Ten thousand years of bitumen transport in the lower Athabasca River, Canada

by

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ABSTRACT

The lower Athabasca River valley in northeastern Alberta, famous for oil sands mining, was also the site of one of North America largest Ice Age floods. During deglaciation, a large proglacial lake, Lake Agassiz, drained catastrophically through the Athabasca River valley. This catastrophic flood eroded deeply into the bitumen-bearing Clearwater and McMurray Formations, transporting and then depositing bitumen in what is now the Peace-Athabasca Delta. Modern erosion of these flood deposits represents an important source of polycyclic aromatic hydrocarbons (PAHs) to the Athabasca River. This erosion occurs primarily at the Big Bend site, a large, 18 m high and 4,200 m wide cut bank, actively eroded by the Athabasca River.

In this thesis, I estimated the contribution of the Big Bend exposure to the sediment and PAH budgets of the lower Athabasca River. The Big Bend is estimated to supply ~410 kt of sediment annually to the lower Athabasca River, which represents ~35 % of the sediment budget between Fort McMurray and the Peace-Athabasca Delta. The erosion of secondary bitumen deposits within the Big Bend exposure is estimated to contribute ~5.3 tons of PAHs to the river each year. PAHs from the Big Bend site are characterized by a unique compositional profile that can be distinguished from other PAH sources. Specifically, the secondary bitumen emplaced within the Big Bend section contains a higher alkylated PA4/PA3 ratio than other PAH sources in the lower Athabasca River region. These other sources of PAHs include primary bitumen from the McMurray Formation, as well as wildfire ash and petroleum coke, which is a by-product of bitumen upgrading. To understand the relative contribution of the various sources of PAHs to the Athabasca River, I compared these results with results from an ambient water quality monitoring program. Water samples were more similar to raw bitumen and Big Bend during months of high-flow, but matched better with forest fire ash and fluid petroleum coke during low-flow periods.

These results suggest the natural bank erosion of the Athabasca River during periods of high discharge plays an important role in supplying PAHs to the lower Athabasca River and the downstream Peace-Athabasca Delta. This study has revealed that the erosion of reworked bitumen at Big Bend is a major source of PAH input to the lower Athabasca River region. This (natural) source of PAHs occurs in addition to inputs resulting from the extraction and processing of bitumen. These industrial inputs have led to increasing burdens of PAHs – and especially alkylated PAHs – across the region. Understanding the fate, biological uptake, and indeed prevalence of the various PAH sources within ecosystems and biota therefore requires additional research.

PREFACE

This thesis contains three chapters. Chapter two is prepared as collaborative works with Drs. Duane G. Froese and Colin A. Cooke. I was responsible for planning and executing the fieldwork, sample collection, laboratory analyses, data processing, and writing the thesis chapters and manuscripts. Joseph Young participated field sampling, and the facies analysis of sampled units.

Chapter 2 is a manuscript prepared for submission as: “Ten thousand years of bitumen transport in the lower Athabasca River, Canada” coauthored by me, Colin A. Cooke, and Duane G. Froese. The manuscript was written by me with editorial contributions from Colin A. Cooke, and Duane G. Froese.

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1.1. Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) are one of the most concerning pollutants in our environment. They are known to be mutagenic and carcinogenic to aquatic life (Myers et al., 2003; Hodson, 2017). The United States Environmental Protection Agency (US EPA) has listed 16 of the non-substituted PAHs as priority pollutants due to their toxicity. Several of these 16 PAHs are known to be potentially cancer causing in humans (Canadian Council of Ministers of the Environment, 2010). Benzo(a)pyrene is one of the PAHs known to be carcinogenic to humans, and is regulated by Health Canada drinking water guideline (Health Canada, 2016). Alkylated PAHs are known to be comparable or more toxic than the parent non-substituted PAHs but are not regulated by Health Canada (Achten and Andersson, 2015).

PAHs are classified as semi-volatile organic compounds with two or more fused aromatic hydrocarbon rings bonded in linear, cluster or angular arrangement (Abdel-Shafy and Mansour, 2016). Alkylated PAHs contain one (or more) alkyl group, and they are expressed as the sum of homologue groups (C1-, C2-, C3-, and C4-) with the identical mass (Canadian Council of Ministers of the Environment, 2010). The heterocyclic sulfur PAH dibenzothiophene (DBT) are useful markers of petroleum in the environment (Stogiannidis and Lane, 2015). PAHs with 2–3 rings are classified as lower molecular weight PAHs whereas PAHs with 3–6 rings are classified as higher molecular weight PAHs (Canadian Council of Ministers of the Environment, 2010). The chemical and physical properties of PAHs are highly dependent on the aromatic hydrocarbon ring numbers and their molecular weight (Canadian Council of Ministers of the Environment, 2010).

The vapor pressure and aqueous solubility of PAHs decrease with increasing number of aromatic hydrocarbon rings and their molecular weight (Stogiannidis and Lane, 2015). PAHs are also hydrophobic and lipophilic (Stogiannidis and Lane, 2015), and the hydrophobicity and lipophilicity of PAHs increases with the number of rings and their molecular weight (Stogiannidis and Lane, 2015). Lower molecular weight PAHs are therefore more soluble in aquatic ecosystems (Stogiannidis and Lane, 2015), and they are more dominant in the gaseous phase in the atmosphere (Galarneau, 2008). In contrast, higher molecular weight PAHs tend to bind to particulates in the water column or atmosphere (Stogiannidis and Lane, 2015; Galarneau, 2008; Kurek et al., 2013).

1.2. Controversy of PAHs in Northeastern Alberta

In Northeastern Alberta, the oil sands (a mixture of bitumen, sand, and water, also known as tar sands) are found predominately in the Cretaceous McMurray and Clearwater Formations. These formations often occur within 75 m of the surface, and as outcrop along the Athabasca River valley and in the valleys of its tributaries. This surficial exposure allows for surface (open-pit) mining activities. A rapid increase in oil sands mining (and processing) activities over the past ~20 years has led to large-scale land use and land cover changes, and elevated concerns over the release of contaminants to aquatic ecosystems, including the Athabasca River (reviewed by Schindler, 2010; Schindler, 2013; Schindler, 2014). Studies initiated in the early 2000s documented an increased concentration of contaminants, including PAHs, in snowpack and river water samples collected near industrial operations relative to samples collected further away from industrial operations (Timoney and Lee, 2009; Kelly et al., 2009). These, and subsequent studies (Hall et al., 2012; Evans et al., 2016; Jautzy et al., 2015; Hebert et al., 2011), have raised concern around the impact of contaminants on the lower Athabasca River, and the downstream Peace-Athabasca Delta.

PAHs are commonly grouped into three major categories: pyrogenic compounds, petrogenic compounds, and biogenic compounds (Wang et al., 1999). Pyrogenic PAHs are generated through the combustion of organic matter or fossil fuels under high temperature without the presence of oxygen (Stogiannidis and Lane, 2015). Petrogenic PAHs are from heavy oil sand bitumen or lighter fuel oil (Wang et al., 2014). Biogenic PAHs are produced by natural biological processes from plants, algae or microorganism (Stogiannidis and Lane, 2015).

PAHs are a key contaminant of concerns within the region because they are released to the environment as a result of oil sands operations. However, there are both natural and anthropogenic sources of PAHs in the region. The natural erosion of the bitumen-bearing Clearwater and McMurray Formations, which occurs as outcrops along the Athabasca River and its tributaries, may be an important source of PAHs to the Athabasca River, its tributaries, and the Peace-Athabasca Delta (Conly et al., 2002; Droppo et al., 2019; Hall et al., 2012). Sediment that contains naturally-eroded bitumen has been found to be toxic to fish development (Droppo et al, 2019). Other natural processes such as forest fires also deposit PAHs to regional watersheds (Wentworth et al., 2018). Anthropogenic sources of bitumen include bitumen dust emitted to the atmosphere during the physical action of open-pit mining (Jautzy et al., 2013), large stock piles of petroleum coke, a by-product of bitumen upgrading (Zhang et al., 2016), and emissions associated with vehicular and industrial heavy machinery. Quantifying the natural load of PAHs to compare with industrial contributions is, therefore, important to understanding the actual impacts of oil sands development.

1.3. Site Geology and background in Northeastern Alberta

The Laurentide ice sheet retreated from the lower Athabasca region towards the northeast of Alberta between 10,500 and 10,000 radiocarbon (^{14}C) years before present (BP) (Rhine and Smith, 1988). Large proglacial lakes were dammed against the margin of the retreating ice sheet (Teller et al., 1983). At 9,900 ^{14}C years BP, the proglacial Lake Agassiz discharged meltwater catastrophically from a northwestern outlet. This mega-flood of meltwater flowed west through the Clearwater River valley before flowing north through the Athabasca River valley (Smith and Fisher, 1993). This catastrophic drainage – through what is now known as the Clearwater-Athabasca Spillway – eventually flowed into glacial Lake McConnell before continuing onto the Arctic Ocean through the Mackenzie River. The level of glacial Lake Agassiz fell by ~50 meters as a result of this catastrophic drainage (Fisher et al., 2002), and an estimated 21,000 km^3 of flood water entered into Arctic Ocean within 1.5 to 3 years at a flow rate of 1.2 to 7.38 x 10^6 m^3/s (Fisher et al., 2002). This resulted in a global sea level rise of 6 cm (Fisher and Smith, 1994).

The catastrophic release of meltwater from Lake Agassiz eroded into the McMurray Formation. This resulted in bitumen being entrained within the flood waters and transported downstream. As mentioned above, the first (standing) body of water encountered by the floodwaters was the glacial Lake McConnell. Glacial Lake McConnell covered parts of what are now the Great Bear Lake, Great Slave Lake and Lake Athabasca basins making it the precursor to the Peace-Athabasca Delta (Smith, 1994). When the floodwaters encountered glacial Lake McConnell, they formed a braided fan delta (Young, 2018). This fan delta captured not only river sand but also significant amounts of the Cretaceous McMurray Formation material (oil sands) from the distal reaches of the Clearwater Athabasca spillway and reworked into the fan delta as bitumen-rich sands and bituballs.

Today, the fan delta formed as part of the glacial Lake Agassiz mega-flood is exposed along the lowermost reaches of the Athabasca River (Young, 2018). The Athabasca River actively incises into this late Pleistocene braided fan delta at the Big Bend site, a large, 18 m high and 4,200 m wide cut bank. The Big Bend consists of four facies – a lacustrine deposit from glacial Lake McConnell at the base, the prodelta heterolithic facies, the delta slope and plain sand, and surficial well-sorted sand (Rhine and Smith, 1988). Bituminous sands are found, primarily, as scattered bituballs with sand and gravel in the Quaternary sand facies of the braided fan delta.

1.4. PAH sources in Northeastern Alberta

In Northeastern Alberta, PAHs are released to the environment by anthropogenic or natural processes (Wrona et al., 2011). Anthropogenic sources would be contributed from the oil sands industry in the lower Athabasca region such as petroleum coke and tailing ponds. The most common natural source PAHs are derived from forest fires and river bank erosion of secondary bituminous sand.

1.4.1. River bank erosion

The natural erosion of exposed bitumen along banks of the Athabasca River and its tributaries is an important source of PAHs to regional aquatic ecosystems (Hall et al., 2012; Droppo et al., 2018). The largest major sediment production and erosion site of the Athabasca River between Fort McMurray and Embarras is the three large meander bends near Embarras, which includes the Big Bend. Erosion at these three-meander bends is estimated to contribute up to 0.35 Mt of sediment annually to the Athabasca River, representing ~65 % of annual sediment load of the lower Athabasca River, which is ~0.55 Mt (Conley et al., 2002).

Other major bank erosion sites occur within tributaries to the Athabsca River. These tributaries, such as Steepbank River and Ells River, cut into the McMurray formation (Headley et al., 2001, Droppo et al., 2018). Total sediment input from all tributaries of the lower Athabasca River was estimated to be ~0.62 Mt/year (Conley et al., 2002). Thus, these tributaries could be important sources of PAHs to the lower Athabasca River (Akre et al., 2004).

1.4.2. Forest fires

Forest fires are another major natural source of PAHs to the atmosphere (emitted in smoke) and to watersheds (left behind as ash) in northeastern Alberta (Gabos et al., 2001; Schuster et al., 2015; Wentworth et al., 2018). Over 2,000,000 hectares of Northern Alberta's coniferous forest (Gabos et al., 2001) burned in more than 15,000 wildfires between 2006 and 2016 (Alberta Wildfire, 2017). At the total burned forest fire site, alkylated PAHs are dominated over the parent PAHs in the sediment (Gabos et al., 2001). In contrast, parent PAH concentrations increased in the air and the surrounding of forest fire region while the total alkylated PAH or DBT were not elevated (Schuster et al., 2015). Higher concentrations of retene were also observed in both air and sediment at the burned site and surrounding indicating input of forest fire (Gabos et al., 2001; Schuster et al., 2015).

1.4.3. Petroleum coke

Petroleum coke is a by-product of upgrading bitumen from oil sands into synthetic crude oil (Shawwa et al., 2001). The by-product petroleum coke is considered as an inexpensive source of carbonaceous absorbent material, and is sold commercially as activated carbon (Shawwa et al., 2001). Delayed and fluid coking are the two major coking processes in the oil sands region (Zhang et al., 2016). The coke of greatest environmental concern is delayed petroleum coke, which is produced through upgrading of bitumen by low temperature coking and catalytic hydrocracking (Manzano et al., 2016). Delayed petroleum coke contains high concentrations of PAHs (up to 26,800 ng/g) while fluid petroleum coke has much lower concentrations of PAHs (up to 170 ng/g) (Zhang et al., 2016). Petroleum coke is stored in large stockpiles on mine sites, and these stockpiles are susceptible to transport by wind (Zhang et al., 2016). These petroleum coke particulates tend to be deposited within ~50 km from the source, but they can travel over 150 km by atmospheric transport (Manzano et al., 2016).

1.4.4. Tailings Ponds

Tailings ponds are storage impoundments containing oil sands process affected water (OSPW) used in the extraction of oil from sand and clay (Small et al., 2015). Every ton of oil sand mined results in up to 0.2 m^3 of OSPW (Small et al., 2015). As of 2015, oil sands tailings ponds covered over 60,000 acres with a total volume of 1,075 million m^3 (Alberta Environment and Parks, 2018). The OSPW contains total PAH concentrations of up to 15.1 μg/kg while tailings ponds sediment contains up to 270,000 μg/g of PAHs (Wang et al., 2014). The potential PAH pathways entering the environment from tailings ponds are from either evaporation of OSPW to air (Galarneau et al., 2014) or groundwater seepage (Ferguson et al., 2009; Holden et al., 2011). The emission rate from tailings ponds is influenced by environmental factors such as air temperature, wind, ice cover in winter months, and rain (Small et al., 2015). Groundwater seepage from tailings ponds aquifer is also a major concern (Holden et al., 2011). Several tailings ponds are located on top of buried sand channels, creating a potential hydrological pathway for OSPW to infiltrate and reach to the underlying sand channel (Holden et al., 2011). Groundwater seepage from tailings ponds is estimated at a rate of 0.0864-5.6 million L/day (Parajulee and Wania, 2014). With the high concentration of both organic and inorganic contaminants in OSPW, the impact on groundwater and surrounding systems could be significant. However, tailings ponds leakage is considered insignificant relation to PAHs particle delivery to the Athabasca River (Droppo et al., 2018).

1.5. Transport of PAHs in Northeastern Alberta

1.5.1. Atmospheric transport to hydrological pathways

PAHs are emitted to the atmosphere through both natural and anthropogenic sources. The major anthropogenic atmospheric PAH sources are from the oil sands industry and include petroleum coke, bitumen particulates, and tailings ponds vapor (Zhang et al., 2016). The major natural input of atmospheric PAHs is from forest fires (Gabos et al., 2001). The total concentration of PAHs in the atmosphere is composed of the concentration in the gas phase plus the concentration in the particle phase (Galarneau, 2008). Whereas PAHs with higher vapor pressure and lower hydrophobicity (e.g. Napthalene) tend to be in gas phase, PAHs with lower vapor pressure and higher hydrophobicity (e.g. Dibenzo[a,h]anthracene) tend to be adsorbed to particulates (Abdel-Shafy and Mansour, 2016). The partition of PAHs between the gas phase and particle phase is rapid and highly dependent on temperature (Galarneau, 2008). The uptake of the gas phase PAHs by particles increases with temperature (Galarneau, 2008); however, desorption of PAHs from particles could take hours during subfreezing temperatures (Galarneau, 2008). The oil sands region is in a subarctic climate zone with annual mean temperature at approximately 0.5 degree Celsius

(Climate Data Organization, 2012). Airborne PAHs released from emission sources in the oil sands region would preferentially adsorb to the particle phase in the atmosphere.

During atmospheric transport, PAHs may undergo atmospheric degradation/or reaction by gas phase reactant and/or solar radiation (Galarneau, 2008). The degradation rate is different with each PAH compound (Galarneau, 2008). The removal of PAHs from the atmosphere is either by dry deposition or wet deposition, and is a function of particle size and meteorological conditions (Baek et al., 1991). Dry deposition occurs when atmospheric particulates settle without precipitation (Abdel-Shafy and Mansour, 2016). The annual dry deposition of parent PAHs over water surfaces in the oil sands region is estimated to be from 330 to 560 µg/m^2 (Zhang et al., 2015). In contrast, alkylated PAHs have a higher dry deposition rate ranging from 3,170 to 4,530 µg/m^2 over water surface due to their high air concentration (Zhang et al., 2015). Wet deposition is defined as the scrubbing of atmospheric PAHs in particulates by precipitation, or the dissolution of gas phase PAHs into precipitation (Abdel-Shafy and Mansour, 2016). The annual mean precipitation in northern Alberta ranges from 400 mm to 500 mm (Alberta Water Portal Society, 2017) in the form of rain or snow. PAHs adsorbed to particulates in the atmosphere are easier to remove than PAHs in the vapor phase by precipitation (Abdel-Shafy and Mansour, 2016). Snow fall is a more effective sink for PAHs than precipitation (Baek et al., 1991). Wet deposition of PAHs is therefore much higher than dry deposition during winter months whereas in non-snow months, dry deposition dominates over wet deposition (Zhang, 2015). Wind pattern plays a critical role in the atmospheric transport of PAHs, with higher deposition rates in the north-south direction than east-west in the oil sands region (Cho et al., 2014).

In the lower Athabasca oil sands region, anthropogenic sources of airborne PAHs are deposited as airborne particulates to the snowpack within 50–80 km from the oil sands upgrading facilities during winter (Kelly et al., 2009; Birks et al., 2017). In spring, the melting of snowpack releases atmospherically-deposited particulates into watersheds as surface runoff (Birks et al., 2017). As the subsurface begins to thaw, surface and groundwater flows increase and leading to increased runoff to the Athabasca River and its tributaries (Gibson et al., 2016). However, Birks et al. (2017) have suggested that the direct release of PAHs in particulates accumulated in snow is not the major source of PAHs to the Athabasca River and its tributaries.

1.5.2. Hydrological transport

The hydrological pathways of PAHs in the Athabasca River can be found in three different phases: (1) dissolved PAHs in the water phase, (2) PAHs in suspended sediment, and (3) PAHs in bedload. Dissolved PAHs concentrations in the water phase are usually low in the Athabasca River with the exception of sites that are near oil sands upgrading facilities (Kelly et al., 2009). This is due to the hydrophobic properties of PAHs, which partition to particulate phases in aqueous environments (Stogiannisdis and Lane, 2015). Natural processes of channel and bank erosion are the main contributors of PAH bounded suspended sediment and bedload sediment in Athabasca River and its tributaries (Droppo et al., 2018). River discharge controls bank retreat rates and sediment contributions to the river (Conley et al., 2002). The higher load of PAHs to the river is observed during the spring melt of snow from May to June/July while PAH load in low-flow period from July/August to October could be 10- to 100- fold lower (Droppo et al., 2018). The spring freshet is the key period of contaminant remobilization and transport (Hall et al., 2012). The river discharge velocity also varies temporally and could affect annual bank retreat rate. For example, in 2011, maximum daily river discharge reached to 4,440 m^3/s. In comparison, 2002 was a dryer year and maximum daily river discharge was only 1,180 m^3/s (Regional Aquatics Monitoring

Program, 2011). During high river discharge, oil sands from the McMurray Formation could break off as large chucks from bank collapse (Barton and Wallace, 1979). These larger chunks of oil sands tend to fuse together in river bedload, which are then transported downstream at a rate of a few centimeters a year (Barton and Wallace, 1979). PAH bounded suspended sediments are derived from atmospheric particulates or erosion of the McMurray Formation from the riverbank or riverbed (Droppo et al., 2018). Suspended sediment eroded from the McMurray Formation is usually fine grained with mainly silts and clay, and coated with hydrophobic oil (Droppo et al., 2018). The suspended sediment in the river within the reach of the McMurray formation tends to be larger in grain size than the parent oil sands material from the river bank, which suggests the eroded material first forms aggregates or flocculates in the water (Droppo et al., 2018). The suspended sediment particle size also decreases downstream, which could be due to a combination of processes, including settling of larger particles by flocculation/deflocculation, formation of flocs, or entrapment of suspended material in the riverbed (Droppo et al., 2018). With the low concentration of PAHs in the dissolved water phase and slow movement of PAHs bounded bedload sediment, suspended sediment PAHs are the main hydrological transport pathway in the Athabasca River.

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CHAPTER 2. Ten thousand years of bitumen transport in the lower Athabasca River, Canada

2.1. Introduction

The Alberta oil sands contains an estimated reserve of 170 billion barrels (bbl) making it the third largest oil deposit in the world (U.S. Energy Information Administration, 2018). A rapid increase in oil sands extraction activities over the past ~20 years have raised concerns around the potential impacts to regional aquatic ecosystems and the downstream Peace-Athabasca Delta (PAD; Gosselin et al., 2010; Hall et al., 2012; Kelly et al., 2009). These concerns led to the establishment of the Canada-Alberta Joint Oil Sands Monitoring (JOSM) Program (Wrona et al., 2011). The JOSM Program provided 50 million dollars per year to fund monitoring, evaluating and reporting activities in the region to understand the cumulative environmental impact of oil sands mining and processing. In 2017, both the federal and provincial governments renewed their commitment to the program, which was renamed the Oil Sands Monitoring (OSM) Program (Dubé et al., 2018).

