Integrated analyses of petroleum biomarkers and polycyclic aromatic compounds in lake sediment cores from an oil sands region

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Abstract

We examined polycyclic aromatic compounds (PACs) and petroleum biomarkers (steranes, hopanes, and terpanes) in radiometrically-dated lake sediment cores from the Athabasca oil sands region (AOSR) and the Peace-Athabasca Delta (PAD) region in Alberta (Canada) to determine whether contributions from petroleum hydrocarbons have changed over time. Two floodplain lakes in the PAD (PAD 30, PAD 31) recorded increased flux of alkylated PACs and increased petrogenic (petroleum-derived) hydrocarbons after ~1980, coincident with a decline of sediment organic carbon content and a rise of bulk sedimentation rate, likely due to increased Athabasca River flow. A large expansion of upstream oilsands mining, upgrading, and refining may also have contributed to the observed shift to more petrogenic hydrocarbons to sediments since the 1980s. Alkylated PAC flux increased in the floodplain lake analyzed within the AOSR (Saline Lake) since the 1970s-1980s, coincident with a sharp rise in sediment organic carbon content and increased contributions of petrogenic hydrocarbons. These changes identify increased supply of petrogenic PACs occurred as Athabasca River floodwaters waned, and may implicate aerial contributions of petrogenic hydrocarbons from oilsands activity. PACs and petroleum biomarkers (steranes, hopanes, and terpanes) in sediment cores from Saline Lake, PAD 30 and PAD 31 revealed a predominance of petrogenic hydrocarbons in these lakes. In contrast, we recorded minimal petrogenic hydrocarbons in the reference lakes outside the surface minable area of the AOSR and PAD (Mariana Lake and BM11), though we noted slight increases in petrogenic contributions to modern (2010-2016) sediments. We show how a combined analysis of PACs and petroleum biomarkers in sediments is useful to quantify petrogenic contributions to lakes with added confidence and highlight the potential for petroleum biomarkers in lake sediment cores as a novel and effective method to track petroleum hydrocarbons in lake sediment.

Keywords: oil sands monitoring; paleolimnology; Peace-Athabasca Delta; Embarras Breakthrough; bitumen

1.0 Introduction

The Athabasca Oil Sands Region (AOSR), one of three distinct crude oil reserves in northern Alberta, produces 1.14 million barrels per day of crude oil (CAPP, 2018). The mining and upgrading of oil sands in the AOSR is an environmentally contentious issue, resulting in significant landscape disturbances, habitat loss, and the release of environmental contaminants, which are harmful to aquatic organisms (Bilodeau et al., 2019; Galarneau et al., 2014; Kelly et al., 2010; Mundy et al., 2019; Rooney et al., 2012). In recent years, the rapid expansion of surface mining raised concerns about the potential release of contaminants into the environment (Korosi et al., 2016; Yang et al., 2014). Several studies showed elevated concentrations of polycyclic aromatic compounds (PACs) and heavy metals within 80 km of upgrading operations in snowpack, water (Kelly et al., 2010, 2009), and lake sediments (Kurek et al., 2013). Additionally, bitumen and its associated PACs are transported downstream into the Peace-Athabasca Delta (PAD) along with other petroleum-derived contaminants, raising questions about the potential impacts on mining and development in the AOSR, and on downstream ecosystems including the PAD (Timoney and Lee, 2009).

The PAD is one of the world's largest inland freshwater deltas, a hydrologically dynamic environment containing many interconnected lakes and channels, all fed by the Athabasca and Peace River watersheds (Jautzy et al., 2015b). The PAD is ~200 km downstream of the surface mining development zone. The public has long raised concerns about potential cumulative environmental effects of the petrogenic hydrocarbons on this downstream region. The Athabasca River has long delivered PACs into the PAD by natural processes, via erosion of bitumen from upstream river banks, as shown by the presence of bitumen-associated PACs in pre-industrial PAD sediments (Hall et al., 2012; Jautzy et al., 2015b). In 1982, a major hydrological event

called the Embarras Breakthrough occurred within the Athabasca sector of the PAD. This has resulted in delivery of large quantities of suspended sediments into lakes along Mamawi Creek (including PAD 30 and, PAD 31 and Mamawi Lake at the creek's terminus (Kay et al., 2019). Significant hydrogeological changes in river water supply and sediment likely affected the concentrations and composition of petrogenic chemicals including PACs through increased flooding events at PAD 31 post-1982 (Hall et al., 2012).

PACs 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 mainly unsubstituted 'parent' PACs (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). Air currents may then transport these PACs long range (Abdel-Shafy and Mansour, 2016; Sofowote et al., 2011). In water, PACs tend to adsorb and partition into sediments due to their hydrophobic nature (Abdel-Shafy and Mansour, 2016; Thienpont et al., 2017). PACs may enter lakes via atmospheric deposition, erosion from the catchment, river transport, and other sources (Hall et al., 2012).

