Tracking the history of Alberta oil sands contaminants using lake sediment cores

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Abstract

Petroleum hydrocarbons are emitted into the environment *via* natural and anthropogenic activities. Once emitted, these hydrocarbons can be transported globally, persisting and accumulating in aquatic ecosystems. In the Alberta oil sands region (AOSR), mining activities have significantly altered and polluted the surrounding aquatic and terrestrial environments with heavy metals and various petroleum hydrocarbons including polycyclic aromatic hydrocarbons (PACs). Though PACs have been tracked through time using dated lake sediment cores, separating natural and anthropogenic PACs can be difficult. In the Peace Athabasca Delta (PAD) this task is especially difficult as this region has been receiving annual inputs of naturally eroded bitumen throughout history. Petroleum biomarkers are unique petrogenic compounds (i.e. derived from petroleum) which may provide a secondary proxy to track mining impacts.

This thesis investigated the impacts of mining activities on the AOSR and the PAD using two different proxies, PAC and petroleum biomarkers. These two regions were compared to reference lakes to the south and northwest of the Athabasca oil sands formation, in order to provide a natural signal, with minimal oil sands mining contamination. Historically deposited PACs and petroleum biomarkers were analysed in radiometrically dated lake sediment cores from the AOSR and the PAD, Alberta. Sediment profiles in the AOSR (Saline Lake) showed increases in PAC fluxes for both alkylated and parent compounds coeval with mining activities. Alkylated PAC fluxes in reference lakes (Mariana Lake and BM11) increased at the height of oil sands development (1990s). PAD lakes showed no statistical increase in PAC flux through time due to high levels of naturally eroded bitumen entering the system. Parent PAC diagnostic ratios, however, showed clear shifts from pyrogenic (primarily wood burning) in pre-development sediments to petrogenically derived PACs in modern sediments, in both AOSR and PAD lakes,

coeval with oil sands development. Petroleum biomarker diagnostic ratios in Saline Lake and PAD lakes remained stable through time, indicating a clear current and historical petroleum signal originating from the AOSR. Reference lakes (Mariana Lake and BM11) showed the greatest change in petroleum biomarkers. Historically, these lakes had signatures uncommon of petroleum sources, however, in recent years petroleum inputs from mining development were revealed by these petroleum biomarkers. This study compared the historical trends of several petroleum hydrocarbons in lake sediment to the historical emissions of these petroleum hydrocarbons from oil sands mining operations. Notably, we show the potential for petroleum biomarkers to trace petroleum hydrocarbon contamination in the environment.

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List of Abbreviations

AOS – Alberta Oil Sands

AOSR – Alberta Oil Sands Region

b/d – Barrels per day

BghiP - Benzo(ghi)perylene

CAPP – Canadian Association of Petroleum Producers

CEQGs – Canadian Environmental Quality Guidelines

CRS – Constant Rate of Supply

DCM - Dichloromethane

ECCC – Environment and Climate Change Canada

EROD - Ethoxy resorufin-O-deethylase

Fla – Fluoranthene

GAM - Gammacerane

GC-MS – Gas Chromatography coupled with Mass Spectrometry

HMW – High Molecular Weight

HPLC – High-Performance Liquid Chromatography

IcdP - Indeno(1,2,3-cd)pyrene

JOSM – Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring

LMW – Low Molecular Weight

PAC – Polycyclic Aromatic Compound

PAD – Peace Athabasca Delta

PAH – Polycyclic Aromatic Hydrocarbon

PCA – Principle Component Analysis

PCR – Polymerase Chain Reaction

Py – Pyrene

TMP - Trimethlypentane

TOC – Total Organic Carbon

UNESCO – United Nations Educational, Scientific and Cultural Organization

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Preface

This thesis is written as a manuscript in accordance to the guidelines provided by the University of Ottawa's Faculty of Graduate and Postdoctoral Studies. Chapter 1 is an introduction to this thesis and provides the necessary background for the manuscript to follow, as well as the primary objective, hypothesis, and predictions of this thesis. Chapter 2 includes a brief introduction, methods, results, and discussion, and is formatted in accordance to Elsevier's guidelines for authors provided by the journal of Environmental Pollution. Chapter 3 summarizes the manuscript and provides concluding remarks and future directions for this research.

Statement of contributions

Chapter 2: Tracking the history of Alberta oil sands contaminants using lake sediment cores

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Chapter 1. General Introduction

1.1 The Peace-Athabasca Delta, Alberta, Canada

The Peace Athabasca Delta (PAD) is the World's largest inland freshwater boreal delta, located in northeastern Alberta, spanning over 6000 km^2 of rivers, channels, lakes, ponds, wetlands, grasslands and boreal forest. The PAD is one of Canada's 15 UNESCO World Heritage Sites, providing an important ecological service to the surrounding area (Hall et al., 2012; Timoney, 2013a; Timoney and Lee, 2009). Protected in 1922 with the creation of Wood Buffalo National Park, the PAD is a major nesting and staging site for numerous species of waterfowl and acts as a connection area for all four North American migratory flyways. In addition to being home to various bird, mammal, and fish species, the PAD provides sustenance and spiritual well-being to the Mikisew Cree, Athabasca Chipewyan First Nations, and Metis peoples who reside in Fort Chipewyan (Timoney, 2013b; Wolfe et al., 2012). Due to its cultural, ecological, and historical value, the PAD was selected as a Ramsar Wetland of International Importance in 1982 (Wolfe et al., 2012).

The deposition of sediments carried by rivers can result in the formation of river deltas like the PAD (Timoney, 2013a). Two major rivers gave rise to the PAD; the Peace River and the Athabasca River. The Athabasca River originates in the Columbia Icefields of the Alberta Rockies. The Peace River originates at the fork of the Finlay and Parsnip Rivers in northern British Columbia. Deltas are highly complex environments, existing at the interface of terrestrial and aquatic transitional zones, resulting in changes through land, water, and air. This makes these regions sensitive to climate change and changes in river management. Consequently, the PAD is subject to multiple stressors such as climate change, upstream industrial development, agriculture, forestry, mining, and resource extraction (Wolfe et al., 2012).

1.2 Alberta Oil Sands, Alberta, Canada

Worldwide, Canada is the fourth largest petroleum producer, generating 5.27 million barrels of crude oil per day (b/d) as of 2018 (U.S. Energy Information Administration, 2018). The Alberta oil sands is the third largest crude oil reserve in the World, containing approximately 170 billion barrels of proven oil (CAPP, 2018; Government of Alberta, 2017). In the late 1960s, commercial production began, using conventional open pit mining techniques to extract oil sands (Conly et al., 2002). Oil sands are a natural mixture of silica sand (85%), water (5%), and bitumen (10%). Bitumen, a heavy and complex hydrocarbon, is solid at room temperature, and contains high levels of nitrogen, sulfur, and heavy metals. This hydrocarbon mixture is too heavy to flow naturally, unless heated or diluted. Canada's oil sands are broken into three distinct regions: the Athabasca, Cold Lake, and Peace River oil sands, covering 142,200 km^2 of boreal forest in northern Alberta. The surface minable area (SMA), found within the Athabasca oil sands region (AOSR) accounts for only 3% of the total oil sands area (4800 km^2) but contains 20% of potential oil. Currently only 895 km^2 of the SMA has been disturbed, with 98% of the SMA under lease. In 2018, Alberta produced approximately 2.65 million b/d of crude bitumen, with production expected to rise to 4.2 million barrels per day by 2035 (CAPP, 2018; Government of Alberta, 2017). As of 2017, Alberta had 50 *in-situ* projects, 200 primary and enhanced recovery projects, 12 bitumen processing plants, and nine approved oil sands mining operations (Government of Alberta, 2017). Evidently, with global oil demands rising (CAPP, 2018), oil sands operations will continue to extract unconventional oil. Congruently, there are numerous environmental problems associated with mining operations that will continue to negatively impact the surrounding environment, ecosystems, and peoples who live off the land. These problems include the disruption and destruction of terrestrial and aquatic habitats, the

accumulation of waste in large tailings ponds, and the release of chemicals and greenhouse gases to the atmosphere (JOSM, 2016).

Several studies have investigated the effects of industrial activities on the distribution of harmful contaminants, such as PACs and heavy metals, into the atmosphere and the surrounding region (Kelly et al., 2010, 2009; Thienpont et al., 2017). Kurek et al. (2013) examined sediments in lakes near oil sands development centers and found alkylated PACs increased significantly at the onset of mining. In recent sediments, PAC concentrations increased 2.5-23 times more than in the pre-mining (pre-1960) sediments (Kurek et al., 2013). Kelly et al. (2009) examined loadings of airborne particulates on snowpack. Snowpack within 50 km from upgrading facilities received 11400 T of particulates including, 391 kg of PACs, which is equivalent to 600 T of bitumen (Kelly et al., 2009). Kelly et al. (2010), also examined heavy metal deposition in the Athabasca River and associated tributaries. Canadian Water Quality Guidelines for the Protection of Aquatic Life (CEQGs) were exceeded for metals including cadmium, copper, lead, mercury, nickel, silver, and zinc in melted snow and/or water (Kelly et al., 2010).

Furthermore, mining by-products from extraction and upgrading of bitumen, including; tailings ponds (Galarneau et al., 2014), pet-coke piles (Crump et al., 2017), mining pits and heavy truck traffic. These are all sources of PACs and heavy metals in the AOSR (Wang et al., 2016). Indigenous communities have also raised concerns regarding community health. Rates of cancers (Douben, 2003), diabetes, and heart problems have all increased since the onset of mining activities, and have been linked to oil sands mining operations (Timoney and Lee, 2009).

1.2.1 The process of oil sands recovery and processing

Oil sands mining consists of three basic steps; extraction, upgrading, and refining, taking raw oil sands and forming usable petroleum products. 1) Extraction; this process is preceded by the removal of overburden from the surface of the oil sands, exposing the petroleum source. Heavy mining shovels then remove the oil sands from the earth, shovel loads weigh approximately 90 tonnes and contain 7-13% bitumen by weight (Shah et al., 2010). Oil sands are then transported to crushers in preparation for extraction. Following crushing, hot water is added to the oil sands creating a slurry (50% solids, 40% water, and 8% bitumen). The slurry is then transported *via* pipelines to the main extraction facility. The slurry is pumped through a Primary Separation Vessel, where bitumen attaches to air bubbles, floating to the top of the slurry and is subsequently recovered in froth storage tanks (60% bitumen, 30% water, and 10% fine solids). The remaining water, silica-sand and debris are pumped to tailings ponds for storage and water recovery. Bitumen froth is mixed with diluent or solvent to reduce mixture viscosity for separation *via* gravity separation units for the final removal of solids and water (98-99.8% bitumen, and up to 2% water + solids) (Giove and Sciarrabba, 2019a). 2) Upgrading; this is the process by which bitumen is transformed into light oil, by fractionation and chemical treatment, removing almost all traces of sulfur, nitrogen, and heavy metals. Approximately 40% of Alberta's bitumen is upgraded into light (sweet) synthetic crude oil before being sold to refineries. First, diluent is recovered from the bitumen and returned to the bitumen production facility. Next the hydrogen to carbon (H:C) ratio is improved through carbon injection (coking) or hydrogen addition (hydroconversion). Heavy (lower value) bitumen is then converted into lighter hydrocarbons using two different methods; fractionation and/or cracking (Berkowitzt and Speightt, 1975). Impurities, such as sulfur and nitrogen, are then removed from the crude oil, a

process known as hydrotreating. Finally, the crude oil is blended together with different liquid fractions that were created during upgrading to produce the desired crude oil, typically known as Synthetic Crude Oil. Currently there are four open pit mining upgrading facilities in Alberta; Suncor, Syncrude, CNRL Horizon and Shell Scotford Upgrader (Giove and Sciarrabba, 2019b). Refining is the final process of turning crude oil into a final product for consumer and industrial use. These products include, gasoline, kerosene, jet fuel, diesel, oil lubricants, asphalts and other consumer products (Berkowitzt and Speightt, 1975). Two types of refineries exist, which allows for the refining of different crude oils. Simple refineries can only process light crude oils with low sulfur content (sweet), whereas, complex refineries can process heavier crude oils with higher sulfur contents (sour) (Giove and Sciarrabba, 2019c).

1.3 Chemical Fingerprinting

1.3.1 Polycyclic Aromatic Compounds

PACs are a group of organic compounds, found ubiquitously in freshwater and marine sediments. Parent PACs are comprised of two or more unsubstituted aromatic rings fused together. Alkylated PACs have various levels of alkyl substitutions added to the main fused ring structure (Douben, 2003; Neff et al., 2005). PACs can include other elements into their fused ring structure, such as organosulfur compounds. These sulfur-containing compounds constitute an expanded list of PAC compounds such as the dibenzothiophenes (DBTs) and benzonaphthothiophenes (BNTs). PACs are produced through the incomplete combustion of organic matter resulting in the formation of thousands of different PAC species. Notably, only 6-16 PACs (Fig.1) are determined to be priority pollutants owing to a lack of understanding of the chemical properties of the other PACs (Keith, 2015; Ukaogo and Igwe, 2015).

The structural differences between parent and their alkylated homologues results in very different chemical and physical properties. These differences can influence exposure pathways, transportation, and environmental fate of the different PACs. For instance, heavily alkylated compounds are generally more toxic than their unsubstituted parent PACs (Lin et al., 2015). Whereas, high molecular weight (HMW) parent PACs tend to have higher carcinogenicity (Manzetti, 2013). The complexity of these compounds has led to a lack of understanding and monitoring of PACs in the environment. The majority of research has focused on the 16 parent polycyclic aromatic hydrocarbons (PAHs) designated by the United States Environmental Protection Agency (US EPA) (Keith, 2015) as priority pollutants, with little research placed on alkylated PACs (Radke et al., 1990).