Within the Athabasca oil sands region, bitumen extraction occurs primarily through open-pit mining. The mining and processing of bitumen are, therefore, important anthropogenic sources of contaminants, including carcinogenic polycyclic aromatic hydrocarbons (PAHs), to the regional aquatic environments (Kelly et al., 2009; Birks et al., 2017). Bitumen is naturally high in PAHs and the mining of bitumen releases oil sands particulates to the atmosphere, which are then deposited in regional watersheds (Manzano et al., 2016). The upgrading of bitumen generates petroleum coke as a by-product, which is stored in large stockpiles near the upgraders. Petroleum coke particulates can also enter the atmosphere, and the subsequent deposition of petroleum coke is an important source of PAHs to regional watersheds (Zhang et al., 2016). Bitumen and petroleum coke deposited on the landscape is then available to be either sequestered (permanently or temporarily) in terrestrial landscapes or transported to downstream environments. Eventually this material may reach the Peace-Athabasca Delta, a Ramsar Wetland of International Importance located ~200 km downstream from the bitumen mining operations near Fort McMurray.

There are also important natural sources of PAHs within the region, including forest fires (Wentworth et al., 2018) and the natural erosion of the bitumen-bearing McMurray Formation by the Athabasca River and its tributaries (Hall et al., 2012). Forest fires emit PAHs to the atmosphere as combustion products (Wentworth et al., 2018) but they may also leave behind ash material that can be washed into watersheds following periods of rainfall (Emmerton et al., 2020). However, natural inputs of bitumen – primarily through the erosion of McMurray Formation – may be one of the most important sources of bitumen to the Athabasca River (Conley et al., 2002; Hall et al., 2012). Natural erosion of bitumen may occur where the McMurray Formation outcrops to regional rivers and streams. These outcrops occur where the McMurray Formation is just a few meters below (or at) the surface, primarily along the lower reaches of the Steepbank, Muskeg, Ells, and MacKay rivers, and along the main-stem of the Athabasca River below the City of Fort McMurray.

In addition to the McMurray Formation itself, bitumen is present within the Quaternary deposits, in secondary (depositional) environments. These outcrops are exposed along the lower reaches of the Athabasca River (hereafter referred to simply as the lower Athabasca River). The largest outcrop of these Quaternary deposits occurs immediately upstream of the Peace-Athabasca Delta within a series of three large meander bends (Conley et al., 2001). These Quaternary sediments are interpreted as part of the post-flood transgression of glacial Lake McConnell, which has been dated between ~10.2 and 9.6 radiocarbon kiloyears before present

(^{14}C ka BP; Young, 2018). This period of deposition follows the catastrophic drainage of Lake Agassiz, a large proglacial lake that formed as the Laurentide Ice Sheet retreated. Meltwater from the Laurentide Ice Sheet flowed west through the Clearwater River valley and then north along the lower Athabasca River. The catastrophic flood also eroded into the McMurray Formation in the Fort McMurray region, exposing bitumen for potential erosion and transport (Smith and Fisher, 1993). During the post flood period, discharge from the northwestern outlet of Lake Agassiz fluctuated but remained stable for another ~400–800 years (Fisher, 2007; Young, 2018). The constant flow of floodwater continued to erode significant amounts of bitumen, and to transport this material downstream, before this material was deposited and reworked into the braided river delta. This bitumen is evident today as discrete horizons of bitumen, bitumen cemented sands, or as "bituballs" entrained within the deltaic sediments of glacial Lake McConnell, which are being actively eroded today by the Athabasca River.

Modern erosion of these cut banks by the Athabasca River is thought to represent an important source of PAHs to the lower Athabasca River and the Peace-Athabasca Delta (Conly et al., 2002). Much of this erosion occurs primarily at "Big Bend", a large, 18 m high cut bank being actively eroded by the Athabasca River (Figure 2.1). This single site, Big Bend, along with two other nearby meander bends, are estimated to supply nearly 65% of the sediment budget of the lower Athabasca River (Conly et al, 2002). Because this sediment contains an abundance of weakly bitumen-cemented sediments, the erosion of these cut banks is a potentially important source of PAHs to the Athabasca River and the PAD.

Here we follow up Conley's 2002 study on Big Bend to estimate annual sediment loading, and, importantly, we quantify natural PAH loading from Big Bend. To accomplish this, we assessed the sedimentology of the Big Bend site to understand how PAHs are distributed across each facies. We then quantified the PAH load supplied to the lower Athabasca River through the erosion of Big Bend.

Big Bend represents just one of many natural and anthropogenic sources of PAHs within the lower Athabasca River region (Kelly et al., 2009; Birks et al., 2017; Manzano et al., 2016; Wentworth et al., 2018; Emmerton et al., 2020; Conly et al., 2002). However, distinguishing between natural and anthropogenic sources as part of regional ambient river quality monitoring has proven difficult (Chambers et al., 2018). In the Fort McMurray region, the surface mining of oil sands releases raw oil sands dust to the atmosphere, which is then deposited across the landscape (Landis et al., 2019). This atmospherically sourced material may then be washed into regional rivers and streams as runoff; however, it is compositionally identical to exposures of the McMurray Formation naturally eroded by the Athabasca River and its tributaries.

A previous study by Akre et al. (2004) demonstrated that Big Bend bituballs could be distinguished from the McMurray Formation bitumen. The Big Bend bituballs exhibited a weathered PAH profile, suggesting compositional changes during or after transport. However, the Arke et al. (2004) dataset was limited to four data points for the Big Bend site. In this study, we further investigate the composition and concentration of PAHs at Big Bend to identify unique fingerprints to allow us to differentiate the secondary bitumen from the McMurray Formation bitumen outcrops upstream of Athabasca River and its tributaries. We then compare these data to new PAH results from other regional sources, including wildfire ash and petroleum coke. Finally, we compare these PAH source data with Athabasca River water quality data collected by the Oil Sands Monitoring Program.

The objectives of this thesis are to: (i) characterize the composition and the concentration of PAHs within Big Bend sediments; (ii) compare Big Bend to other regional PAH sources; (iii) determine the flux of PAHs contributed by Big Bend to the Lower Athabasca River; and (iv) determine if the input of PAHs from Big Bend can be detected from the regional surface water quality monitoring program.

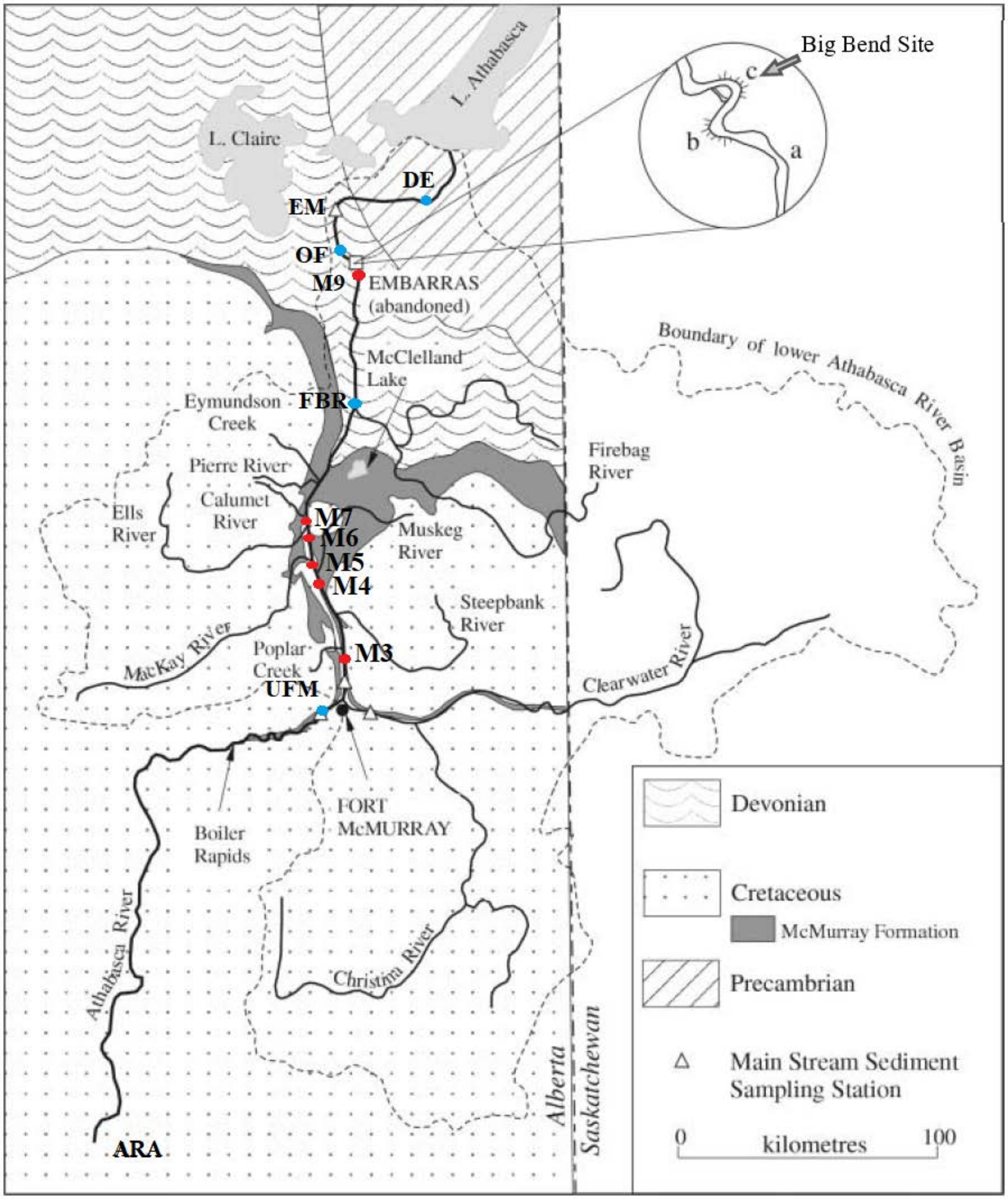

Figure 2.1. The Lower Athabasca map showing the Big Bend site, McMurray Formation and Alberta Environment and Park (AEP) and Environment and Climate Change Canada (ECCC) water sampling station. The Big Bend is an erosional meander bend located near Embarras. The Big Bend is marked as "c" on the top right of the map. The AEP and ECCC water sampling stations are located from upstream to downstream of the Athabasca River. AEP sites – Upstream – Athabasca (ARA), Upper Fort McMurray (UFM), Firebag River (FBR), Old Fort (OF) and Devil's Elbow (DE) – Downstream. ECCC sites – Upstream – M3, M4, M5, M6, M7, and M9 – Downstream. Main stream sediment sampling station – Upper Fort McMurray (UFM), and Embarras (EM) (modified from Conly et al., 2002).

2.2. Methods

2.2.1. Study site

The Athabasca River flows over a distance of nearly 1,400 km covering a drainage area of approximately 160,000 km^2. The river begins as meltwater from the Columbia Icefield in Jasper National Park, Alberta, Canada. The Athabasca River flows east-northeast across the plains, before turning northeast to Fort McMurray. The river then flows north eventually feeding into the Peace-Athabasca Delta and Lake Athabasca. The Athabasca River is a source of water for many communities, businesses, agricultural, industrial, and private users, and supports a significant fishery in the region, including numerous oil sands mining and upgrading operations, which occur within downstream of the confluence with the Clearwater River (here simply referred to as the lower Athabasca River). The lower Athabasca river accounts for a drainage area of approximately 58,000 km^2 (Conly et al., 2002) and includes several tributaries that cut into the McMurray Formation including the Clearwater, Steepbank, MacKay, Ells, Muskeg and Firebag rivers (Figure 2.1).

The lower Athabasca River region has a dry cool summer and a cold winter. In Fort McMurray area, the lowest mean daily temperature is -17.4 ºC in January and the highest mean daily temperature is 17.1 ºC in July (1981-2010; Environment and Climate Change Canada, 2021). The mean annual precipitation is 418.6 mm with May to October usually occurring as rainfall and November to April as snowfall (1981-2010; Environment and Climate Change Canada, 2021). The highest mean precipitation is in July at 80.7 mm as rainfall with the lowest mean precipitation in February at 13.2 mm as snowfall. The precipitation volume is ~6 times higher in summer than in winter.

To quantify the composition and concentration of PAHs from Big Bend to the Athabasca River, we mapped the horizontal and vertical extent of the sedimentological facies along the cut bank. A Lasertech 100XL laser range finder, with a vertical accuracy of ± 0.2 m, was used to measure the thickness of each unit across the entire meander bend at 19 locations (AK01 to AK19) not including the uppermost aeolian sand (Figure 2.2). We sampled sediment at one-meter intervals vertically at four locations (LAR1, LAR2, LAR3, and LAR4) and at 50-cm intervals at LAR5 (Figure 2.2); bituballs within each unit were also sampled. All samples were immediately frozen at –20 ºC upon returning to the laboratory to avoid loss of the volatile PAHs.

To characterize the concentration and composition of PAHs from other sources, we also obtained samples of (i) raw bitumen from a surface mining site in the Fort McMurray region, (ii) wildfire ash collected by Alberta Environment and Parks in early May 2016 (i.e., during the Horse River Wildfire), and (iii) fluid and delayed petroleum coke from bitumen upgrading facilities in Fort McMurray region. The raw bitumen samples collected are considered to be "unweathered" samples of bitumen from the McMurray Formation, whereas the bituballs in Big Bend represent secondary deposits of bitumen that may have altered during erosion, transport, or post-deposition.

2.2.2 Polycyclic aromatic hydrocarbons (PAHs) analyses

Big Bend sediments were classified into four types, following Young (2018): McConnell mud, prodelta sediment, braided river sand, and bituballs. Braided river sands were screened to avoid bituballs mixed within the sample. Raw bitumen from surface mining site and wildfire ash were also submitted for analysis (Table A.3.). In total, 20 unsubstituted PAH compounds and 26 alkylated PAHs were quantified. These included the US EPA priority 16 PAHs, biphenyl, dibenzothiophene, benzo(e)pyrene, retene, and perylene, and their C1–C4 alkylated PAHs forms (Table 2.1). PAHs were analyzed by Method MSU-021A modified from US EPA Method 1625B and US EPA Method 8270C/D (Semi-volatile Organic Compounds by Isotope Dilution GC/MS). Samples were spiked with deuterated surrogate standards and then extracted by Soxhlet extraction with dichloromethane. The extracts were cleaned by silica gel column and gel permeation column chromatography. The final extracts were analyzed by low-resolution mass spectrometry (LR-MS) using an RTX-5 capillary GC column. The final concentrations of target analyte were calculated by isotope dilution quantitation method using the deuterated surrogates. The PAHs method from SGS-AXYS Analytical Services is accredited to ISO/IEC17025 by the Canadian Association for Laboratory Accreditation (CALA). The laboratory detection limit results are listed in supplemental information (Table A.1). Quality control data can be found in appendix B.

Table 2.1. Polycyclic aromatic hydrocarbons analyte list at SGS AXYS Laboratory.

PAH	Short name	Rings	Molecular weight (g/mol)	PAH	Short name	Rings	Molecular weight (g/mol)
Naphthalene	N	2	128	C1-Fluoranthenes/Pyrenes	FLPY1	4	216
C1-Naphthalenes	N1	2	142	C2-Fluoranthenes/Pyrenes	FLPY2	4	230
C2-Naphthalenes	N2	2	156	C3-Fluoranthenes/Pyrenes	FLPY3	4	244
C3-Naphthalenes	N3	2	170	C4-Fluoranthenes/Pyrenes	FLPY4	4	258
C4-Naphthalenes	N4	2	184	Benz[a]anthracene	BaA	4	228
Biphenyl	B	2	154	Chrysene	C	4	228
C1-Biphenyls	B1	2	168	C1-Benzo[a]anthracenes/Chrysenes	BaAC1	4	242
C2-Biphenyls	B2	2	182	C2-Benzo[a]anthracenes/Chrysenes	BaAC2	4	256
Acenaphthylene	AY	3	152	C3-Benzo[a]anthracenes/Chrysenes	BaAC3	4	270
Acenaphthene	AE	3	154	C4-Benzo[a]anthracenes/Chrysenes	BaAC4	4	284
C1-Acenaphthenes	AE1	3	168	Benzo[b]fluoranthene	BbF	5	252
Fluorene	F	3	166	Benzo[j,k]fluoranthenes	BjkF	5	252
C1-Fluorenes	F1	3	180	Benzo[e]pyrene	BeP	5	252
C2-Fluorenes	F2	3	194	Benzo[a]pyrene	BaP	5	252
C3-Fluorenes	F3	3	208	C1-Benzofluoranthenes/Benzopyrenes	BFP1	5	266
Anthracene	A	3	178	C2-Benzofluoranthenes/Benzopyrenes	BFP2	5	280
Phenanthrene	PA	3	178	Dibenz[a,h]anthracene	DA	5	278
C1-Phenanthrenes/Anthracenes	PA1	3	192	Perylene	PER	5	252
C2-Phenanthrenes/Anthracenes	PA2	3	206	Benzo[ghi]perylene	BghiP	6	276
C3-Phenanthrenes/Anthracenes	PA3	3	220	Indeno[1,2,3-cd]pyrene	IP	6	276
C4-Phenanthrenes/Anthracenes	PA4	3	234	Dibenzothiophene	DBT	3	184
Retene	RET	3	234	C1-Dibenzothiophenes	DBT1	3	198
Fluoranthene	FL	4	202	C2-Dibenzothiophenes	DBT2	3	212
Pyrene	PY	4	202	C3-Dibenzothiophenes	DBT3	3	226
				C4-Dibenzothiophenes	DBT4	3	240

2.2.3. Other PAHs Data source

Data on the concentration and composition of PAHs within the Athabasca River were obtained from the Surface Water Quality Monitoring component (Cooke et al., 2018) of the Oil Sands Monitoring Program (Wrona et al., 2011). Surface water sampling stations were located from multiple locations along the Athabasca River, including: at the town of Athabasca, at Fort McMurray, upstream of the Firebag River, at Old Fort and at Devil's Elbow (Figure 2.1 and Table A.2). These monitoring stations span a distance of ~514 km, and the station at the town of Athabasca occurs upstream of McMurray Formation outcrops to the river (Wrona et al., 2011, Cooke et al., 2018). The Big Bend site is located 13 km upstream of Alberta Environment and Parks water monitoring station at Old Fort (58°15'9.76"N, 111°24'52.74"W).

Big Bend represents one of many potential sources of PAHs to the Athabasca River. Other sources include natural erosion of the McMurray Formation by the Athabasca River and its tributaries, atmospheric deposition of bitumen dust generated during surface mining of the McMurray Formation, atmospheric deposition of fluid petroleum coke (Zhang et al., 2016) and delayed petroleum coke (a by-product of bitumen upgrading) (Zhang et al., 2016), and the wash-in or atmospheric deposition of wildfire ash (e.g., the large 2016 Fort McMurray Wildfire). To understand the relative importance of each of these sources on regional water quality, we obtained samples of McMurray Formation bitumen, delayed petroleum coke, fluid petroleum coke, and forest and urban ash were submitted to the same lab, SGS AXYS, for PAH analysis (Table A.3).

2.2.4. Carbon stable isotope ($\delta^{13}C$) and carbon content (% C) analyses

All sediments from the Big Bend site were submitted to the University of Alberta Biogeochemical Analytical Service Laboratory for $\delta^{13}C$ and % C analyses. Samples were analyzed for $\delta^{13}C$ ratios and % C using a Vario Pyrocube elemental analyzer coupled to an IsoPrime VisIon continuous-flow isotope ratio mass spectrometer (CF-IRMS). $\delta^{13}C$ ratios (‰) were determined using the following equation:

$$\delta R \text{ ‰} = ((R_{sample}/R_{standard})-1) \times 1000$$

where R_{sample} was the ratio of $^{13}C/^{12}C$ in the sample, and $R_{standard}$ for ^{13}C is referenced to that in air. The laboratory also used NIST 8415 whole egg powder SRM as an in-house $\delta^{13}C$ (-23.99 ‰) and % C (59.2 %) QA/QC check every 20 samples throughout analyses. The precision for the in-house standard is $\delta^{13}C \pm 0.01$ ‰ and % C ± 0.2 %.

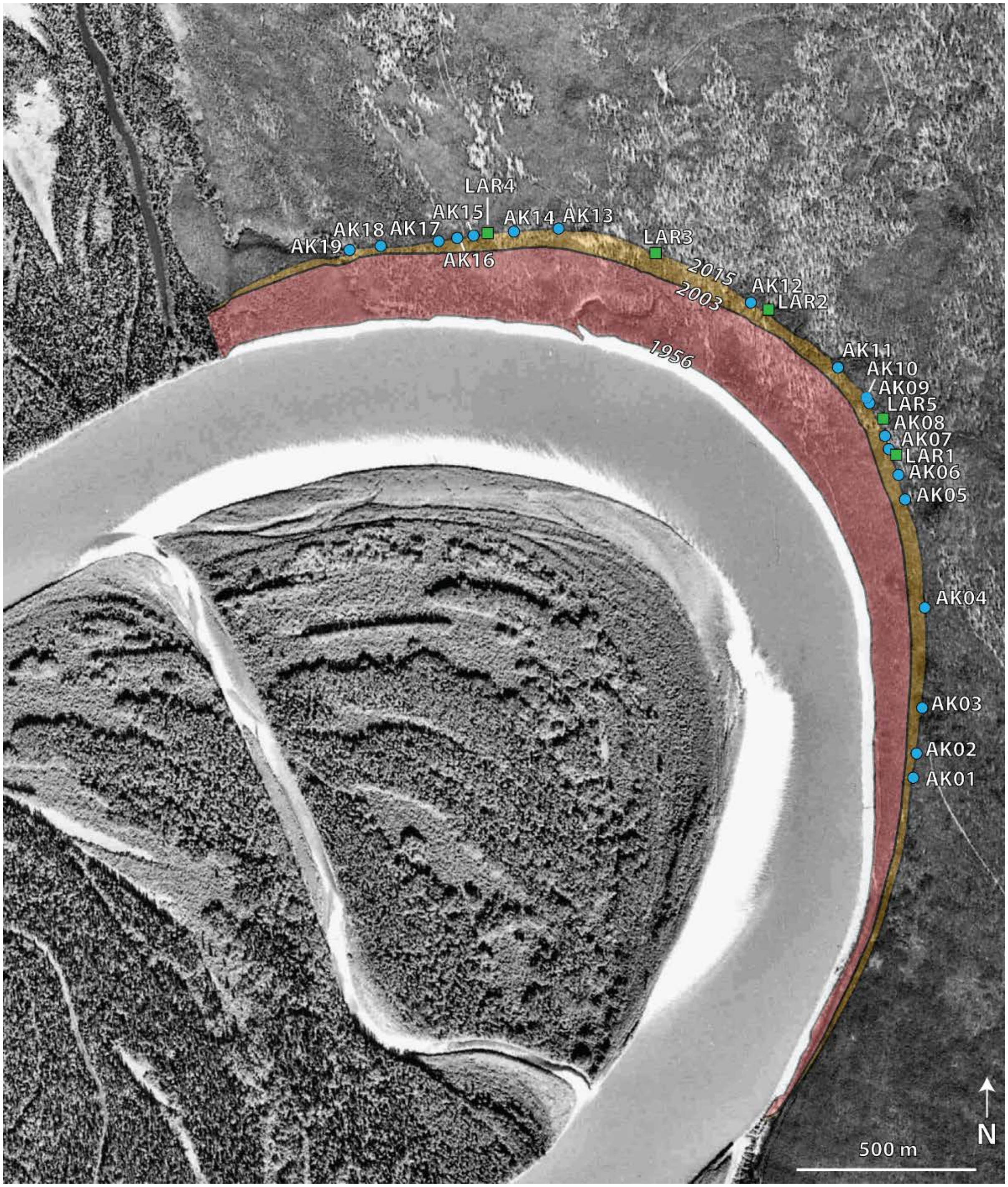

Figure 2.2. Big Bend retreat map (1956-2015) and sampling sites. The area of retreat (Red and yellow) is estimated to be ~625000 m^2 from 1956-2015. The yellow shows the retreat area from 2003-2015 estimated to be ~140000 m^2. Samples were collected for analysis from north to south of Big Bend - North - LAR4, LAR3, LAR2, LAR5, LAR1- South. Stratigraphic logs were measured at nineteen sites from south to north AK01 to AK19.

