three sites. In addition, historical (1989 to 2011) snowmelt data were available for three of the previously-mentioned rivers (Firebag - five sites, Muskeg - five sites, and Steepbank - four sites), although for a given year, the data did not always span the entire snowmelt period. The resulting data set contained data from 27 continuous and 56 partial snowmelt periods.

Supporting environmental data

Discharge data were obtained from the Water Survey of Canada (WSC). Discharge has been measured near the downstream sites on each of the five tributaries since the 1970s by the WSC, except for the High Hills River, which has discharge records only since 2011. Daily discharge was estimated for upstream sites by scaling discharge data from outlet sites by drainage area of the upstream site.

Information on bedrock geology, location relative to the river’s incisement of the McMurray formation and stage of mine development (i.e., pre-development; early land clearing, development and production; or subsequent expansion

or upgrading) in the watershed were determined for each site. Geographic Information Systems (GIS) base layers were compiled from public sources (e.g., NRCan Atlas of Canada v6, <http://atlas.nrcan.gc.ca>) whereas historical oil sands areas, agreements, leases, boundaries, mineable area and approval boundaries were compiled from the former Energy Resource Conservation Board, now the Alberta Energy Regulator, and available from the Province of Alberta (e.g., Alberta Environment 2009, Alberta Energy 2013), as well as from registrations submitted by operators in accordance with Alberta’s Environmental Protection and Enhancement Act. Timing of development was determined using information disseminated by industry sources, including company websites; 43-101 SEDAR investor reports (www.sedar.com); and historical information (GIS) previously compiled by federal and provincial agencies (as above).

Data analysis / Statistical Approach

Current water chemistry

Water chemistry data from April 2012 to March 2015 were combined into a single data set (available on the Canada-Alberta Oil Sands Environmental Monitoring Information Portal <http://donnees.ec.gc.ca/data/substances/monitor/surface-water-quality-oil-sands-region/tributary-water-quality-oil-sands-region/>) to establish the current state of water quality for Athabasca River tributaries. Average, minimum and maximum values were calculated for all parameters as well as the percentage of observations exceeding Canadian Environmental Quality Guidelines for the Protection of Aquatic Life (CCME 2010) or Alberta Surface Water Quality Guidelines for the Protection of Aquatic Life (AESRD 2014).

Spatial and temporal trends in the distribution of contaminants in Athabasca River tributaries were assessed for select parameters:

- Diss Se, diss As and total V. These three elements have been previously associated with oil sands development.
- Mercury (THg and MeHg). Mercury has been routinely identified as a contaminant of concern in the oil sands region. In addition, mercury in fish is a recognized threat to subsistence consumers.

- Polycyclic aromatic compounds (PACs). PACs are currently one of the greatest concerns for chronic pollution in the oil sands, given their prominence in bitumen and in petroleum coke, a byproduct of bitumen upgrading. Concern has centered on whether PACs, which occur naturally in hydrocarbon bearing deposits, are released to aquatic ecosystems, through natural or through anthropogenic pathways.

Concentrations were compared (1) among some or all five tributaries with oil sands mining activity in their watersheds (Ells, Firebag, Mackay, Muskeg, and Steepbank rivers, all at downstream sites) to assess variability among tributaries, (2) between upstream and downstream sites on individual rivers to determine changes in contaminants along rivers, and (3) to discharge to examine hydrologic controls of contaminant inputs. When this report was prepared, not all data were available, verified or interpreted. Consequently, interpretation of patterns in diss Se, diss As and total V was limited to 3 tributaries (Ells, Muskeg, and Steepbank rivers) over 3 years (2012-2014). Patterns in mercury were examined for all five tributaries but only using 2012 data. Concentrations of total (Σ PAC) were compared for three tributaries (Mackay, Muskeg, Steepbank) for 2012 and 2013.

Historical water chemistry

The historical database of diss Se, diss As and total V measurements (2 March to 1 November, 1972 to 2010) was used to determine the range of concentration and instantaneous daily loads in the tributaries of the Athabasca and Clearwater rivers between 1972-2010. Daily load was calculated as the product of concentration and daily discharge, and expressed in kg per day.

To establish regional reference concentrations (i.e., for all Athabasca River tributaries, collectively, in the oil sands region), concentrations of diss Se, diss As and total V were compared (1) between sites upstream of the McMurray formation versus those in or downstream of the McMurray formation; (2) between sites upstream of development versus those situated downstream but sampled prior to development; and (3) over the 38 year period for sites upstream of development. If the three elements showed little spatial variation (upstream versus down-

stream of the McMurray formation, or upstream versus downstream of future development) or temporal variation (38 years, 1974-2010), the data from sites upstream of development as well as downstream, but sampled prior to development, were pooled and used to calculate "reference" concentrations.

The historical pH database during snow melt (1989-2014) was used to determine the frequency of snowmelt acidification events in Athabasca River tributaries. Acidification events (expressed as duration, in fraction of days, from when pH first fell below 7.0 until pH rose above 7.0) were determined for each site and year. Also, episodes of low pH (pH<6.5) were identified. The severity (duration \times magnitude) of each snowmelt acidification event was estimated as the duration (d_i as portion of day) of each pH measurement <7.0 multiplied by the inverse of that pH measurement (pH_i), summed for the duration of an acidification event (Equation 1).

$$\text{Severity} = \sum_{i=1}^n (d_i * \frac{1}{pH_i}) \quad (\text{Equation 1})$$

Results

Progress Relative to the Joint Implementation Plan

As a result of increased efforts by AESRD, Hatfield Consultants and EC under the JOSM, a large number of tributary sites were visited, many at high frequency, between April 2012 and March 2015. Previously, a total of 43 tributary sites were monitored by AESRD or Hatfield Consultants with, at most, monthly sample collection (Table 1). Under the JOSM, 62 sites were monitored: 14 sites with high frequency (daily or alternate days during snow melt and thereafter decreasing) by EC, and 48 sites monitored monthly, seasonally or annually by either AESRD or Hatfield Consultants. Intensive sampling at 14 sites by EC resulted in 2083 water samples collected between 2012 and 2015 (1832 water samples +399 replicates or blanks), with analysis resulting in 163 measurements of metal, ion, nutrient, mercury and PAC concentrations per sample (Table 3). Similarly, sampling by AESRD / Hatfield Consultants resulted in 717 tributary samples, each analyzed for 149 parameters.

Current state of water quality of Athabasca River tributaries (2012-2015 JOSM data)

Water quality of Athabasca River tributaries in Canada's oil sands region is heavily influenced by the presence of the underlying Cretaceous bedrock, comprised of shale, sandstone and limestone. The waters are moderately hard (average alkalinity of 108 mg/L CaCO₃) because of their mineral content, particularly Mg²⁺, Ca²⁺ and bicarbonate (8.53, 27.71 and 137.07 mg/L, respectively) (Table 4). This mineral content results in an average conductivity of 241±4 µS/cm and total dissolved solids concentration of 139±2 mg/L. Together, the alkalinity and mineral content (along with an average pH of 7.72±0.05, 1989-2014) indicate moderate sensitivity to acid rain (Zimmerman & Harvey 1979-1980). Concentrations of nitrogen and phosphorus (indicators of nutrient status) are typically low to moderate, indicative of oligotrophic to mesotrophic conditions. Concentrations average

0.14 mg/L total and 0.03 mg/L total dissolved phosphorus, and 0.91 mg/L total nitrogen, 0.08 mg/L nitrogen as nitrate+nitrite, and 0.04 mg/L nitrogen as total ammonia (Table 4).

Streamwater concentrations of anions, cations and nutrients are strongly influenced by seasonal patterns in discharge. Concentrations of dominant ions were greatest prior to snow melt. For example, anions such as chloride, fluoride and sulphate were greatest in winter grab samples with maximum concentrations of 40.4, 0.26 and 75.1 mg/L, respectively, observed in April 2014. Likewise, total ammonia and nitrate+nitrite concentrations were greatest during winter (January and March). As a result, conductivity and total dissolved solids also peaked during late winter. In contrast, concentrations of particulate material were greatest during high flow events: total suspended solids, total nitrogen and total phosphorus all peaked during snow melt and summer rainfall events.

Table 3. Number of water samples collected from Athabasca River tributaries by Environment Canada (EC) or Alberta Environment and Sustainable Resource Development (AESRD)/Hatfield Consultants as part of the Canada-Alberta Joint Oil Sands Implementation Plan for Oil Sands Monitoring (2012-2014).

Watershed	EC				Total no. samples	AESRD / Hatfield No. of samples
	No. of samples		No. of QA/QC samples			
	Grab samples	Auto-samples	Duplicates	Blanks		
Beaver						6
Calumet						6
Clearwater						52
Ells	260	121	27	37	445	49
Eymundson						9
Firebag	186		31	39	256	44
High Hills	68		12	18	98	12
Mackay	170	243	21	28	462	67
McLean						3
Mills						3
Muskeg	204		30	35	269	348
Pierre						9
Poplar						25
Red Clay						9
Steepbank	360	220	54	67	701	60
Tar						6
Unnamed (Big)						9
TOTAL	1248	584	175	224	2231	717

Bitumen is made up of hydrocarbons (i.e., organic compounds containing only carbon and hydrogen) but also “impurities” such as nitrogen, sulphur and heavy metals. Many metals (notably vanadium, nickel, molybdenum, mercury, aluminum, antimony, arsenic, cadmium, chromium, copper, iron, lead, strontium, uranium, zinc), as well as other elements (e.g., selenium) have been associated with bitumen extraction and related oil sands operations (Kelly et al. 2009, 2010). Under the JOSM, 44 metals and metalloids, as well as selenium, were analyzed for both total and dissolved forms; mercury was analyzed for both total and methyl mercury. Of these 46 elements, 18 have either Canadian Environmental Guidelines for the Protection of Aquatic Life (CCME 2010), Alberta Surface Water Quality Guidelines for the Protection of Aquatic Life (AERSD 2014), or both (Table 4). While several elements occasionally exceeded guidelines (e.g., <5 % of all samples for total Cd, total Cr, total Ag, total Zn, total As, total Se), several frequently exceeded guidelines (i.e., >10 % of samples exceeding guidelines for total Al, total Cu, total Fe; 2012-2015 data; Table 4). Concentrations of total and methyl mercury in all 2012 tributary samples were below CCME guidelines. Exceedance of water quality guidelines for certain metals and metalloids sampled from lower Athabasca tributaries during the JOSM was not unexpected: aluminium, copper and iron often exceeded aquatic life guidelines during 1998-2000 surveys of the Steepbank, Mackay and Ells rivers (Headley et al. 2005) and sulphide, total aluminium, total chromium, total iron and total phenols exceeding guidelines were reported by RAMP (2015) for a number of tributaries sampled in 2014.