1.3.2 Sources and Environmental Fate of PACs in Aquatic Ecosystems

PACs are predominantly hydrophobic, of low solubility in water, and semi-volatile. PACs readily adsorb to particulate matter and other oily substances, facilitating transportation of these compounds into water, soil, and air. Transportation of PACs occurs primarily in the solid phase (79-93%), therefore, sedimentation and accumulation of PACs in riverbeds and lake sediments is the primary path for PAC accumulation in the environment (Manzetti, 2013). PACs are primarily produced from pyrogenic and petrogenic sources (Abdel-Shafy and Mansour, 2016; Neff et al., 2005; Ukaogo and Igwe, 2015). Pyrogenic PACs are produced through high temperature combustion, generating HMW PACs with a greater abundance of unsubstituted parent compounds. Conversely, petrogenic PACs are formed at lower temperatures during diagenesis and petroleum formation. They are typically of low molecular weight (LMW) and consist of more alkylated compounds (Abdel-Shafy and Mansour, 2016; Thienpont et al., 2017; Timoney and Lee, 2011). Therefore, alkylated PACs are directly connected to production and

refining of bitumen and crude oils. Within crude oils, parent PACs constitute 1-3% of total PACs; alkylated PACs comprise more than 90% (Bence et al., 1996). Clear connections between petrogenic PACs have been characterized in the AOSR, due to the dominance of alkylated PACs (Kelly et al., 2009). Alkylated PACs are released through mining extraction processes and upgrading processes, natural erosion, and leaching from bitumen outcrops (Conly et al., 2002; Evans et al., 2016). Recently, studies have provided evidence that open pit mining may be contributing significantly to the contamination of aquatic ecosystems (Kelly et al., 2009; Kurek et al., 2013).

Research in the PAD has focused primarily on characterising PACs from petrogenic sources and linking them to river discharge. Jautzy et al. (2015) used compound specific isotopic signatures (δ^2H and $\delta^{13}C$) in lake sediments from PAD lakes to determine the presence of petroleum coke, a particulate dust emitted by oil sands processing. The spatial differences in δ^2H and $\delta^{13}C$ showed evidence of long-range transport (~150 km) of anthropogenically derived PACs to the PAD (Jautzy et al., 2015a). Alexander and Chambers (2016), reported that heavy metals (arsenic, selenium and vanadium) that were present in bitumen upstream, were also found in sediments downstream. Interestingly, heavy metal concentrations downstream were found to be higher as a result of mining operations in recently deposited sediments (Alexander and Chambers, 2016). The complex nature of the PAD has made it difficult to determine if the PAC signature in the PAD has increased as a result of mining practices in the AOSR or whether the PAC signal been the result of centuries of bitumen erosion into the PAD.

1.3.3 Petroleum Biomarkers in the Alberta Oil Sands

Petroleum biomarkers play a key role in identifying the source of petroleum products; this is known as chemical fingerprinting (Wang et al., 2007). Petroleum biomarkers can be

emitted with other petroleum products such as PACs and n-alkanes, allowing for source identification of rocks and oils. Petroleum biomarkers consist of hopanes, steranes, and terpanes, and are derived from previously living organisms (Table 1). Highly resistant to degradation, petroleum biomarkers are excellent tools for evaluating oil biodegradation, genesis, and the maturation of petroleum products (Brooks et al., 1988; Wang et al., 2013; Yang et al., 2011). Hopanes, steranes, and terpanes are formed and preserved exclusively in petroleum reservoirs and are distinct from their biological precursors (Zumberge, 1987). Historically, petroleum biomarkers have been used by geochemists in characterization of oil in terms of (1) oil-oil and oil-source rock correlation, (2) types of precursor organic material present in source rocks, (3) ranking of oils thermal maturity, (4) evaluation of in-reservoir degradation, (5) determination of depositional environment, and (6) providing information on petroleum source rock age (Wang et al., 2007). Therefore, petroleum biomarkers offer accuracy and precision for petrogenic source identification, compared to PACs and alkanes, which have multiple environmental sources. Within the AOSR and the PAD, petroleum biomarkers can be useful tools to understand the movement of petroleum-based pollution.

1.3.4 Using Sediment Cores to Track Historical Changes

Lake sediment cores provide a natural archive of environmental conditions, both spatially and temporally (Korosi et al., 2016). Routinely, sediment cores are used to infer historic depositional trends in environmental contaminants, including metals and persistent organic pollutants. Lake sediment cores may also preserve the fossil remains of aquatic biota, including daphnia and diatoms, which are routinely used as model organisms in ecotoxicology (Korosi et al., 2017). Advancements in paleolimnology have allowed for the recovery of high-resolution sediment cores that can be sectioned and dated, providing a reconstruction of past ecosystems.

Analysis of these cores can help overcome a lack of long-term monitoring data in regions that have undergone anthropogenic change, particularly the AOSR. Recently, a large body of research has demonstrated the effectiveness of using lake sediment cores to reconstruct the depositional environment of lakes within the AOSR (Jautzy et al., 2013; Korosi et al., 2016; Manzano et al., 2017; Thienpont et al., 2017). An analysis of dated lake sediment cores from the AOSR, may provide a better understanding of contaminants released by surface mining activities.

1.4 Thesis Objectives and Hypothesis

AOSR and the PAD are two highly dynamic regions in northern Alberta, affected by oil sands mining operations. Oil rich sediments are transported *via* air currents, and eroded bitumen is dispersed through the watershed *via* the Athabasca River. Studies performed in the AOSR and the PAD have advanced the understanding of the impacts mining operations have on the environment (Hall et al., 2012; Kelly et al., 2010, 2009; Kurek et al., 2013; Thienpont et al., 2017; Timoney and Lee, 2009).

PACs are of concern in the AOSR due to their relative abundance in the region and their toxic and pervasive properties. PAC contamination in the AOSR provides strong evidence of oil sands emissions to the region. However, given that PACs may also be produced by fuel burning, forest fires, volcanic activity, and other natural phenomena, these PAC sources must also be considered.

Petroleum biomarkers such as terpanes, hopanes and steranes, may hold the key to these questions because they are source specific compounds originating from petroleum. These petroleum biomarkers have been used as indicators of source rock origin in oil spills (Wang et

al., 2007). The use of these highly specific compounds could help further pinpoint sources of PACs in the AOSR and develop the evidence for the regional impacts of oil sands mining operations.

The primary aim of this thesis is to evaluate the chemical signatures of PACs and petroleum biomarkers in the AOSR and the PAD. By comparing selected lakes from the AOSR and PAD, a proper contrast of the chemical fingerprint of PACs and petroleum biomarkers can be assessed as indicators of change. In order to guide this assessment of chemical fingerprinting, an analysis in lake sediment cores of parent and alkylated PACs, as well as petroleum biomarkers was completed. Environmentally relevant bituminous PACs were analysed in all lakes. Petroleum biomarkers (terpanes, hopanes, and steranes) were analysed in sediment cores for the first time in the PAD and the AOSR, to determine their use as potential indicators of petrogenic sources in these complex regions.

The following chapter of this thesis provides an in-depth analysis of PACs and petroleum biomarkers in lake sediment profiles of the AOSR and the PAD. Here I investigated the utility of petroleum biomarkers as a tool to accurately identify the input and origin of bituminous compounds in the PAD and AOSR lakes.

I hypothesize that mining activities in the AOSR have altered aquatic systems in the region and in the PAD. I predict that: (1) petrogenic PAC loadings in lakes in the AOSR and the PAD have increased in lake sediments coeval with oil sands mining operations; and (2) petroleum biomarkers composition has changed in lake sediments coeval with oil sands mining, in the AOSR and the PAD.

Table 1: Petroleum biomarker used for oil forensics

Name	Code	Target ion
Terpanes		
C_{21} terpane	C_{21} T	191
C_{22} terpane	C_{22} T	191
C_{23} terpane	C_{23} T	191
C_{24} terpane	C_{24} T	191
Hopanes		
C_{27} 18A-hopane II (Ts)	Ts	191
C_{27} 17A-hopane (Tm)	Tm	191
C_{29} αβ hopane	C_{29} αβ H	191
C_{30} αβ hopane	C_{30} αβ H	191
C_{31} (S) hopane	C_{31} (S) H	191
C_{31} (R) hopane	C_{31} (R) H	191
C_{32} (S) hopane	C_{32} (S) H	191
C_{32} (R) hopane	C_{32} (R) H	191
C_{33} (S) hopane	C_{33} (S) H	191
C_{33} (R) hopane	C_{33} (R) H	191
C_{34} (S) hopane	C_{34} (S) H	191
C_{34} (R) hopane	C_{34} (R) H	191
C_{35} (S) hopane	C_{35} (S) H	191
C_{35} (R) hopane	C_{35} (R) H	191
Gammacerane	GAM	191
Steranes		
C_{27} αββ sterane	C_{27} αββ S	218
C_{28} αββ sterane	C_{28} αββ S	218
C_{29} αββ sterane	C_{29} αββ S	218

Chapter 2. Tracking the history of Alberta oil sands contaminants using lake sediment cores

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Abstract

Historically deposited polycyclic aromatic compounds (PACs) and petroleum biomarkers were examined in radiometrically dated lake sediment cores from the Athabasca oil sands region (AOSR) and the Peace Athabasca Delta (PAD) in Alberta, Canada to track impacts from oil sands mining operations in the region. Since the onset of mining development, various chemical contaminants including PACs have increased in aquatic ecosystems. Sediment PAC records from lakes in the AOSR showed higher petrogenic contributions coinciding with regional oil sands development, compared to historically high levels found in the PAD. Parent PAC diagnostic ratios showed clear shifts from pyrogenic (primarily wood burning) in pre-development sediments to petrogenically derived PACs in modern sediments, for both AOSR and PAD lakes, coeval with oil sands development. Changes in alkylated PAC fluxes were seen in Saline Lake at the onset of oil sands development (1970s) and Mariana Lake and BM11 during heightened oil sands development (1990s), along with parent PAC fluxes changing in Saline Lake (1970s) and BM11 (1990s). PAD lakes showed no statistical change in PAC fluxes through sediment profiles. Petroleum biomarker diagnostic ratios were stable in sediment profiles for Saline Lake, PAD 30 and PAD 31, indicating a historical petroleum source from the AOSR. Mariana Lake showed the greatest change in biomarkers followed by BM11, these reference lakes had signatures uncommon of petroleum sources, however, in recent years petroleum inputs from mining development has shifted these petroleum biomarker ratios. This study compared historical patterns of petroleum hydrocarbons in lake sediment to historical emissions of these chemicals from oil sands mining operations. In particular, we show the potential for petroleum biomarkers to track petroleum hydrocarbon contamination in the environment.

1.0 Introduction

Globally Canada is the fourth largest petroleum producer, generating 5.27 million barrels per day (b/d) as of 2018 (U.S. Energy Information Administration, 2018). The Alberta oil sands are the third largest crude oil reserve in the world, with three distinct regions: Athabasca, Cold Lake, and Peace River. Combined, these regions occupy an area of 142,000 km^2 across northern Alberta (Canadian Association of Petroleum Producers) (CAPP, 2018), slightly larger in size than England. An estimated 170 billion barrels of oil are recoverable by current extraction methods: open pit mining (1.14 million b/d) and *in-situ* extraction (1.51 million b/d) (CAPP, 2018). The Athabasca Oil Sands Region (AOSR) contains the only bitumen deposits that are <75 m below the Earth's surface, covering an area of 4,800 km^2 (Government of Alberta, 2017). In the late 1960s, commercial production began using conventional open pit mining techniques (Conly et al., 2002). With increasing global energy demands, it is projected that oil sands production will increase by 150% by 2025 (CAPP, 2018), from the currently produced 2.5 million b/d (Government of Alberta, 2017).

Oil sands surface mining and upgrading in the AOSR is an environmentally contentious issue, resulting in significant landscape disturbances, habitat loss, and water quantity/quality issues (Galarneau et al., 2014; Kelly et al., 2010). In recent years, the rapid expansion of surface mining has raised concerns about the potential release of contaminants into the environment (Korosi et al., 2016; Yang et al., 2014). Several studies have shown elevated concentrations of polycyclic aromatic compounds (PACs) and heavy metals within 50-80 km of upgrading operations in snow pack, water, (Kelly et al., 2010, 2009) and lake sediments, 2.5-23 times higher than pre-mining (1960) sediments (Kurek et al., 2013).

Oil sands upgraders, pet-coke piles, tailings ponds (Galarneau et al., 2014), mine pits, and truck traffic are all sources of PACs in the AOSR (Wang et al., 2016). Studies conducted in the AOSR have shown that exposure to PACs can cause morphological deformities in amphibians and fish, as well as EROD (Ethoxy resorufin-O-deethylase) induction, and increased mortality (Colavecchia et al., 2004; Rankouhi et al., 2005; Timoney and Lee, 2009). Recently, Mundy et al. (2019) demonstrated high EROD and *Cyp1a4* mRNA induction in avian hepatocytes in wetlands near mining operations (≤10 km). Human health issues have also been raised by local Indigenous communities in the region. They are concerned about putative effects, such as increased rates of cancer (Douben, 2003), diabetes, and heart problems, which have been linked to areas influenced by oil sands mining (Irvine et al., 2014; Timoney and Lee, 2009).