2.3. Results

2.3.1. The Big Bend site

The Big Bend site is a braided delta consisting of three main lithofacies from bottom to top: (i) lacustrine mud deposits from glacial Lake McConnell (Figure 2.3a); (ii) prodelta heterolithic facies with silty clay and sand rythmites (Figure 2.3b); and (iii) braided river sands (Figure 2.3c) (Rhine and Smith, 1988; Young, 2018). Importantly, deposits of reworked bitumen, sourced from the Cretaceous McMurray Formation, occur as distinct horizons within the braided river sand facies. These bitumen deposits are largely found as cross sets of imbricated bituballs within the sandy facies (Figure 2.3d). Bitumen material is also found as a weak cement in the glacial Lake McConnell and prodelta heterotlithic facies. These facies are capped by aeolian sands deposited during the mid-Holocene (Rhine and Smith, 1988).

The Big Bend site has a length of ~4,200 m with an average height of 17.7 m from the river surface level measured in October 2017 (Figure A.1). The upstream end has a height of ~18 m whereas the downstream end of the Big Bend has an elevation of ~14 m. The highest elevation is at the center of the Big Bend site where the bank height is ~21 m. The McConnell mud, which vary between 1.5 to 5.0 m in thickness, begin at ~1,800 m from the upstream end of Big Bend and continue to the distal end. The prodelta sediment facies varies in thickness from 3 to 11 m across the site. There is a missing section for both McConnell mud and prodelta sediment from ~2,000 m to 3,400 m from the upstream end (Figure A.1). The missing section of McConnell mud and prodelta sediment was incised by the paleo Athabasca river and consists entirely of sandy facies. The braided river sand facies range from 9 to 15 m in thickness across the section. Bituball deposits occur as distinct layers of imbricate clasts at various elevations primarily within the braided river sands. The total thickness of the bituballs horizons is estimated to be ~3 m vertically of the vertical sections based on repeat measurements. The McConnell mud extends ~5 m above river level (a.r.l) to below the river surface level across the Big Bend as measured by ground penetration radar (Jol and Smith, 1991). Thus, the average height for Big Bend is ~22.7 m with the average thickness of McConnell mud, prodelta sediment, and braided river sands to be ~6 m, 3 m, and 14 m, correspondingly. Thus, we estimate the McConnell mud, prodelta sediment, braided river sands and bituballs accounts for ~27 %, 13 %, 47 % and 13 % of total surface area of the Big Bend exposure, respectively.

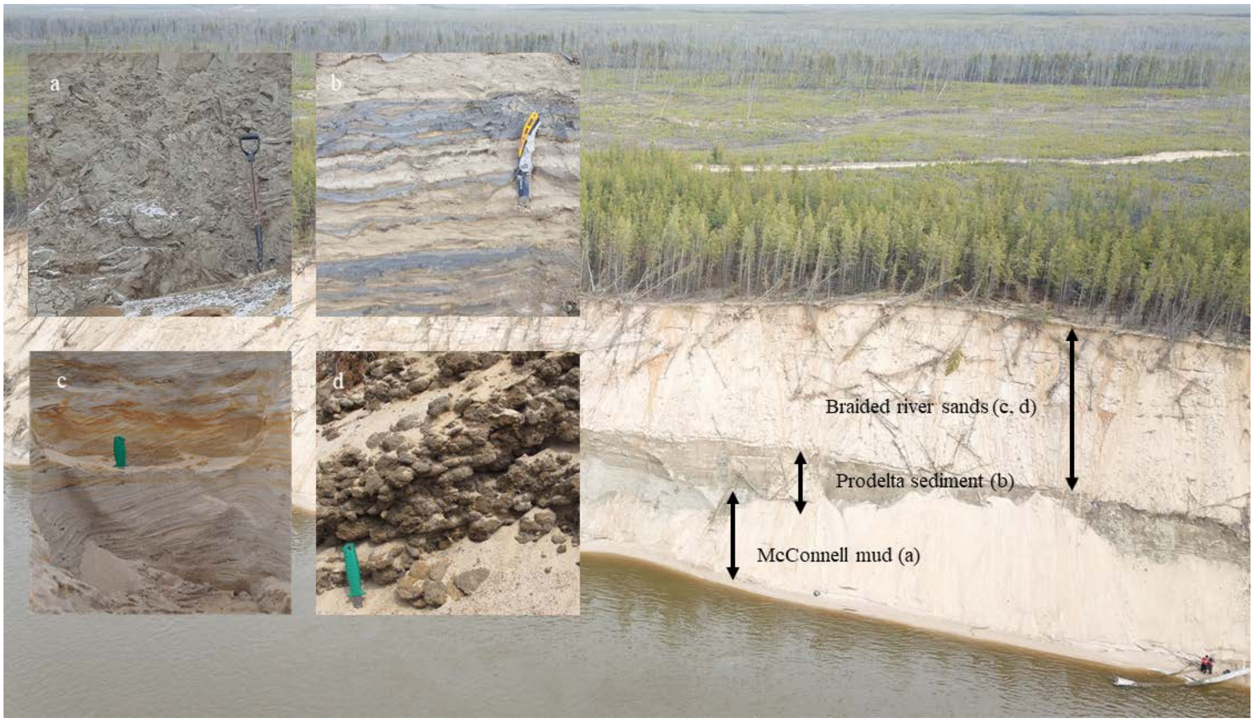

Figure 2.3. The erosional meander bend of Athabasca River known as Big Bend by Embarras. a) McConnell mud. b) Prodelta sediment. c) Braided river sands. d) Bituballs found in braided river sands.

2.3.2. PAH concentrations and distributions in Big Bend sediment

The Big Bend site was sampled for PAH analyses at 5 locations (LAR1 – LAR5) (Figure 2.4). The upstream end LAR1 and LAR5 consist of a bottom 5 m of McConnell mud, 5 m of prodelta sediment and ~10 m of braided river sands, whereas both sites LAR2 and LAR3 are formed predominately by braided river sands. Site LAR4 on the downstream end consists of 3 m McConnell mud overlain by 17 m of braided river sands. Total PAH concentrations at Big Bend ranged from 3 ng/g to 188,028 ng/g (Figure 2.4, Table A.4). The McConnell mud had median and mean PAH concentrations of 3,861 ng/g and 5,341 ± 3,717 ng/g (n = 8), respectively. The prodelta sediment above the McConnell mud had median and mean PAH concentrations of 4,053 n/g and 11,148 ± 18,092 ng/g, respectively (n = 6). In terms of PAH species, both McConnell mud and prodelta sediment were found to have a similar concentration of parent PAHs, total alkylated PAHs, and total dibenzothiophenes (DBT) including C1-C4 alkylated dibenzothiophenes (Figure 2.5). The braided river sands were characterized by lower PAH concentrations [median: 44 ng/g and a mean: 400 ± 1,156 ng/g (n = 17)]. The relative abundance of parent PAHs, alkylated PAHs and DBTs found in the braided river sands are 19 %, 81 %, and 9 %, respectively. The highest PAH concentrations at Big Bend were found within the bituball horizons in the braided river sands. Bituball samples had median and mean PAH concentrations of 75,912 ng/g and 76,518 ± 68,845 ng/g, respectively (n = 10). The bituballs varied in total PAH concentrations from 680 ng/g to 188,023 ng/g. The relative abundance of parent PAHs, alkylated PAHs and DBTs in the bituballs are 5 %, 95 %, and 24 %, respectively. Alkylated PAHs are an indicator of a petrogenic origin, and alkyl-PAHs comprise 91 %, 90 %, 81 % and 95 % of total PAHs for in the McConnell mud, prodelta sediment, braided river sands, and bituballs, respectively. This suggests the PAHs content in the McConnell mud, prodelta sediment and Big

Bend bituballs have a common petrogenic oil source. The lower percentage of alkylated PAHs content in the braided river sands suggest a mix of other (non-petrogenic) PAHs.

As with PAHs, the Big Bend bituballs have a similar carbon isotope ratio of -29.0 ‰ (Table A.6, figure A.2.) to the Athabasca bitumen -29.6 ‰ (Jha et al., 1979) suggesting bituballs are the same bitumen as McMurray Formation bitumen. The McConnell muds and prodelta sediment grouped together in terms of carbon content and $\delta^{13}C$ signatures, with median carbon concentrations of 1.2 % and 1.7 %, and median $\delta^{13}C$ ratio of -16.3 ‰ and -17.6 ‰, respectively (Figure A.2 and A.3). This suggests a common carbon source for these two units (Algae; Fenton & Ritz, 1988). The carbon in the clay and silt of both the McConnell mud and prodelta sediments are likely trapping organic material like PAHs from the bituballs particles washed down from the braided river sand facies, which a significant PAH concentration can be found in these two units. The carbon isotope and carbon content in the braided river sands were found to be -27.0 ‰ and 0.1 %, respectively (n = 75) (Figure A.2 and A.3). The braided river sand facies are formed mainly of quartz sand, and the low carbon content in the braided river sands do not preserve significant organic material from the bituballs; however, some of the samples of the braided river sands had a $\delta^{13}C$ signature that was similar to the bituballs carbon isotope ratio (Figure A.2). This suggests bitumen is mixed within some of the braided river sands.

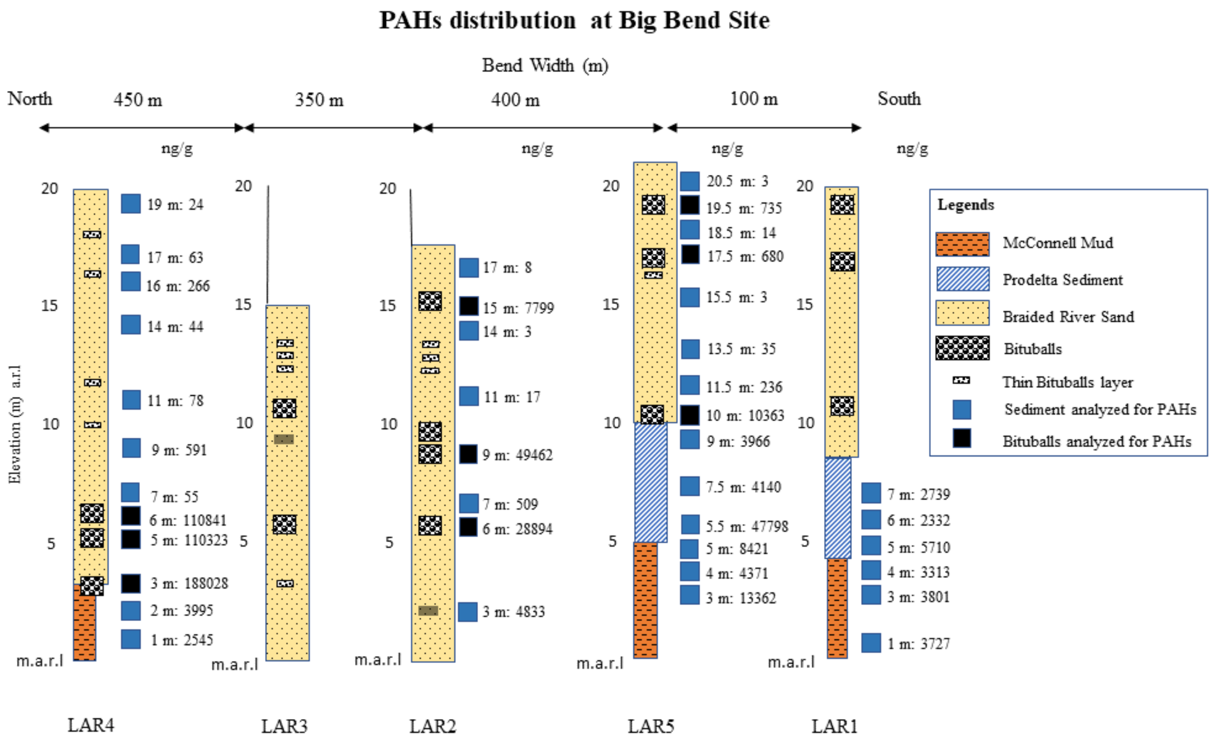

Figure 2.4. PAH distributions at the Big Bend site from north to south. The reworked bitumen (Bituballs) labelled in black are mainly in the braided river sands. Elevation above river level (m) and total PAH concentrations (ng/g).

2.3.3. PAH concentrations in sources

Our results from Big Bend indicate it is an important source of PAHs to the lower Athabasca River. But there are other important natural and anthropogenic sources of PAHs as well, including the natural erosion of the McMurray Formation upstream, and the transport of wildfire ash and the input of petroleum coke. Raw bitumen (obtained from mining sites) had the highest concentrations of total PAHs among other bitumen sources averaging 383,278 ± 50,755 ng/g (n = 6) (Table A.5). Natural exposures of the McMurray Formation within Athabasca River tributaries were also high in PAHs, averaging 215,741 ± 83,840 ng/g (n = 5). The delayed petroleum coke had an average mean total PAH concentrations of 921,390 ± 528,037 ng/g (n = 2), whereas our one sample of fluid petroleum coke had the lowest total PAH concentrations of

613 ng/g. These much lower PAH concentrations in fluid petroleum coke are consistent with the findings of Zhang et al. (2016) who noted that delayed petroleum coke contained much higher concentrations of PAHs than fluid petroleum coke. Finally, wildfire ash had an average mean of total PAH concentrations of 10,666 ± 8,866 ng/g (n = 15).

The raw bitumen and tributary bitumen PAH concentrations were, on average, five and three-fold higher than the Big Bend bituballs, respectively (Table A.5). Lower PAH concentrations in the bituballs from Big Bend may reflect their mode of formation. When physically examining the bituballs, they are found to be less “sticky” with less raw/oil bitumen content than the raw bitumen. PAHs in the bituballs may have been lost during transport to Big Bend, lost post-deposition due to diagenesis, or the lower PAH concentration could simply reflect the fact that bituballs are a mix of bitumen and riverbed sand (Figure A.4). This might explain the decreasing trend in PAH concentrations observed from raw bitumen to tributary bitumen to Big Bend bituballs. The various PAH concentrations in different bitumen horizon at different river bank height might also describe the differences in river velocity during the post paleo flood period. The higher PAH concentrations observed in bituballs at the lower part of exposure suggest greater availability of bitumen immediately after the catastrophic flood of Lake Agassiz.

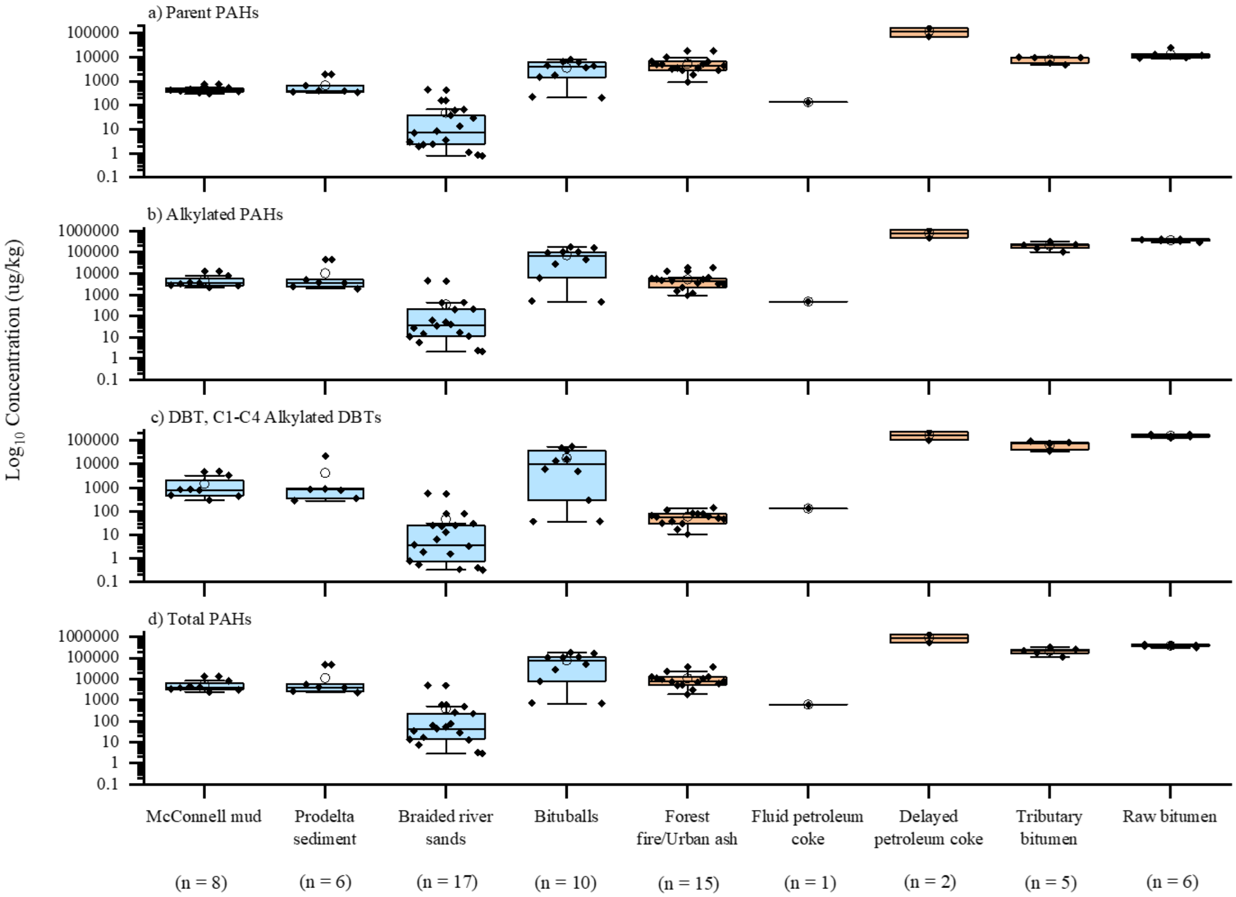

Figure 2.5. PAHs concentration distribution of a) Parent PAHs, b) Alkylated PAHs, c) DBTs, and d) Total PAHs for Big Bend sediment - McConnell mud, prodelta sediment, braided river sands, and bituballs, and regional sources – Forest fire/urban ash, fluid petroleum coke, delayed petroleum coke, tributary bitumen and raw bitumen.

2.3.4. PAH composition in sources

The composition of Big Bend bituballs is compared with other sources (forest fire/urban ash, fluid petroleum coke, delayed petroleum coke, tributary bitumen and raw bitumen) in figures 2.6 and 2.7. There are clear compositional differences in the sums of parent PAHs, alkylated PAHs, and DBTs among the sources.

The most obvious difference was between ash (pyrogenic) and the other (petrogenic) sources. Ash samples had nearly equal amounts of parent and alkylated PAHs, and almost no

DBTs. Ash samples had much higher relative abundances of retene (~10 %) than the petrogenic source materials (~0.5 %) (Figure 2.7). While previous authors have noted that retene may be a useful marker for the input of forest fire ash (Gaboes et al., 2001; Schuster et al., 2015), our results suggest that the relative abundance (or lack thereof) of DBTs may also be a simple but highly indicative marker distinguishing between petrogenic and pyogenic sources of PAHs in the oil sands region. Both types of petroleum coke were characterized by ~20% DBTs and higher relative concentrations of parent PAHs than in samples of bitumen (Figure 2.6). This indicates compositional changes in PAHs during the coking process. Finally, the raw bitumen, tributary bitumen, and Big Bend bituballs show similar PAH compositional profiles with a high abundance of alkylated PAHs (97 %, 96 % and 89 %, respectively).

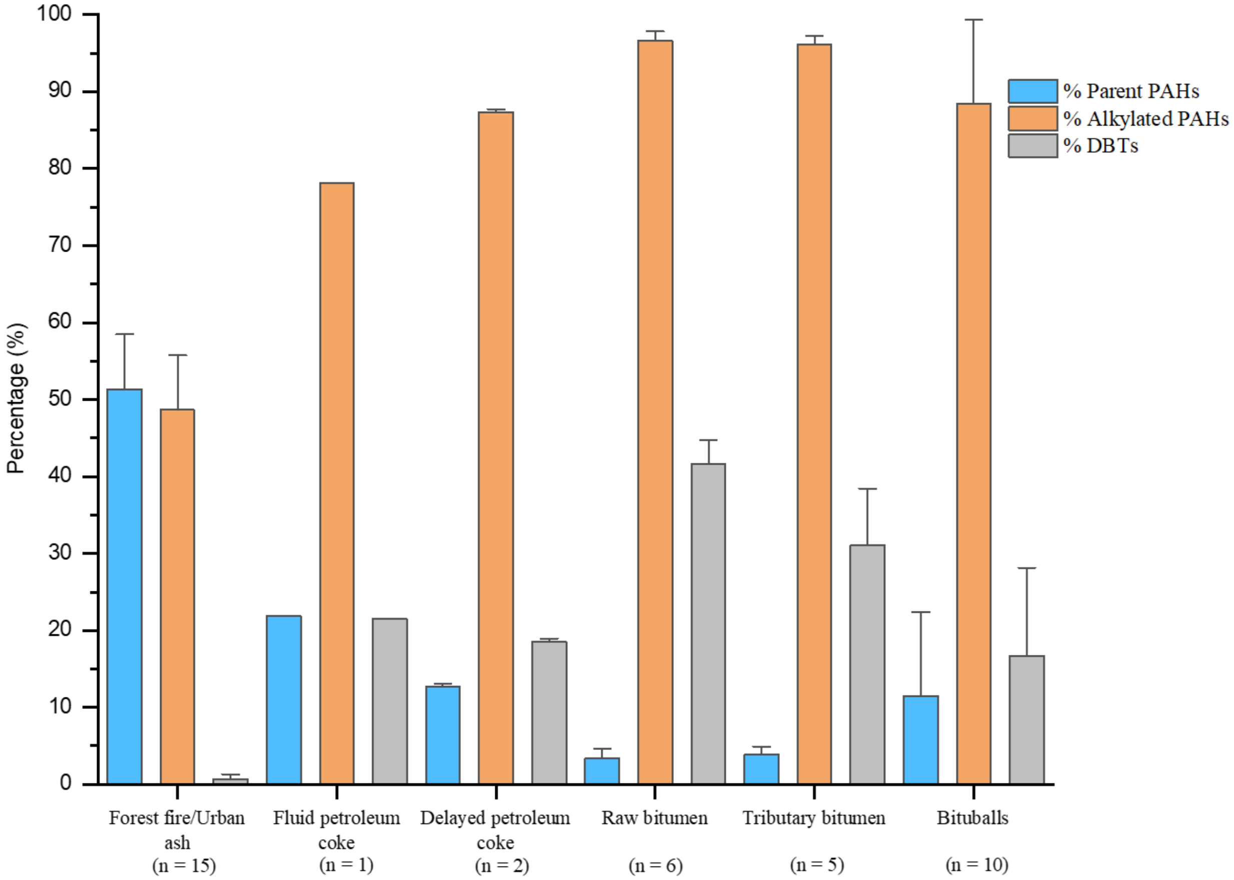

Figure 2.6. PAHs composition distribution of Parent PAHs, Alkylated PAHs, and DBTs for forest fire/urban ash, petroleum coke, raw bitumen, tributary bitumen, and Big Bend bituballs.