Polycyclic aromatic compounds (PACs) are currently one of the greatest concerns for chronic pollution in the oil sands, given their prominence in bitumen. A total of 52 PACs were analyzed including unsubstituted PACs (unPACs, n=25), alkylated PACs (aPACs, n=22) and dibenzothio-phenes (DBTs, n=5). Although aPACs and DBTs are the main PACs associated with petrogenic sources, only unPACs have Canadian Environmental Guidelines for the Protection of Aquatic Life (CCME 2010). For these, only pyrene was observed to occasionally exceed the established guidelines for total concentration in water (e.g., <5 % of all samples, Table 4). It should be noted that all PAC concentrations (both measured and

guidelines values) are for the dissolved fraction; however, because of their hydrophobic nature, most PACs bind to particulate matter.

During the past 10 years, a number of studies have been conducted that measured water quality of Athabasca River tributaries in Canada’s oil sands region (e.g., Kelly et al. 2010, Guéguen et al. 2011, Lavoie et al. 2011, RAMP 2015, Gerner et al. 2016, Shotyk et al. 2017). Comparisons are difficult to make because of variation in analytical methods, time of year and frequency of sampling, and sites sampled. For example, Guéguen et al. (2011) sampled two Athabasca tributaries downstream of Fort McMurray (Mackay and Muskeg) between June-August 2008 and 2009, with samples analyzed for total and dissolved metals (Cd, Co, Cu, Ni, Pb) as well as total and dissolved ions (Ca, Mg), dissolved nutrients (DOC, NO_3^- , PO_4^{3-} , SO_4^{3-}), total suspended solids, conductivity and pH. In contrast, Shotyk et al. (2017) sampled five tributaries downstream of Fort McMurray in October 2014, with samples analyzed for 17 dissolved metals. In general, a good agreement is often found between concentrations of “conventional parameters” (i.e., physical measures as well as ions and nutrients). However, as Huang et al. (2016) observed in their review of metal characterization and distribution in the Alberta oil sands region, analytical techniques used to determine metals in the oils sands region vary widely, making numerical comparisons difficult.

Table 4. Concentrations of major parameters in the Firebag, Ells, Mackay, Muskeg and Steepbank rivers sampled as part of the Canada-Alberta Joint Oil Sands Implementation Plan for Oil Sands, and comparison to water quality guidelines for protection of aquatic life, where available. Units are µg/L unless otherwise indicated. When guideline calculations required input on water hardness, a value of 108.05 mg/L CaCO₃ was used. All data are from EC records (2012-2015) except mercury (total and methyl) which are combined EC and Alberta data; mercury data are for 2012 only.

Parameter (µg/L unless indicated)	JOSM data (2012 – 2015)					Guide-line	Frequency of observations exceeding guideline (%)
	mean	min	max	Lower 95 %	Upper 95 %		
Physical							
TSS mg/L	87.78	1.00	2310	77.11	98.45	30.00c	40.1%
Alkalinity CaCO ₃ mg/L	108.05	17.06	349.15	104.92	111.17		
pH	7.88	6.69	8.57	7.87	7.89		
conductivity	241.36	40.40	915.00	234.15	248.58		
TDS	138.63	20.50	534.03	134.41	142.84		
Ions							
Ca	27.71	0.05	93.70	26.88	28.54		
Mg	8.53	0.005	28.60	8.27	8.79		
Na	10.85	0.001	106.00	10.26	11.44		
K	1.49	0.01	5.24	1.45	1.54		
Cl	2.12	0.01	40.40	1.96	2.28		
F	0.11	0.01	0.27	0.10	0.11		
SO ₄ mg/L	10.33	0.01	75.10	9.79	10.87		
Metals							
Al (total)	46.91	1.10	1080	41.38	52.45	100.00c	62.9 %
Be (total)	0.07	< 0.01	1.78	0.06	0.07		
Cd (total)	0.02	< 0.01	0.52	0.02	0.02	0.17 c 2.3c	0.92 % 0.0 %
Cr (total)	1.65	0.01	49.20	1.46	1.84	8.90c	4.2 %
Cu (total)	1.83	0.02	35.20	1.64	2.01	2.53c	17.8 %
Fe (total)	2778	160	61200	2541	3016	300.00c	98.6 %
Hg (total) ng/L	2.61	0.11	14.58	2.35	2.87	26c	0 %
Hg (methyl) ng/L	0.06	0.010	0.362	0.056	0.072	4c	0 %
Pb (total)	0.91	0.01	23.20	0.80	1.02	3.51c	6.9 %
Mo (total)	0.36	0.01	2.62	0.35	0.38	73.00c	0.00 %
Ni (total)	2.33	0.02	42.80	2.12	2.55	101.37c	0.00 %
Ag (total)	0.01	< 0.01	0.26	0.01	0.01	0.25c 0.10b	1.3 %
Sr (total)	114	17.5	540	110	118		
Tl (total)	0.02	< 0.01	0.48	0.02	0.02	0.80c	0.00 %
U (total)	0.18	0.01	1.88	0.17	0.19	15c 33c	0.0 % 0.0 %
V (total)	3.38	0.04	84.80	3.00	3.77		
Zn (total)	5.60	0.20	143.00	5.00	6.20	30.00c	3.4 %

Metalloids								
As (total)	1.26	0.17	21.10	1.17	1.36	5.00c	3.4 %	
As (diss)	0.50	0.01	1.50	0.48	0.51			
Sb (total)	0.04	< 0.01	0.45	0.04	0.05			
Nitrogen & Phosphorus								
N (total) mg/L	0.91	0.24	4.32	0.89	0.93			
N (diss) mg/L	0.62	0.22	1.29	0.61	0.64			
NH ₃ (un-ionized) mg/L	< 0.01	< 0.01	0.03	< 0.01	< 0.01	0.019b,c	0.2 %	
NH ₃ (total) mg/L	0.04	0.01	0.98	0.04	0.05			
NO ₃ +NO ₂ -mg/L	0.08	0.01	0.85	0.08	0.09	3.00c	0.0 %	
P (total) mg/L	0.14	0.02	2.16	0.13	0.15			
P (diss) mg/L	0.03	< 0.01	0.11	0.03	0.03			
Nonmetals								
Se (total)	0.11	0.01	1.49	0.10	0.11	1.00c	0.4 %	
Se (diss)	0.06	0.01	0.43	0.05	0.06			
v in dissolved fraction								
ΣPACs ₍₅₂₎	0.92	< 0.01	18.65	0.77	1.08	-	-	
Acenaphthene	< 0.01	< 0.01	0.02	< 0.01	< 0.01	5.8c	0.0 %	
Anthracene	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.012c	0.0 %	
Benzo[a]anthracene	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.018c	0.0 %	
Benzo[a]pyrene	< 0.01	< 0.01	0.01	< 0.01	< 0.01	0.015c	0.0 %	
Fluoranthene	< 0.01	< 0.01	0.02	< 0.01	< 0.01	0.04c	0.0 %	
Fluorene	< 0.01	< 0.01	0.02	< 0.01	< 0.01	3c	0.0 %	
Naphthalene	0.05	< 0.01	0.24	0.04	0.06	1.1c	0.0 %	
Phenanthrene	< 0.01	< 0.01	0.05	< 0.01	0.01	0.4c	0.0 %	
Pyrene	< 0.01	< 0.01	0.06	< 0.01	0.01	0.025c	2.2 %	

^b AESRD 2014

^c CCME 2010 (Note: if short-term and long-term guidelines were available for the same chemical, both are presented. For NO₃+NO₂, the CCME guideline is 13 mg/L which is equivalent to 3 mg/L NO₃+NO₂-N).

Dissolved selenium, dissolved arsenic and total vanadium in Athabasca River tributaries

Current water chemistry

As part of the JOSM, seasonal and inter-annual (2012-2014) patterns in three elements known to be associated with oil sands mining were compared for three tributaries with similar patterns and magnitude of discharge (Ells, Muskeg, and Steepbank rivers). Concentrations of diss As, diss Se and total V varied among the three study rivers, with average (± 1 SE) concentrations (April 2012 – November 2014) at sites closest to the river mouths being highest for the Ells River:

- diss As ($\mu\text{g/L}$): 0.72 ± 0.02 Ells, 0.48 ± 0.01 Steepbank, 0.32 ± 0.01 Muskeg,
- diss Se ($\mu\text{g/L}$): 0.109 ± 0.002 Ells, 0.056 ± 0.004 Steepbank, 0.034 ± 0.001 Muskeg,
- total V ($\mu\text{g/L}$): 8.28 ± 1.40 Ells, 3.25 ± 0.38 Steepbank, 0.43 ± 0.02 Muskeg.

Seasonal patterns in diss As, diss Se and total V concentrations were similar among the three rivers, with concentrations strongly correlated with discharge ($r^2 \geq 0.85$, $p < 0.01$); hence, concentrations were typically greatest during snow melt (e.g., 9 April to 29 May), peaking at values of $1.31 \mu\text{g/L}$ diss As, $0.43 \mu\text{g/L}$ diss Se and $84.8 \mu\text{g/L}$ total V (with all peaks observed in the Ells River during snow melt 2013) (Fig. 2). Water quality guidelines are not in place for total vanadium, or for arsenic and selenium in dissolved form. Concentrations of total selenium and total arsenic rarely exceeded water quality guidelines (Table 4).