PACs are produced by the incomplete combustion of organic material, forming compounds with two or more fused aromatic rings. These compounds are separated into two groups: pyrogenic and petrogenic PACs (Neff et al., 2005; Zhang et al., 2015). Pyrogenic PACs are produced through the high temperature combustion of organic material, creating unsubstituted parent compounds (Timoney and Lee, 2011). Petrogenic PACs are formed over geologic timescales under geothermal temperature and pressure conditions, creating predominantly alkylated versions of parent compounds (Douben, 2003; Thienpont et al., 2017; Timoney and Lee, 2011). Once released into the environment, atmospheric transport allows for global dispersion (Abdel-Shafy and Mansour, 2016). In water, PACs tend to adsorb and partition into sediments due to their hydrophobic nature (Abdel-Shafy and Mansour, 2016; Thienpont et al., 2017; Ukaogo and Igwe, 2015). As a result, PAC concentrations in lake sediments within the AOSR have increased coeval with bitumen extraction in the region (Evans et al., 2016; Kurek et al., 2013). Bitumen, and its associated PACs, are transported downstream into the Peace

Athabasca Delta (PAD), raising questions about the potential impact of the AOSR on downstream populations and communities (Timoney and Lee, 2009).

The PAD is one of the world's largest inland river deltas, a hydrologically dynamic environment containing many interconnected lakes and channels, all fed by the Athabasca and Peace River watersheds (Jautzy et al., 2015b). Although the PAD is >200 km downstream of the surface mining development zone, it receives PACs from mining operations *via* atmospheric transport (Jautzy et al., 2015a; Kelly et al., 2009). In addition, the Athabasca River has transported PACs into the PAD for hundreds of years, as clearly shown by the erosion of bitumen from upstream river banks (Hall et al., 2012; Jautzy et al., 2015b). There is some evidence of increased PAC concentrations in pre-industrial PAD sediments (Hall et al., 2012). As a result, PAC concentrations can be highly variable through time (Evans et al., 2016) and consequently there is still public concern regarding the potential downstream cumulative environmental effects of the oil sands industry on this region and its communities (Hall et al., 2012). Recently, Hebert (2019) reported elevated mercury levels in the eggs of aquatic birds in the PAD, during years of high flow. High mercury levels have been equated to anthropogenic activities within the AOSR: land disturbances, atmospheric releases, and dust from roads and tailings ponds (Hebert, 2019). Alexander and Chambers (2016), concluded that heavy metal concentrations associated with bitumen, were higher downstream of mining operations in post-development sediments (Alexander and Chambers, 2016). Fortunately, different organic proxies, such as petroleum biomarkers, may provide key information on the impact of industrial activities and natural bitumen seeps on regions such as the PAD.

Petroleum biomarkers have been frequently used to investigate ancient sediments and petroleum sources (Wang et al., 2013; Yang et al., 2011). Three groups of petroleum biomarkers

(hopanes, terpanes, and steranes), are formed and preserved exclusively in petroleum reservoirs, making them useful for oil forensics (Zumberge, 1987). Recently, these petroleum biomarkers have been used for source identification, differentiation of oils, and monitoring of oil weathering (Wang et al., 2013). Petroleum biomarkers are derived from formerly living organisms and are found in crude oils, rocks, and sediments; there is little to no structural change through time compared to most aromatic compounds (Wang et al., 2016, 2006b). Petroleum biomarkers are highly abundant in oils, thermodynamically stable, and have high source specificity (Wang et al., 2016). In fact, petroleum biomarkers from a 25-year-old oil spill in Lesser Slave Lake, Alberta, were not significantly degraded in surface (0-4 cm) and sub-surface (30-40 cm) sediments, when compared to heavily weathered PACs (Wang et al., 1998). Consequently, petroleum biomarkers in the bitumen-rich environment of the AOSR may provide an important tool to accurately identify the source of PACs, as natural or anthropogenic in the environment.

Lake sediment cores provide a natural archive of environmental conditions, both temporally and spatially (Korosi et al., 2016). They can be analysed to help overcome a lack of long-term monitoring data in any region that has undergone anthropogenic change. In the AOSR, lake sediment cores can be a tool to track these changes, as a result of mining activities. A large body of scientific studies have demonstrated the effectiveness of using lake sediment cores to reconstruct depositional histories of contaminants in lakes within the AOSR (Jautzy et al., 2013; Manzano et al., 2017; Thienpont et al., 2017). A chronological analysis of deposition in dated lake sediment cores may provide a better understanding of the sources and contaminants released by surface mining activities within the AOSR (Korosi et al., 2016).

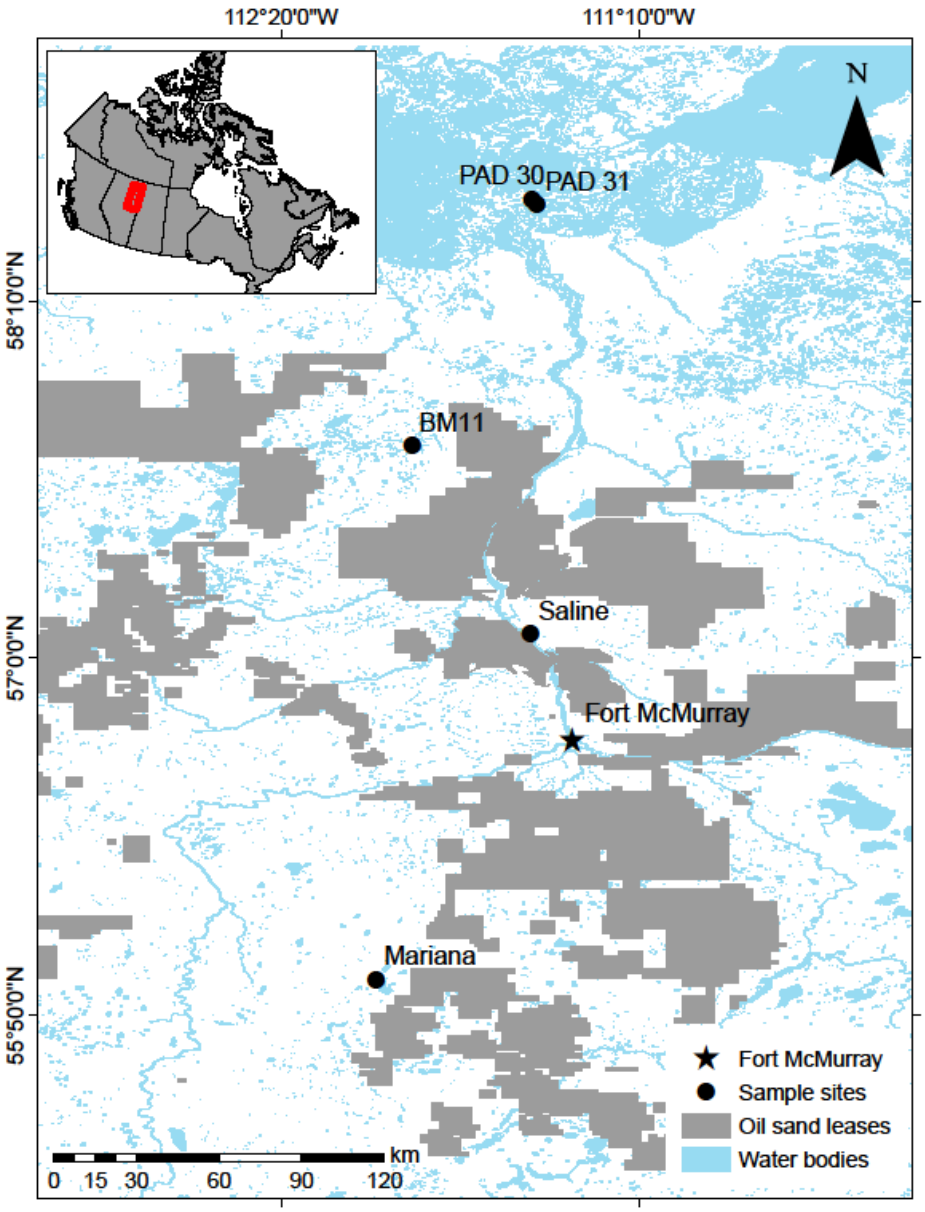
The objective of this study is to determine if mining operations in Alberta's oil sands have altered the PAC and petroleum biomarker composition of lake sediments collected from the

AOSR and the PAD. Increases in future mining operations result in more barrels of oil mined per day, and the amount being upgraded. As a result, it is expected that future oil extraction will increase regional contaminant inputs. The combined use of both petroleum biomarkers and PACs should provide a more complete understanding of the source and extent of contamination to lakes in these regions over the past century. We examined two lakes in the PAD, one heavily impacted site in the AOSR, and two relatively unimpacted sites (hereafter referred to as reference sites) in the AOSR. I hypothesize that (1) petrogenic PACs in the AOSR and the PAD increased in lake sediments coeval with oil sands production and (2) the petroleum biomarkers composition in the AOSR and the PAD changed in lake sediments coeval with increased oil sands production emissions.

2.0 Methods

2.1 Study Sites and Sample Collection

This study was conducted in the Municipality of Wood Buffalo near Fort McMurray, Alberta and in the PAD. Both PAD 30 and PAD 31 are located downstream of the Athabasca River and receive flood waters on an annual basis. BM11, located in the south eastern section of the Birch Mountains, is a remote lake, 43 km north of the nearest mining upgrader. Saline Lake is directly adjacent to the Athabasca River and is less than 5 km from the nearest mining upgrader. Mariana Lake is approximately 100 km southwest of the city of Fort McMurray. Mariana Lake and BM11 were selected as reference sites due to their distance from oil sands upgraders.



402

403 **Fig.1.** Map of study region, identifying sampling locations in the Athabasca oil sands region:
404 Saline Lake (57°04'41.81" N, 111°31'20.43" W), BM11 (57°41'35.97" N, 111°54'26.08" W),
405 and Mariana Lake (55°57'02.35" N, 112°01'34.97" W), and sampling location in the Peace
406 Athabasca Delta: PAD 30 (58°30'N, 111°31'W) and PAD 31 (58°29'N, 111°30'W). Oil sands
407 leases currently being utilized by mining companies are shown in grey (2015).

408

409 Lake sediment cores were collected from PAD 30 in September 2016, and PAD 31 in

410 September 2010, and lake sediment cores from BM11, Mariana Lake, and Saline Lake were

411 collected in June 2017. Sediment cores from the AOSR were collected using a gravity corer and
412 sectioned at 0.5 cm intervals using a vertical extruder, whereas sediment cores from the PAD
413 were sectioned at 1 cm intervals. Sediments from PAD 30 and PAD 31 were kept in Whirl-Pak®
414 bags at 4°C at the University of Waterloo, Ontario, Canada. Sediments from the AOSR were
415 kept in Whirl-Pak® bags at -20°C at the University of Ottawa, Ontario, Canada.

416 *2.2 Laboratory analysis – Dating sediment cores*
417

418 Each lake sediment core was ^{210}Pb dated using an Ortec High Purity Germanium Gamma
419 Spectrometer (Advanced Measurement Technology Ink, Oak Ridge, TN, USA) at the University
420 of Ottawa. Chronologies based on excess ^{210}Pb activities were constructed with the constant rate
421 of supply (CRS) model using ScienTissiMe (Barry's Bay, ON, Canada). Efficiency corrections
422 were made using Certified Reference Material (312 and 385) from the International Atomic
423 Energy Association (Vienna, Austria).

424 *2.3 PAC and Biomarker analysis*
425

426 The target analytes were the 16 US EPA priority PAHs, benzonaphthothiophene and
427 dibenzothiophene and their respective alkylated forms (Table S3). Sediments (20-30 g wet
428 weight (wwt.)), containing a minimum of 0.5 g total organic carbon (TOC), were weighed.
429 Water was first removed from the sediments through centrifuging and the subsequent addition of
430 Diatomaceous earth (Thermo Scientific). Samples were then spiked with a Deuterated mixture:
431 Naphthalene (D8, 99.5%), Acenaphthene (D10, 99%), Phenanthrene (D10, 98%),
432 Benz[a]Anthracene (D12, 98%), Perylene (D12, 98%) and N-Tetracosane (D50,98%),
433 (Cambridge Isotope Laboratories Inc. Tewksbury, MA, USA). PACs were extracted using an
434 accelerated solvent extractor (ASE-200, Dionex Corporation, Sunnyvale, CA, USA), using 50:50

acetone:hexane based on US EPA method 3540C modified for accelerated solvent extraction. Solvent and water were separated using liquid-liquid extraction and then rinsed three times using 5 mL of hexane. Samples were evaporated down to 2 mL under a gentle stream of nitrogen (TurboVap, Biotage, Charlotte, NC, USA) and centrifuged to remove any remaining particles and water. Samples were subsequently evaporated down to 1 mL under a gentle stream of nitrogen. Samples were then fractionated using silica gel (Grade 644) (6g) column chromatography (Fisher S7441). To separate the F1 (petroleum biomarkers) and F2 (PACs) fractions: we used 22 mL hexane and 35 mL 50:50 dichloromethane (DCM):hexane, respectively.

The F1 fraction was evaporated down to 1 mL in 2,2,4-Trimethylpentane (TMP). Samples were evaporated into 1 mL TMP and spiked with internal standard, p-Terphenyl (D_{14}, 98) 10ul and then quantified using gas chromatography coupled with mass spectrometry. Standards included hopanes and steranes (NIST 2266) in TMP (Sigma-Aldrich, Oakville, ON, Canada), as well as C8-C40 Alkanes Calibration Standard (Bellefonte, PA, USA). F2 samples were evaporated down to 1 mL for sulphur and pigment removal using preparative liquid chromatography (GPC clean-up via modified US EPA method 3640a on Envirogel™ GPC columns (Waters), automated with Agilent 1200 series preparative HPLC system). Samples were evaporated into 1 mL TMP and spiked with internal standard, p-Terphenyl (D_{14}, 98) 10ul, for quantification using Gas Chromatography coupled with Mass Spectrometry (GC-MS). All solvents were high grade Optima® from Fisher Chemicals, except TMP.