Looking at concentrations of individual PAH offers additional insights into the compositional differences among the various sources (Figure 2.7). Forest fire/urban ash and fluid petroleum coke are dominated by 2–3 rings unsubstituted parent PAHs, and the alkylated PAHs homologues of naphthalene and phenanthrene/anthracene (Figure 2.7a and 2.7b). Ash samples had low concentrations of the 4–5 rings unsubstituted parent PAHs and alkylated PAHs homologues. In contrast, delayed petroleum coke has a PAH pattern more similar to the raw bitumen with a low abundance of 2–3 rings unsubstituted parent PAHs and their alkylated PAH homologues (Figure 2.7c). However, ash, fluid petroleum coke and delayed petroleum coke exhibit a similar distribution pattern of alkylated phenanthrene/anthracene with $C_1 > C_2 > C_3$ but with C_4 having the highest abundance (Figure 2.7a, 2.7b and 2.7c). This unique distribution pattern of alkylated phenanthrene/anthracene in these samples is different from bitumen (Figure 2.7d, 2.7e, and 2.7f). Both fluid petroleum coke and delayed petroleum coke displayed a mix of both pyrogenic and petrogenic characteristics with a significant abundance of alkylated PAHs homologues of fluoranthene/pyrene, benzo(a)anthracene/chrysene and dibenzothiophene. The alkylated fluoranthene/pyrene and benzo(a)anthracene/chrysene had a distribution pattern of $C_1 > C_2 > C_3 > C_4$ whereas alkylated dibenzothiophene had a bell-shaped distribution which was also found in the raw bitumen (Figure 2.7d). The strong presence of 4–5 rings PAHs likely reflects the fact that petroleum coke is a by-product of the high-temperature upgrading of bitumen into synthetic crude oil (Shawwa et al., 2001); the PAH signature of petroleum coke therefore includes a mix of both the source material and the process by which it was created.

The PAH profiles for raw bitumen, tributary bitumen and Big Bend bituballs are characterised by a similar PAH distribution pattern (Figure 2.7d, 2.7e, and 2.7f). All the bitumen and bituball samples show high concentrations of the alkylated homologues of naphthalene, fluorene, phenanthrene/anthracene, fluoranthene/pyrene, benzo(a)anthracene/chrysene and dibenzothiophene. The PAH profiles of the bitumen also show evidence that oil degradation has occurred. Degradation of PAH compounds increases with decreasing number of aromatic rings and alkylation (Yang, 2011). The oil degradation process can be observed in the 2–3 rings of alkylated homologues of naphthalene, fluorene, phenanthrene/anthracene and dibenzothiophene with the distribution pattern of $C_0 < C_1 < C_2 < C_3 < C_4$ except DBTs in raw bitumen, which is dominated with DBT3. The alkylated C1 to C4 naphthalene have the lowest concentration and composition relative to other alkylated C_1 to C_4 PAH homologues in the PAH profiles. This results in the 2-ring alkylated naphthalene being the most susceptible to weathering due to their volatile properties (Yang, 2011). The 4-ring alkylated homologues of fluoranthene/pyrene and benzo(a)anthracene/chrysene appear to be more stable with a bell-shaped distribution pattern in all bitumen samples as they are more resistant to degradation.

Differences in the PAH profiles for raw bitumen, tributary bitumen, and Big Bend bituballs reflect variable amounts of weathering (Figure 2.7d, 2.7e, and 2.7f). A strong weathering pattern can be observed in the abundances of the alkylated PA1–PA4 and alkylated DBT1–DBT4. The slope of PA1 to PA4 distribution pattern increases from raw bitumen to tributary bitumen to Big Bend bituballs with increasing dominance of PA4 (Figure 2.7d, 2.7e, and 2.7f). A similar distribution pattern change can be seen in DBT1 to DBT4. The raw bitumen starts with a bell-shaped distribution pattern (Figure 2.7d). The pattern changed in tributary bitumen with increasing DBT4 concentration (Figure 2.7e). Ultimately, we see a sharp slope distribution pattern in Big Bend bituballs with high abundances of DBT4. The DBT1 to DBT4 composition decrease from 41.6 % in raw bitumen to 31.1 % in tributary bitumen to 16.7 % in Big Bend bituballs. The higher dominance of PA4 and DBT4 are indicative of weathering (Wang et al., 1999; Stogiannidis and Lane, 2015), suggesting the Big Bend bituballs were weathered during or after transport and deposition. Overall, the Big Bend bituballs are characterized by different distribution patterns than the other sources of PAHs we analyzed, including forest fire/urban ash and petroleum coke. Big Bend bituballs, however, show a distribution pattern most similar to raw bitumen and tributary bitumen sources.

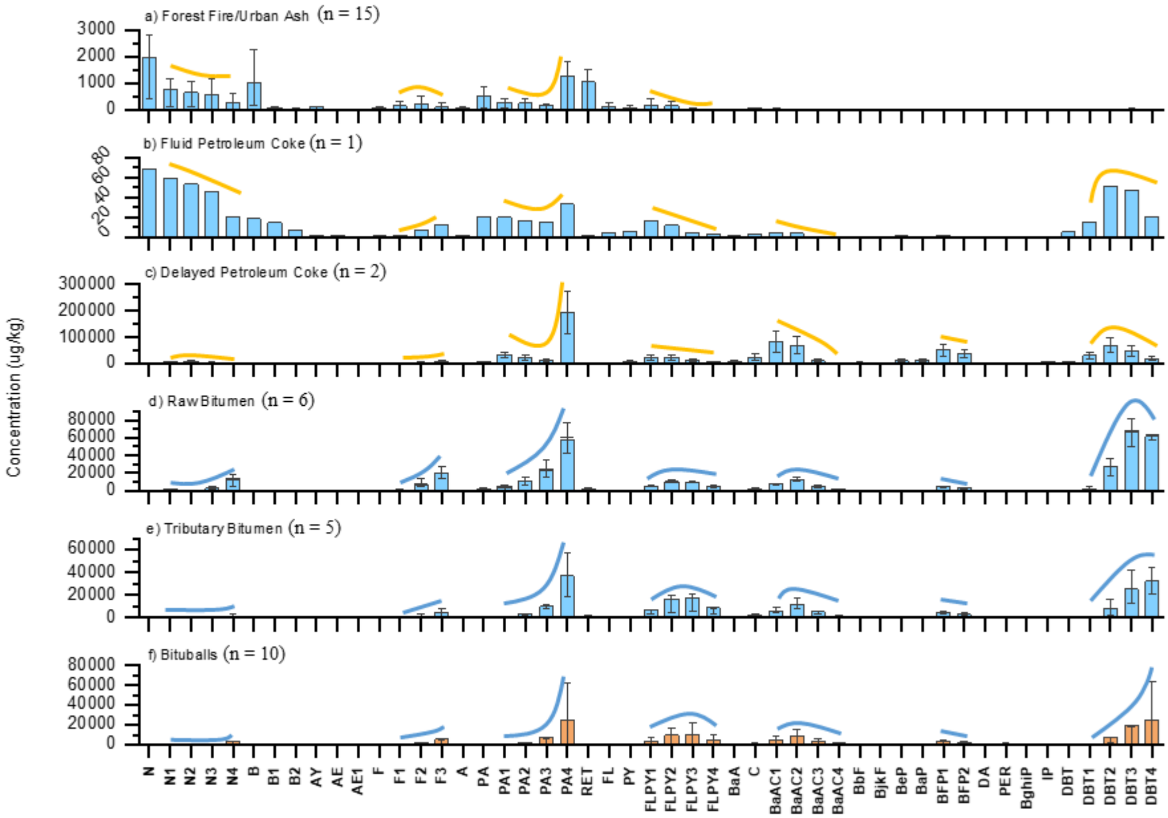

Figure 2.7. Concentration profile of polycyclic aromatic hydrocarbons. Bar graphs showing average concentration for a) forest fire/urban ash, b) fluid petroleum coke, c) delayed petroleum coke, d) raw bitumen, e) tributary bitumen, and f) Big Bend bituballs.

2.3.4.1. Diagnostic ratios for PAHs compounds in Big Bend Sediment

Previous studies have used diagnostic ratios in an attempt to distinguish between pyrogenic and petrogenic sources of PAHs to various media (Birks et al., 2017; Evans et al., 2016). The diagnostic ratio applies the physical, chemical, and thermal stability of PAHs to identify various sources (Wang et al., 1999). In this study, diagnostic ratios are applied to distinguish between pyrogenic and petrogenic PAHs in Big Bend and other potential natural input sources including forest fire/urban ash, raw bitumen and tributary bitumen.

2.3.4.2. Pyrogenic Index (PI)

The pyrogenic index (PI) is the ratio of the sum of 3–6 ringed parent PAHs (AY, AE, A, FL, BaA, BeP, BghiP, IP, DA) relative to the sum of 5 alkylated PAHs homologues (N(1–4), PA(1–4), DBT(1–4), F(1–3), FLPY(1–4), BaAC(1–4)) (Wang et al., 2014). A PI <0.05 indicates a heavy fuel or crude oil PAH source while a PI ratio between 0.8 and 2.0 suggest pyrogenic source(s) (Wang et al., 2014). A PI ratio range from 0.05–0.8 suggest a mix of pyrogenic and petrogenic sources.

The PI ratio of the McConnell mud, prodelta sediment, and Big Bend bituballs are 0.03, 0.04, and 0.03, respectively. These ratios are all consistent with a petrogenic sources (Figure 2.8a). In contrast, the braided river sands PI ratio is slightly higher at 0.09, which indicates a mix of pyrogenic and petrogenic PAH sources. Compared to other PAH sources in the region, the PI ratio of the forest fire/urban ash, fluid petroleum coke, delayed petroleum coke, raw bitumen and tributary bitumen are 0.10, 0.04, 0.07, 0.01, and 0.01, respectively (Figure 2.8b). The PI ratio of forest fire/urban ash and braided river sands are similar suggesting the braided river sands incorporated natural pyrogenic sources of PAHs. The PI ratio is useful in distinguishing natural pyrogenic sources from bitumen sources in the lower Athabasca region which the PI ratio is 3 to 10-fold higher than the bitumen. However, anthropogenic pyrogenic sources such as fluid petroleum coke and delayed petroleum coke have a more similar PI ratio to bitumen sources. This might be due to petroleum coke are by-product of bitumen retaining similar PI ratio. Big Bend bitumen PI ratio is also found to be similar to both raw bitumen and tributary bitumen which do not provide unique signature to distinguish among the petrogenic sources. As the PI ratio are very similar among both petroleum coke and the bitumen sources, PI ratio does not allow us to clearly distinguish sources in the environment of the lower Athabasca region.

2.3.4.3. PA4/PA3 Ratio

To further investigate the potential for weathering to alter the PAH composition of bitumen within Big Bend we used the alkylated PA4/PA3 ratio (Figure 2.9). The higher molecular weight alkylated PA4 is more resistant to weathering than PA3 (Wang et al., 1999; Stout et al., 2001). Thus, higher PA4/PA3 ratios suggest a more weathered sample.

The PA4/PA3 ratio increased from raw bitumen (2.2) to tributary bitumen (5.2) to Big Bend bituballs (11.1) (Figure 2.9). This increasing trend also agrees with the weathering pattern observed in DBTs (Figures 2.6 and 2.7). These weathering ratios reflect the histories of these three types of bitumen samples.

The PA4/PA3 ratio is also examined in water PAHs data for Athabasca River in figure A.5. In the modern river data, the PA4/PA3 ratio increased from Fort McMurray (1.9) to Firebag River (2.9), and reached to highest ratio when the river reached Old Fort, immediately downstream of Big Bend (3.5). The ratio then decreased further downstream at Devil's Elbow (2.9) (Figure A.5). This suggests an influx of weathered bituminous material entering the Athabasca River between the Firebag River and Old Fort. As there are no other PAH sources between Firebag River and Old Fort (Conly, 2002), the PAH source is most likely from Big Bend weathered bitumen material. A similar result was reported by Glozier et al. (2018) who found the PA4 concentration captured by semi-permeable membrane device (SPMD) increased when the river reached the bituminous area at Fort McMurray (M3), and started to decrease at the end of bituminous area from Ells River (M7) to Embarras Airport (M9) (M9 is located immediate upstream of Big Bend). This suggests PA4 concentrations reflect the influx of petrogenic PAHs source between M3 to M7. The PA4 could therefore be a useful tool in identifying areas of bitumen input in the lower Athabasca River whereas PA4/PA3 ratio could provide information on the weathering state.

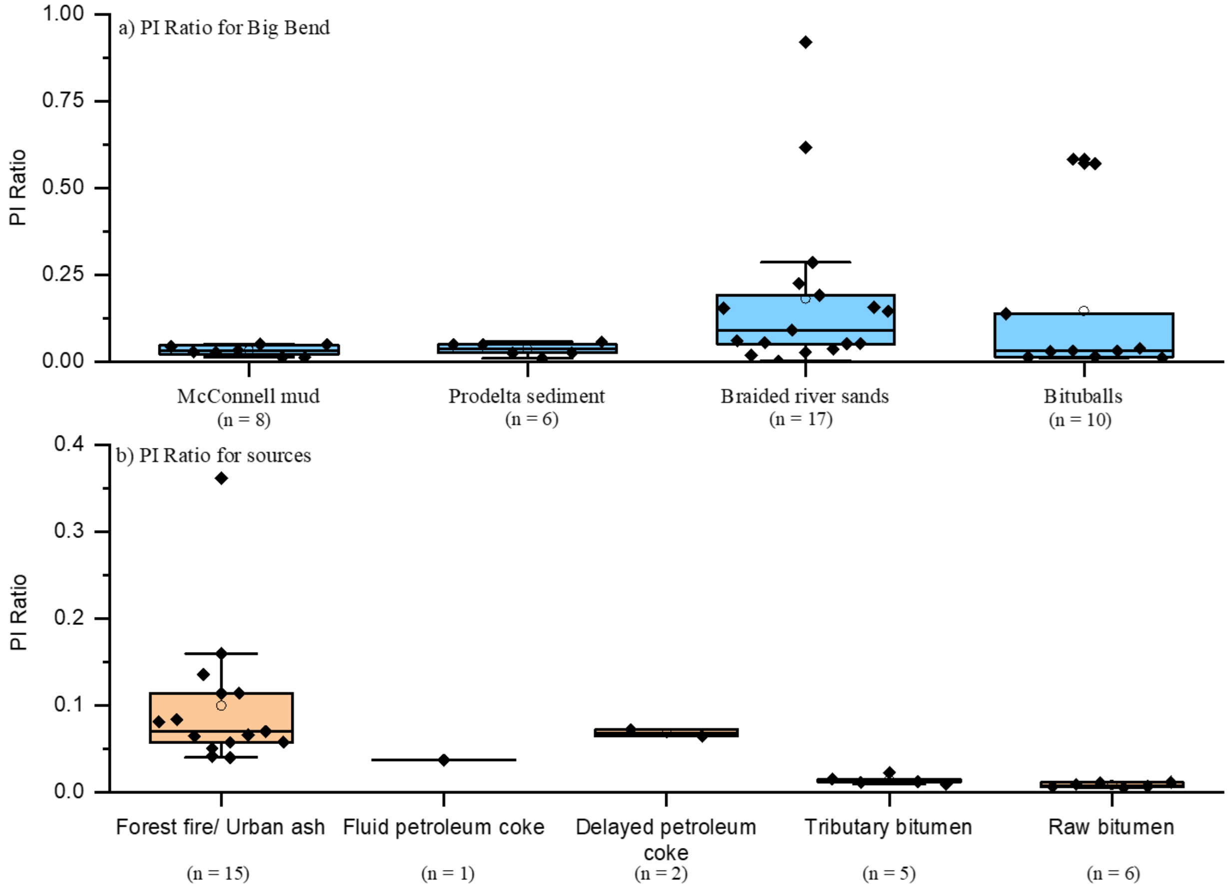

Figure 2.8. a) Pyrogenic ratio for Big Bend: McConnell mud, prodelta sediment, and Big Bend bituballs.b) Pyrogenic ratio for sources: Forest fire/urban ash, fluid petcoke, delayed petroleum coke, tributary bitumen, and raw bitumen.

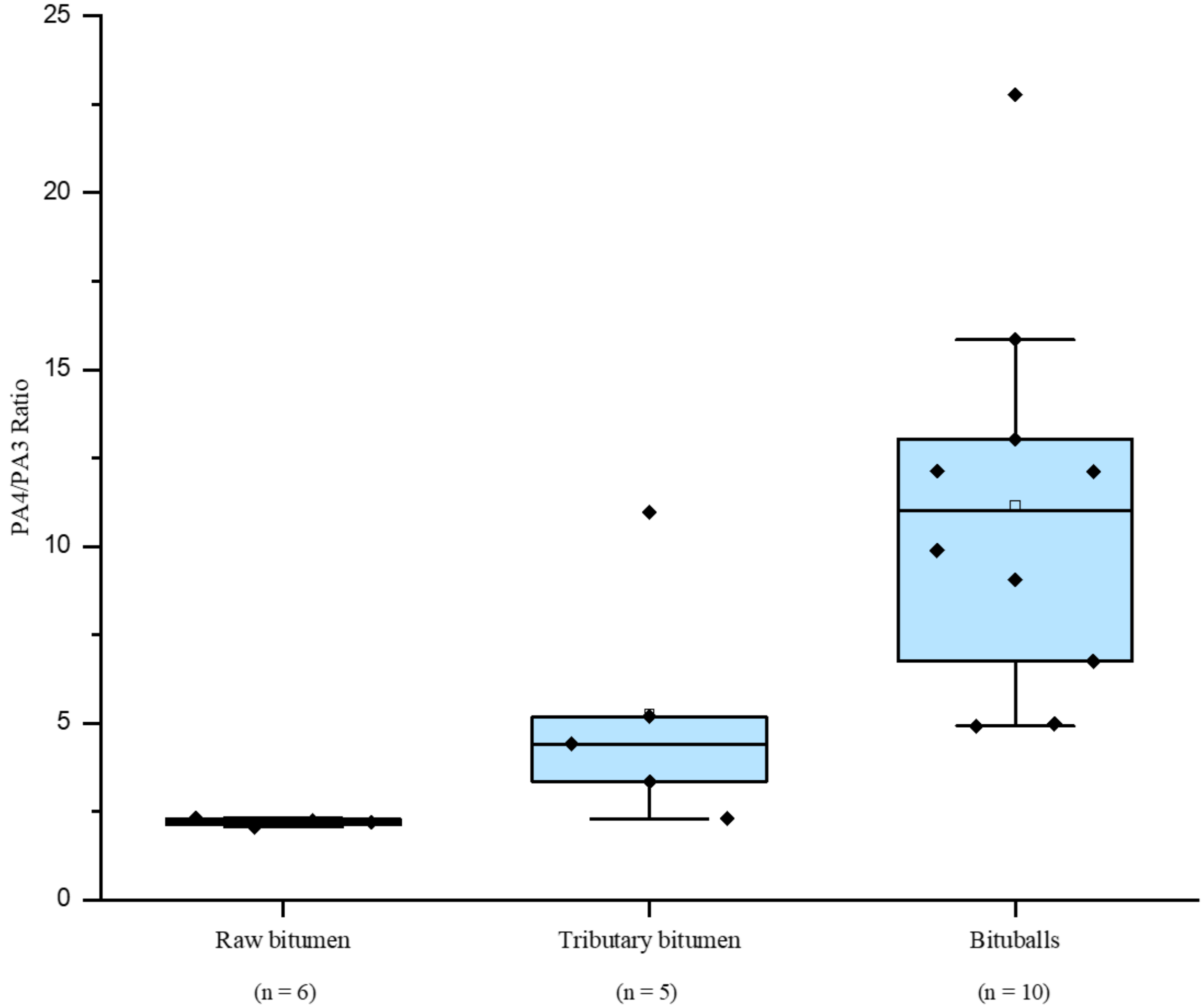

Figure 2.9. PA4/PA3 weathering ratio raw bitumen, tributary bitumen, and Big Bend bituballs.

2.3.4.4. Source and weathering ratio analysis

Dibenzothiophenes, which are heterocyclic sulfur-bearing PAHs, are useful to assess an oil source origin and the degree of weathering (Stogiannidis and Lane, 2015). The alkylated groups of dibenzothiophene and phenanthrene degrade and weather proportionally (Douglas et al., 1996). Thus, the double ratio plot of DBT2/PA2 vs DBT3/PA3 had been used by regulatory agencies to identify parties responsible for oil spill accidents such as the Exxon Valdez in Alaska (Brown and Boehm, 1993; Douglas et al., 1996). Alkylated chrysene weathers at a faster rate than alkylated dibenzothiophene (Evans et al, 2016). The double ratio plot of BaAC2/DBT2 vs BaAC3/DBT3 provides information on oil weathering and biodegradation (Brown and Bohem, 1993).