Preliminary comparison of sites sampled upstream of development versus near the mouth of the rivers showed that concentrations of certain parameters, for example diss Se, were greater ($p < 0.05$) at downstream sites (Fig. 3, left panel). Multiplying measured concentrations ($\mu\text{g/L}$) by average daily flow (m^3/day), and then summed for each hydrologic year, gives an estimate of the total quantity (or load, kg/year) of each element exported from a given site. For example, in the case of the Muskeg River, downstream load was 3x to 6x greater than upstream values for total V, diss Se and diss As ($p < 0.04$) (Fig. 3, right panel).

Historical water chemistry

Analysis of historical water chemistry for seven tributaries to the lower Athabasca and Clearwater rivers showed that concentrations of diss As, diss Se and total V did not differ between sites upstream of the McMurray formation versus those downstream of the formation ($F_{1, 306} \leq 0.93$, $p \geq 0.34$; Fig. 4 white circles). Furthermore, concentrations did not differ between sites upstream of development versus those situated downstream but sampled prior to development ($F_{1, 306} \leq 0.92$, $p \geq 0.34$; Fig. 4 white circles). Finally, analysis of change in water chemistry at upstream sites over the 38-year study period showed no changes in concentration over time ($F_{1, 306} \leq 1.02$, $p \geq 0.32$). Given that pre-development values for diss As, diss Se and total V showed little spatial (upstream versus downstream of the McMurray formation, or upstream versus downstream of future development) or temporal variation (38 years, 1972-2010), concentrations from all upstream sites and downstream sites sampled prior to development were pooled to calculate "reference" concentrations: 0.54 ± 0.02 (0.05) $\mu\text{g/L}$ diss As, 0.16 ± 0.01 (0.01) $\mu\text{g/L}$ diss Se, and 0.83 ± 0.05 (0.09) $\mu\text{g/L}$ total V (mean \pm SE (95th percentile)).

Comparison of historical total V, diss Se, and diss As measurements from reference sites (i.e., upstream sites and downstream sites sampled prior to development) versus sites downstream of development showed that concentrations of all three elements were greater ($p \leq 0.01$) downstream of development (Fig. 4, left panels, grey squares versus white circles). Similarly, river loads (calculated as measured concentrations multiplied by average daily flow) were greater ($p \leq 0.01$) at sites downstream of development compared to reference loads (Fig. 4, right panels, grey squares versus white circles).

Muskeg River —a case study

The Muskeg River was the site of a case study to assess changes in concentrations and loads over time, and in relation to stage of mining development. It was chosen because sufficient sampling had been conducted there, pre- versus post-development and upstream versus downstream, to support statistically rigorous comparisons. The 12 historical sites on the river were grouped into three aggregate sites to facilitate Analysis

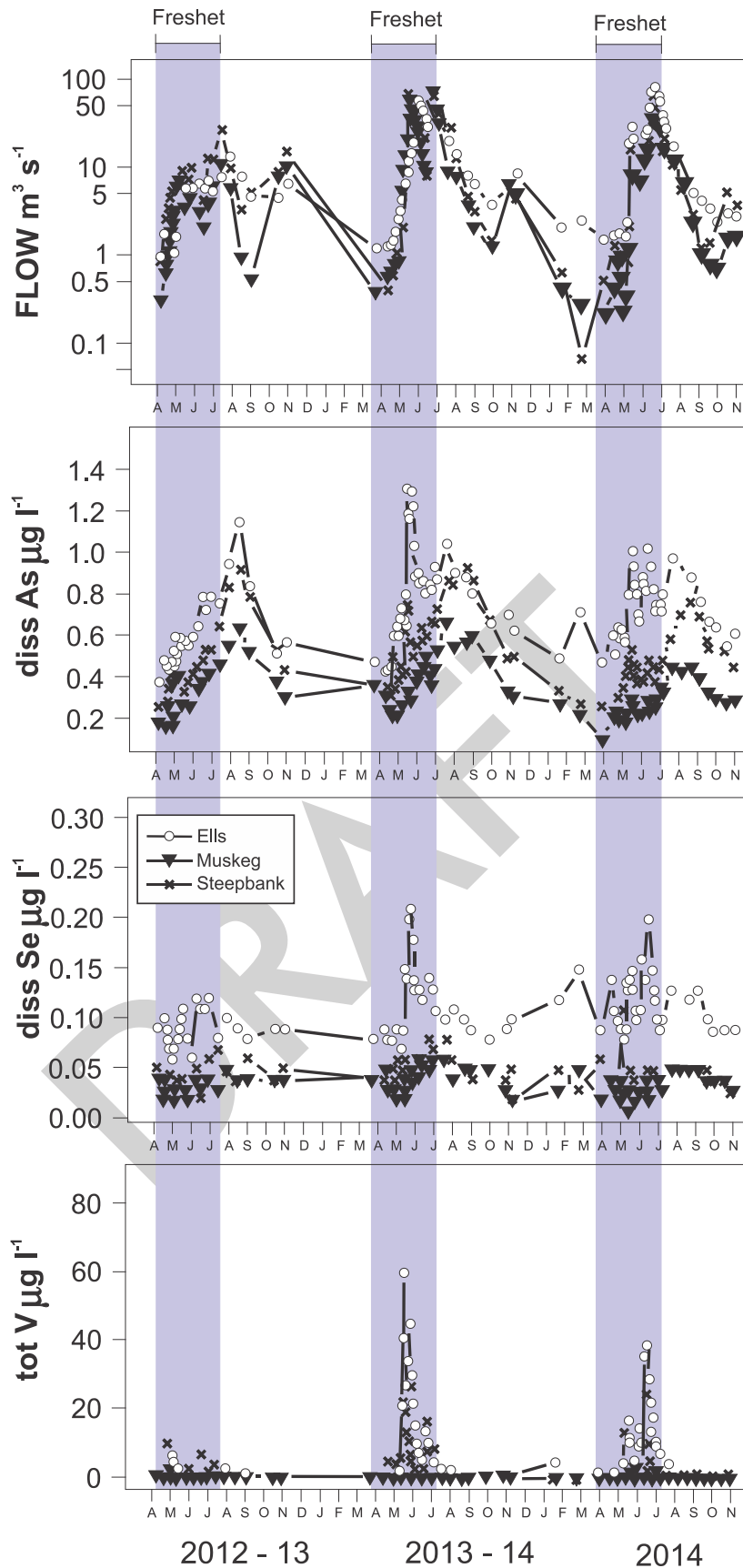


Figure 2. Seasonal and inter-annual variation in discharge and concentration of dissolved arsenic (diss As), dissolved selenium (diss Se) and total vanadium (total V) near the mouths of three tributaries of the Athabasca River (Ells, Muskeg, Steepbank).

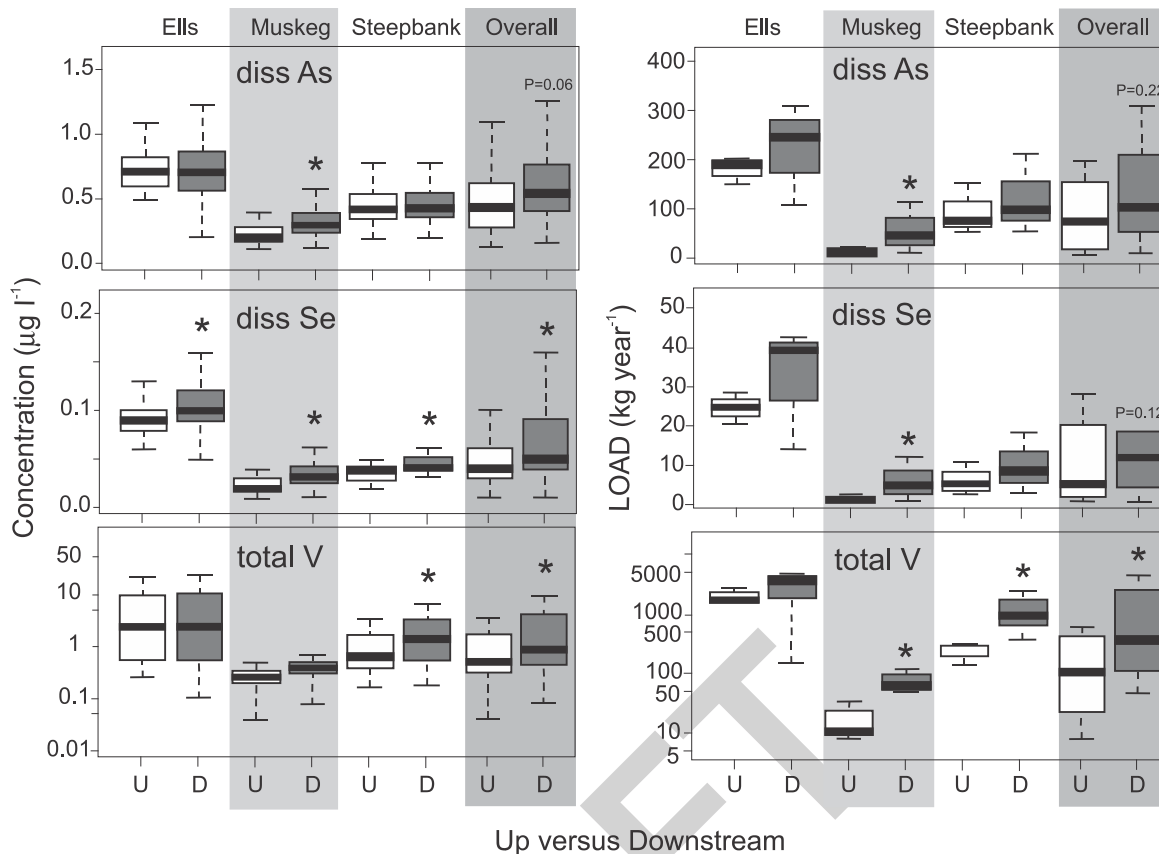


Figure 3. Mean annual (2012-2014) concentrations (left panel) and loads (right panel) of dissolved arsenic (diss As), dissolved selenium (diss Se) and total vanadium (total V) at upstream and downstream sites on three tributaries of the Athabasca River (Ells, Muskeg, Steepbank). Significant differences ($p < 0.05$) are identified (*) between upstream and downstream sites on the same river (Ells, Muskeg or Steepbank) or the three rivers overall.

of Variance (ANOVA) comparisons with similar sample sizes (degrees of freedom ≥ 40 per site per element): MU7, situated upstream of development; MU4, situated just downstream of development; and MU1 (near the river mouth), situated downstream of development as well as incisement of the McMurray formation (Fig. 5a).