2.4 Statistical Analyses

Diagnostic ratios of PACs were calculated because they have proven useful for distinguishing pyrogenic versus petrogenic PACs in the environment (De La Torre-Roche et al.,

2009; Yunker et al., 2002). The ratios calculated included: 1) Fluoranthene (Fla) / pyrene (Py) ratio = Fla/(Fla+Py) and 2) Indeno(1,2,3-cd)pyrene (IcdP) / Benzo(g,h,i)perylene (BghiP) ratio = IcdP/(IcdP+BghiP).

Statistical analyses were performed using R statistical computing environment (v3.5.2). To explore the variations between both regions and between lakes downcore profiles, we conducted a principle component analysis (PCA) on the relative abundance of PACs. The PCA biplots were conducted using 'prcomp' function in the 'vegan' package. Using the "Kendall" package, we conducted Mann-Kendall trend tests on PAC fluxes, PAC diagnostic ratios, and petroleum biomarker diagnostic ratios. This was done in order to compare temporal trends between our study lakes.

3.0 Results and Discussion

3.1 PAC depositional history comparisons through time

Alkylated and parent PAC fluxes in the AOSR increased in surface sediments, with consistently greater fluxes in alkylated PACs than in parent PACs (Fig.2). In Saline Lake, alkylated PACs increased in the late 1970s, coinciding with the onset of mining activities in the AOSR (CAPP, 2018) (Fig.2C). Historically, alkylated PAC fluxes in Saline Lake were greater than in reference lakes. This suggests that impacted lakes had historically elevated PAC fluxes, which may be the result of erosion of bitumen into surrounding waterbodies (Hall et al., 2012; Jautzy et al., 2015a, 2015b). Interestingly, alkylated PACs in Mariana Lake and BM11 increased in recent sediments (>1990s), indicating that these recent increases in alkylated PACs were not confined exclusively to lakes directly affected by oil sands development. At Mariana Lake, a convenience store and gas station were constructed in 1970 (Cormier, 2008). This may have

resulted in increased petroleum emissions adjacent to the lake, in addition to vehicle traffic associated with the nearby highway. Runoff from motorways is one of the most important sources of anthropogenic hydrocarbons to sediments (Stout and Wang, 2016), which has possibly impacted Mariana Lake. The recent rise (2.5cm, 2002) in alkylated PACs in BM11 could be explained by the deposition of petrogenic PACs, such as naphthalenes, phenanthrenes, dibenzothiophenes, and chrysenes, as a result of regional atmospheric transport from mining activities. Page et al. (1999) concluded that sediment associated PACs may remain unchanged for years, providing clues as to the type of anthropogenic activities in a region, based on the types of PACs present.

PAC fluxes in PAD lakes were greater than those in the AOSR (Fig.2). This may be caused by the continual input of naturally eroded bitumen into the Athabasca River (Hall et al., 2012) as well as annual downstream PAC transport into the Delta from mining activities. PAD 31 had a history of flooding, with recorded flooding events pre-1940s and post-1982. The decrease in PACs in 1996 (8.5 cm) and 1947 (17.5 cm) (Fig.2B) are indicative of flooding events. Hall et al. (2012) compared sediment PACs from these flood prone years (pre-1940s and post-1982) to a known flood event in 2007 and found similar PAC compositions thus confirming the historical flooding events that we see in PAD 31 (Fig.2B). While there are no documented flooding events in PAD 30, the decreased parent and alkylated PAC fluxes in 1964 (12cm) suggest a flooding event occurred. Alkylated PAC fluxes in PAD 30 then increased in 1975 (10cm), coinciding with increased oil sands development in the AOSR (Kelly et al., 2009). Notably, the PAC flux in PAD 31 increased later (1996) than PAD 30 (1969), despite PAD 30 and PAD 31 being hydrogeologically connected.

3.2 Changes in PACs through time

We used diagnostic ratio cross-plots to investigate PAC trends in lake sediment cores. Fluoranthene and pyrene (Fla/[Fla+Py]) were plotted along the y-axis denoting pyrogenic and petrogenic sources (Fig.3). Values lower than 0.4 denoted petrogenic sources and values greater than 0.5 denoted pyrogenic sources (De La Torre-Roche et al., 2009). Plotted along the x-axis are Indeno(1,2,3-cd)perylene and benzo(ghi)pyrene (IcdP/[IcdP+BghiP]). Values less than 0.2 denote petrogenic sources and values above 0.5 denote pyrogenic sources. Values between 0.2-0.5 denote petroleum combustion (Yunker et al., 2002).

Parent PAC diagnostic ratio cross-plots for PAD 30 indicated that diagnostic ratios for Fla/(Fla+Py) shifted from pyrogenic signatures to petroleum combustion signatures in recent sediments (10.5cm, 1975), though IcdP/(IcdP+BghiP) ratios remained relatively unchanged (Fig.3A). Similarly, PAC diagnostic ratios in PAD 31 were similar to those of PAD 30 (Fig.3B). A recent study by Evans et al. (2016), demonstrated that the PAD and the western section of Lake Athabasca were dominated by petrogenic sources as evidenced by low Fla/(Fla+Py) ratios (<0.4). Notably, IcdP/(IcdP+BghiP) did not indicate petrogenic sources and was dominated by a petroleum combustion signature (Evans et al., 2016). Similar trends were observed in the lakes we sampled: low molecular weight (LMW) (2-3 ringed) PACs (as evident by the decrease in Fla/[Fla+Py]) and petroleum combustion signatures in high molecular weight (HMW) (4-6 ringed) PACs indicated that petrogenic sources dominated within the PAD after the onset of mining activity (1970s). Therefore, the results presented herein, and elsewhere (Evans et al., 2016) demonstrate that petrogenic sources appear to be driving the PAC profiles within PAD lakes.

In Saline Lake, PAC fluxes provided a record of oil sands mining operations, as evidenced by a shift from pyrogenic to petrogenic sources in the late 1970s, marking the onset of bitumen mining in the region (CAPP, 2018) (Fig.3C). Visually, parent and alkylated PACs increased coeval with PAC fluxes in modern sediments (BM11, Mariana Lake, PAD 30, PAD 31, and Saline Lake) (Fig.2). PAC diagnostic ratios in BM11 shifted towards petrogenic sources for both diagnostic ratios, suggesting inputs from mining activities in modern sediments (5.5cm, 1971) (Fig.3D). In Mariana Lake, Fla/Py ratios decreased in 1972, possibly due to the construction of a gas station and convenience store, which opened in 1970 (Cormier, 2008) approximately 80 m for the lake (Fig.2E). In 2008, the stores closed to construct an additional lane on nearby highway 63. Interestingly, alkylated PAC fluxes increased in 2013, further shifting the PAC composition towards more petrogenic sources (Fig.3E). It follows that decreased values of Fla/(Fla+Py) and IcdP/(IcdP+BghI) in modern sediments have been shown to indicate a greater source of petrogenic PACs (Jautzy et al., 2013; Kurek et al., 2013; Thienpont et al., 2017).

Table 1

Result of Mann-Kendall trend test: p-value (p), and rank correlation coefficient (τ) of the PAC flux in each lake for sum parent and alkylated PAC flux, and PAC diagnostic ratios (Fla/Py = Fla/(Fla+Py) and (IcdP/BghiP = IcdP/(IcdP+BghiP)). Bold font denotes statistical significance, α = 0.05.

Lake	∑Parent		∑Alkyl		Fla/Py		IcdP/BghiP	
	τ	p	τ	p	T	p	τ	p
BM11	0.600	**0.013**	0.527	**0.029**	-0.663	**0.009**	-0.782	**1.08E-03**
Mariana	0.384	0.0630	0.538	**0.009**	-0.912	**7.15E-06**	-0.912	**7.15E-06**
Saline	0.855	**3.42E-04**	0.818	**6.14E-04**	-1	**2.62E-05**	-0.891	**1.86E-04**
PAD 30	0.200	0.474	0.467	0.074	-0.822	**1.28E-03**	-0.467	0.074
PAD 31	0.022	1	0.289	0.283	-0.556	**0.032**	-0.644	**0.012**

548 We used the Mann-Kendall test to determine whether sources and composition of PACs
549 deposited into these lakes has changed significantly over time. Diagnostic ratios with negative τ
550 values, suggest a shift from pyrogenic to petrogenic PAC sources (Ravindra et al., 2008;
551 Thienpont et al., 2017). In both our AOSR and PAD lakes, diagnostic ratios had statistically
552 negative τ values ($p<0.05$) thus supporting a shift from pyrogenic and petrogenic PAC sources,
553 except for PAD 30 (IcdP/BghiP) (Table 1). Shifts from pyrogenic to petrogenic sources occur in
554 Saline Lake, PAD 30, and PAD 31, coincide with the onset of mining activities (1970s) for both
555 ratios. Interestingly, the reference sites Mariana Lake and BM11 diagnostic ratios shift later (mid
556 1990s, IcdP/BghiP and 2013 and 1982 for Fla/Py, respectively) and less drastically than
557 impacted sites. In Saline Lake and BM11, ∑parent and ∑alkylated PACs had statistically
558 positive τ values (Table 1), indicating an increase in PAC flux towards the top of the sediment
559 core. In Saline Lake, the increase in near surface PACs can be attributed to mining, due to
560 increased levels of benzonaphthothiophenes, dibenzothiophenes and chrysenes, PACs commonly
561 associated with oil sands mining (Fig.2C). In BM11, deposition of these same compounds,
562 transported *via* prevailing winds (Environment and Climate Change Canada) (ECCC, 2019)
563 across the oil sands has resulted in near surface PAC flux increases in recent years (2000s). In
564 Mariana Lake, the τ value is significantly positive and thus suggests an increase in the deposition
565 of ∑alkylated PACs; this may be the result of vehicle traffic on highway 63 (Fig.2E). Korosi et
566 al. (2016), reported on the impact of vehicle traffic on winter roads to PAC concentrations in
567 subarctic Canadian lakes. While they reported higher levels of alkylated PACs in water and
568 sediment samples from lakes adjacent to roads, (relative to reference lakes), they could not
569 conclusively link vehicle traffic to increased PAC values (Korosi et al., 2016). Thus, while our
570 results suggest a possible link between vehicle traffic and increased PAC deposition, further

analysis of heavy metals in sediment profiles may provide additional proxies to determine whether this relationship is significant.

3.3 Petroleum Biomarker Changes in Lake Sediments

To investigate downcore changes in petroleum biomarkers in lake sediments, we examined petroleum biomarker diagnostic ratios (Table 2). All lakes showed statistical changes in petroleum biomarker diagnostic ratios (Table 2). Diagnostic ratios with marked (^{1}) p-values are statistically significant. However, the effective size for these analyses is low (10-12 intervals per lake), therefore p-values slightly above 0.05 are not considered significant. Visual inspection of raw data supports this determination (Table S4-8). Small changes in petroleum biomarkers do not equate to shifts in source as values can vary through replicates (Yang et al., 2011).

The use of petroleum biomarker diagnostic ratios more properly reflects the differences of the target biomarker distribution between samples, reducing concentration effect size. These ratios have been used as defensible indices for identification, correlation, and differentiation of spilled oils (Peters and Moldowan, 1993; Wang et al., 2006a). Matching ratios may indicate a correlation between a suspected source and a sample (Wang et al., 2007). To this effect, comparing diagnostic ratios may help identify similar petroleum sources in sediment profiles. Petroleum biomarker diagnostic ratios in Saline Lake, PAD 30, and PAD 31 did not track the history of mining activity as evidenced by the PAC diagnostic ratios throughout the cores. Interestingly, petroleum biomarkers in Mariana Lake did track recent (early 2000s) anthropogenic activity: biomarker ratios (C_{23}/C_{30}, C_{24}/C_{30}, $C_{30}/\sum C_{31\text{-}35}$, $C_{31}(S)/C_{31}(R)$, and $\sum$Steranes/$\sum$Terpanes) showed the greatest fluctuation in values through time (Table 2). While these ratios increase, we cannot attribute these shifts to oil sands mining operations. Mariana Lake is situated outside the oil sands mining zone, and the prevailing winds move to the

595 northwest, towards the oil sands. These shifts were coincident with development along the
596 highway and the highway's later expansion. Prior to the 2000s, petroleum biomarker diagnostic
597 ratios in Mariana Lake were near zero, suggesting no petroleum sources present in the lake
598 (Table S5). The thermodynamic stability of petroleum sources is based on the ratio of (S) and
599 (R) configurations, which denotes the enantiomer of petroleum biomarkers, as chiral molecules.
600 Stable petroleum sources have a 1:1 mixture of (S) and (R) configurations (Dastillung and
601 Albrecht, 1976). In PAD 30, PAD 31, and Saline Lake, (C_{31}(S)/C_{31}(R), C_{34}(S)/C_{35}(S),
602 C_{34}(R)/C_{35}(R) ratios were near 1 (Table S6-8), indicative of a thermally stable petroleum source,
603 e.g. bitumen. In Mariana Lake, these ratios increased through time, suggesting that a continual
604 petroleum source was entering the system. Consequently, vehicle traffic appears to be the major
605 factor influencing the PAC concentrations and petroleum biomarkers in Mariana Lake.
606 Bryselbout et al. (1998) reported higher thermal maturity of petroleum on pine species found
607 along highways compared to urban roadways (Bryselbout et al., 1998). Similarly, Mariana Lake
608 petroleum biomarker ratios for S and R configurations increased through time (Table S5), which
609 may be the result of petroleum entering the lake from the nearby highway. Comparatively,
610 petroleum biomarker shifts in BM11 were likely caused by the atmospheric deposition of
611 petroleum sources from oil sands mining development. Consequently, these results indicate that
612 petroleum biomarkers can be used as proxies to determine when petroleum sources entered
613 historically uncontaminated lake systems. Similarly, increased terpane diagnostic ratios (C_{23}/C_{30}
614 and C_{24}/C_{30}) in BM11 are increasing towards levels seen in raw Alberta oil sands samples (Yang
615 et al., 2011). Interestingly, hopane ratios (C_{30}/$\sum C_{31\text{-}35}$ and C_{31}(S)/C_{31}(R)) increased in Saline
616 Lake, as was also in Mariana Lake. An increase in hopanes may suggest an increase in industrial
617 activity, and thus we did not expect to see such increases in our reference lake. The increase in

hopane diagnostic ratios in Saline Lake may be the result of vehicle exhaust from mining activities near Saline Lake and traffic along highway 63, near Mariana Lake. Notably, PAD 31 petroleum biomarkers have remained stable through the sediment profile (Table 2), coeval with bitumen erosion into the PAD. Interestingly, PAD 30 terpane diagnostic ratios have shifted through the sediment profile.