The source ratio DBT2/PA2 vs DBT3/PA3 for all-natural PAHs sources is depicted in figure 2.10. As expected, the ash samples have a ratio that is unique from the raw bitumen, tributary bitumen, and Big Bend bituballs. Compared to all other types of samples, the source ratios for bituballs are tightly grouped together, suggesting bituballs across Big Bend came from a similar source. The majority of samples from the bitumen and bituballs appear to be grouped together with subgroups observed in the raw bitumen and tributary bitumen. The subgroups of source ratio observed in raw bitumen and tributary bitumen suggest different source ratio within McMurray Formation. This also agrees with Droppo et al.'s (2018) suggestion that spatial and chemical differences exist within the McMurray Formation in the oil sands region. The bituballs source ratio overlaps with raw bitumen and tributary bitumen suggesting the bituballs were only eroded from a source region of McMurray Formation. This also agrees with the double ratio plot DBT2/PA2 vs DBT3/PA3 in the study by Akre et al. (2012), which suggest the different facies of sediment from the Embarras cut bank sharing similar source as the upstream sediment due to same river system and oil sands formation.

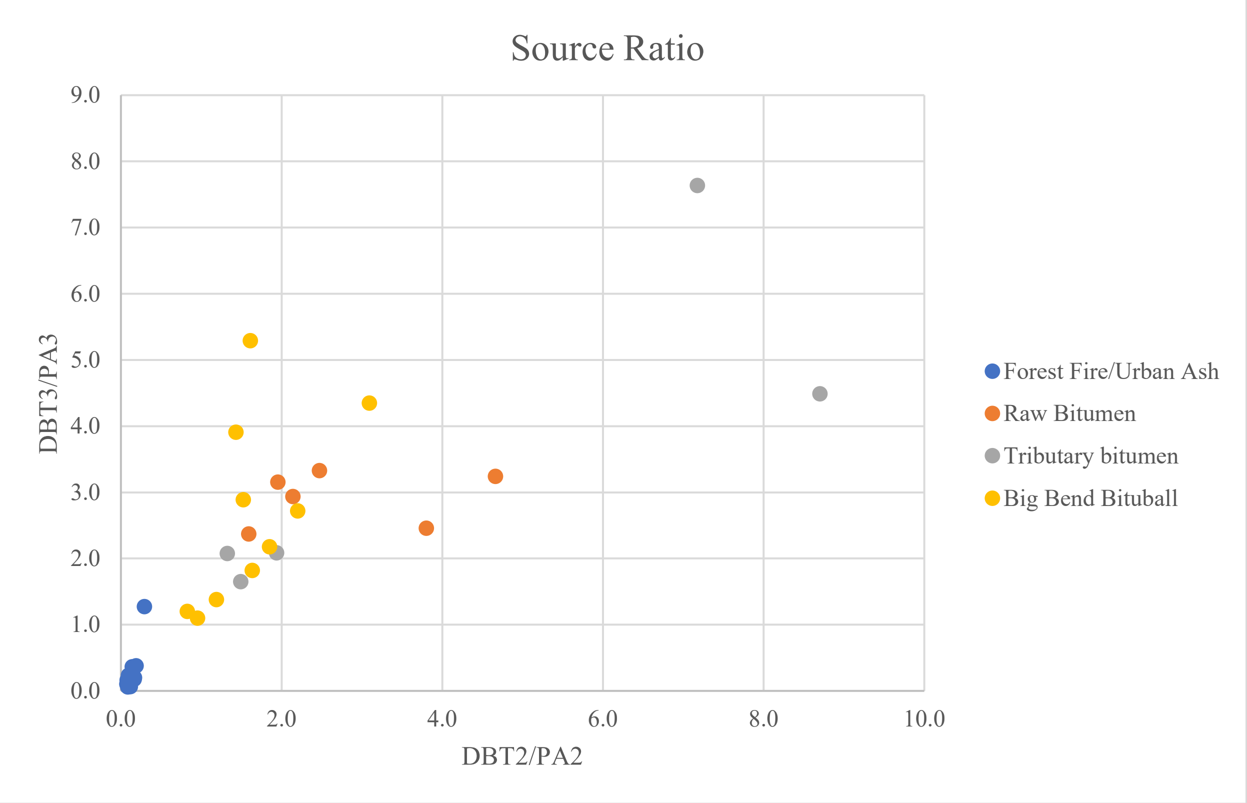

Figure 2.10. DBT2/PA2 vs DBT3/PA3 source ratio analysis for forest fire/urban ash, raw bitumen, tributary bitumen, and Big Bend bituballs.

The weathering ratios of BaAC2/DBT2 vs BaAC3/DBT3 are shown in figure 2.11. Lower ratios indicate less weathering as BaAC2 and BaAC3 are more weather resistance than DBT2 and DBT3. An increasing trend of weathering ratio are observed from raw bitumen < tributary bitumen < Big Bend bituballs, which are also observed in the PA4/PA3 ratio. Raw bitumen is buried deep underneath in the McMurray Formation of the oil sands region with less chance of exposing to photodegradation and biodegradation. In contrast, the tributary bitumen were freshly exposed to river erosion, and weathering. A wide range of BaAC2/DBT2 ratio (1.9-29.0) is observed in the Big Bend bituballs suggesting different stage of weathering in the samples collected. This also agrees with Arke et al. suggestion that bitumen at Big Bend was deposited during different periods of time with different length of exposure to environment before buried by clean sand (2012).

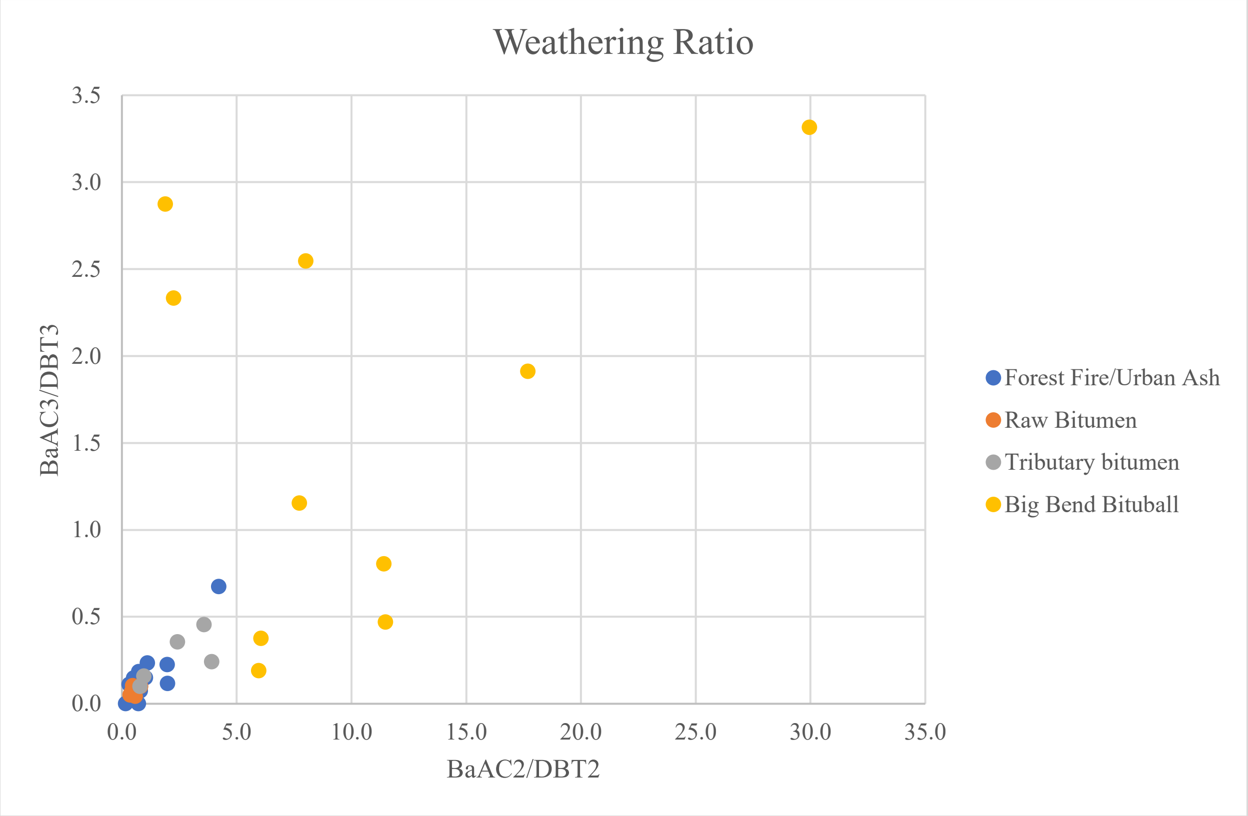

Figure 2.11. BaAC2/DBT2 vs BaAC3/DBT3 weathering ratio analysis for forest fire/urban ash, raw bitumen, tributary bitumen, and Big Bend bituballs.

2.3.4.5. Source ratio comparison

Three diagnostic ratios were used to evaluate Big Bend PAH data to the regional sources. We found PA4/PA3 ratio is the most useful diagnostic ratio to distinguish among different bitumen sources with similar PAH profile in the lower Athabasca region. The other common approaches for source identification of PI ratio, and source and weathering ratio are useful to distinguish pyrogenic sources from petrogenic sources but was not as successful within the similar petrogenic sources and petroleum coke having the same bitumen origin. Future studies could use the PA4/PA3 as the diagnostic ratio for fingerprinting Big Bend bitumen.

2.3.5. Sediment load at Big Bend

The Athabasca River is actively eroding the Big Bend site. Time series images from aerial photography at a scale of 1:16000 (1956), along with satellite images from Landsat 20 m (2008) and Sentinel 10 m (2012-2015) were used to estimate the bank retreat rate. Between 1956 and 2015, the average annual surface area loss was 10,400 m^2 (Figure 2.2). To estimate the material lost to river transport, we multiplied this surface area loss by the average bulk density of each lithofacies. An average bulk density of 1.7 t/m^3 was used for clay, silt, and sand (Conly et al., 2002), while 2.0 t/m^3 was used for bituballs horizons (Berkowitz and Speight, 1975). The annual sediment input from the McConnell mud, prodelta sediment, and braided river sands are ~107 kt, 51 kt, and 191 kt, respectively, with bituballs contributing another ~62 kt each year to the river. The sum of total annual sediment load from different facies at Big Bend would approach ~410 kt. This is slightly higher than an early estimation of ~350 kt by Conly et al. (2002).

To put the sediment load from Big Bend in a broader regional context for the Athabasca River, we obtained total suspended sediment concentrations and discharge data from the regional oil sands monitoring program (Cooke et al., 2018). The sediment load of the Athabasca River is shown in figure 2.12. Between 2012 and 2014, the mean annual suspended sediment load at M3, by Fort McMurray, was 3,800 kt. Downstream at M7, by the Ells River, the mean annual suspended sediment load was 4,540 kt. The amount of suspended sediment contributed to the Athabasca River between the M3 and M7 monitoring stations would, therefore, be ~740 kt (Table A.7.). There is 115 km of river between M7 and Big Bend; however, the only tributary of note in this river stretch is the Firebag River with an estimated sediment load 28 kt. Bank erosion from the Athabasca River itself between M7 and Big Bend likely contributes very little sediment due to both the highly resistant nature of the bank material and the broad nature of the river in this stretch (Conly et al., 2002). The Big Bend contributions from the site are estimated at 410 kt/year. We estimate the total annual sediment load for the lower approximately one-third of the Athabasca River (including tributaries) to be 1,178 kt. The total sediment annual mean input from all tributaries from Fort McMurray (M3) to Big Bend between 2012 and 2014 is 152 kt representing ~13 % of the annual sediment budget for the lower Athabasca River (Yi, 2019). The tributaries sediment contribution is slightly lower to the estimation by Conly et al. of 210 kt from downstream of Fort McMurray to Embarras (2002) (Table A.8.). With all potential sediment inputs accounted for, the net balance would be 1,026 kt eroded through the bank erosion from M3 monitoring station to the Big Bend site excluding tributaries (Yi, 2019). This is much higher than Conly et al.'s estimation of 550 kt (2002) from upstream Fort McMurray to Embarras suggesting increasing in-channel erosion and sediment load from Athabasca River over a ~20-year period (Table A.8.). The sediment supply from the Big Bend site alone, therefore, represents

~35 % of the sediment budget, and ~40 % of the in-channel sediment contribution of the lower Athabasca River between Fort McMurray and Embarras. This makes Big Bend exposure one of the largest single sediment supply sources in the Athabasca River.

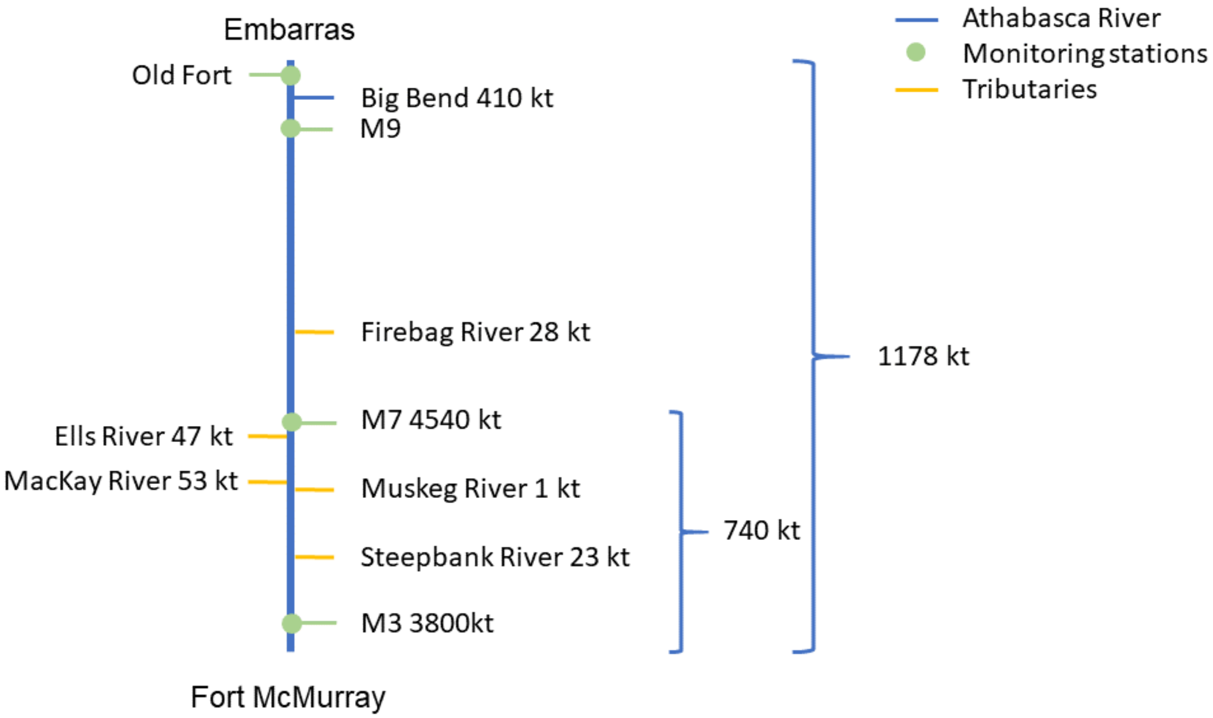

Figure 2.12. Sediment load of Athabasca River from Fort McMurray to Embarras. M3 and M7 monitoring station provide information on the measured sediment load.

2.3.6. PAHs load at Big Bend

The load of PAHs from Big Bend to the Athabasca River was estimated by using the annual sediment load for each unit multiplied by the median PAH concentration for the corresponding unit. The annual PAH load from the McConnell mud (including 5 m below river level), prodelta sediment, and braided river sands were ~0.41 t, 0.21 t, and 0.003 t, respectively. The McConnell mud and prodelta sediments are fine-grained and, therefore, much of this material is likely transported as suspended sediment (rather than as bed sediment) by the Athabasca River contributing ~0.62 t. The largest PAH load is from bituballs imbricated in the braided river sands, which contribute ~4.67 t of PAHs accounting for 88 % of the total PAH load from the Big Bend site. The total annual PAH load from Big Bend directly released into the Athabasca River would approach to ~5.29 t. In comparison, the annual mean PAH loading from tributaries in the Athabasca River is estimated to be ~0.15 t (Yi, 2019). By comparison, the anthropogenic atmospheric PAHs mass deposition is 1.97 t for the 50 km within the major development of the oil sands region during the winter months (Manzano et al., 2016). However, the actual atmospheric PAH mass loading to the Athabasca River remains unclear. This therefore makes Big Bend the largest known PAHs source loading directly to the lower Athabasca River.

2.3.7. PCA Analysis of PAHs sources in lower Athabasca River Region

To link sources and receptors of PAHs, we compared the composition of PAHs within each of the sources we characterized with Athabasca River water quality data using Principal Component Analysis (PCA). PCA is a multivariate analytical method that reduces the dimensionality of a large dataset that would otherwise be difficult to interpret. PCA does this while preserving as much variability as possible by creating new uncorrelated variables that successively maximize variance. PCA analysis was performed using CANOCO version 5.11 (ter Braak and Šmilauer, 2012). For results that were below detection limit, those results were assigned as “0” value which were 16 % of the 15,696 PAH data. The PCA analyses were completed on a correlation matrix with variables centred and standardized to account for different units of measurement.

Petrogenic sources dominate the first principal component axis (PC1, x-axis) with high concentrations of C4 phenanthrene and C4 dibenzothiophene (Figure 2.13). In contrast, pyrogenic sources dominate the second principal component axis (PC2, y-axis) with higher concentrations of the lighter volatile parent PAHs naphthalene, biphenyl, retene, phenanthrene, alkylated PAHs C1–C3 naphthalene, and C2 dibenzothiophene. These grouping reflect in the PAH profiles in figure 2.7. The petrogenic sources are found to have greater abundance of alkylated PAHs, which dominate PC1. Parent PAHs are found to be in relatively low concentration in the petrogenic sources. On the PC1 axis, the petrogenic sources are found to be in high concentration of PA4, and DBT4. The high concentration of PA4 and DBT4 in these petrogenic sources suggest these samples are heavily weathered, which the lighter C1–C3 alkylated of phenanthrene and dibenzothiophene were degraded. Within the petrogenic sources, the raw bitumen is found to be with higher abundance of PA4, whereas Big Bend sediment, bituballs, and tributary bitumen, are found to be in higher concentration of DBT4. The molecular weight of PA4 is lighter than DBT4. As the raw bitumen is buried in the oil sands region, it would be able to preserve the lighter PAHs such as PA4. The Big Bend sediment and tributary sediment were more exposed to weathering, heavier PAHs such DBT4 would be better preserved from weathering.

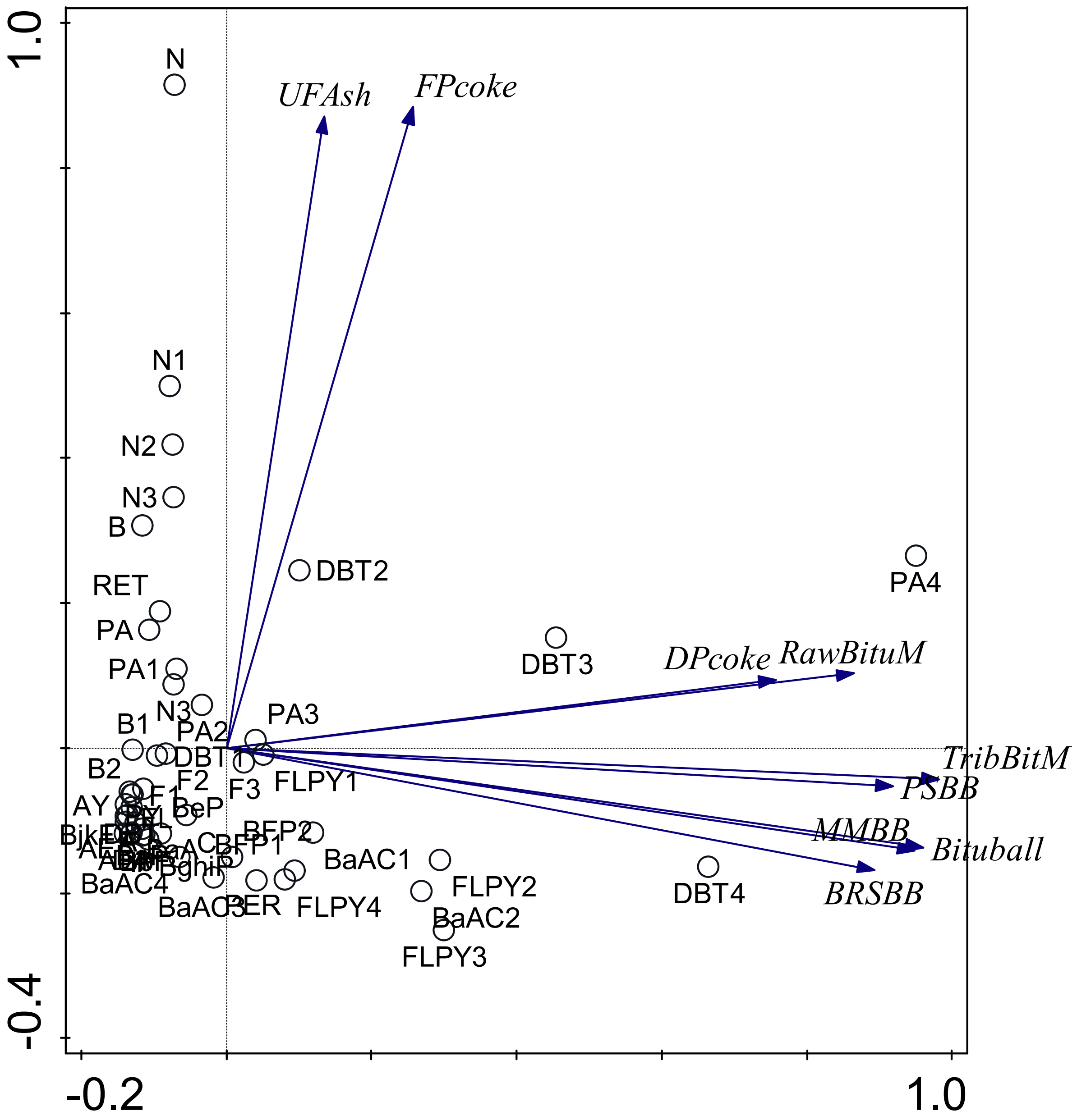

Figure 2.13. PCA analysis of natural PAHs sources forest fire/urban ash (UFAsh), raw bitumen (RawBituM), tributary bitumen (TribBitM), McConnell mud (MMBB), prodelta sediment (PSBB), braided river sands (BRSBB), Big Bend bituballs (Bituball) and anthropogenic PAH sources: fluid petroleum coke (FPcoke), delayed petroleum coke (DPcoke).