Comparing water chemistry from the three aggregate sites showed that concentrations of diss As, diss Se and total V did not differ ($p \geq 0.13$) between the upstream site (MU7 from 1976-2009) and the two downstream sites sampled prior to development (MU1 and MU4 from 1972-1996) (Fig. 5b). Hence, in the absence of development, concentrations did not increase with distance downstream or with passage along the McMurray formation. Moreover, analysis of diss As, diss Se and total V concentrations at the upstream site over the 33-year study period showed no significant change over time ($p \geq 0.06$; Fig. 5c). Pre-development values for

diss As, diss Se and total V showed little spatial variation (i.e., upstream versus downstream of future development, or with exposure to the McMurray formation) or temporal variation (33 years, 1976-2009). Concentrations from all upstream sites and downstream sites sampled prior to development were pooled to calculate "reference" concentrations for the Muskeg River.

Comparison of concentrations of diss As, diss Se and total V among three sites (MU7, MU4 and MU1) and three development stages (prior to, early, and subsequent development) showed significant interactions between site location and development stage (ANOVA $F_{1,236} \geq 14.73$, $p \leq 0.01$). Concentrations of all three elements were greatest (Tukey's HSD, $p \leq 0.01$) during the early stage of mine development at MU4, the site situated closest to active development (13-35 % greater than reference). Kelly et al (2010) similarly observed that concentrations of metals such as cadmium and zinc were correlated with

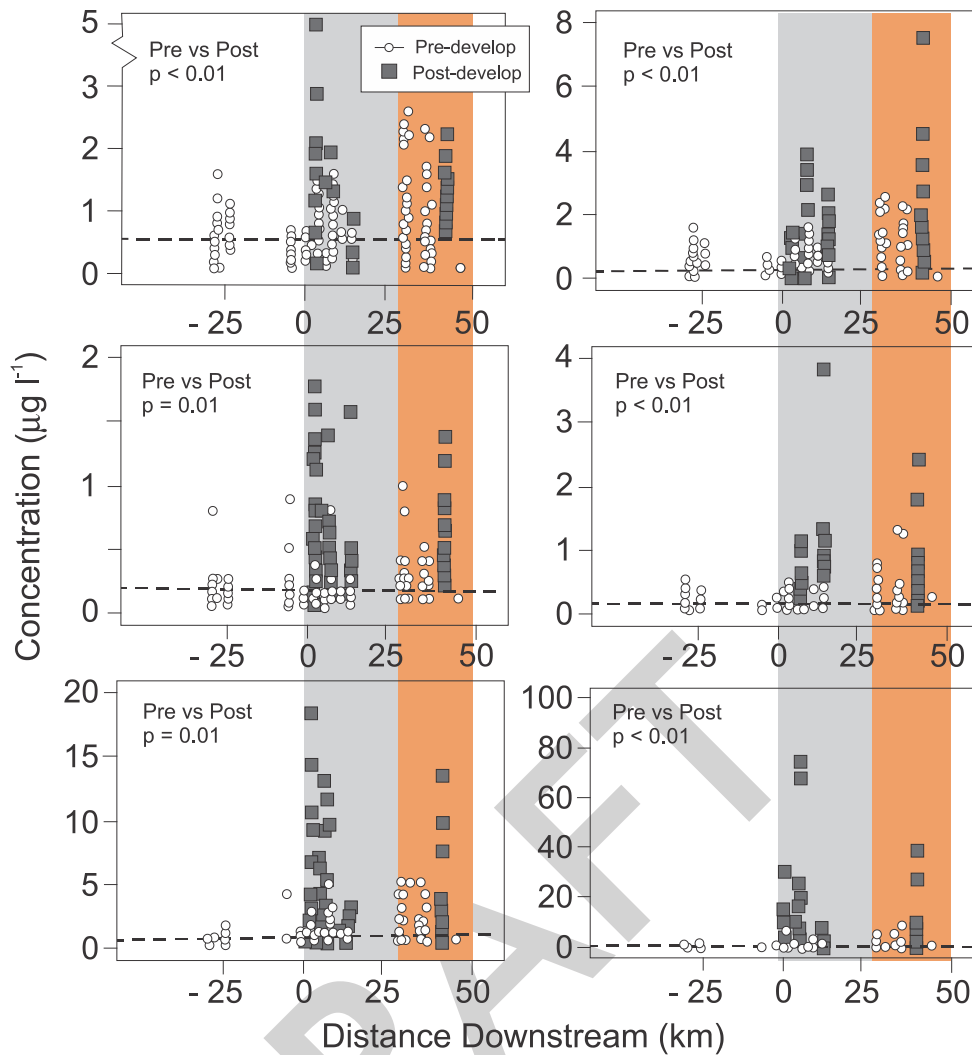


Figure 4. Historical (1972-2010) concentrations (left panels) and daily loads (right panels) of dissolved arsenic (diss As), dissolved selenium (diss Se) and total vanadium (total V) sampled at sites located upstream or downstream of development, showing data for seven study tributaries combined. The upstream limit of development was set as 0 km on each tributary. The shaded area (0 to 50 km) represents distance downstream of development; orange shading identifies the area below incisement of the bitumen-bearing McMurray geological formation. Dashed lines show average reference concentrations or loads, which did not change with river distance ($p \geq 0.34$). Concentrations and loads of all three elements post-development were greater than reference values (ANCOVA $p < 0.01$) and increased with distance downstream of development.

the extent of land disturbance in the watershed. Concentrations of diss Se were also elevated (Tukey's HSD, $p < 0.01$) during the subsequent development phase at the furthest downstream site (21 % greater than reference).

Similarly, analysis of daily loads (kg/day) showed significant effects of site location and development stage on diss Se and total V (ANOVA,

$F_{2, 126} \geq 8.53$, $p < 0.01$), and significant interactions between site location and development stage on diss As (ANOVA, $F_{3, 126} = 3.69$, $p < 0.01$). Thus, during the early phase of mine development, diss As, diss Se and total V loads were 34 to 126 % greater immediately downstream of development and 47 to 148 % greater at the furthest downstream site compared to reference loads (Tukey's HSD, $p \leq 0.01$) (Fig. 5c).

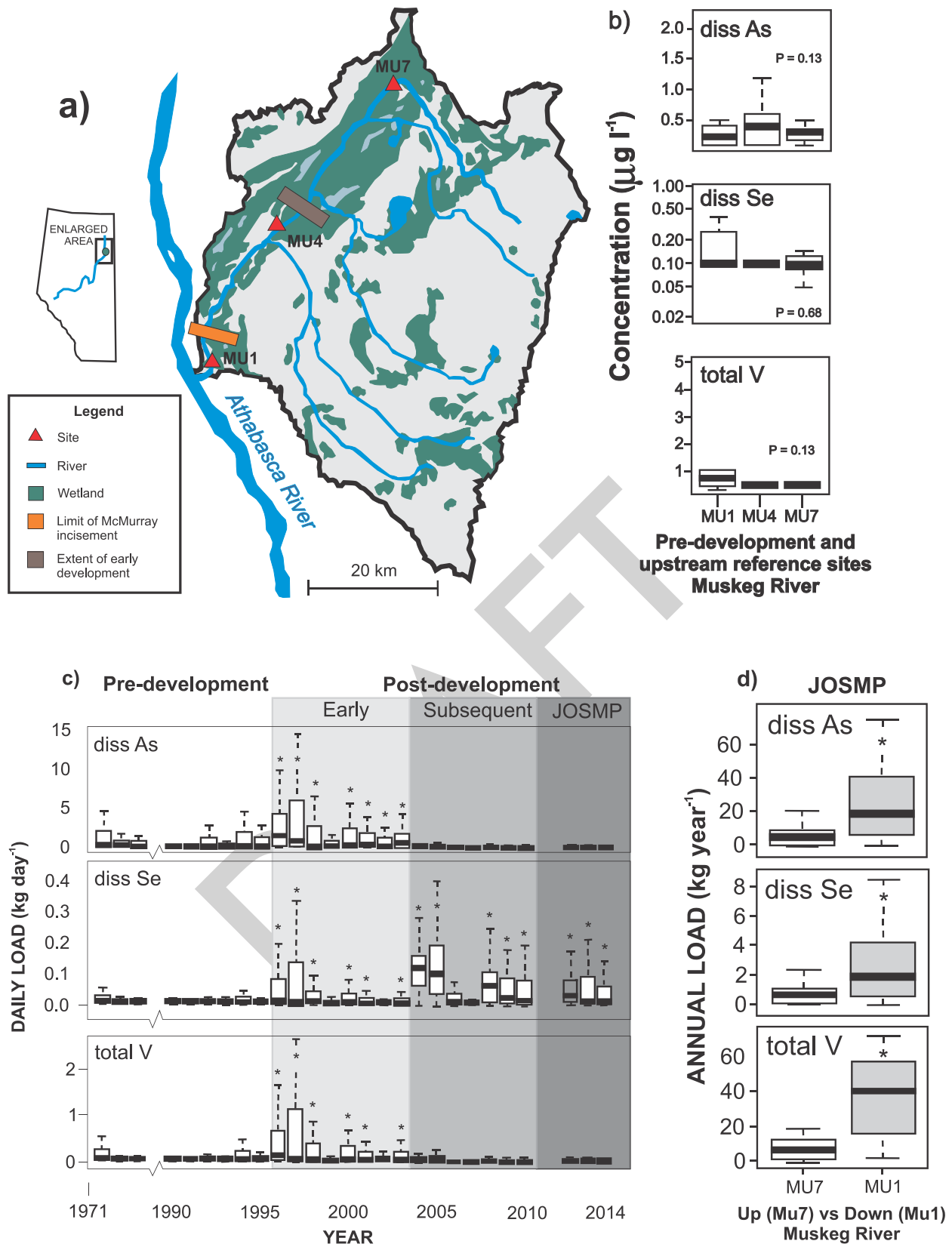


Figure 5. Muskeg River watershed showing: (a) the three aggregate study sites: MU7, situated upstream of development; MU4, situated just downstream of development and; MU1 (near the river mouth), situated downstream of development as well as incisement of the McMurray formation; (b) concentrations of dissolved As, dissolved Se and total V at the upstream site (MU7) and two downstream sites sampled prior to development; (c) average daily loads (kg/day) of dissolved As, dissolved Se and total V at the downstream site (MU1), with the stage of mining operations identified for the period of record; (d) annual loads (2012-2014 only) of dissolved As, dissolved Se and total V at upstream (MU7) and downstream (MU1) sites.