Overall, Saline Lake, PAD 30, and PAD 31 had the same levels of petroleum biomarkers across all diagnostic ratios (Table S6-8). These results indicated exposure to a common petroleum source: bitumen. In contrast, BM11 had different concentrations of diagnostic ratios, which suggested that this lake received minimal loadings of petroleum biomarkers. Biomarkers in Mariana Lake increased towards the beginning of the 21st century suggesting a greater source input of petroleum biomarkers in modern sediment

Table 2

Result of Mann-Kendall trend test (p = p-value, τ = rank correlation coefficient) of the petroleum biomarker diagnostic ratios in each lake. Bold font denotes statistical significance, α = 0.05.

Diagnostic Ratios	**BM11**		**Mariana**		**Saline**		**PAD 30**		**PAD 31**	
	τ	p	τ	p	τ	p	τ	p	τ	p
C_{23}/C_{24}	-0.24	0.35	0.23	0.30	0.48	0.05[1]	0.67	**0.01**	-0.21	0.47
C_{23}/C_{30}	0.58	**0.02**	0.84	**9.16E-05**	-0.04	0.94	0.64	**0.01**	0.30	0.28
C_{24}/C_{30}	0.61	**0.01**	0.77	**4.29E-04**	-0.40	0.12	0.52	**0.05**	0.33	0.23
C_{29}/C_{30}	-0.28	0.27	-0.33	0.14	-0.77	**1.62E-03**	0.09	0.79	0.27	0.32
Ts/Tm	0.59	0.03[1,2]	-0.03	0.94	-0.49	0.05[1]	0.22	0.46	0.14	0.65
$C_{30}/\sum C_{31\text{-}35}$	0.33	0.22	0.84	**1.52E-04**	0.56	**0.03**	0.49	0.06	0.45	0.09
C_{31}(S)/C_{31}(R)	0.54	**0.03**	0.89	**4.71E-05**	0.61	**0.01**	-0.04	0.93	0.54	**0.04**
C_{34}(S)/C_{35}(S)	NA	NA	NA	NA	0.20	0.44	-0.09	0.79	0.30	0.28
C_{34}(R)/C_{35}(R)	NA	NA	NA	NA	0.20	0.44	0.03	1.00	-0.11	0.72
C_{27}abb/C_{29}abb	NA	NA	0.43	0.05[1]	0.48	0.05[1]	-0.02	1.00	-0.51	0.05[1]
∑Steranes/∑Terpanes	0.15	0.58	0.60	**0.01**	-0.10	0.75	-0.50	0.06	-0.36	0.20

[1] Not biologically significant

[2] Only 2 values were obtained for this diagnostic ratio, therefore not significant

3.4 Multivariate analysis of lake sediment cores

PCAs were conducted on the stratigraphic profiles of parent PACs, alkylated PACs, and petroleum biomarkers to visualize changes in the relative abundance of PACs and petroleum biomarkers through time. The resulting figures (Fig.4-5, Fig. S7-S9) show the PCAs for each lake with the five variables contributing most to the total variance as arrows.

Parent and alkylated naphthalene and benzonaphthothiophene were the primary contributors to the variance in the PCAs (Fig. 4-5). These two compounds were major contributors to the variance in all lakes with their directionality shifting towards modern sediments. The loadings at the top of the cores were larger than those at the bottom (Fig.2), driving the change in the PCAs (Fig 4-5). Naphthalene explained much of the PCA variance and its presence may be attributed to forest fires. Vila-Escale et al. (2007), reported high levels of naphthalene after a forest fire in Spain, with PAC values taking 15-22 months to return to background levels (Vila-Escale et al., 2007). Annual forest fires, particularly the fire of 2015 which damaged parts of Fort McMurray may be the cause of high naphthalene values in modern sediments. Bitumen extraction and upgrading in the AOSR would explain the presence of benzonaphthothiophene, a common petrogenic PAC (Kelly et al., 2009). Other important petrogenic PACs, including dibenzothiophene and chrysene, have been shown to play an important role in explaining the variance, generally mirroring the directionality of benzonaphthothiophene. These compounds are known petrogenic PACs (Kelly et al., 2009; Wang et al., 2014), further supporting our rationale that petrogenic PAC input in these lake systems is caused by mining operations in the AOSR.

4.0 Conclusions

In the AOSR and the PAD, there is evidence of increased PACs as the result of anthropogenic activity in modern sediments. Among all sites considered in this study, the industrial impact is most evident in lakes closer to the surface mining and upgrading activities in the AOSR. Clear shifts from pre-industrial pyrogenic emissions to petrogenic PACs have been detected in sediment profiles corresponding to the mid-1970s. Interestingly, petroleum biomarkers in the PAD and AOSR did not track a change to petrogenic sources in sediment profiles, as was predicted. We attribute this lack of shift in petroleum biomarkers to the natural composition of the area, the very composition that makes it suitable for mining activity. In reference lakes, PAC concentrations show increases in alkylated PACs, along with diagnostic ratio shifts towards petrogenic sources. These increases suggest that anthropogenic activities related to mining may be impacting our reference lakes in recent sediments. Petroleum biomarker diagnostic ratios show similar results, increasing in modern sediments, suggesting a petroleum signal in reference lakes (>1990s) that was not present prior to oil sands mining. Notably, our reference lakes were not pristine through the sediment profile, yet they provide a strong comparison to contaminated lakes in the AOSR and the PAD. Reference lakes have PAC fluxes up to three orders of magnitude lower than lakes in the AOSR and the PAD, providing a significant difference in impact. Consequently, we propose the use of petroleum biomarkers in lake sediment profiles in areas outside of naturally occurring, petroleum-rich, rock formations. The shift in the biomarker composition in response to recent anthropogenic activity was detectable in our reference environments because of the naturally low historical levels of petroleum biomarkers. It is critical to continue to provide context on the environmental impacts

of oil sands mining and processing at a local and regional level, given the projected growth in the region.

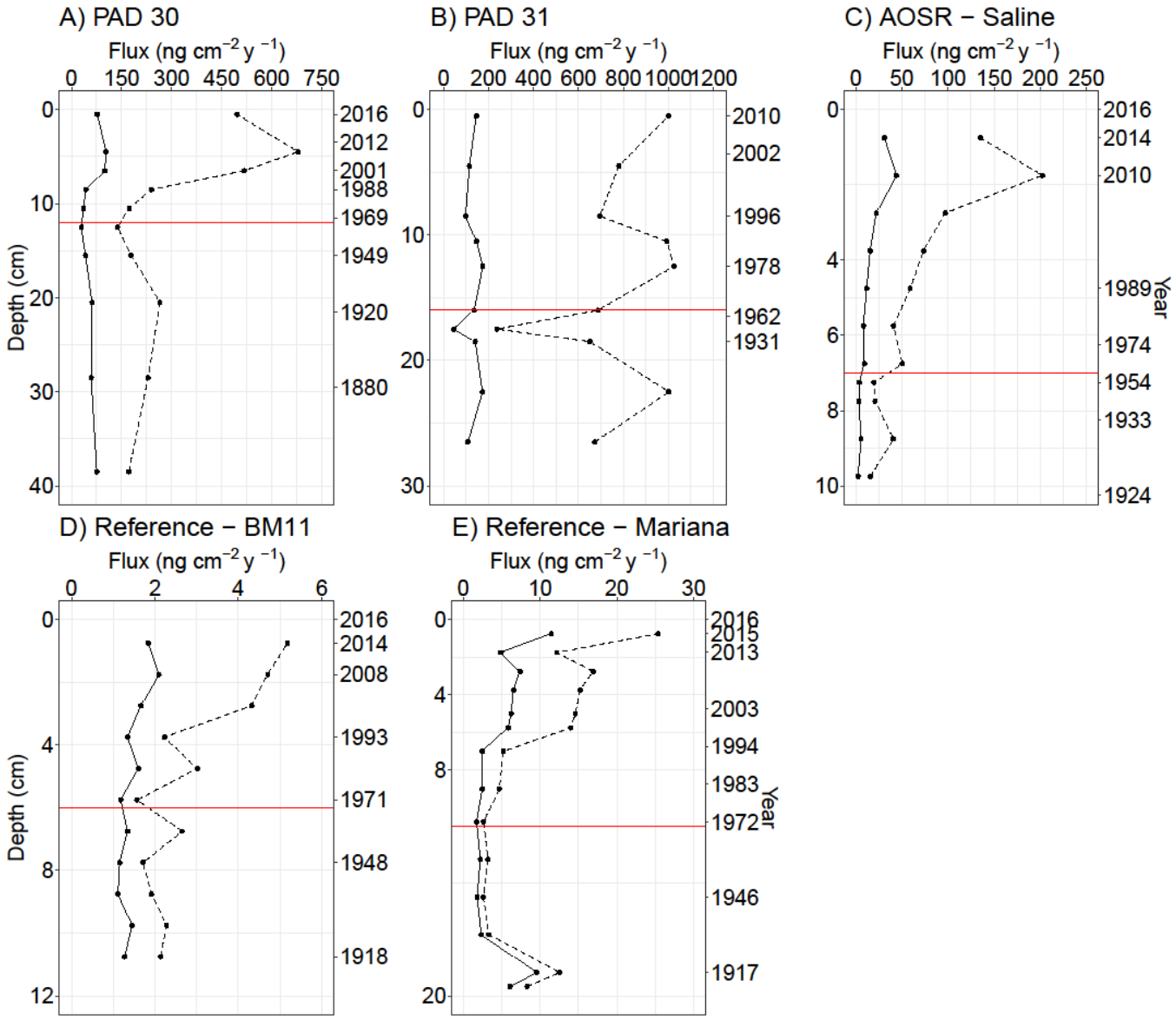


Fig.2. Line plot of PAC flux (ng cm^{-2} y^{-1}) versus depth (cm) for each lake down core. Depth is shown on the left y-axis and the corresponding date (year) is shown on the right y-axis. Solid lines represent parent PACs and the dashed line represents alkylated PACs. Red line indicates the beginning of oil sands production (1967).

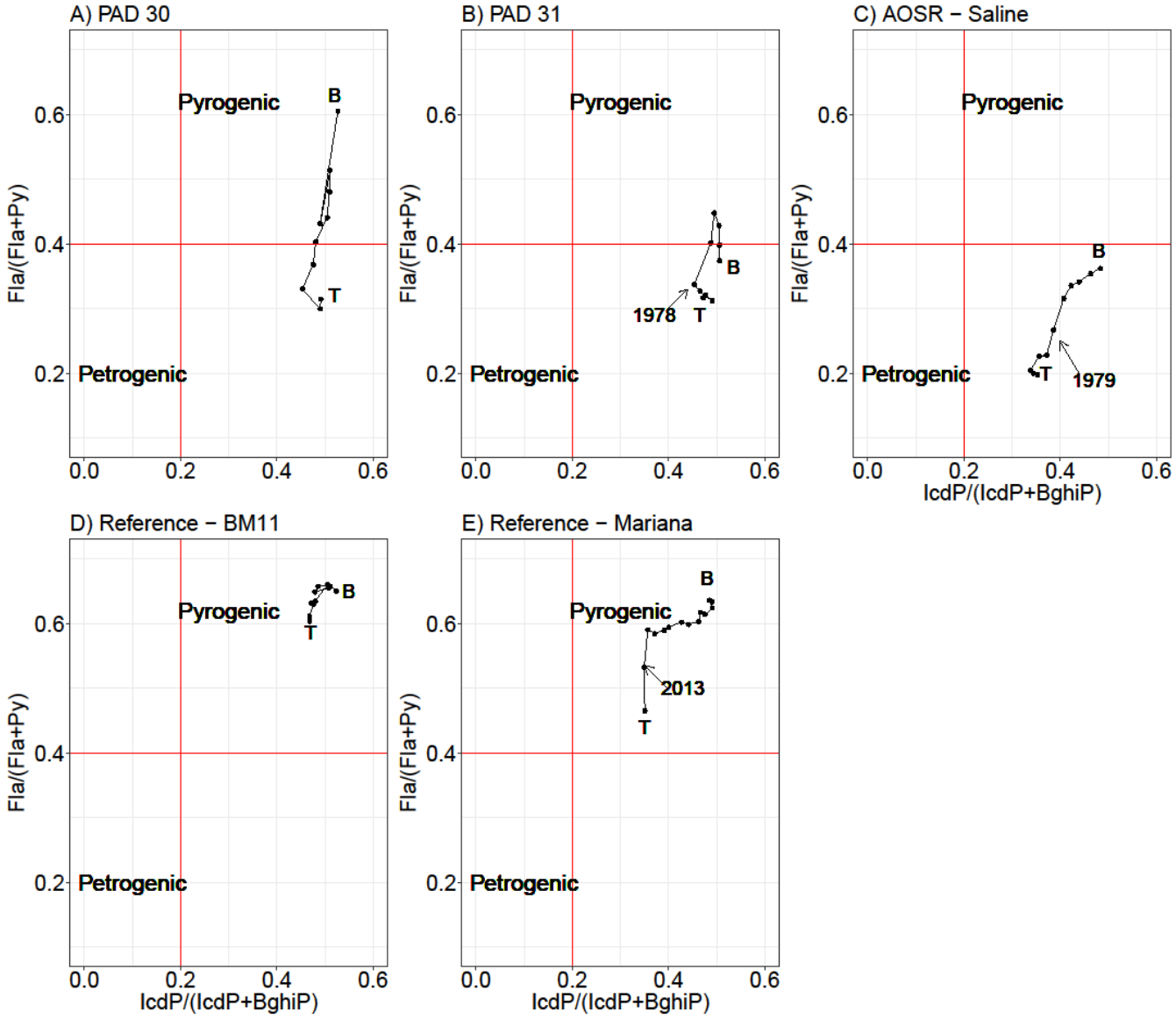


Fig.3. Plots showing PAC composition of lake sediment cores from the five study sites in relation to the PAC diagnostic ratios Fluoranthene/Pyrene, (F/(FLA+Py)) and Indeno(1,2,3-cd)pyrene(IcdP) / Benzo(g,h,i)perylene(BghiP), (IcdP/(IcdP + BghiP)). Data points are connected to show the sequence of sediment deposition. (B) indicates the bottom of each core (time before industrial development) and (T) indicated the top of the core (most recent sediment, deposited during industrial development). Red lines indicate separations from petrogenic and pyrogenic space.