2.4. Discussion

Big Bend is an important source of PAHs to the lower Athabasca River. To understand if the regional monitoring program could detect the input of PAHs from Big Bend, and from the other potential sources of PAHs characterized as part of this study, we compared the composition of PAH sources (Raw bitumen, tributary bitumen, Big Bend bituballs, fluid petroleum coke, delayed petroleum coke, and urban/forest fire) to the composition of PAHs in water samples collected by Environment and Climate Change Canada and Alberta Environment and Parks as part of the Oil Sands Monitoring Program (Cooke et al., 2018; Wrona et al., 2011). We made this comparison using a principal components analysis (PCA). Within the PCA, we also included discharge, which varies seasonally. In 2016 – 2018, the average river discharge rate spring/summer months (May to October) reached as high as 1,031 m^3/s, whereas winter discharge (November to April) fell as low as 281 m^3/s (07DD001; Environment Canada and Climate Change, 2021). For this reason, the Athabasca River PAHs water data for each monitoring stations are further averaged into high-flow (May to October) and low-flow (November to April) results.

Water samples collected from the most upstream site (at the town of Athabasca) and at the most downstream site (Devil's Elbow) sampling stations grouped together during low-flow (Figure 2.14). These stations had PAH compositions that matched closely with the composition of forest fire/urban ash and petroleum coke, suggesting a predominance of pyrogenic, rather than petrogenic, PAHs. In contrast, water PAH samples collected at Fort McMurray, Firebag River and Old Fort monitoring stations grouped between fluid petroleum coke and the cluster of petrogenic sources characterized by positive PC1 scores and negative PC2 scores. This suggests water PAH composition at these sites are characterized by a mixture of both pyrogenic and petrogenic sources. Bank erosion would be minimal during periods of low-flow, which likely increases the contribution from pyrogenic sources such as fluid petroleum coke or urban/forest fire ash are deposited through atmospheric transport as airborne particulates to the snowpack onto the Athabasca River in the region (Kelly et al., 2009; Birks et al., 2017).

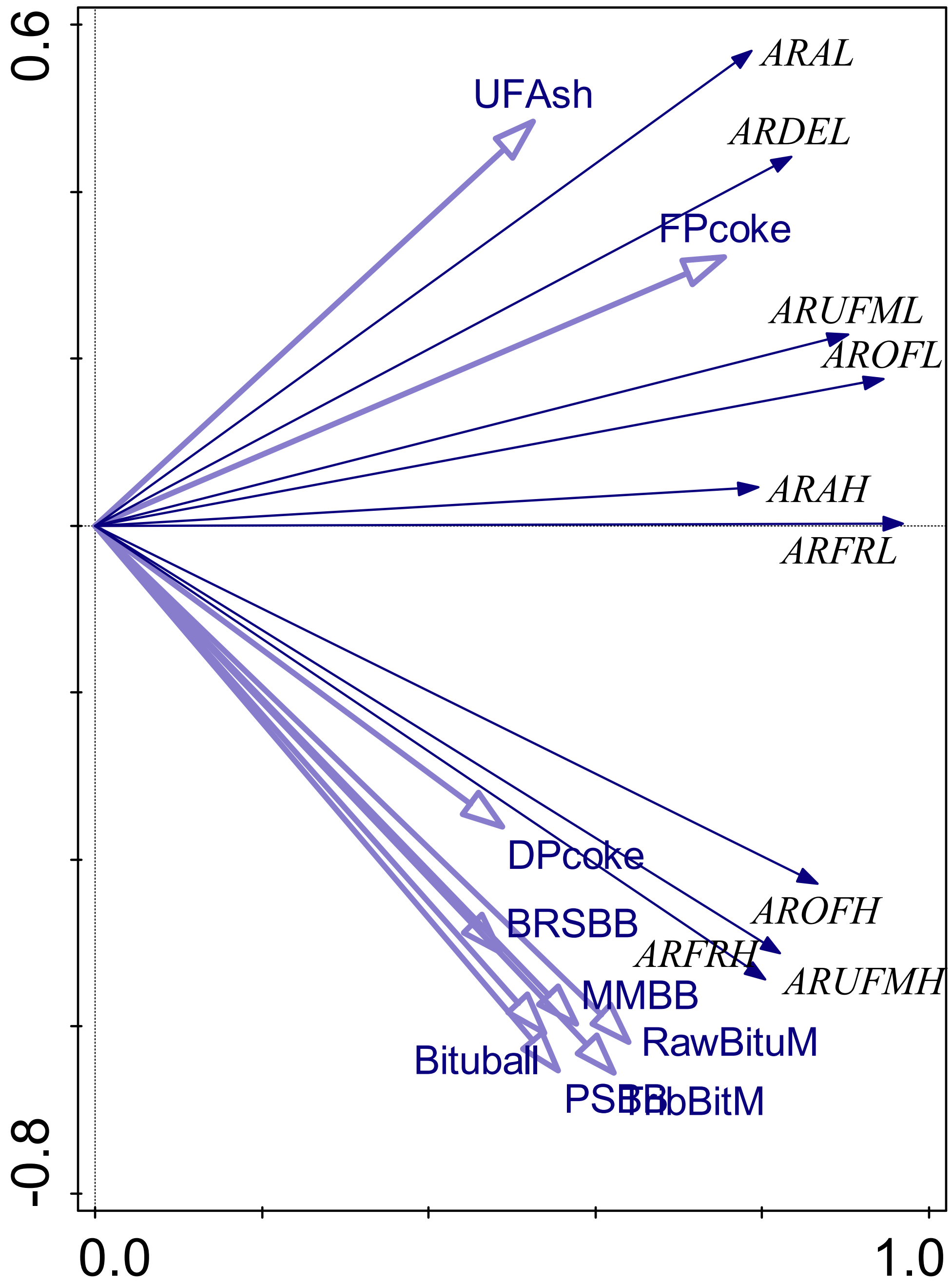

Figure 2.14. PCA analysis of PAHs in surface water from AEP water sampling stations located from upstream to downstream of the Athabasca River. Upstream – Athabasca (ARA), Upper Fort McMurray (UFM), Firebag River (FBR), Old Fort (OF) and Devil's Elbow (DE). (L: low flow. H: high flow) vs natural PAH sources: forest fire/urban ash (UFAsh), raw bitumen (RawBituM), tributary bitumen (TribBitM), McConnell mud (MMBB), prodelta sediment (PSBB), braided river sands (BRSBB), Big Bend bituballs (Bituball); Anthropogenic sources: fluid petroleum coke (FPcoke), delayed petroleum coke (DPcoke).

During periods of high discharge, water samples from the town of Athabasca (ARAH) are characterized by high PC1 scores and very low PC2 scores, which are a closer match to pyrogenic sources than petrogenic sources. In contrast, water samples collected from Fort McMurray, upstream of the Firebag River and at Old Fort during high-flow are characterized by PAH compositions that are grouped closely with the composition of raw bitumen, tributary and Big Bend sediments. Interestingly, the pyrogenic delayed petroleum coke is found to be among the petrogenic sources. Delayed petroleum coke is characterized by high abundance of PA4 (Figure 2.7c). Thus, we would predict to see an increase in the PA4/PA3 ratio downstream of the delayed petroleum coke piles that are located along the edge of the Athabasca River. Indeed, there is increase in the PA4/PA3 ratio from a ratio of ~2 at the Fort McMurray station to a ratio of ~3 at Firebag River station. These ratios are still well below that of delayed petroleum coke (~14) but the small increase may indicate the input of some delayed petroleum coke to this reach of the Athabasca River. However, overall, these low ratios suggest most of the PAHs present in the water may be ultimately derived from bitumen. The spring freshet is the key period of contaminant remobilization and transport (Hall et al., 2012). During high river flow discharge, bitumen is liberated from the McMurray Formation and may even break off as large chucks from bank slippage (Barton and Wallace, 1979; Droppo et al., 2018). This suggests high river flow discharge is responsible for in-channel erosion of bitumen from the McMurray Formation to Athabasca River, but may also include bituballs from the Big Bend site.

2.4.1. PCA Analysis of Water PAHs data in lower Athabasca River Region

Water PAH concentrations from monitoring stations (The town of Athabasca, Fort McMurray, upstream of the Firebag River, Old Fort and Devil's Elbow) along the Athabasca

River were also evaluated using a PCA on absolute concentrations to understand the compositional differences from each station during low river flow discharge and high river flow discharge (Figure A.6). During low-flow periods, PAH concentrations within the Athabasca River at Fort McMurray, Old Fort, and Devil's Elbow are grouped together on the bottom right of the biplot with no obvious PAH compound associations. This suggests water data from these monitoring stations have minimal PAH input during low-flow periods. During high-flow periods, water PAH concentrations from Fort McMurray, Firebag River and Old Fort are grouped together in the biplot with a higher abundance of PA4. The high abundance of PA4 in water from these stations also aligns with the higher abundance of PA4 observed in the petrogenic sources (raw bitumen, tributary bitumen and Big Bend bituballs; Figure 2.7d, 2.7e, and 2.7f). PA1, PA2 and PA3 which are associated with atmospheric PAH source (Figure 2.7a, 2.7b, and 2.7c) are not grouped with any monitoring stations during high-flow period. This suggests atmospheric PAH sources including urban ash/forest fire, urban petroleum coke, and delayed petroleum coke have minimal impact to the Athabasca River during high flow. The other highest PAH concentration compound DBT4 in the petrogenic source is found to not be as closely related to the water composition in Fort McMurray, Firebag river or Old Fort during high-flow. This might reflect the greater abundance of PA4 in suspended sediment relative to DBT4. As the Athabasca River travels down from Fort McMurray to the Old Fort station, the Fort McMurray station is found to have a high composition of PA4 in the biplot. Then, the PA4 concentrations decrease at the Firebag River station. The PA4 is found to be in high abundance again when the Athabasca River reached to Old Fort station. This suggests there are two major bitumen inputs in the Athabasca River during high-flow period – the in-channel erosion near Fort McMurray region, and meander bend erosion at Big Bend. PA4 could be a bitumen input indicator in the Athabasca River.

2.4.2. Water Monitor Program

The Athabasca River is monitored through Surface Water Quality Monitoring (Cooke et al., 2018) of the Oil Sands Monitoring Program (Wrona et al., 2011). Total PAHs in the Athabasca River during the high-flow period from 2016 to 2018 are depicted in figure A.7. The median PAH concentrations for the Athabasca, Fort McMurray, Firebag River, and Old Fort were 146 ng/L, 102 ng/L, 142 ng/L and 172 ng/L, respectively. The change in water PAH concentrations from the Firebag River to Old Fort increased by 30 ng/L. Downstream of the Firebag River to Big Bend, there is no other bank erosion or bitumen source between Firebag River to Old Fort except for Big Bend (Conly et al., 2002). The mean annual discharge volume of Athabasca River at Embarras is ~16,533,333 dam^3 during the high-flow period from 2016 to 2018 (07DD001, Environment Canada and Climate Change, 2021). Thus, the total PAH loading in water (Total + suspended) from Firebag River to Old Fort would be ~0.50 t. With the annual PAH loading from Big Bend is ~5.29 t, the surface water monitoring program is only able to capture less than 10 % of PAHs that are deposited to river by Big Bend. The bottom of Big Bend cliff is McConnell mud and prodelta sediment. These McConnell mud and prodelta would be directly eroded into suspension phase in Athabasca River. The annual PAH loading from McConnell mud and prodelta sediment is 0.62 t. This suggests Surface Water Quality Monitoring program is capturing what is eroded directly from McConnell mud and prodelta sediment. The PAH loading of bituballs was not detected suggesting PAH content in the bituballs did not dissolve or break off as particulates to the water phase in the river.

Approximately 88 % of the PAH load from Big Bend are derived from the bituballs horizons imbricated in the braided river sand facies. During bank erosion, Big Bend bituballs are likely deposited in the Athabasca River as large clasts of bituballs or individual bituballs as bedload. The current surface water quality program by Alberta Environment and Parks (AEP) performs grab sampling for PAH analyses from the river surface, it therefore may not capture the PAHs contributed as bedload.

The results summarized above suggest that Big Bend is an important source of both sediment and PAHs to the Athabasca River. Our revised estimate of erosions rates at Big Bend and our new data on PAH concentrations within the cutbank suggest an annual supply of ~410 kt of sediment and ~5.29 t of PAHs to the Athabasca River. This input makes Big Bend one of the most important sources of PAHs to the Athabasca River. However, the long-term fate of this material, and its availability to biota, remain unknown. Moreover, this supply is in addition to the supply of PAHs derived from mining activities within the basin. There is a large and growing body of evidence demonstrating that the extraction and processing of bitumen had led to increasing burdens of PAHs – and especially alkylated PAHs – across the region. This evidence comes in the form of both snowpack samples (Kelly et al., 2009; Manzano et al., 2016; Ahad et al., 2021), lake sediments (Kurek et al., 2013), lichen (Graney et al., 2017; Landis et al., 2019), and moss (Zhang et al., 2016). In addition, PAHs that result directly from upgrading (i.e., petroleum coke) and A predominance of alkylated PAHs is also evident in traditional foods (Golzadeh et al., 2021). In addition, PAHs supplied by petroleum coke may carry novel compounds (e.g., nitrogen heterocyclic PAHs; Chibwe et al., 2019) and new evidence suggests they can be fingerprinted in the environment using compound specific isotopic ratios (Ahad et al., 2021). Additional research is therefore clearly needed to understand spatial and temporal trends in the relative contribution of these various sources, and to investigate the fate, biological uptake, and indeed prevalence of the various PAH sources within ecosystems across the region.

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CHAPTER 3. Conclusions and future work

3.1 Summary of research

The Athabasca River cuts through the oil sands development region from Fort McMurray to the Peace-Athabasca Delta. Multiple potential anthropogenic or natural PAHs sources could increase PAH concentrations within the river. This research was conducted to: (i) characterize the composition and the concentration of PAHs within Big Bend sediments; (ii) compare Big Bend to other regional PAHs sources; (iii) determine the flux of PAHs contributed by Big Bend to the Lower Athabasca River; and (iv) determine if the input of PAHs from Big Bend can be detected from the regional surface water quality monitoring program. The main conclusions of this study are summarized as follow:

i. The PAHs profile and carbon isotope signature of Big Bend bituballs suggest they originated from the McMurray Formation. The highest PAH concentrations within Big Bend sediment are bituballs with median and mean of 75,912 ng/g and 76,518 respectively. However, bituballs PAH concentrations are lowest among other bitumen sources in the McMurray Formation of the lower Athabasca River region. The McConnell mud and prodelta sediment also have a significant amount of PAHs with median and mean of 3,861 ng/g and 5,341 ± 3,717 ng/g, and 4,053 n/g and 11,148 ± 18,092 ng/g, respectively.

ii. PAHs within Big Bend bituballs show compositional differences with pyrogenic sources fluid petroleum coke, delayed petroleum coke and forest fire/urban ash but show compositional similarities with upstream petrogenic bitumen sources raw bitumen, and tributaries bitumen. However, Big Bend bituballs can be characterized by PA4/PA3 ratio from other bitumen sources.

iii. The bank erosion of Big Bend alone contributed 5.29 t of PAHs annually to the lower Athabasca River. This makes Big Bend the largest source of PAHs to the lower Athabasca River. Much of this material is delivered to the river during periods of high discharge. Within Big Bend PAHs loading, 0.62 t of McConnell mud and prodelta sediment were eroded into suspended sediment in water phase. The 4.67 t of bituballs were likely eroded as bed sediment.

iv. The ambient surface water quality monitoring program did record a change in PAH composition suggesting a petrogenic PAH input at Big Bend, and was effective capturing the PAH loading of suspended sediment from McConnell mud and prodelta sediment at Big Bend. However, it did not capture the PAH loading of bituballs in Big Bend as most bituballs from Big Bend are likely transported as bedload.

3.2 Suggestions for future work

The erosion of Big Bend represents the largest continuous input of PAHs to the lower Athabasca River in which the potential impact to the Peace-Athabasca Delta and downstream communities are significant. Some suggestions for future work expanding off this thesis include:

i. Studying the fate of bituballs over long range transport is essential when the bituballs are transported to downstream to the Peace-Athabasca Delta, which is the largest freshwater inland river delta in North America. As the Big Bend bituballs are found to be “less sticky” than the raw bitumen, the bituballs might be more prone to break up during long range transport in the river. The Big Bend PAHs could eventually be transported as suspended sediment in water phase. The toxicity of bituballs toward aquatic life should be studied.

ii. Most PAHs from Big Bend are likely transported as bedload. Current surface water monitoring program can only detect water phase PAHs. As such, it is clear that additional sampling method to capture the bedload PAHs will be needed.

iii. The McConnel mud and prodelta sediment are contributing an annual PAH loading of ~0.62 t as suspended sediment directly to Athabasca River. The immediate impact to downstream Peace-Athabasca Delta should be evaluated.

iv. The Big Bend demonstrated natural bank erosion is one of the largest PAH sources in the lower Athabasca River. The newly estimated in-channel sediment erosion of Athabasca River from downstream of For McMurray (M3) to downstream of Ells River (M7) is estimated to be ~616 kt (Table A.7.). This is higher than original estimated ~200 kt in channel erosion between Fort McMurray to Embarras in table A.8. (Conly et al., 2002). The upstream of Athabasca River might be eroding outcrops of McMurray Formation as observed of increasing PA4/PA3 ratio between Fort McMurray to Firebag River (Figure A.5). Mapping of other in-channel bank erosion sources would be essential to identify the actual loading of the natural PAH sources to the lower Athabasca river.

v. In this study, we identified the unique weathering characteristics of PA4/PA3 ratio in bituballs which is significantly higher than raw bitumen and tributary bitumen. The PA4/PA3 ratio could be useful in identifying the input of Big Bend bituballs in the lower Athabasca River, and could be applied to the lower Athabasca River region.

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Appendix A: Supplemental Information

Table A.1. SGS AXYS Lab polycyclic aromatic hydrocarbons in solid detection limit.

PAH	Short name	Rings	Detection Limit (ng/g)
Naphthalene	N	2	0.5
C1-Naphthalenes	N1	2	1
C2-Naphthalenes	N2	2	1
C3-Naphthalenes	N3	2	1
C4-Naphthalenes	N4	2	1
Biphenyl	B	2	0.1
C1-Biphenyls	B1	2	1
C2-Biphenyls	B2	2	1
Acenaphthylene	AY	3	0.5
Acenaphthene	AE	3	0.5
C1-Acenaphthenes	AE1	3	1
Fluorene	F	3	0.5
C1-Fluorenes	F1	3	1
C2-Fluorenes	F2	2	1
C3-Fluorenes	F3	3	1
Anthracene	A	3	0.5
Phenanthrene	PA	3	0.5
C1-Phenanthrenes/Anthracenes	PA1	3	1
C2-Phenanthrenes/Anthracenes	PA2	3	1
C3-Phenanthrenes/Anthracenes	PA3	3	1
C4-Phenanthrenes/Anthracenes	PA4	3	1
Retene	RET	3	0.5
Fluoranthene	FL	4	0.5
Pyrene	PY	4	0.5
C1-Fluoranthenes/Pyrenes	FLPY1	4	1
C2-Fluoranthenes/Pyrenes	FLPY2	4	1
C3-Fluoranthenes/Pyrenes	FLPY3	4	1
C4-Fluoranthenes/Pyrenes	FLPY4	4	1
Benz[a]anthracene	BaA	4	0.5
Chrysene	C	4	0.5
C1-Benzo[a]anthracenes/Chrysenes	BaAC1	4	1
C2-Benzo[a]anthracenes/Chrysenes	BaAC2	4	1
C3-Benzo[a]anthracenes/Chrysenes	BaAC3	4	1
C4-Benzo[a]anthracenes/Chrysenes	BaAC4	4	1
Benzo[b]fluoranthene	BbF	5	0.5
Benzo[j,k]fluoranthenes	BjkF	5	0.5
Benzo[e]pyrene	BeP	5	0.5
Benzo[a]pyrene	BaP	5	0.5

C1-Benzofluoranthenes/Benzopyrenes	BFP1	5	1
C2-Benzofluoranthenes/Benzopyrenes	BFP2	5	1
Dibenz[a,h]anthracene	DA	5	0.5
Perylene	PER	5	0.5
Benzo[ghi]perylene	BghiP	6	0.5
Indeno[1,2,3-cd]pyrene	IP	6	0.5
Dibenzothiophene	DBT	3	1
C1-Dibenzothiophenes	DBT1	3	1
C2-Dibenzothiophenes	DBT2	3	1
C3-Dibenzothiophenes	DBT3	3	1
C4-Dibenzothiophenes	DBT4	3	1