Daily loads of diss Se were also elevated during the subsequent phase of development (Tukey's HSD, $p \leq 0.01$). Daily loads calculated as part of the JOSM (2012-2014) were consistent with values observed for the historical record in the Muskeg River (1972-2010) (Fig. 5c).

Analysis of data collected during the JOSM showed that annual loads of diss As, diss Se and total V were $>200\%$ greater downstream compared to upstream of development for the Muskeg River ($p \leq 0.04$) (Fig. 5d). Differences in upstream versus downstream loads varied seasonally: differences were greatest during freshet for diss As (12.99 ± 8.15 versus 3.00 ± 1.46 kg/y for downstream versus upstream respectively, $p = 0.03$) but greatest during the open water period for diss Se and total V (both $>4x$ greater, $p = 0.04$ and $p < 0.01$ for diss Se and total V, respectively). Export (i.e., load standardized for catchment area, expressed as kg/year/km²) of diss As, diss Se and total V were also $>2.6x$ greater between upstream and downstream sites sampled during the JOSM. For example, export of total V was 2.8 times greater from upstream to downstream (0.02 ± 0.01 to 0.06 ± 0.02 kg/yr/km²; $F_{1,4} = 12.10$, $p = 0.02$; Tukey's). Research is continuing to determine the relative contributions from natural sources versus mining development at the downstream sites sampled during the JOSM.

Mercury in Athabasca River tributaries

Total mercury (THg) concentrations varied among five tributary rivers (Ells, Mackay, Firebag, Muskeg and Steepbank rivers) in 2012. Average annual concentrations at the mouth of each river, from highest to lowest, were Mackay (3.87 ± 2.13 ng/L) $>$ Steepbank (3.41 ± 2.26 ng/L) $>$ Ells (2.75 ± 2.36 ng/L) $>$ Firebag (1.88 ± 1.18 ng/L) $>$ Muskeg (1.32 ± 0.53 ng/L). Seasonal patterns were similar among the five rivers, with concentrations closely following hydrological discharge and reaching up to ~ 12 ng/L during high flow periods (Fig. 6). Patterns in methyl mercury (MeHg) concentrations were slightly different than those for THg, with highest average concentrations in the Mackay and Ells rivers and lowest in the Firebag River (average annual MeHg concentrations in order of highest to lowest at the mouth of each river: Mackay (0.12 ± 0.10 ng/L) $>$ Ells (0.08 ± 0.07 ng/L) $>$ Muskeg (0.07 ± 0.06 ng/L) $>$ Steep-

bank (0.05 ± 0.04 ng/L) $>$ Firebag (0.04 ± 0.03 ng/L)). Although MeHg concentrations did increase during high flow periods, the highest MeHg concentrations (up to ~ 0.35 ng/L) were observed during the mid-late summer months (late June to mid-August) when MeHg production via microbial pathways is known to be highest in aquatic ecosystems such as lakes and wetlands (Compeau and Bartha 1985, Benoit et al. 2003). These results suggest both runoff and active MeHg production within each river's watershed are sources of MeHg to the five study rivers. Water quality guidelines for MeHg and total Hg were not exceeded.

In the Firebag, Muskeg, and Steepbank rivers, where both upstream and downstream sites were sampled during summer 2012 (4-April to 27-August), upstream and downstream THg concentrations were not significantly different on the Firebag River (2.13 ± 1.27 versus 2.00 ± 1.20 ng/L), but were significantly higher at downstream sites on the Muskeg (1.5 ± 0.44 versus 1.37 ± 0.52 ng/L) and Steepbank (2.76 ± 1.50 versus 3.51 ± 2.37 ng/L) rivers (Fig. 6). These results indicate that inputs of THg, such as catchment runoff, are higher near the river mouth than further upstream on the Muskeg and Steepbank rivers.

Average annual THg and MeHg concentrations in the five Athabasca tributaries were comparable to those observed in other Canadian rivers, including those in the Arctic, sub Arctic and southern regions of Canada, including the North Saskatchewan River at Edmonton, Alberta, and several tributaries of Lake Ontario in southern Ontario. MeHg concentrations in the Mackay River were elevated and similar to those observed in the Churchill, Mackenzie, and Niagara rivers, which are known to be influenced by MeHg export from local wetlands or delta lakes where MeHg production is elevated (Graydon et al. 2009, Kirk & St. Louis 2009, Denkenberger et al. 2014) (Table 5).

The quantity of THg and MeHg entering the Athabasca River from the Steepbank, Muskeg, Firebag, Ells and McKay rivers during summer 2012 was calculated by multiplying measured concentrations (ng/L) by average daily flow (m³/day). Although THg concentrations in the Firebag River were the lowest of all five rivers, due to higher flows, the Firebag was the larg-

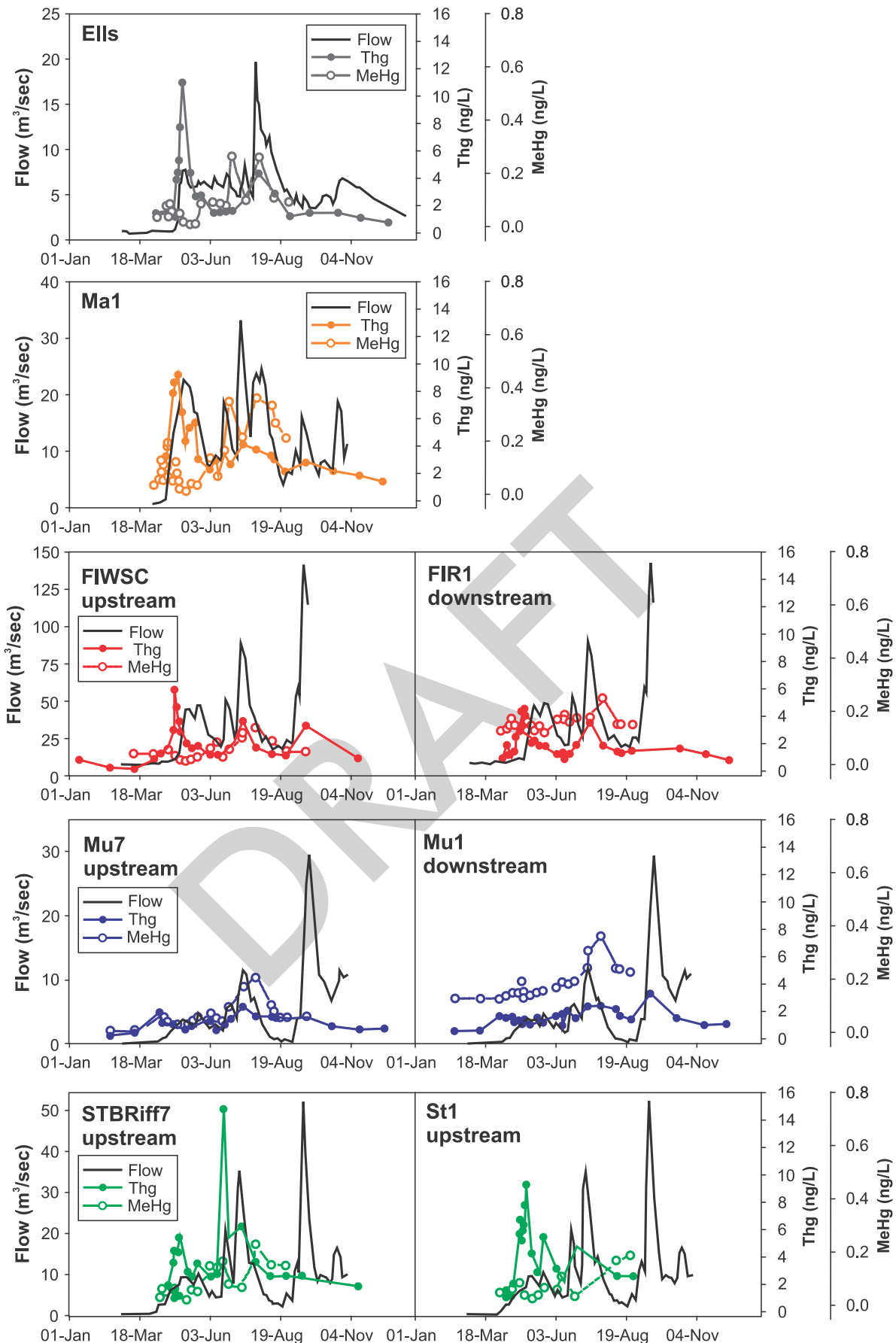


Figure 6. Figure 6. River discharge (m^3/sec) and concentrations of both total mercury (THg) and methyl mercury (MeHg; ng/L) in five major tributaries of the Athabasca River (Ells, Mackay, Firebag, Muskeg and Steepbank rivers) throughout 2012. Site abbreviations are explained in Table 2.

Table 5. Average annual concentrations of total mercury (THg) and methyl mercury (MeHg) in various regions of Canada, including the high Arctic, sub-Arctic, southern Canada, and five major Athabasca River tributaries (Muskeg, Mackay, Steepbank, Ells, and Firebag rivers).