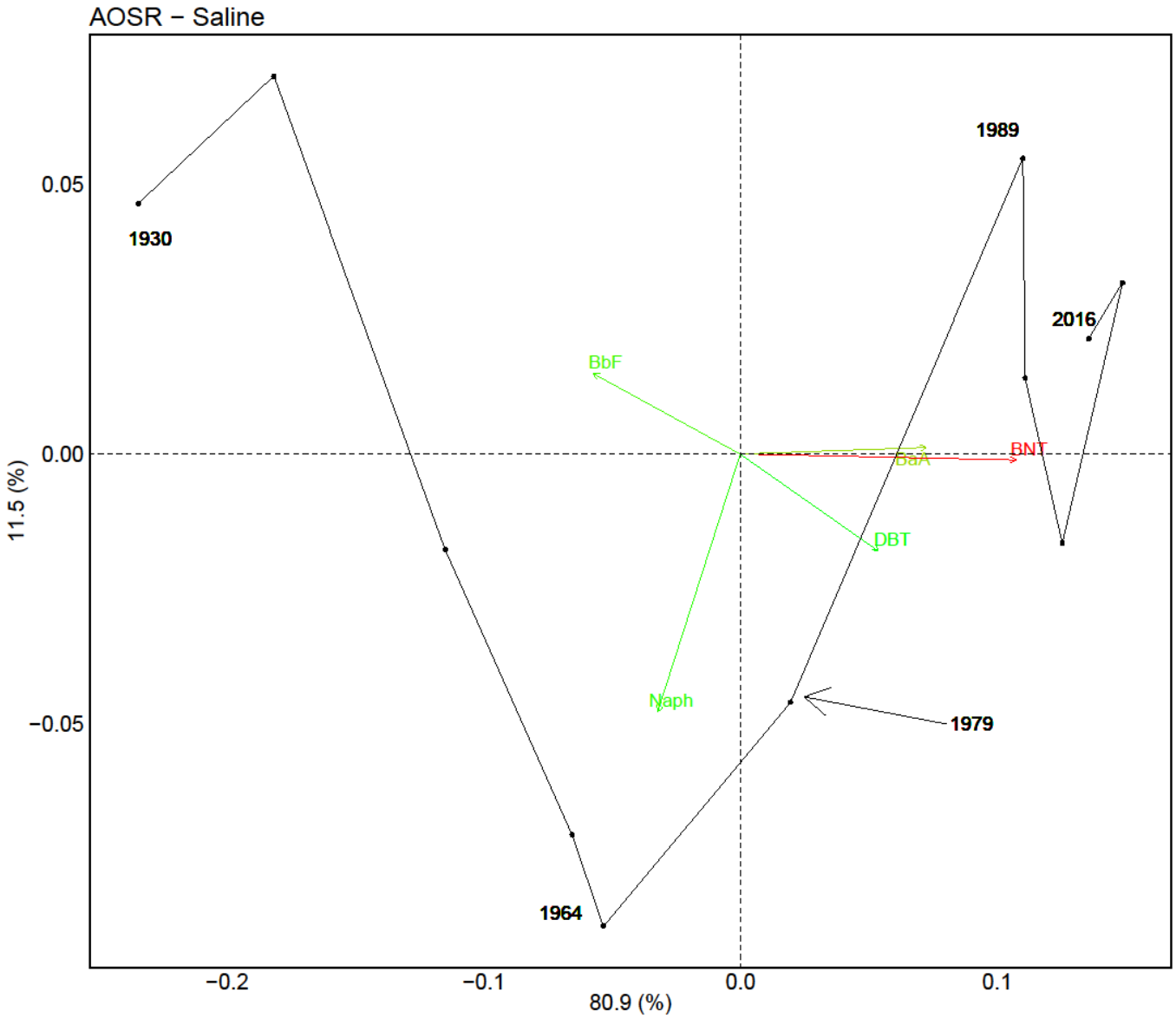


Fig.4. Ordination plot of principle components for each lake down core for parent PACs, data from lake sediment cores. Each biplot shows sample scores and parent PACs as explanatory variables. Arrows indicate the contribution of the 5 most important explanatory variables (red arrows have highest contribution and green arrows have the lowest contribution). An arrow shows directional change from bottom to top of the core with dates marking the oldest and newest interval in the sediment core.

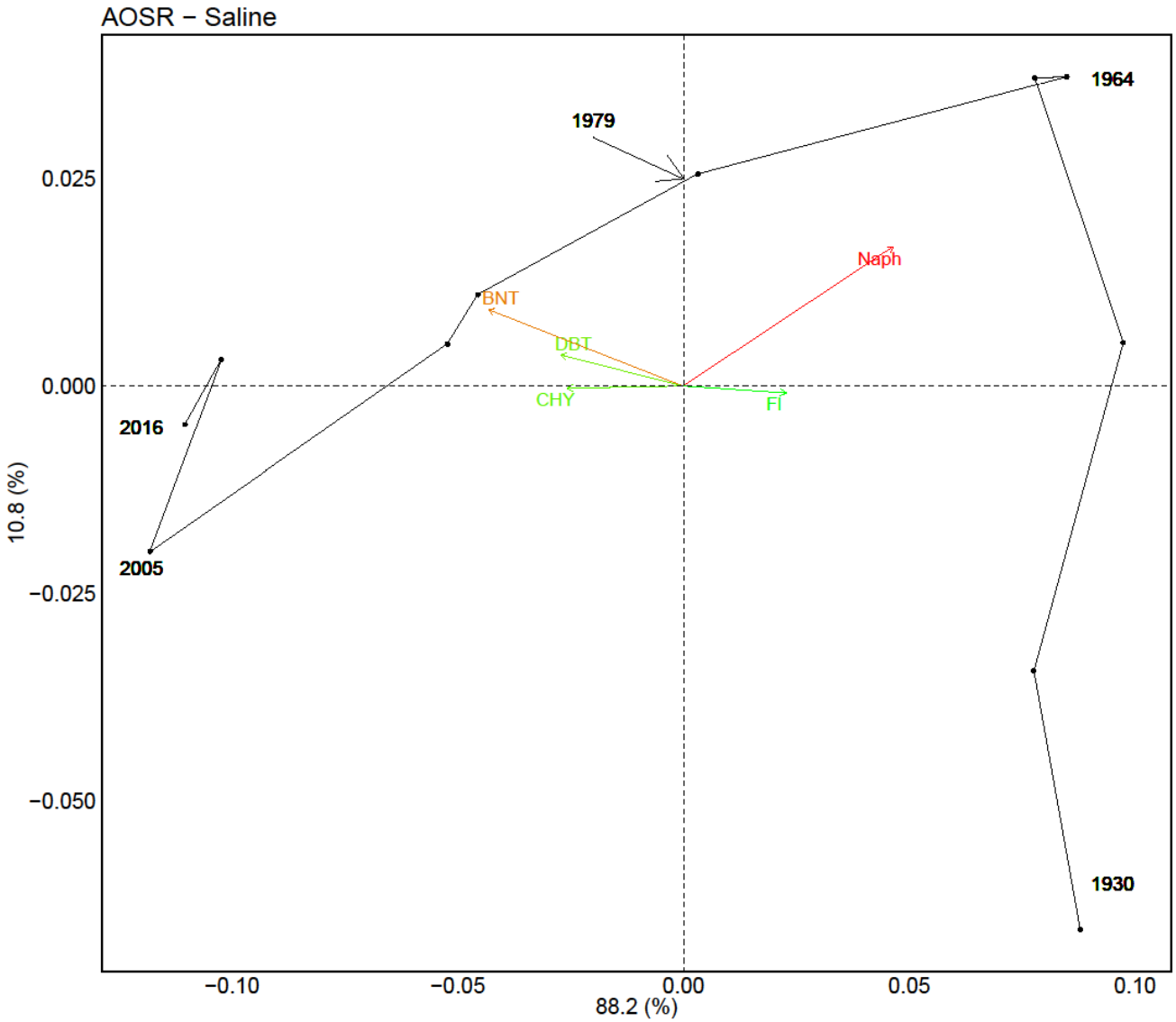


Fig.5. Ordination plot of principle components for each lake down core for alkylated PACs, data from lake sediment cores. Each biplot shows sample scores and alkylated PACs as explanatory variables. Arrows indicate the contribution of the 5 most important explanatory variables (red arrows have highest contribution and green arrows have the lowest contribution). An arrow shows directional change from bottom to top of the core with dates marking the oldest and newest interval in the sediment core.

Supplementary Information

Table S3: Targeted PAC analytes

Polycyclic Aromatic Compounds	Abbreviation
16 US EPA Priority PAHs	
Naphthalene	Naph
Acenaphthylene	Acl
Acenaphthene	Ace
Fluorene	Fl
Phenanthrene	Phen
Anthracene	An
Fluoranthene	Fla
Pyrene	Py
Benz(a)anthracene	BaA
Chrysene and triphenylene	Chy
Benzo(b)fluoranthene	BbF
Benzo(k)fluoranthene	BbK
Benzo(a)pyrene	BaP
Indeno(1,2,3-cd)pyrene	IcdP
Dibenz(a,h)anthracene	DA
Benzo(ghi)perylene	BghiP
Additional PACs	
Dibenzothiophene	DBT
Benzonaphthothiophene	BNT

Table S4: Down core petroleum biomarker diagnostic ratios for BM11

Diagnostic Ratios	**Sediment core depth intervals (cm) Diagnostic Ratios**										
	0.5-1	1.5-2	2.5-3	3.5-4	4.5-5	5.5-6	6.5-7	7.5-8	8.5-9	9.5-10	10.5-11
C_{23}/C_{24}	1.24	1.28	1.64	2.13	1.82	1.17	2.26	0.00	2.36	3.30	1.20
C_{23}/C_{30}	0.12	0.07	0.08	0.08	0.06	0.03	0.08	0.06	0.06	0.05	0.05
C_{24}/C_{30}	0.10	0.06	0.05	0.04	0.03	0.03	0.04	0.00	0.02	0.02	0.04
C_{29}/C_{30}	0.70	0.82	0.82	0.75	0.81	0.80	0.82	0.80	0.74	0.84	0.93
Ts/Tm	0.31	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$C_{30}/\sum C_{31\text{-}35}$	0.11	0.10	0.10	0.08	0.09	0.09	0.09	0.09	0.10	0.09	0.09
C_{31}(S)/C_{31}(R)	0.07	0.07	0.05	0.91	0.06	0.06	0.05	0.06	0.06	0.05	0.00
C_{34}(S)/C_{35}(S)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_{34}(R)/C_{35}(R)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_{27}abb/C_{29}abb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\sum$Steranes/$\sum$Terpanes	0.04	0.10	0.11	0.10	0.08	0.09	0.06	0.12	0.02	0.09	0.08

Table S5: Down core petroleum biomarker diagnostic ratios for Mariana Lake

Diagnostic Ratios	**Sediment core depth intervals (cm)**												
	0.5-1	1.5-2	2.5-3	3.5-4	4.5-5.5	5.5-6	8.5-9.5	10.5-11	12.5-13	14.5-15	16.5-17	18.5-19	19-20
C_{23}/C_{24}	1.46	1.31	2.05	1.10	1.45	1.11	1.84	1.20	1.63	1.35	1.52	0.00	0.74
C_{23}/C_{30}	0.24	0.26	0.27	0.19	0.18	0.17	0.21	0.14	0.11	0.07	0.07	0.06	0.05
C_{24}/C_{30}	0.17	0.20	0.13	0.17	0.12	0.15	0.12	0.12	0.07	0.05	0.05	0.00	0.07
C_{29}/C_{30}	1.29	1.22	1.11	1.29	1.43	1.46	1.69	1.29	1.37	1.38	1.30	1.44	1.34
Ts/Tm	0.00	0.00	0.00	0.00	0.30	0.34	0.35	0.37	0.00	0.00	0.00	0.00	0.00
$C_{30}/\sum C_{31\text{-}35}$	0.14	0.13	0.14	0.14	0.13	0.13	0.11	0.12	0.11	0.09	0.08	0.07	0.08
$C_{31}(S)/C_{31}(R)$	0.24	0.24	0.21	0.30	0.21	0.21	0.20	0.16	0.15	0.13	0.11	0.11	0.10
$C_{34}(S)/C_{35}(S)$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$C_{34}(R)/C_{35}(R)$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_{27}abb/C_{29}abb	1.02	1.86	0.97	1.59	1.02	0.97	1.06	1.20	1.37	0.00	0.00	0.00	0.00
$\sum$Steranes/$\sum$Terpanes	0.87	0.40	0.44	0.53	0.49	0.42	0.54	0.49	0.33	0.10	0.07	0.09	0.07