Table A.2. Alberta Environment and Park water sampling site for PAHs analysis

Site Description	Matrix	Sampling Date	Latitude	Longitude
Athabasca River at Athabasca OCT2016 16SWE00124	Water	2016-10-01	54.722	-113.286
Athabasca River at Athabasca JAN2017 17SWE00003	Water	2017-01-01	54.722	-113.286
Athabasca River at Athabasca FEB2017 17SWE00016	Water	2017-02-01	54.722	-113.286
Athabasca River at Athabasca MAR2017 17SWE00025	Water	2017-03-01	54.722	-113.286
Athabasca River at Athabasca SEP2016 16SWE00116	Water	2016-09-01	54.722	-113.286
Athabasca River at Athabasca OCT2017 17SWE00084	Water	2017-10-01	54.722	-113.286
Athabasca River at Athabasca NOV2017 17SWE00108	Water	2017-11-01	54.722	-113.286
Athabasca River at Athabasca DEC2017 17SWE00115	Water	2017-12-01	54.722	-113.286
Athabasca River at Athabasca JAN2018 18SWE00004	Water	2018-01-01	54.722	-113.286
Athabasca River at Athabasca FEB2018 18SWE00022	Water	2018-02-01	54.722	-113.286
Athabasca River u/s Ft. McMurray SEP2016 16SWE00117	Water	2016-09-01	56.720	-111.406
Athabasca River u/s Ft McMurray OCT2016 16SWE00127	Water	2016-10-01	56.720	-111.406
Athabasca River u/s Ft McMurray FEB2017 17SWE00017	Water	2017-02-01	56.720	-111.406
Athabasca River u/s Ft McMurray MAR2017 17SWE00027	Water	2017-03-01	56.720	-111.406
Athabasca River u/s Ft McMurray JUN2017 17SWE00052	Water	2017-06-01	56.720	-111.406
Athabasca River u/s Ft McMurray AUG2017 17SWE00071	Water	2017-08-01	56.720	-111.406
Athabasca River u/s Ft McMurray OCT2017 17SWE00086	Water	2017-10-01	56.720	-111.406
Athabasca River u/s Ft McMurray DEC2017 17SWE00116	Water	2017-12-01	56.720	-111.406
Athabasca River u/s Ft McMurray JAN2018 18SWE00008	Water	2018-01-01	56.720	-111.406
Athabasca River u/s Ft McMurray FEB2018 18SWE00026	Water	2018-02-01	56.720	-111.406
Athabasca River u/s Firebag River-LB SEP2016 16SWE00118	Water	2016-09-01	57.724	-111.379
Athabasca River u/s Firebag River-RB SEP2016 16SWE00119	Water	2016-09-01	57.724	-111.379
Athabasca River u/s Firebag River-RB OCT2016 16SWE00130	Water	2016-10-01	57.724	-111.379
Athabasca River u/s Firebag River-LB OCT2016 16SWE00129	Water	2016-10-01	57.724	-111.379
Athabasca River u/s Firebag River - LB NOV2016 16SWE00138	Water	2016-11-01	57.724	-111.379
Athabasca River u/s Firebag River - RB NOV2016 16SWE00139	Water	2016-11-01	57.724	-111.379
Athabasca River u/s Firebag River-RB FEB2017 17SWE00019	Water	2017-02-01	57.724	-111.379
Athabasca River u/s Firebag River-LB FEB2017 17SWE00018	Water	2017-02-01	57.724	-111.379
Athabasca River u/s Firebag River -RB APR2017 17SWE00037	Water	2017-04-01	57.724	-111.379
Athabasca River u/s Firebag River - RB JUN2017 17SWE00055	Water	2017-06-01	57.724	-111.379
Athabasca River u/s Firebag River - RB AUG2017 17SWE00072	Water	2017-08-01	57.724	-111.379
Athabasca River u/s Firebag River-RB OCT2017 17SWE00088	Water	2017-10-01	57.724	-111.379
Athabasca River u/s Firebag River - RB NOV2017 17SWE00111	Water	2017-11-01	57.724	-111.379
Athabasca River u/s Firebag River - RB DEC2017 17SWE00117	Water	2017-12-01	57.724	-111.379
Athabasca River u/s Firebag River - RB JAN2018 18SWE00011	Water	2018-01-01	57.724	-111.379
Athabasca River u/s Firebag River - RB FEB2018 18SWE00029	Water	2018-02-01	57.724	-111.379
Athabasca River u/s Firebag River - RB MAR2018 18SWE00042	Water	2018-03-01	57.724	-111.379
Athabasca River at Old Fort SEP2016 16SWE00120	Water	2016-09-01	58.328	-111.518
Athabasca River at Old Fort OCT2016 16SWE00132	Water	2016-10-01	58.328	-111.518
Athabasca River at Old Fort NOV2016 16SWE00140	Water	2016-11-01	58.328	-111.518
Athabasca River at Old Fort FEB2017 17SWE00020	Water	2017-02-01	58.328	-111.518
Athabasca River at Old Fort JUN2017 17SWE00056	Water	2017-06-01	58.328	-111.518
Athabasca River at Old Fort OCT2017 17SWE00090	Water	2017-10-01	58.328	-111.518
Athabasca River at Old Fort AUG2017 17SWE00073	Water	2017-08-01	58.328	-111.518
Athabasca River at Old Fort NOV2017 17SWE00112	Water	2017-11-01	58.328	-111.518
Athabasca River at Old Fort DEC2017 17SWE00118	Water	2017-12-01	58.328	-111.518
Athabasca River at Old Fort JAN2018 18SWE00012	Water	2018-01-01	58.328	-111.518
Athabasca River at Old Fort MAR2018 18SWE00043	Water	2018-03-01	58.328	-111.518
Athabasca River d/s Devil's Elbow FEB2017 17SWE00022	Water	2017-02-01	58.447	-111.186
Athabasca River d/s Devil's Elbow DEC2017 17SWE00119	Water	2017-12-01	58.447	-111.186
Athabasca River d/s Devil's Elbow JAN2018 18SWE00013	Water	2018-01-01	58.447	-111.186
Athabasca River d/s Devil's Elbow MAR2018 18SWE00044	Water	2018-03-01	58.447	-111.186

Table A.3. Samples submitted for PAHs analysis at SGS AXYS Laboratory – Forest fire/urban ash, petroleum coke, tributary bitumen and raw bitumen

Site Description	Matrix	Sampling Date	Latitude	Longitude
RAC	Urban Ash	2016-04-12	56.726	-111.392
YAC	Urban Ash	2016-04-12	56.725	-111.390
YBC	Urban Ash	2016-04-12	56.703	-111.360
YWC	Urban Ash	2016-04-12	56.702	-111.345
Unnamed Creek ~1km d/s M3	Forest Fire Ash	2016-05-11	56.838	-111.411
Hangingstone River ~2km u/s Mouth	Forest Fire Ash	2016-05-12	56.679	-111.362
Hangingstone ~1km u/s Mouth	Forest Fire Ash	2016-05-12	56.704	-111.374
Horse River Near Mouth	Forest Fire Ash	2016-05-12	56.710	-111.399
Clearwater River at WSC Gauge near Draper	Forest Fire Ash	2016-05-12	56.685	-111.256
Christina River above Confluence with Clearwater River	Forest Fire Ash	2016-05-12	56.664	-111.055
NW Timberlea in Fort McMurray	Forest Fire Ash	2016-05-12	56.763	-111.480
Athabasca River ~2km u/s M3	Forest Fire Ash	2016-05-13	56.815	-111.407
Athabasca River below Fort McMurray	Forest Fire Ash	2016-05-13	56.780	-111.402
Athabasca River 2km u/s of golf course	Forest Fire Ash	2016-05-13	56.694	-111.453
Clearwater River ~3km u/s Mouth	Forest Fire Ash	2016-05-13	56.692	-111.293
Petroleum coke from John Martin	Fluid Petroleum Coke	Unknown	Unknown	Unknown
Petroleum coke CNRL	Delayed Petroleum Coke	Unknown	Unknown	Unknown
Petroleum coke Suncor	Delayed Petroleum Coke	Unknown	Unknown	Unknown
Steepbank River approx. 10km u/s WSC Gauge	Tributary Bitumen	2016	56.980	-111.299
Steepbank River	Tributary Bitumen	2016	N/A	N/A
Ells River	Tributary Bitumen	2016	N/A	N/A
Steepbank River Oil Sand – East bank	Tributary Bitumen	Unknown	Unknown	Unknown
Steepbank River Oil Sand – West bank	Tributary Bitumen	Unknown	Unknown	Unknown
Muskeg River u/s Jackpine Creek	Raw Bitumen	2018	57.264	-111.473
Fort McMurray Surface Mining Site	Raw Bitumen	Unknown	Unknown	Unknown
Fort McMurray Surface Mining Site	Raw Bitumen	Unknown	Unknown	Unknown
Fort McMurray Surface Mining Site Suncor	Raw Bitumen	Unknown	Unknown	Unknown
Fort McMurray Surface Mining Site CNRL	Raw Bitumen	Unknown	Unknown	Unknown
Oil Sand from Under Water	Raw Bitumen	Unknown	Unknown	Unknown

Table A.4. Big Bend samples analyzed for polycyclic aromatic hydrocarbons at SGS AXYS Laboratory.

Site ID	Sampling Height (m.a.r.l)	AXYS Lab ID	Sediment Unit	Sampling Date	Latitude	Longitude	∑ PAHs (ng/g)
LAR1	1	L30298-1	McConnell Muds	2016-07-30	58.252	-111.414	3727
LAR1	3	L30298-2	McConnell Muds	2016-07-30	58.252	-111.414	3081
LAR1	4	L30298-3	McConnell Muds	2016-07-30	58.252	-111.414	3313
LAR1	5	L30298-4	Prodelta Sediment	2016-07-30	58.252	-111.414	5710
LAR1	6	L30298-5	Prodelta Sediment	2016-07-30	58.252	-111.414	2332
LAR1	7	L30298-6	Prodelta Sediment	2016-07-30	58.252	-111.414	2739
LAR2	3	L30298-18	Braided River Sands	2016-07-31	58.255	-111.419	4832
LAR2	6	L30299-4	Braided River Sands	2016-07-31	58.255	-111.419	28894
LAR2	7	L30298-19	Braided River Sands	2016-07-31	58.255	-111.419	509
LAR2	9	L30299-5	Braided River Sands	2016-07-31	58.255	-111.419	49462
LAR2	11	L30298-20	Braided River Sands	2016-07-31	58.255	-111.419	17
LAR2	14	L30298-21	Braided River Sands	2016-07-31	58.255	-111.419	13
LAR2	15	L30299-6	Braided River Sands	2016-07-31	58.255	-111.419	7799
LAR2	17	L30298-22	Braided River Sands	2016-07-31	58.255	-111.419	8
LAR4	1	L27373-3	McConnell Muds	2016-07-31	58.257	-111.432	2454
LAR4	2	L27373-4	McConnell Muds	2016-07-31	58.257	-111.432	3995
LAR4	3	L27373-5	Braided River Sands	2016-07-31	58.257	-111.432	188028
LAR4	5	L27373-6	Braided River Sands	2016-07-31	58.257	-111.432	110323
LAR4	6	L27373-7	Braided River Sands	2016-07-31	58.257	-111.432	110841
LAR4	7	L30298-23	Braided River Sands	2016-07-31	58.257	-111.432	55
LAR4	9	L30298-24	Braided River Sands	2016-07-31	58.257	-111.432	591
LAR4	11	L27373-8	Braided River Sands	2016-07-31	58.257	-111.432	78
LAR4	14	L30298-25	Braided River Sands	2016-07-31	58.257	-111.432	44
LAR4	16	L27373-9	Braided River Sands	2016-07-31	58.257	-111.432	266
LAR4	17	L30298-26	Braided River Sands	2016-07-31	58.257	-111.432	63
LAR4	19	L27373-10	Braided River Sands	2016-07-31	58.257	-111.432	29
LAR5	3	L30298-7	McConnell Muds	2017-10-13	58.253	-111.415	13362
LAR5	4	L30298-8	McConnell Muds	2017-10-13	58.253	-111.415	4371
LAR5	5	L30298-9	McConnell Muds	2017-10-13	58.253	-111.415	8421
LAR5	5.5	L30298-10	Prodelta Sediment	2017-10-13	58.253	-111.415	47998
LAR5	7.5	L30298-11	Prodelta Sediment	2017-10-13	58.253	-111.415	4140
LAR5	9	L30298-12	Prodelta Sediment	2017-10-13	58.253	-111.415	3966
LAR5	10	L30299-1	Braided River Sands	2017-10-13	58.253	-111.415	102363
LAR5	11.5	L30298-13	Braided River Sands	2017-10-13	58.253	-111.415	236
LAR5	13.5	L30298-14	Braided River Sands	2017-10-13	58.253	-111.415	35
LAR5	15.5	L30298-15	Braided River Sands	2017-10-13	58.253	-111.415	3
LAR5	17.5	L30299-2	Braided River Sands	2017-10-13	58.253	-111.415	680
LAR5	18.5	L30298-16	Braided River Sands	2017-10-13	58.253	-111.415	14
LAR5	19.5	L30299-3	Braided River Sands	2017-10-13	58.253	-111.415	735
LAR5	20.5	L30298-17	Braided River Sands	2017-10-13	58.253	-111.415	3

Table A.5. Polycyclic aromatic hydrocarbon concentrations for regional sources

Regional PAH Sources	n	Mean ∑ Parent PAHs (ng/g)	Mean ∑ Alkylated PAHs (ng/g)	Mean ∑ Dibenzothiophenes (DBTs) (ng/g)	Mean ∑ PAH (ng/g)	Standard deviation ∑ PAH (ng/g)
Forest Fire/Urban Ash	15	5285	5381	61	10666	8866
Fluid Petroleum coke	1	134	479	132	613	N/A
Delayed Petroleum coke	2	115623	805767	169400	921391	528038
Raw Bitumen	6	13132	370146	159263	383278	50756
Tributary Bitumen	5	7897	207844	65758	215741	83840
Big Bend Bituballs	10	3607	72911	18376	76518	68846

Table A.6. Samples analyzed for stable isotopes at BASL Laboratory.

Site ID	Sample Height (m.a.r.l)	Sediment Unit	Sampling Date	Sample Matrix	$\delta^{13}C$ (‰)
LAR1	13	Braided River Sand	2016-07-30	Bituballs	-28.9
LAR1	15	Braided River Sand	2016-07-30	Bituballs	-28.9
LAR1	18	Braided River Sand	2016-07-30	Bituballs	-30.0
LAR2	6	Braided River Sand	2016-07-31	Bituballs	-28.7
LAR2	9	Braided River Sand	2016-07-31	Bituballs	-29.0
LAR2	10	Braided River Sand	2016-07-31	Bituballs	-29.0
LAR3	5	Braided River Sand	2016-07-31	Bituballs	-29.7
LAR3	10	Braided River Sand	2016-07-31	Bituballs	-29.1
LAR3	11	Braided River Sand	2016-07-31	Bituballs	-28.9
LAR3	12	Braided River Sand	2016-07-31	Bituballs	-28.9
LAR4	3	Braided River Sand	2016-07-31	Bituballs	-28.9
LAR4	6	Braided River Sand	2016-07-31	Bituballs	-27.4
LAR4	10	Braided River Sand	2016-07-31	Bituballs	-29.5
LAR4	18	Braided River Sand	2016-07-31	Bituballs	-29.6
LAR5	10	Braided River Sand	2017-10-13	Bituballs	-29.7
LAR5	17.5	Braided River Sand	2017-10-13	Bituballs	-29.3
LAR5	19.5	Braided River Sand	2017-10-13	Bituballs	-29.7
				Mean	-29.1
				Standard deviation	0.6

Table A.7. TSS Loading from 2012 to 2014 for lower Athabasca River (Yi, 2019).

Total Suspended Sediment (TSS) Loading (2012-2014)	
Athabasca River net sediment load	**Sediment Load kt**
Athabasca River at Fort McMurray (M3)	4540
Athabasca River at Firebag River (M7)	3800
Difference	740
Firebag River (downstream of M7)	28
Big Bend at Embarras	410
Net load from Fort McMurray (M3) to Big Bend	1178
Tributaries	
Steepbank River	23
Muskeg River	1
MacKay River	53
Ells River	47
Total tributaries input from M3 to M7	124
Firebag River (downstream of M7)	28
Net tributaries load	152
Net balance in-channel erosion (excluding tributaries)	1026
In-channel erosion from M3 to M7 (excluding tributaries)	616

Table A.8. TSS Loading from 1976 to 1984 for lower Athabasca River (Conly et al., 2002).

Total Suspended Sediment (TSS) Loading (1976-1984)	
Athabasca River mainstem stations	**Sediment Load kt**
Athabasca River at Embarras (EM)	6350
Athabasca River at upstream Fort McMurray (UFM)	5180
Difference	1170
Tributaries	
Clearwater River at Draper	410
Other tributaries	210
Total tributaries input	620
Net balance in-channel erosion (excluding tributaries)	550
Big Bend at Embarras	350
In-channel erosion excluding Big Bend	200

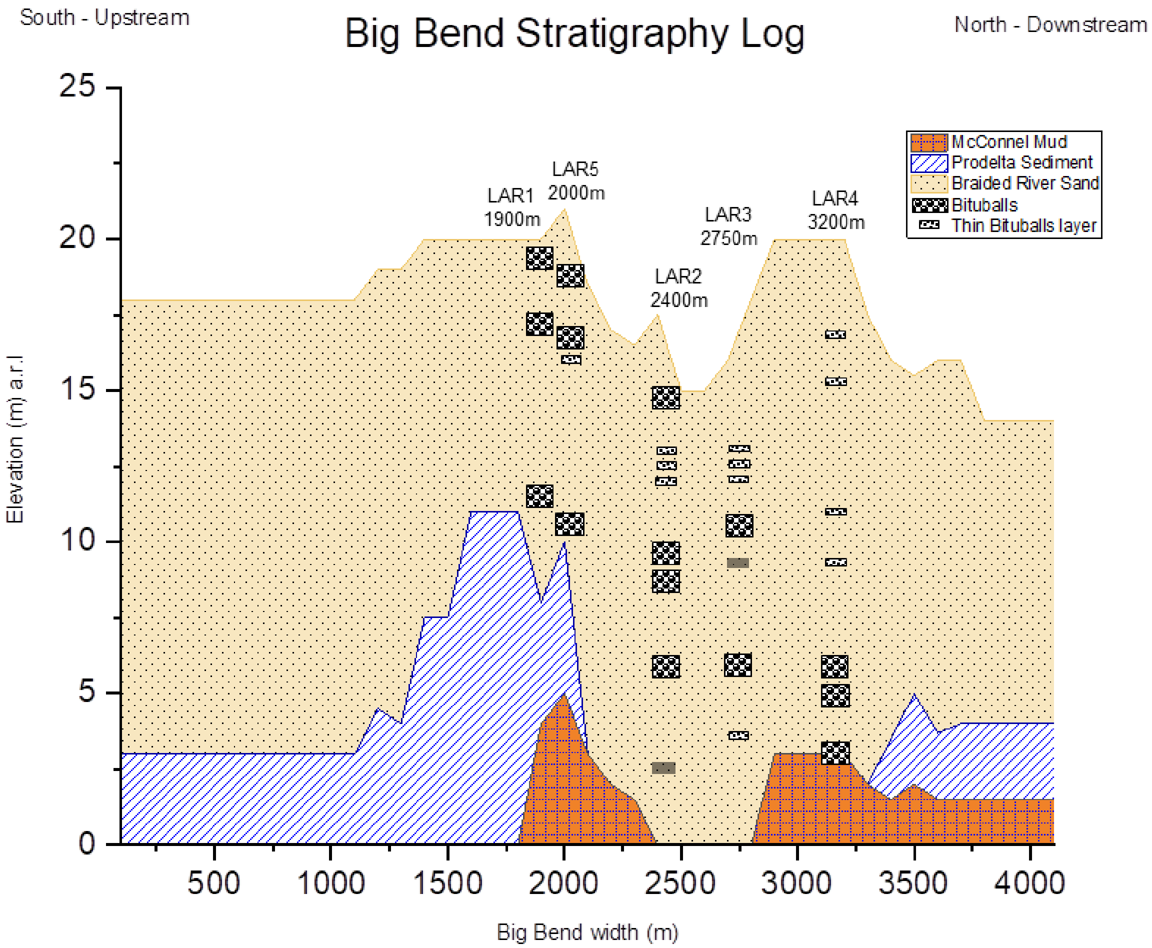

Figure A.1. Big Bend stratigraphy log. Bituball distrbutions are shown for the sampling sites LAR1 to LAR5.

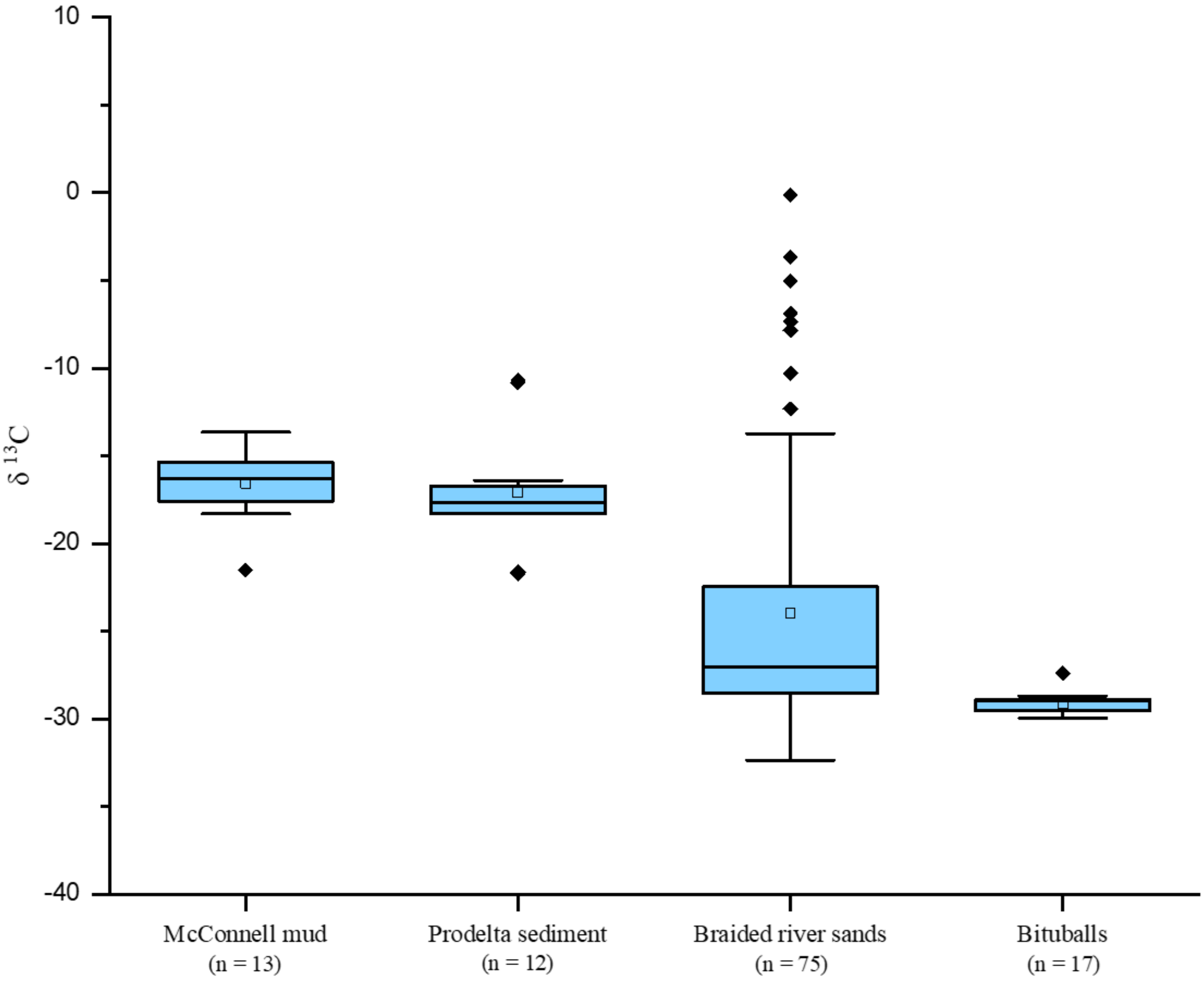

Figure A.2. Carbon isotope ratio of McConnell mud, prodelta sediment, braided river sands, and Big Bend bituballs