River	Sampling year	n	THg (ng/L)	MeHg (ng/L)	Source
High Arctic					
Cornwallis Island streams	1994-2006	7	1.2 ± 1.1	0.07 ± 0.06	Amyot et al. 2012
Ellesmere Island streams	2005	4	1.1 ± 0.7	0.04 ± 0.03	Amyot et al. 2012
Sub Arctic					
Mackenzie River	2003-2005	37	7.0 ± 4.3	0.09 ± 0.03	Amyot et al. 2012
Mackenzie River tributaries	2003-2005	20	6.3 ± 2.9	0.07 ± 0.04	Leitch et al. 2007
Churchill River	2003-2007	34	2.0 ± 0.8	0.18 ± 0.09	Kirk and St. Louis 2009
Nelson River	2003-2007	66	0.9 ± 0.3	0.05 ± 0.03	Kirk and St. Louis 2009
Southern Canada					
North Saskatchewan River	2005-2006	29	1.5 ± 2.6	0.06 ± 0.05	Kirk and St. Louis 2009
St. Lawrence River	2009-2010	23	0.3 ± 0.2	0.07 ± 0.08	Denkenberger et al. 2014
Black River	2009-2010	23	2.5 ± 1.5	0.09 ± 0.11	Denkenberger et al. 2014
Niagara River	2008-2009	34	0.8 ± 0.5	0.11 ± 0.24	Denkenberger et al. 2014
Humber River	2008-2009	29	2.0 ± 1.1	0.06 ± 0.05	Denkenberger et al. 2014
Trent River	2008-2009	33	0.9 ± 0.6	0.07 ± 0.11	Denkenberger et al. 2014
Athabasca River tributaries					
Ells River	2012	26	2.8 ± 2.4	0.08 ± 0.07	This report
Mackay River	2012	33	3.9 ± 2.1	0.12 ± 0.10	This report
Firebag River	2012	31	1.9 ± 1.2	0.04 ± 0.03	This report
Muskeg River	2012	37	1.3 ± 0.5	0.07 ± 0.06	This report
Steepbank River	2012	25	3.4 ± 2.3	0.05 ± 0.04	This report

est exporter of THg to the Athabasca River over summer 2012. Summer 2012 THg exports in order of highest to lowest were Firebag (780 g) > Mackay (686 g) > Steepbank (406 g) > Ells (255 g) > Muskeg (75 g). Due to the high flows and elevated MeHg concentrations of the Mackay River, the Mackay was the largest exporter of MeHg to the Athabasca River: Mackay (33 g) > Firebag (25 g) > Ells (10 g) > Steepbank (7 g) > Muskeg (6 g). Mercury export is largely controlled by hydrologic discharge and catchment size, which varies by a factor of approximately 5 for the five Athabasca tributaries: Firebag (568,700 ha) > Mackay (556,600 ha) > Ells (270,900 ha) > Muskeg (143,400 ha) > Steepbank (136,500 ha). Because of this variability in catchment size, areal THg and MeHg exports were also calculated. The Steepbank River was by far the largest exporter of THg per ha of catchment area: Steepbank (29.7 g/ha) > Firebag (13.7 g/ha) > Mackay (12.3 g/ha) > Ells (9.4 g/ha) > Muskeg (5.2 g/ha). The Mackay and Steepbank rivers were the largest exporters of MeHg on an areal basis: Mackay (0.58 g/ha) > Steepbank (0.49 g/ha) > Firebag (0.43 g/ha) > Muskeg (0.41 g/ha) > Ells (0.37 g/ha). These large exports of MeHg from the Mackay and Steepbank are likely due to the extensive network of wetlands on the catchments of these two rivers. In fact, preliminary results indicate a strong relationship ($r^2=0.72$,

$p<0.01$) between wetland extent (specifically bogs and fens) and areal MeHg export, suggesting that bog and fens are significant contributors of MeHg to surrounding water bodies. Investigations are continuing using a GIS approach to examine potential drivers of THg and MeHg export to the Athabasca River from these five tributaries, including the extent of various wetland types, various industrial developments, and natural bitumen deposits.

Polycyclic Aromatic Compounds in Athabasca River tributaries

As a first step in evaluating the present state of water quality in tributaries to the Athabasca River, seasonal patterns in concentrations of total polycyclic aromatic compounds (Σ PAC) were compared for three tributaries: Mackay, Muskeg, Steepbank. Concentrations of Σ PAC in the rivers were highest in late-April and early-May in both 2012 and 2013 (Fig. 7). Average Σ PAC concentrations were higher in 2012 in the Steepbank (2012: 2.14, 2013: 0.63 mg/L), and Muskeg rivers (2012: 0.6, 2013: 0.38 mg/L), while the Mackay River showed higher Σ PAC concentrations in 2013 (2012: 1.54, 2013: 3.17 mg/L). The quantity (i.e., load) of PACs entering the Athabasca River from the Mackay, Muskeg and Steepbank rivers was calculated by multiplying

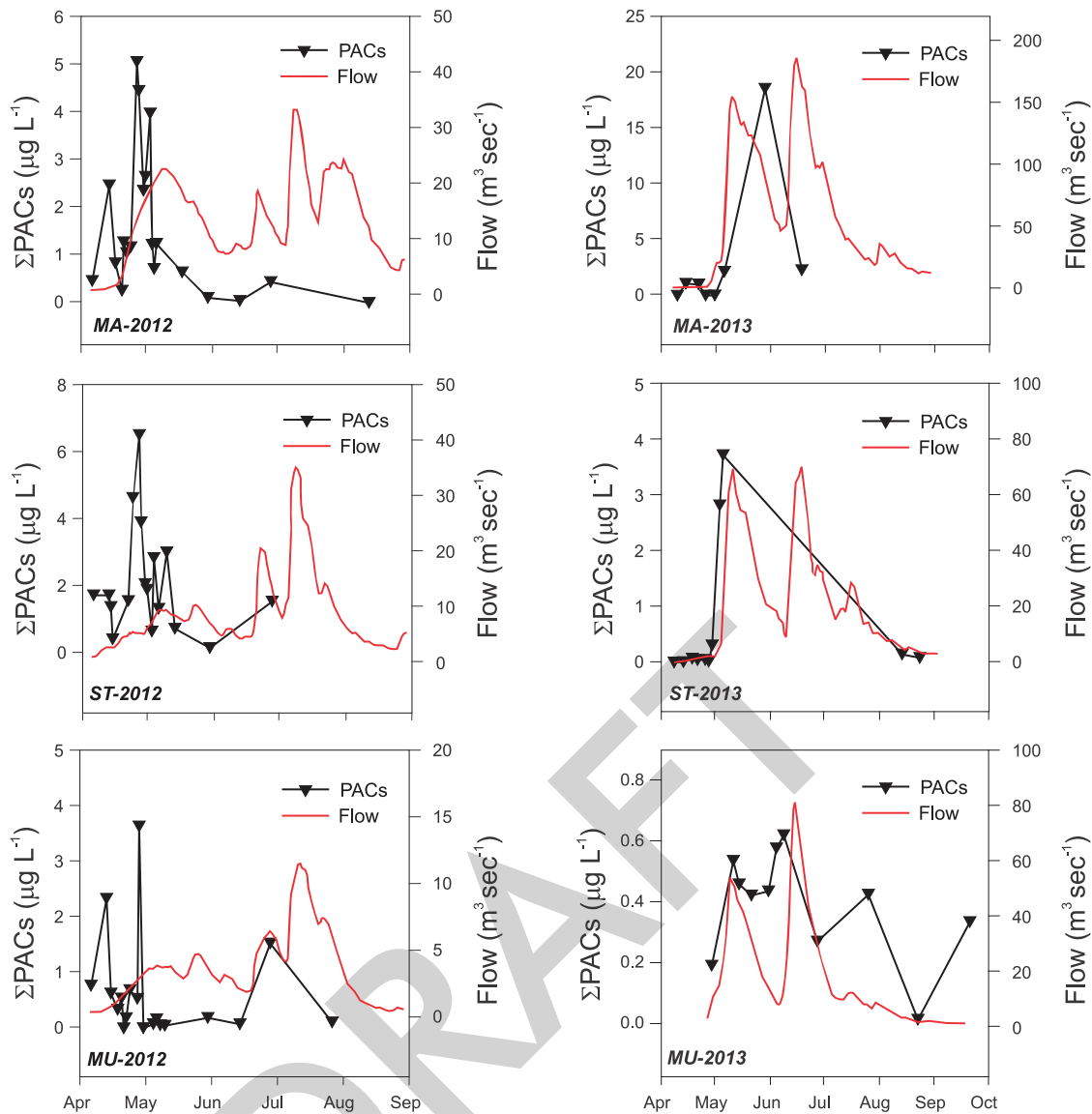


Figure 7. River discharge and concentrations of total polycyclic aromatic compounds (Σ PACs) near the mouths of three Athabasca River tributaries (MA1 on the Mackay, MU1 on the Muskeg, and ST1 on the Steepbank) in 2012 and 2013.

measured concentrations by average daily flow. Loads of Σ PAC were elevated during spring (late-April and early-May in 2012 and 2013) in all rivers (Fig. 8). Additionally, a second pulse of Σ PAC export was observed during early June 2013 in the Muskeg and Steepbank rivers (Fig. 8). These observations are consistent with previous reports indicating that spring snow melt can be an important source of PACs to local aquatic environments (Kelly et al. 2009). However, other factors, such as natural erosion of geologic formations should be considered. Comparison of sites located upstream and downstream of major industrial developments for the Muskeg River showed that downstream loads were significantly higher in 2012 and 2013 (Fig. 9).

The PAC distribution in the Mackay and Steepbank rivers was generally dominated by aPACs. The contribution of DBTs was higher in the first months of sampling, and decreased after the loadings spiked in early spring. However, DBTs were not significant contributors to Muskeg River Σ PAC loadings in either year (i.e., DBTs were not detected in most samples).