Table S6: Down core petroleum biomarker diagnostic ratios for Saline Lake

Diagnostic Ratios	**Sediment core depth intervals (cm)**										
	0.5-1	1.5-2	2.5-3	3.5-4	4.5-5	5.5-6	6.5-7	7-7.5	7.5-8	8.5-9	9.5-10
C_{23}/C_{24}	1.88	1.76	1.86	1.81	1.78	1.82	1.79	1.77	1.68	1.79	1.69
C_{23}/C_{30}	0.47	0.45	0.46	0.47	0.46	0.43	0.42	0.45	0.44	0.48	0.56
C_{24}/C_{30}	0.25	0.25	0.25	0.26	0.26	0.24	0.23	0.25	0.26	0.27	0.33
C_{29}/C_{30}	0.80	0.78	0.80	0.83	0.83	0.81	0.81	0.84	0.84	0.87	0.98
Ts/Tm	0.32	0.32	0.33	0.35	0.33	0.35	0.37	0.35	0.36	0.35	0.34
$C_{30}/\sum C_{31\text{-}35}$	0.49	0.48	0.49	0.50	0.48	0.47	0.46	0.49	0.44	0.44	0.46
C_{31}(S)/C_{31}(R)	1.21	1.21	1.19	1.16	1.14	1.12	1.06	1.24	1.08	1.12	1.02
C_{34}(S)/C_{35}(S)	1.07	1.01	0.89	0.98	1.00	0.99	0.91	0.96	1.06	1.02	0.81
C_{34}(R)/C_{35}(R)	1.35	1.59	1.26	1.19	1.05	1.53	1.58	1.43	1.44	1.07	1.11
C_{27}abb/C_{29}abb	1.28	1.06	1.14	1.34	1.09	1.03	0.99	1.30	0.95	1.06	0.85
∑Steranes/∑Terpanes	0.13	0.13	0.14	0.14	0.14	0.16	0.15	0.15	0.12	0.14	0.13

Table S7: Down core petroleum biomarker diagnostic ratios for PAD 30

Diagnostic Ratios	**Sediment core depth intervals (cm)**									
	0-1	4-5	6-7	8-9	10-11	12-13	15-16	20-21	28-29	38-39
C_{23}/C_{24}	1.76	1.78	1.71	1.71	1.45	1.11	1.32	1.39	1.42	1.07
C_{23}/C_{30}	0.59	0.52	0.45	0.40	0.32	0.22	0.27	0.30	0.39	0.23
C_{24}/C_{30}	0.33	0.29	0.26	0.23	0.22	0.20	0.20	0.22	0.28	0.21
C_{29}/C_{30}	0.95	0.99	0.91	0.86	0.92	0.95	0.88	0.89	0.95	0.93
Ts/Tm	0.36	0.35	0.35	1.17	0.41	0.38	0.35	0.29	0.37	0.35
$C_{30}/\sum C_{31\text{-}35}$	0.52	0.47	0.44	0.39	0.42	0.30	0.37	0.36	0.42	0.41
C_{31}(S)/C_{31}(R)	0.97	1.00	1.00	0.99	0.78	0.58	0.66	0.90	1.06	1.02
C_{34}(S)/C_{35}(S)	1.01	1.02	1.08	0.91	0.00	0.00	0.00	1.07	1.10	1.04
C_{34}(R)/C_{35}(R)	1.13	1.01	1.29	0.00	0.00	0.00	0.00	1.33	1.72	0.00
C_{27}abb/C_{29}abb	1.04	1.03	0.99	2.17	3.89	2.52	2.03	1.48	1.01	1.55
∑Steranes/∑Terpanes	0.11	0.15	0.18	0.18	0.31	0.14	0.18	0.22	0.18	0.26

Table S8: Down core petroleum biomarker diagnostic ratios for PAD 31

Diagnostic Ratios	**Sediment core depth intervals (cm)**									
	0-1	4-5	8-9	10-11	12-13	16-17	17-18	18-19	22-23	26-27
C_{23}/C_{24}	1.63	1.67	1.53	1.74	1.63	1.70	1.68	1.59	1.76	1.67
C_{23}/C_{30}	0.48	0.46	0.36	0.52	0.46	0.41	0.37	0.37	0.45	0.44
C_{24}/C_{30}	0.29	0.28	0.24	0.30	0.28	0.24	0.22	0.24	0.26	0.26
C_{29}/C_{30}	0.92	0.93	0.87	0.94	0.91	0.99	0.84	0.82	0.90	0.90
Ts/Tm	0.34	0.34	0.37	0.32	0.34	0.29	0.32	0.29	0.33	0.39
$C_{30}/\sum C_{31\text{-}35}$	0.47	0.48	0.46	0.48	0.45	0.29	0.36	0.34	0.39	0.42
C_{31}(S)/C_{31}(R)	1.05	0.92	1.01	0.95	0.88	0.75	0.75	0.66	0.80	0.89
C_{34}(S)/C_{35}(S)	0.91	1.11	0.98	0.98	1.25	0.60	0.69	0.63	0.91	0.88
C_{34}(R)/C_{35}(R)	1.22	1.32	1.16	1.36	1.29	0.00	1.53	0.00	1.22	1.78
C_{27}abb/C_{29}abb	0.84	0.76	0.77	0.88	0.94	1.28	1.41	1.39	1.12	0.91
∑Steranes/∑Terpanes	0.14	0.14	0.17	0.15	0.16	0.18	0.19	0.17	0.14	0.17

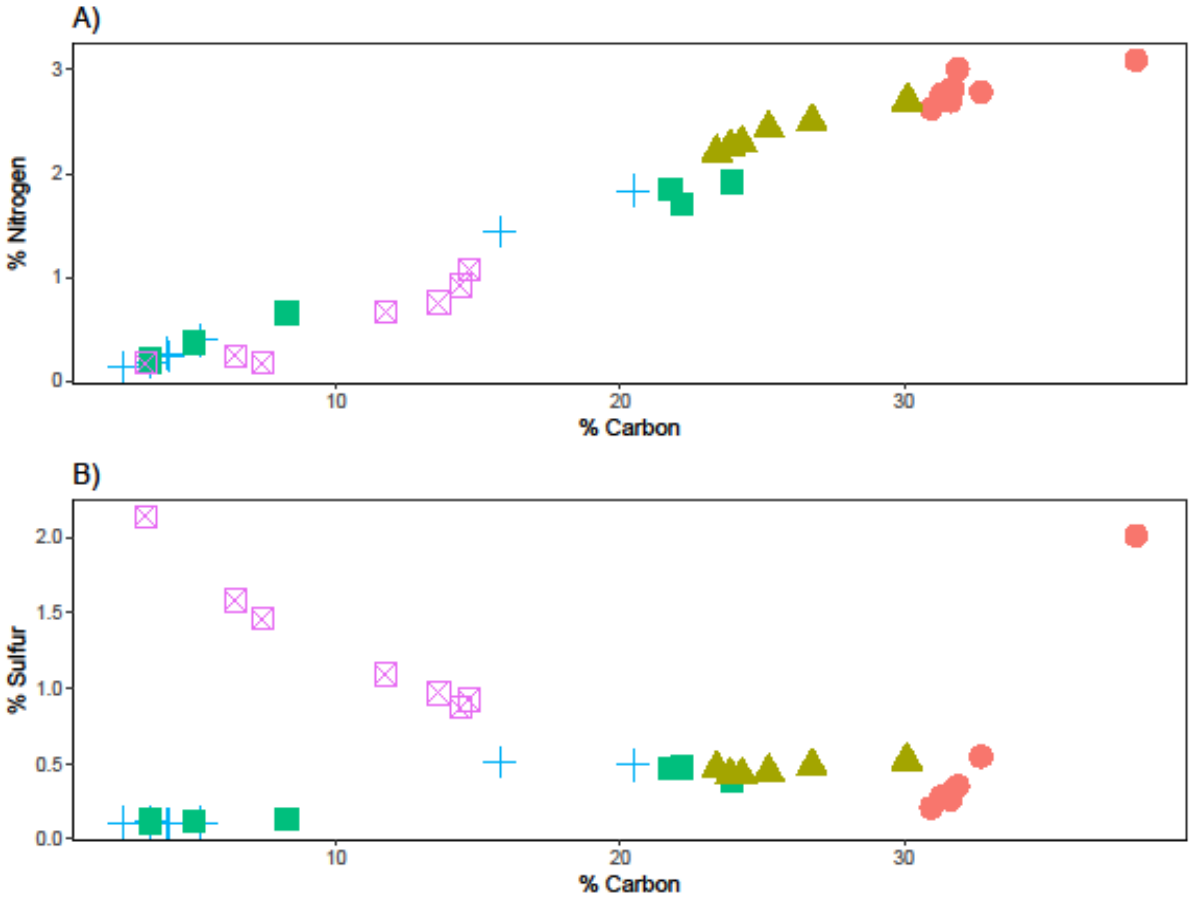


Figure S6: A) Scatter plots of percent organic carbon versus percent nitrogen, and B) percent carbon versus percent sulfur, for down core lake sediments from BM11 (circles), Mariana (triangles), PAD 30 (squares), PAD 31 (cross), Saline (box).

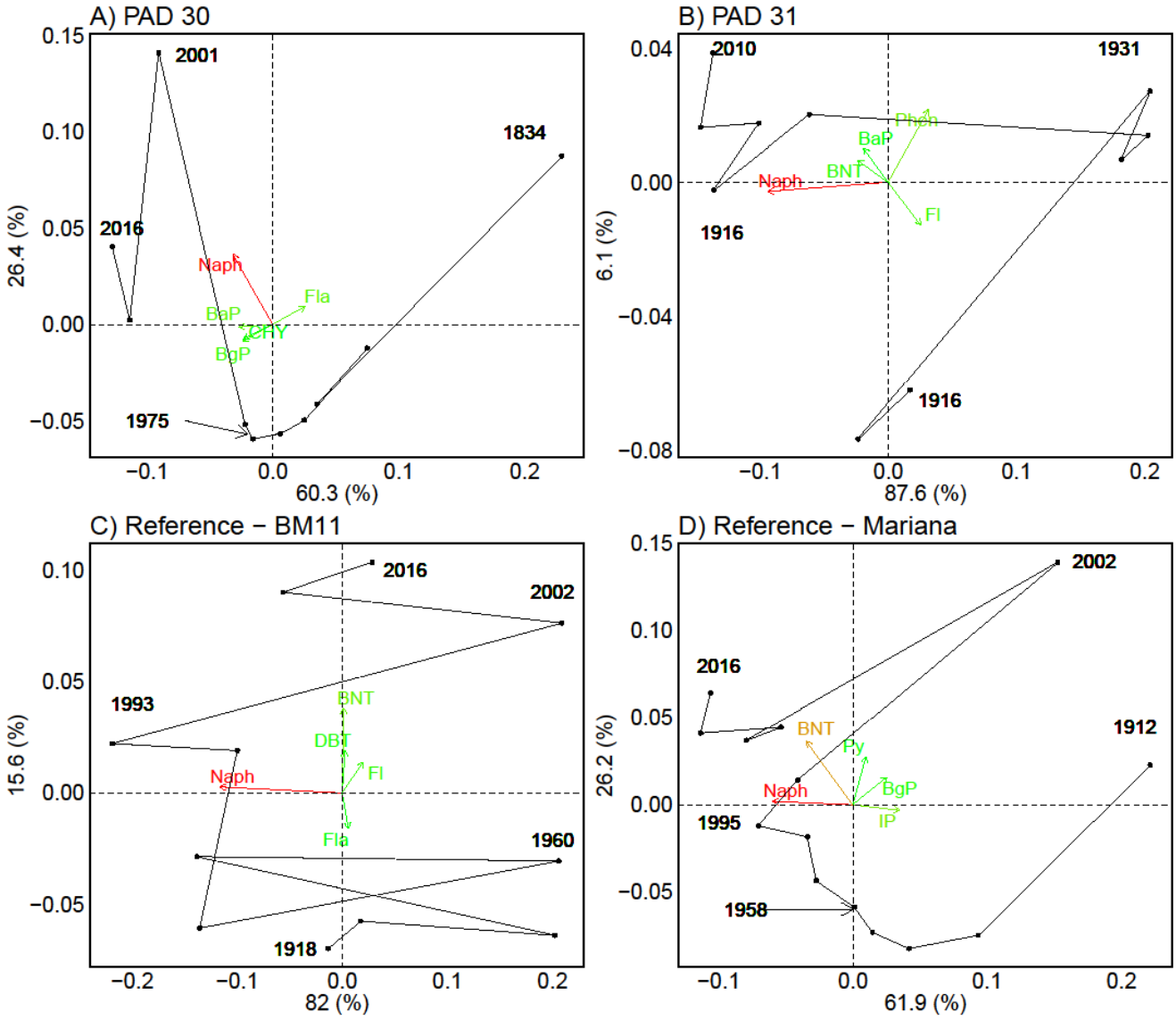


Figure S7: Ordination plot of principle components for each lake down core for parent PACs, data from lake sediment cores. Each biplot shows sample scores and parent PACs as explanatory variables. Arrows indicate the contribution of the 5 most important explanatory variables (red arrows have highest contribution and green arrows have the lowest contribution). An arrow shows directional change from bottom to top of the core with dates marking the oldest and newest interval in the sediment core.