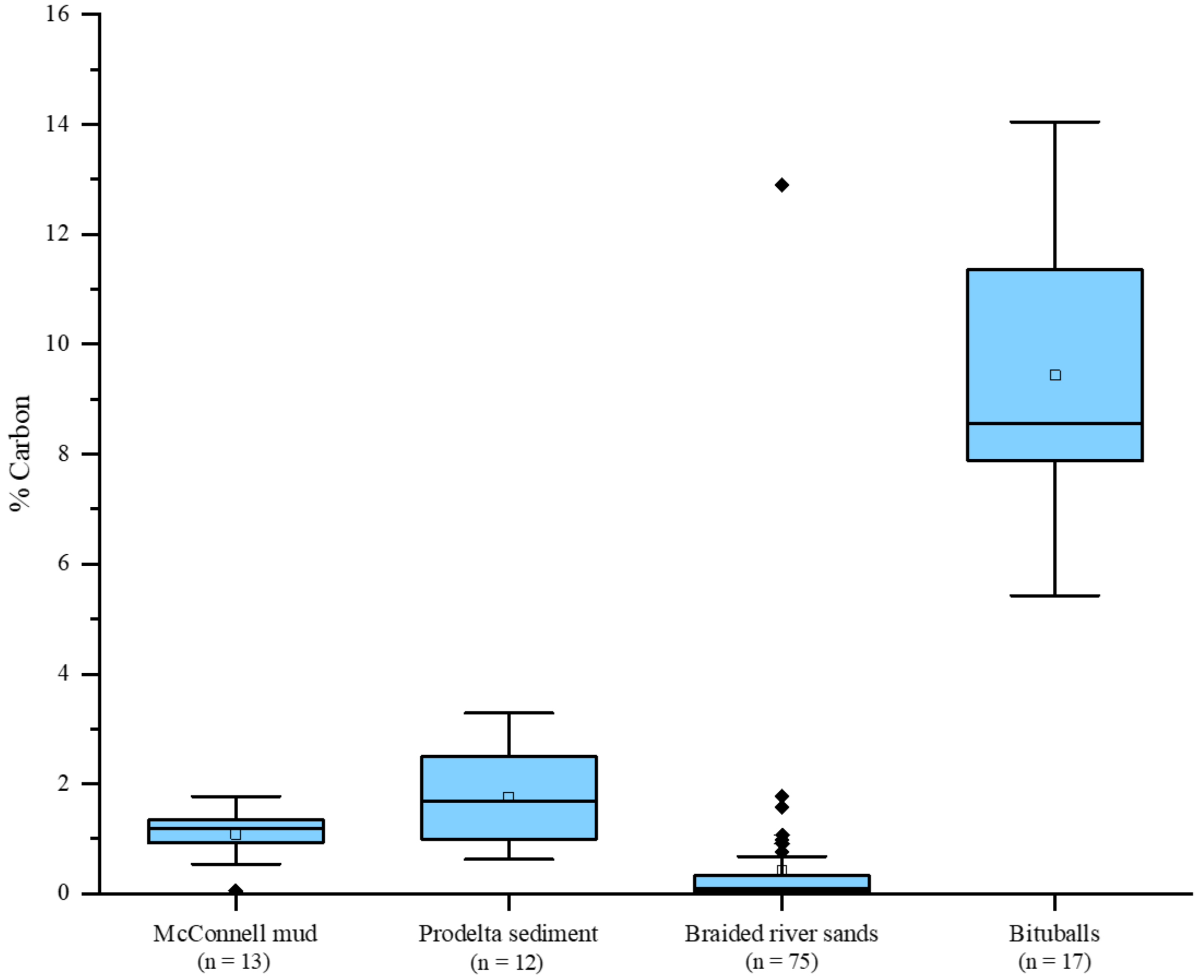

Figure A.3. Carbon content of McConnell mud, prodelta sediment, braided river sands, and Big Bend bituballs

Figure A.4. Big Bend bituballs divided in half.

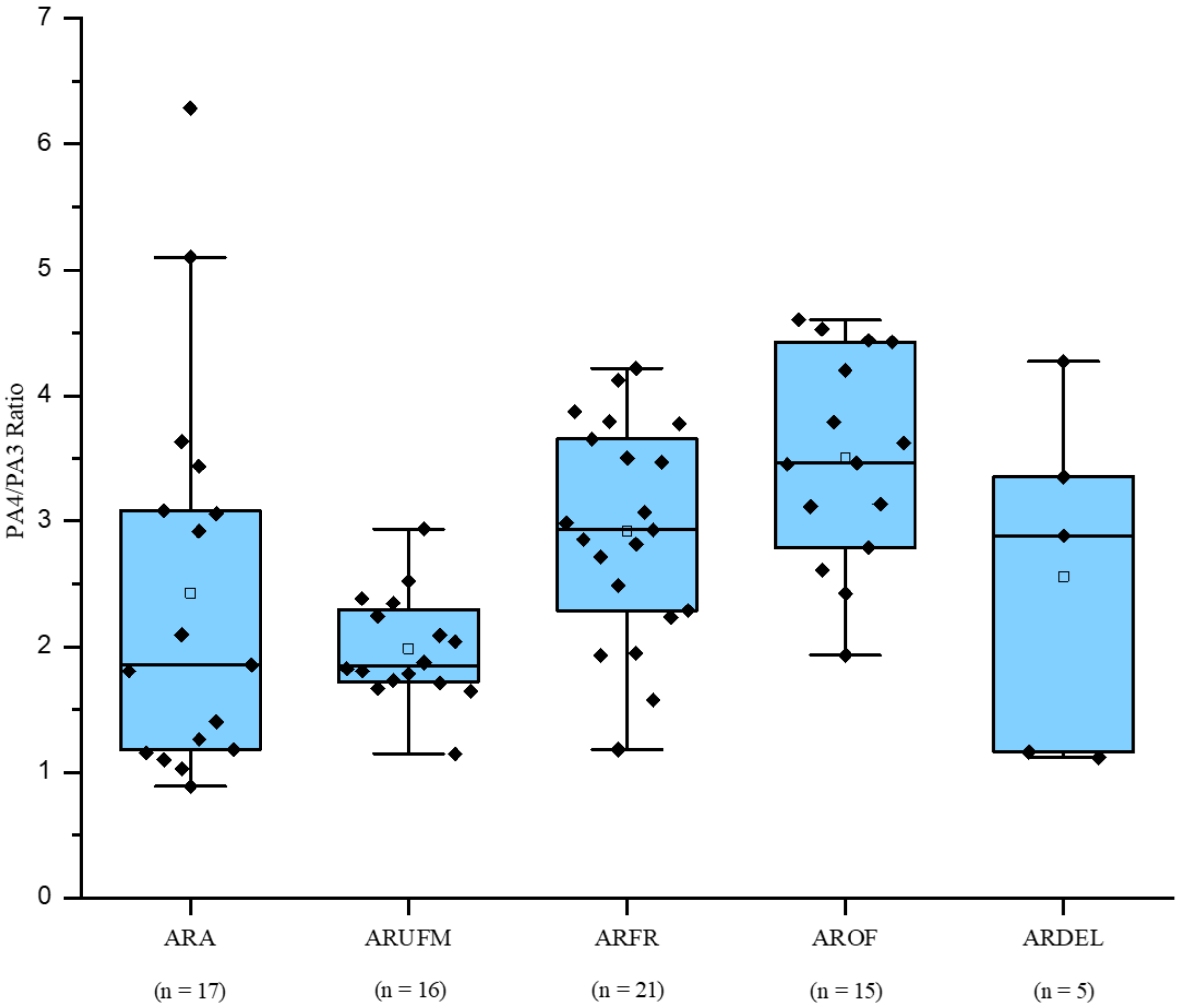

Figure A.5. PA4/PA3 ratio for Athabasca River during high flow period.ARA - town of Athabasca, ARUFM - Upper Fort McMurray, ARFR - Firebag River, AROF - Old Fort, AR-DE – Devil's Elbow

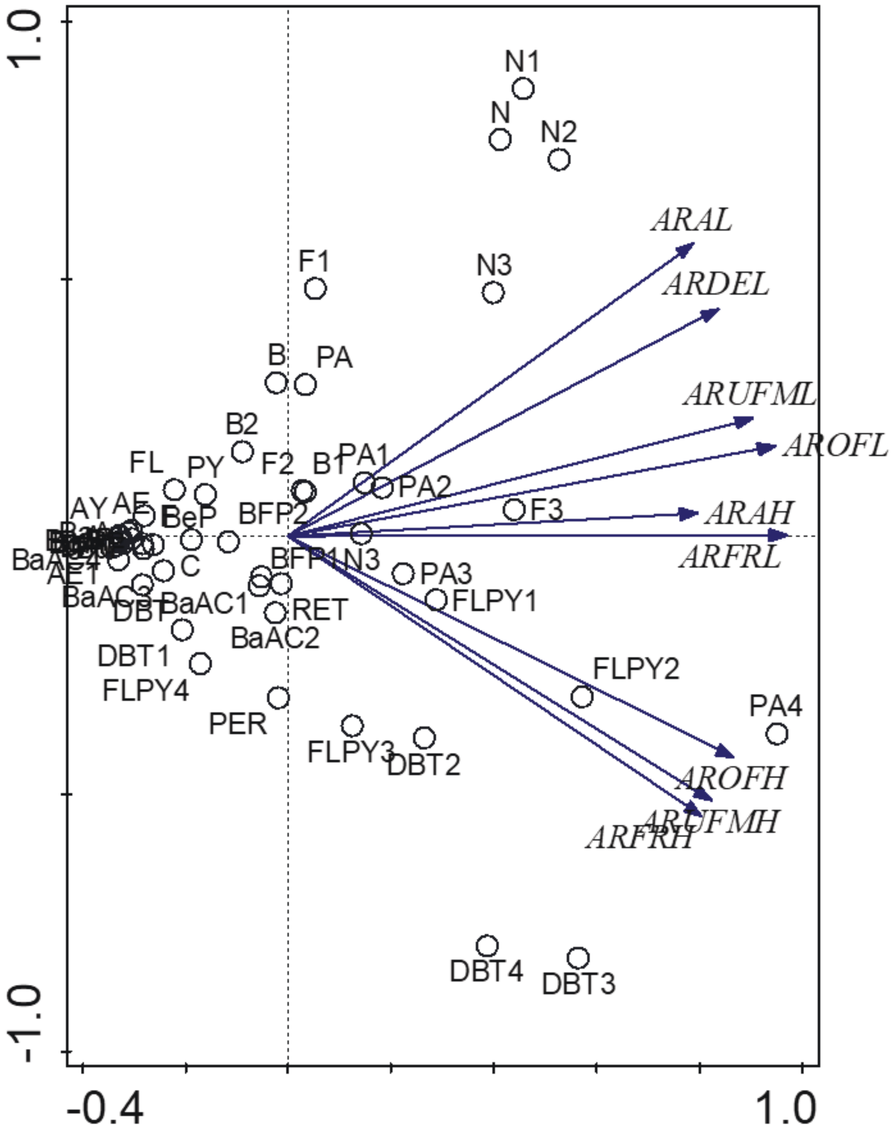

Figure A.6. PCA analysis of Athabasca River. ARA - town of Athabasca, ARUFM - Upper Fort McMurray, ARFR - Firebag River, AROF - Old Fort, AR-DE – Devil's Elbow. The data are further divided into lowe period (L) and high flow period (H)

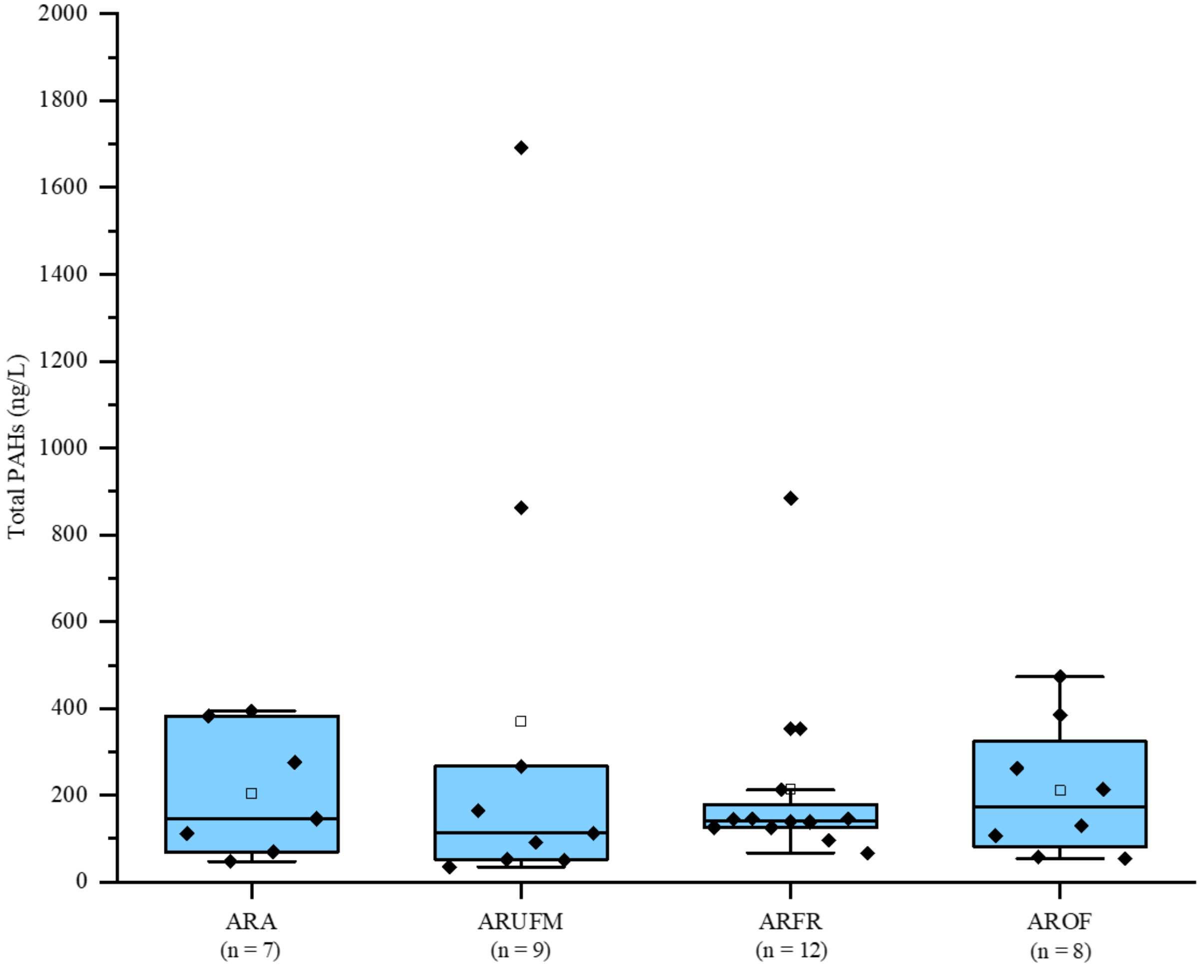

Figure A.7. Total Polycyclic aromatic hydrocarbons in water for Athabasca River during high flow period. ARA - town of Athabasca, ARUFM - Upper Fort McMurray, ARFR - Firebag River, AROF - Old Fort

Appendix B: Quality Control

Table B.1. Results of 7 method blanks, including the percent of samples in which the conger was detected and mean values of those detections for each conger.

Conger	% detected	Mean concentration of detects (ng/g)	Standard deviation (ng/g)
Naphthalene	71	1.6	1.6
C1-Naphthalenes	57	0.7	0.5
C2-Naphthalenes	43	1.4	0.7
C3-Naphthalenes	43	1.2	1.5
C4-Naphthalenes	14	3.3	-
Biphenyl	86	0.7	0.8
C1-Biphenyls	43	2.7	3.3
C2-Biphenyls	86	8.4	15.1
Acenaphthylene	14	0.2	-
Acenaphthene	14	0.3	-
C1-Acenaphthenes	0	-	-
Fluorene	29	0.2	0.0
C1-Fluorenes	0	-	-
C2-Fluorenes	14	0.3	-
C3-Fluorenes	14	4.7	-
Anthracene	29	0.3	0.3
Phenanthrene	86	0.7	0.6
C1 Phenanthrenes/Anthracenes	0	-	-
C2 Phenanthrenes/Anthracenes	57	0.4	0.3
C3-Phenanthrenes/Anthracenes	29	0.3	0.2
C4-Phenanthrenes/Anthracenes	0	-	-
Retene	14	0.1	-
Fluoranthene	100	0.3	0.3
Pyrene	100	0.3	0.3
C1-Fluoranthenes/Pyrenes	14	0.4	-
C2-Fluoranthenes/Pyrenes	0	-	-
C3-Fluoranthenes/Pyrenes	0	-	-
C4-Fluoranthenes/Pyrenes	0	-	-
Benz[a]anthracene	57	0.2	0.1
Chrysene	100	0.2	0.2
C1-Benzo[a]anthracenes/Chrysenes	14	0.5	-
C2-Benzo[a]anthracenes/Chrysenes	14	0.2	-
C3-Benzo[a]anthracenes/Chrysenes	0	-	-
C4-Benzo[a]anthracenes/Chrysenes	0	-	-
Benzo[b]fluoranthene	0	-	-
Benzo[j,k]fluoranthenes	0	-	-
Benzo[e]pyrene	0	-	-
Benzo[a]pyrene	0	-	-
C1-Benzofluoranthenes/Benzopyrenes	0	-	-
C2-Benzofluoranthenes/Benzopyrenes	14	1.0	-

Perylene	0	-	-
Dibenz[a,h]anthracene	57	0.6	0.6
Indeno[1,2,3-cd]pyrene	71	0.7	0.6
Benzo[ghi]perylene	14	0.6	-
Dibenzothiophene	29	0.5	0.3
C1-Dibenzothiophenes	14	0.6	-
C2-Dibenzothiophenes	57	1.6	1.3
C3-Dibenzothiophenes	29	0.5	0.3
C4-Dibenzothiophenes	14	0.3	-

Table B.2. Results of 4 duplicates, including the mean relative percent difference (RPD) for each conger.

Conger	Mean RPD (%)	Standard deviation (%)
Naphthalene	17.6	22.6
C1-Naphthalenes	11.5	13.7
C2-Naphthalenes	24.4	31.4
C3-Naphthalenes	25.3	37.3
C4-Naphthalenes	31.1	35.8
Biphenyl	10.8	11.3
C1-Biphenyls	10.3	7.5
C2-Biphenyls	10.2	2.6
Acenaphthylene	-	-
Acenaphthene	2.3	1.8
C1-Acenaphthenes	6.7	4.4
Fluorene	14.1	8.2
C1-Fluorenes	15.2	13.3
C2-Fluorenes	14.2	16.8
C3-Fluorenes	15.6	20.7
Anthracene	-	-
Phenanthrene	15.0	4.9
C1 Phenanthrenes/Anthracenes	24.4	30.9
C2 Phenanthrenes/Anthracenes	19.8	25.9
C3-Phenanthrenes/Anthracenes	10.4	14.3
C4-Phenanthrenes/Anthracenes	13.0	9.1
Retene	17.3	19.3
Fluoranthene	20.6	25.8
Pyrene	9.0	10.8
C1-Fluoranthenes/Pyrenes	11.7	9.5
C2-Fluoranthenes/Pyrenes	11.5	6.5
C3-Fluoranthenes/Pyrenes	12.4	8.2
C4-Fluoranthenes/Pyrenes	16.5	11.4
Benz[a]anthracene	28.2	32.9
Chrysene	10.2	11.4
C1-Benzo[a]anthracenes/Chrysenes	11.5	15.4
C2-Benzo[a]anthracenes/Chrysenes	11.4	14.7
C3-Benzo[a]anthracenes/Chrysenes	13.4	9.9
C4-Benzo[a]anthracenes/Chrysenes	17.9	25.8
Benzo[b]fluoranthene	11.4	13.4
Benzo[j,k]fluoranthenes	14.3	20.5
Benzo[e]pyrene	7.0	6.0
Benzo[a]pyrene	25.3	32.6
C1-Benzofluoranthenes/Benzopyrenes	7.0	6.5
C2-Benzofluoranthenes/Benzopyrenes	10.1	4.0
Perylene	30.9	49.5
Dibenz[a,h]anthracene	12.7	7.0
Indeno[1,2,3-cd]pyrene	6.7	8.1

Benzo[ghi]perylene	3.9	3.0
Dibenzothiophene	7.5	5.3
C1-Dibenzothiophenes	19.0	31.9
C2-Dibenzothiophenes	13.9	16.8
C3-Dibenzothiophenes	17.3	21.7
C4-Dibenzothiophenes	8.2	10.1

Table B.3. Results of 7 matrix spikes, including the mean percent of recovery for each conger.

Conger	Mean percent of recovery (%)	Standard deviation (%)
Naphthalene	94.6	3.4
C1-Naphthalenes	-	-
C2-Naphthalenes	-	-
C3-Naphthalenes	-	-
C4-Naphthalenes	-	-
Biphenyl	100.6	4.6
C1-Biphenyls	-	-
C2-Biphenyls	-	-
Acenaphthylene	99.1	2.1
Acenaphthene	102.6	7.0
C1-Acenaphthenes	99.1	-
Fluorene	77.1	6.6
C1-Fluorenes	-	-
C2-Fluorenes	-	-
C3-Fluorenes	-	-
Anthracene	99.7	3.3
Phenanthrene	100.8	2.3
C1 Phenanthrenes/Anthracenes	-	-
C2 Phenanthrenes/Anthracenes	-	-
C3-Phenanthrenes/Anthracenes	112.0	-
C4-Phenanthrenes/Anthracenes	-	-
Retene	99.5	12.3
Fluoranthene	100.1	3.9
Pyrene	99.3	3.6
C1-Fluoranthenes/Pyrenes	-	-
C2-Fluoranthenes/Pyrenes	-	-
C3-Fluoranthenes/Pyrenes	-	-
C4-Fluoranthenes/Pyrenes	-	-
Benz[a]anthracene	101.3	3.4
Chrysene	101.3	3.3
C1-Benzo[a]anthracenes/Chrysenes	-	-
C2-Benzo[a]anthracenes/Chrysenes	-	-
C3-Benzo[a]anthracenes/Chrysenes	-	-
C4-Benzo[a]anthracenes/Chrysenes	-	-
Benzo[b]fluoranthene	99.1	3.6
Benzo[j,k]fluoranthenes	102.2	3.3
Benzo[e]pyrene	104.3	5.7
Benzo[a]pyrene	101.8	2.7
C1-Benzofluoranthenes/Benzopyrenes	-	-
C2-Benzofluoranthenes/Benzopyrenes	-	-
Perylene	102.2	3.0
Dibenz[a,h]anthracene	101.7	3.4
Indeno[1,2,3-cd]pyrene	100.9	3.5
Benzo[ghi]perylene	101.5	2.5

Dibenzothiophene	100.6	3.2
C1-Dibenzothiophenes	-	-
C2-Dibenzothiophenes	-	-
C3-Dibenzothiophenes	-	-
C4-Dibenzothiophenes	-	-