Investigations are continuing using a GIS approach to examine drivers of upstream versus downstream differences in PAC concentrations and loads, including the influence of geologic formations and various types of industrial developments in the area. Additionally, Σ PAC load-

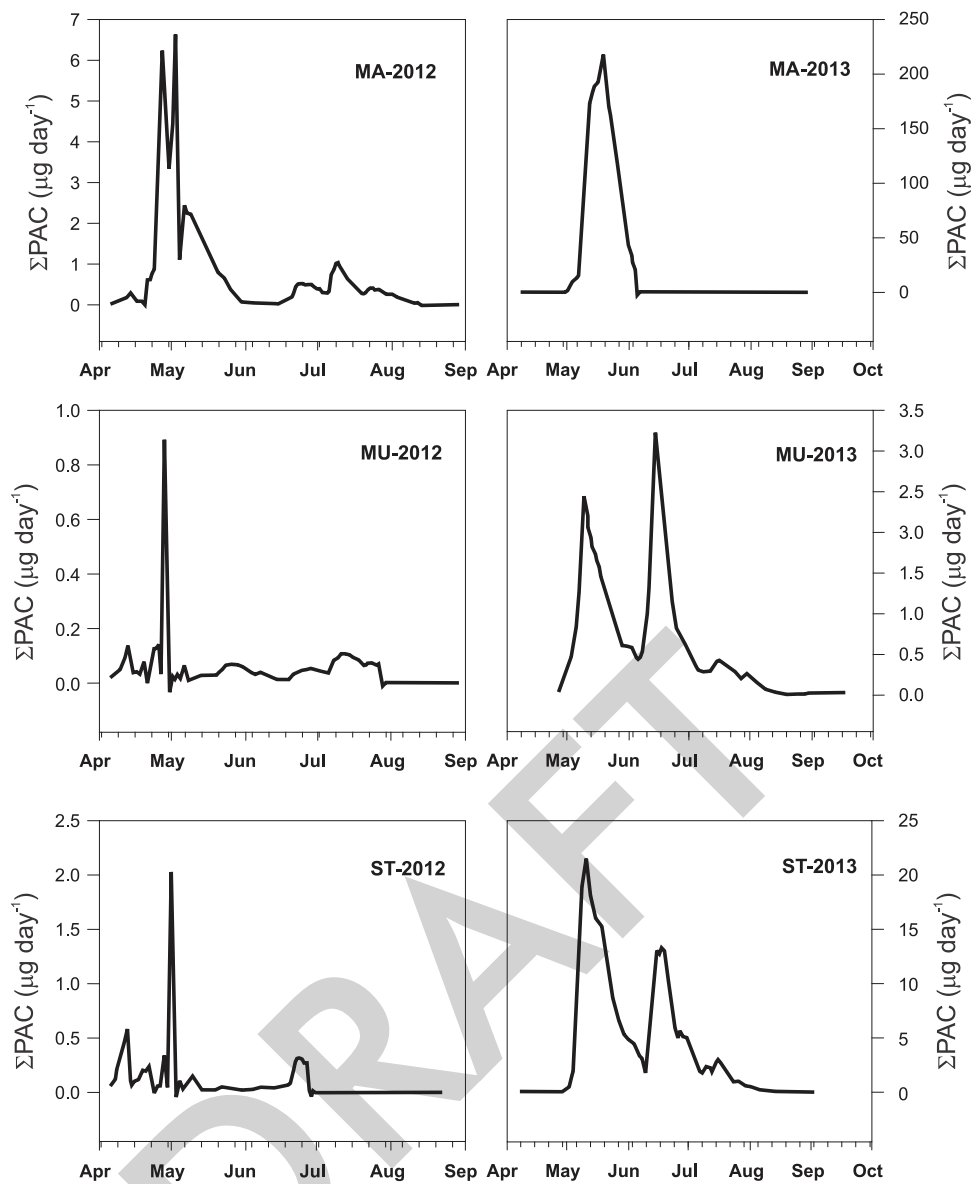


Figure 8. Daily loads of total polycyclic aromatic compounds (Σ PACs) near the mouths of three Athabasca River tributaries (MA1 on the Mackay, MU1 on the Muskeg, and ST1 on the Steepbank) in 2012 and 2013.

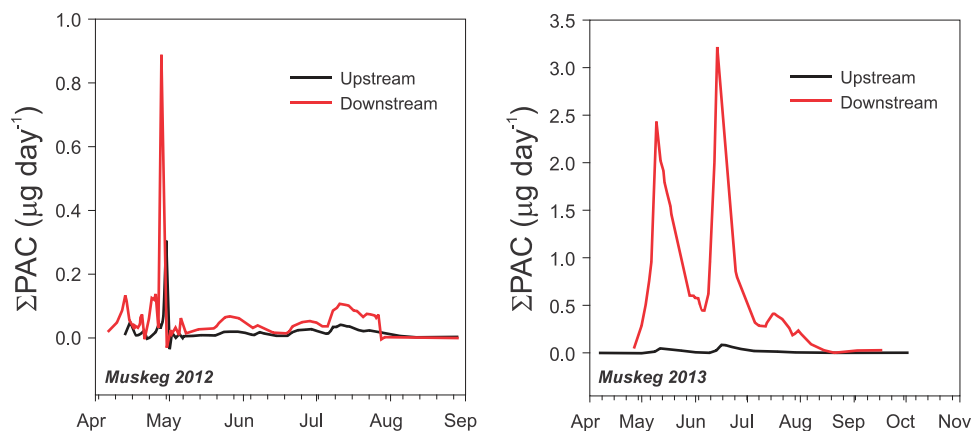


Figure 9. Daily loads of total polycyclic aromatic compounds (Σ PACs) at upstream and downstream sites on the Muskeg River in 2012 and 2013.

ings will be compared to other contaminants to better understand the impact of major industrial developments in the area.

Snowmelt acidification of Athabasca River tributaries

Episodic acidification refers to a decrease in acid neutralizing capacity and pH, often occurring during snowmelt or rain events (e.g., Jeffries et al. 1979, Cooper et al. 1987, Schindler 1988, Davies et al. 1992, Wigington et al. 1996, Kowalik et al. 2007). Brief periods (typically <1 day) of episodic acidification occur naturally as a result of flushing or seepage of organic acids from soil (Wellington and Driscoll 2004) and dilution of acid neutralizing base cations such as Ca^{2+} and Mg^{2+} (Wigington et al. 1996). Acidic rainfall or pre-existing acidic deposition in snow may exacerbate these natural processes and result in low pH episodes of even greater magnitude (decreases of one or more pH units) and extent (days-to-weeks). Because oil sands operations produce acidifying emissions and large tracks of northeastern Alberta are acid-sensitive, the extent (frequency, duration and severity) of episodic acidification during snow melt was examined for five tributaries draining Canada's oil sands region.

Assessment of 83 snowmelt events on five Athabasca river tributaries between 1989 and 2014 showed that 32 of these snow melts (39 %) exhibited acidification ($\text{pH}<7$) episodes (Table 6; Alexander et al. 2017). When present, snowmelt acidification occurred between 7 April and 14 May, lasting on average 31 ± 13 days (mean \pm SE, range <1 to 69 days, all years and sites collectively).

Analysis of 2012-2014 data showed that snowmelt concentrations of 11 priority pollutants and Al were always higher during low pH episodes (<6.5) compared to non-episodes ($\text{pH}>7.5$) (Fig. 10). Moreover, dividing the pH episodes into baseflow versus flood conditions showed that concentrations were always greatest under low pH (<6.5) flood conditions compared to both low pH baseflow conditions and non-episodes ($\text{pH}>7.5$). This finding is consistent with reports from elsewhere (e.g., Dickson 1978, Lawrence 2002) that acidification episodes are often associated with high stream flows and can cause mobilization and transport of contaminants such as metals from the land base to adjacent water courses.

Table 6. Snowmelt acidification of five watersheds in Canada's oil sands region over a 25-year (1989-2014) period.

River	Total No. ¹ snowmelt events	No. (%) snowmelts with $\text{pH}<7$	Min pH during episodes (ΔpH) ²	Duration of $\text{pH}<7$ episodes (mean)	Relative Severity Index (mean \pm 1SE)
Firebag	22	5 (23%)	5.9 (1.75)	12-d	0.29 \pm 0.07
High Hills	3	2 (67%)	5.5 (0.96)	12-w	0.47 \pm 0.11
Mackay	6	2 (33%)	5.3 (2.56)	6-w	0.43 \pm 0.11
Muskeg	40	14 (35%)	5.8 (1.42)	25-d	0.46 \pm 0.12
Steepbank	12	9 (75%)	5.0 (2.73)	17-d	0.40 \pm 0.19
Total	83	32 (39%)		31-d	

¹ Not all sites were sampled every year for each river.

² Calculated using the method outlined in Fölster et al. (2007); Erlandsson et al. (2010).