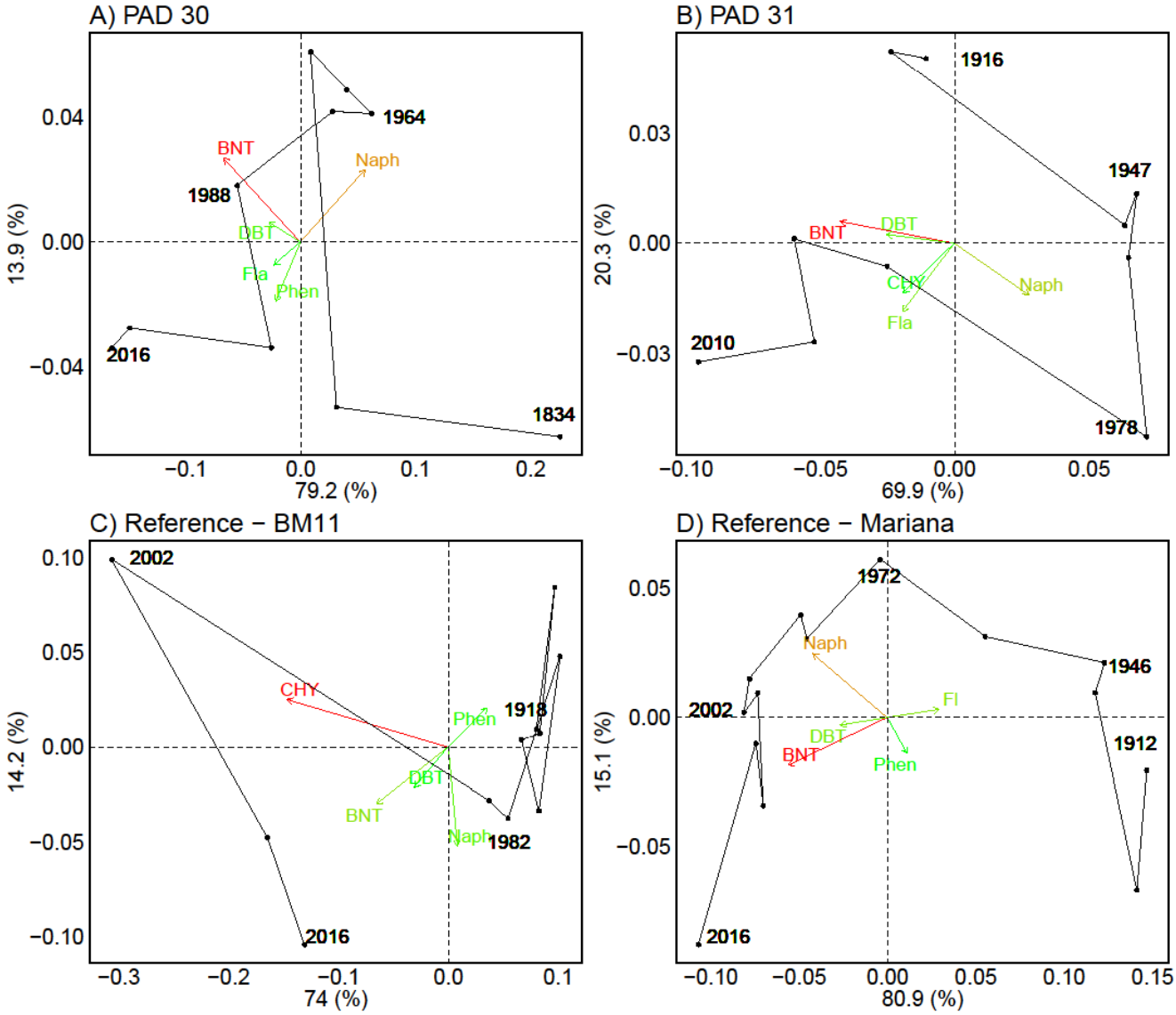


Figure S8: Ordination plot of principle components for each lake down core for alkylated PACs, data from lake sediment cores. Each biplot shows sample scores and alkylated PACs as explanatory variables. An arrow shows directional change from bottom to top of the core with dates marking the oldest and newest interval in the sediment core.

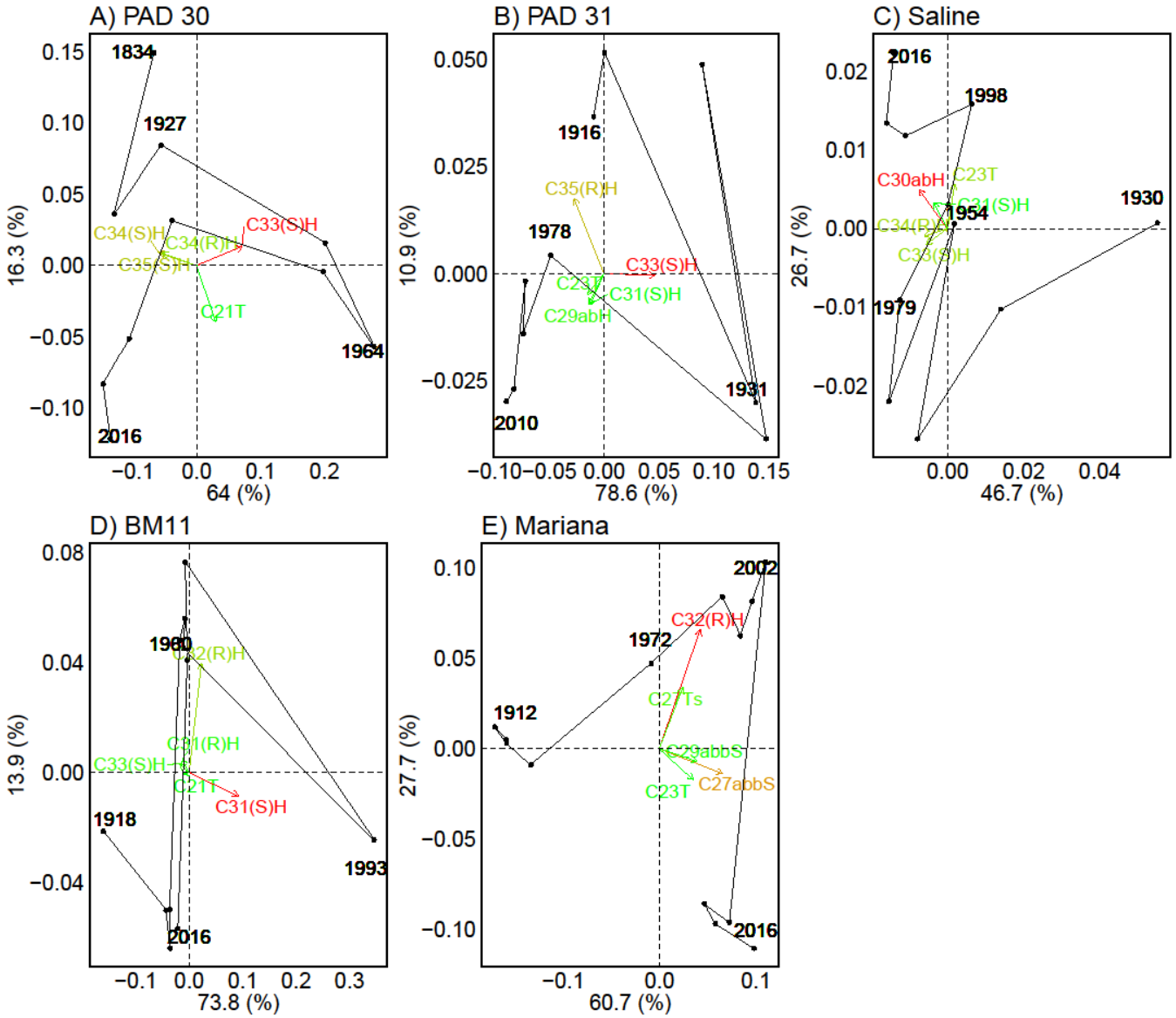


Figure S9: Ordination plot of principle components for each lake down core for biomarkers, data from lake sediment cores. Each biplot shows sample scores and biomarkers as explanatory variables. An arrow shows directional change from bottom to top of the core with dates marking the oldest and newest interval in the sediment core.

Chapter 3. Conclusion

To my knowledge, the results presented in this thesis are the first to analyse petroleum biomarkers in sediment profiles across the AOSR and the PAD. The aim of this thesis was to evaluate PACs and petroleum biomarkers as proxies for mining activities to better understand their impacts on a temporal and spatial scale. This was achieved by

(1) Measuring the concentration and distribution of PACs and petroleum biomarkers in sediment profiles in addition to characterizing their petrogenic or pyrogenic origins (Chapter 2).

I have taken the preliminary steps in using petroleum biomarkers in sediment profiles as proxies of mining activities and have added to the current knowledge of down core PAC profiles in the AOSR and the PAD.

3.1 Study Outcomes

Chapter 2 provides an in-depth analysis of PACs and petroleum biomarkers (hopanes, steranes and terpanes) in sediment profiles of selected lakes in three regions: The Peace Athabasca Delta and the oil sands region and reference lakes outside of the AOSR. Although many studies have examined the PACs in sediment profiles in the AOSR and the PAD, this thesis is the first to our knowledge to evaluate the use of petroleum biomarkers in sediment profiles, to track mining activities (extraction and upgrading) in northern Alberta. The results of this study confirmed the initial prediction that PACs would increase in modern sediments (post 1970s) as a result of oil sands mining and upgrading, in the AOSR and the PAD. Higher concentrations of alkylated PACs associated with bitumen sources (benzonaphthothiophenes, dibenzothiophenes and chrysenes) were elevated in the AOSR and PAD when compared to

reference lakes. PACs in reference lakes did show increases in PACs in modern sediments (>1990s) as a result of atmospheric deposition of petrogenic PACs (BM11) and vehicle emissions (Mariana Lake). Lakes within the PAD showed evidence of the hydrogeologic connection between the AOSR and the PAD, based on loading of bituminous PACs, which are present in PAD 30 and PAD 31. Further evidence of shifts from pyrogenic sources to petrogenic sources are shown in PAC diagnostic ratios. All lakes showed shifts in modern sediments towards petrogenic sources as seen by decreases in Fla/Py and IcdP/BghiP ratios. Petroleum biomarkers have shown their importance in identifying changes in sources from pyrogenic to petrogenic. However, these results were only seen in Mariana Lake and BM11, where clear increases of petroleum biomarkers may be connected to vehicle traffic in the region and atmospheric deposition respectively. The use of petroleum biomarkers in regions with historical oil signatures, such as the AOSR and PAD, cannot provide further information regarding industrial activities, as these biomarkers are historically present due to these bitumen rich source rocks. In areas without petroleum sources, petroleum biomarkers may be able to provide information on the addition of petroleum sources into a system. Further examination of petroleum biomarkers in historically clean areas, which have later been exposed to anthropogenic activities, could provide a better understanding of the impacts of petroleum sources and their movement through the environment.

3.2 Future Directions

Through this study, we have determined that mining operations in the AOSR have resulted in increased PACs within the region and downstream in the PAD. The use of petroleum biomarkers, as indicators of petroleum source inputs, have proven to be promising proxies of anthropogenic change. Petroleum biomarkers have clearly tracked petroleum source increases in

reference lakes and provided evidence for when petroleum entered a lake system. However, in areas historically rich with petroleum, such as the AOSR and the PAD, shifts are not apparent, as sediments are already rich with these biomarkers. Using petroleum biomarkers in historically untouched environments, with respect to petroleum sources, such as the Arctic, would provide important information on petroleum source additions. With increased commercial shipping through the more frequently opened Arctic Ocean (Canadian Shipping Act, 2001), anthropogenic impacts will be of greater interest to governments and environmental regulators. This diverse landscape is extremely fragile and will continue to change with increased inputs of anthropogenic source contamination, including petroleum (Casper, 2009). The addition of oil sources such as crude oils, diesel, and gasoline, will have significant impacts on the environment. If these oil compounds can be tracked within the Arctic, researchers, may have a better understanding of when this contamination arrived and from what sources.

Furthermore, the shifts and trends of PACs in sediment profiles provide valuable information on mining influences on a temporal and spatial scale. However, PACs are of concern because of their toxic, mutagenic and carcinogenic properties (Douben, 2003; Evans et al., 2016). Determining if PAC have increased as a result of mining activities, creating hazards to humans and wildlife should be examined more closely. Toxicity testing of PAC extracts from sediment profiles would provide strong evidence for changes in toxicity through time. These analyses would provide evidence of mining impacts through time relating to both humans and wildlife.

Previously, studies have focused on surface grab or individual PAC exposure studies (Gauthier et al., 2004; Goswami et al., 2016; Medunić et al., 2016), providing a vast amount of information on the toxicity of specific PACs. However, PACs interact in complex mixtures,

making toxicity testing difficult as each mixture has a unique signal (White, 2002). In the AOSR and PAD, PACs have been present for millions of years, therefore, a petrogenic signal has always been present in these environments (Hall et al., 2012). Downcore toxicity testing of sediments could provide valuable information on the impact of mining activities in the AOSR and the PAD. Tracking the toxicity of PACs and heavy metals emitted from oil sands mining operations into lake sediments through high throughput PCR arrays would yield information on the history of toxicity in the region. Determining how shifts in PACs have affected this baseline of toxicity would be highly important for local communities and local biologists.

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