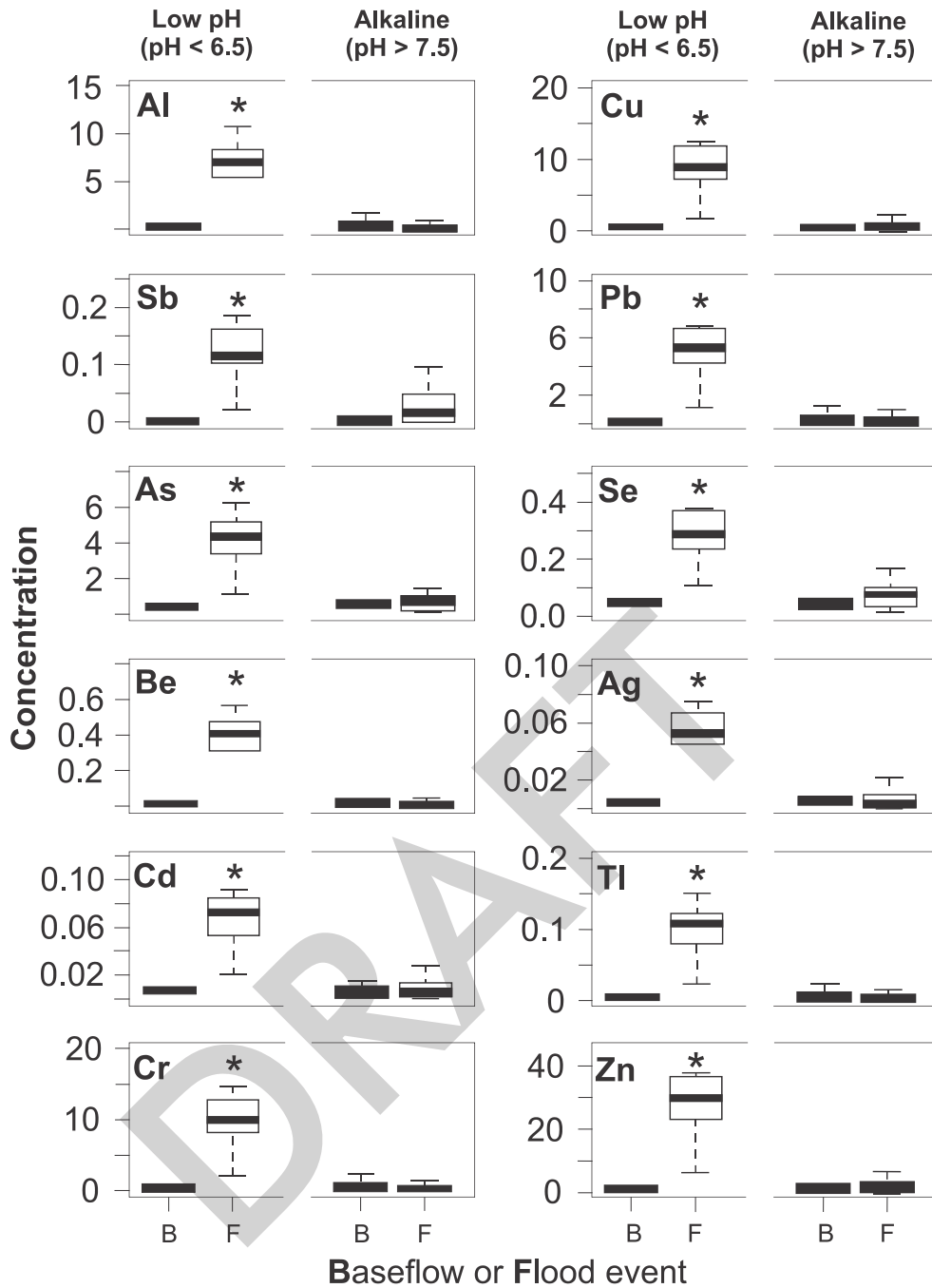


Figure 10. Comparison of the median concentration (\pm interquartile range) of total aluminium and 11 priority pollutants ($\mu\text{g/L}$) in five tributaries of the Athabasca River during snow melt (2 March to 14 June for 2012-2014). The data are split into hydrologic periods of base flow (B) or flood (F) (grey and white boxes, respectively) during low pH ($\text{pH} < 6.5$) versus alkaline pH ($\text{pH} > 7.5$) episodes.

Theme Assessment

Impacts of industrial development

Given the limited time period of JOSM data (three years), assessing impacts of development on contaminant export is challenging. However, analysis will continue and involve a GIS approach to identify whether increases in contaminant concentrations, loads and export between upstream reference sites and sites downstream of development are related to industrial development, natural bitumen deposits and the extent of various wetland types. Analysis of historical water chemistry data (1972-2010) from Athabasca River tributaries did, however, show that concentrations and loads of total V, diss Se and diss As were greater downstream of development compared to measurements from reference sites. Moreover, a case study conducted on the Muskeg River (1972-2009 data) showed that concentrations and loads of the same three elements were greatest during the early land-clearing stage of mine development, with dissolved selenium remaining elevated during the subsequent expansion stage of development.

Identification of reference condition

Analysis of historical water chemistry data (1972-2010) from Athabasca River tributaries showed that it is possible to identify reference chemical conditions (i.e., water chemistry associated with pre-development conditions). Providing chemical concentrations measured prior to development were analyzed using comparable methods and concentrations show little spatial (i.e., upstream versus downstream) or inter-annual variation, measurements from all upstream sites and downstream sites sampled prior to development can be pooled to calculate regional reference concentrations. As part of the JOSM tributaries monitoring program, regional reference concentrations were calculated for three variables: 0.54 ± 0.02 (0.05) $\mu\text{g/L}$ diss As, 0.16 ± 0.01 (0.01) $\mu\text{g/L}$ diss Se, and 0.83 ± 0.05 (0.09) $\mu\text{g/L}$ total V (mean \pm SE (95th percentile)). In future, regional reference concentrations for Athabasca River tributaries will be determined for other parameters as stated within Appendix B of the Lower Athabasca Water Quality Monitoring Program – Phase 1 (Government of Canada and Alberta, 2011).

Integration with other themes

As well as providing water quality measurements to identify changes associated with mine development, data collected as part of the Athabasca River tributaries monitoring program establishes the environmental conditions for aquatic biological communities. For example, snow collected from the frozen surface of the Athabasca main stem and Athabasca tributaries was shown not to affect larval fish survival or development (McMaster et al. 2018), establishing that water chemistry during these snowmelt periods was not toxic. Similarly, assessment of benthic macroinvertebrate composition from tributary sites showed that in the absence of development, the invertebrate communities did not change between sites situated upstream of the McMurray formation versus sites exposed to the McMurray formation (Culp et al. 2018). This finding is consistent with tributary water quality results showing that diss As, diss Se and total V concentrations did not increase with passage along the McMurray formation.

Water quality observations obtained as part of the Athabasca River tributaries monitoring program also serve as input to water quality models. Under the JOSM, water quality models are being run for the Athabasca River main stem to track the transport and fate of contaminants (Droppo et al. 2018); the tributaries program contributes information on contaminant loads exported from major tributaries. In future, modelling of contaminant sources, transport and fate in Athabasca River tributaries will be conducted; the JOSM tributary data underpins this modelling activity.

The tributaries water quality data also complement the JOSM work on atmospheric deposition of metals to the snow pack. This study showed that the loads of mercury and other metals were greatest near major mining developments, and decreased with distance from development (Kirk et al. 2014; Kirk et al. 2018). Data analysis is underway to relate the loads of metals in the snow to the loads discharged from the tributaries during snow melt.

Future research needs in support of monitoring

Results of studies conducted as part of the JOSM tributary water quality theme have pointed

to new research efforts that would assist with answering key JOSM questions. Proposed new research efforts include:

- Addition of filtered total and methyl mercury to evaluate mercury uptake by biota.
- Analysis of a larger suite of PACs, particularly ones more indicative of local sources, for better source identification (for example, heterocyclic PACs associated with petroleum coke and other sources in the region (Manzano et al. 2017)).
- Measurements of emissions to the atmosphere (from stacks, blowing dust, etc.) to establish quantities of contaminants deposited on the snow pack and into surface waters.
- Analysis of historical and current data to establish regional reference concentrations for all water chemistry parameters (in addition to the regional reference values already calculated for diss As, diss Se, and total V).
- Comparison of contaminant loads in the snow pack versus in streamwater during freshet to determine the extent to which contaminants in the snow pack are transported to proximate streams.
- Further analysis of the data collected under the JOSM to establish regional fluxes of contaminants in tributaries to the Athabasca River in relation to mine development.
- Geospatial analysis of the JOSM data to better relate upstream versus downstream differences in concentrations and loads to industrial development, land disturbance, atmospheric deposition, type and extent of wetlands, and geologic formations.

Monitoring recommendations

The goal of the new monitoring program started under the JOSM was to provide an integrated regional monitoring program that delivers (1) information needed for strategic decisions, (2) core results on the accumulative environmental state and the relationships between system drivers and environmental response, and (3) a decision framework that sets out triggers or decision thresholds that identify when specific

stations or monitoring intensity should be scaled back or ramped up. To achieve this goal, major recommendations from the Athabasca River tributaries monitoring program are as follows:

1. To continue monitoring water quality and discharge at the same sites, both upstream and downstream, on major tributaries. Tributary results highlighted differences in concentrations, loads and export between upstream and downstream sites. Analysis of historical data (particularly from the Muskeg River) also documented the need for sufficient sampling upstream versus downstream of development (and, where possible, pre- versus post-development) to support statistically rigorous analysis of the effects of development on water quality.

2. To continue frequent water sampling during snow melt. Results from the Athabasca River tributaries monitoring program also identified snow melt as an important period (and likely the most important period of the year) for transport and delivery of potential contaminants (metals, metalloids, selenium, PACs) through tributaries to the Athabasca main stem.

3. To ensure comparable data among analytical labs. Under the Athabasca River tributaries monitoring program, concentrations of metals, metalloids and selenium measured as part of the EC, AESRD and Hatfield Consultants programs could not be combined as the laboratories used extraction techniques that were not comparable.

Although the ideal monitoring program would maintain flow-weighted sampling (i.e., sampling more frequently during high discharge associated with snowmelt and rain events) at upstream and downstream sites on the five major tributaries to the Athabasca River, it is recognized that such high intensity sampling (and associated laboratory intensity) may not be sustainable.

These options could be considered:

- Sampling three tributaries (each with upstream and downstream sites) at high frequency every year, and including the remaining two tributaries in the sampling campaign every 3-5 years.

- Reducing the frequency of sampling. Sample frequency should be maintained at 3x per week during snow melt but could quickly transition thereafter to weekly sampling and, in turn, monthly sampling. With further data analysis, it may be possible to identify an automated measurement (e.g., conductivity, total dissolved solids) associated with snowmelt water quality and use this measurement to determine when snowmelt sample frequency should be curtailed.

Other recommendations that would benefit the Athabasca River tributaries monitoring program are these:

- Addition of filtered total and methyl mercury sampling. Filtered mercury sampling is logistically demanding because it requires filtering of samples the same day of collection. This information is needed, however, as methyl mercury speciation is an important driver of methyl mercury uptake by biota.
- Inclusion of a larger suite of PACs. By analyzing samples for a greater number of PACs, especially ones more indicative of local sources, there is a greater likelihood of identifying sources of contamination.

Ultimately, successful continued implementation of the new monitoring program started under the JOSM will provide an integrated regional monitoring program that delivers (1) information needed for strategic decisions, (2) core results on the accumulative environmental state and the relationships between system drivers and abiotic environmental response, and (3) a decision framework that sets out triggers or decision thresholds that identify when specific station numbers or monitoring intensity should be scaled back or ramped up.

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