In this study, we assessed the potential for petroleum biomarkers to track petrogenic sources to freshwater lake sediment cores. Studies have also used petroleum biomarkers (hopanes, terpanes, and steranes) to investigate petrogenic sources in the environment (Wang et al., 2013; Yang et al., 2011). Petroleum biomarkers are recalcitrant biomolecules from deceased organisms, found ubiquitously in crude oils, rocks, and sediments, that undergo little structural change over time (Wang et al., 2016, 2006) . Several studies have used petroleum biomarkers for petroleum source identification, differentiation of oils, and monitoring of oil weathering (e.g.

88 Wang et al., 2013) due to their thermodynamic stability and high source specificity (Wang et al.,
89 2016). Consequently, analysis of petroleum biomarkers in lake sediment cores may accurately
90 track contributions from fossil fuel mining and processing to freshwater environments.

91 We assessed PACs and petroleum biomarkers in sediment cores from all five lakes to
92 determine if petrogenic sources can be estimated by these two independent classes of
93 compounds. We hypothesized that: (1) petrogenic contributions of petroleum biomarkers and
94 PACs are higher in the AOSR and the PAD than in upland reference lakes outside the AOSR; (2)
95 petrogenic contributions of petroleum biomarkers and PACs in the AOSR increased in lake
96 sediments coeval with the onset of oil sands production; and (3) the Embarras Breakthrough
97 increased petrogenic PACs and petroleum biomarkers coeval with post-1982 flooding events in
98 the PAD. The combined use of both petroleum biomarkers and PACs in sediments provides
99 independent proxies of petrogenic contamination to lakes in these regions over the past century,
100 thus we predict that conclusions drawn from each should be similar.

101 **2.0 Methods**

102 *2.1 Study Sites and Sample Collection*

103 We conducted this study in the Municipality of Wood Buffalo near the community of
104 Fort McMurray, Alberta, and in the PAD, which is mainly (80%) located within Wood Buffalo
105 National Park (Fig.1). Sediment cores from three Athabasca River floodplain lakes provided an
106 opportunity to assess contaminant transport via mainly fluvial pathways. Saline Lake is centrally
107 located within the AOSR, within 5 km from the nearest mining upgrader and the zone of known
108 aerial contaminant deposition (Cooke et al., 2017; Kirk et al., 2014; Klemt et al., 2020). Saline
109 Lake is situated directly adjacent to the Athabasca River, and thus receives episodic inputs of
110 river floodwater. However, declining river flows in recent decades has led to reduced frequency

of flooding, and nearby lakes show evidence of increased deposition of contaminants via aerial pathways as flood influence has waned (Klemt et al., 2020). Lakes PAD 30 and PAD 31, are located in the Athabasca Delta, and are situated ~ 1 km apart and on opposite sides of Mamawi Creek, and thus approximate replicate sites for the goals of this study (Fig.1). However, PAD 31 lies at slightly lower elevation than PAD 30 and is slightly more flood-prone. Nevertheless, PAD 30 and PAD 31 have similarly experienced three episodes of distinctive hydrological conditions and contaminant deposition since 1700 (Hall et al., 2012; Kay et al., 2020, 2019; Wolfe et al., 2008). Prior to ~1700 until ~1940, the lakes were inundated under a high-stand of Lake Athabasca (under a former embayment now partially occupied by Mamawi Lake) supported by elevated Athabasca River flow. After ~1940, Lake Athabasca levels declined and both lakes entered an isolated, closed-drainage hydrological phase of infrequent or absent flooding despite their location adjacent to Mamawi Creek, which was a relict (non-flowing) channel at that time. After July 1982, both lakes entered a third phase when they became increasingly prone to river flooding following avulsion of the Embarras River into Cree and Mamawi creeks (an event known as the Embarras Breakthrough), which has routed increasing volumes of Athabasca and Embarras river flow to the low lying areas where these lakes are located. Increased delivery of river-supplied sediment after the Embarras Breakthrough is visually detected as an abrupt horizon in sediment cores from dark brown organic-rich material before the Embarras Breakthrough to light grey mineral-rich sediment after (Kay et al., 2019).

Reference lakes potentially receive mid- and far-field deposition via the atmosphere, respectively. BM11 is located in a remote south-eastern section of the Birch Mountains, approximately 40 km north of the nearest upgrader. Mariana Lake is approximately 120 km south-west of the nearest upgrader facility (which upgrades heavy oils into synthetic crude), and

lies ~ 150 m from Alberta Highway 63. Highway 63 was constructed in the 1960s, and vehicular traffic increased markedly after it was twinned in 2008. A convenience store and gas station were built within 80 m of Mariana Lake in 1970 and closed in 2008 (Cormier, 2008). We selected Mariana Lake and BM11 as reference sites (sites outside the range of oilsands influence) because of (1) their distance from oil sands upgraders, and (2) they were outside the PAD and the surface minable area of the AOSR.

We collected lake sediment cores from PAD 30 in June 2016, PAD 31 in September 2010, and BM11, Mariana Lake, and Saline Lake in June 2017. A gravity corer extracted bottom sediments, which we then sectioned at 0.5 cm intervals (Saline Lake, Mariana Lake, and BM11) or 1 cm intervals (PAD 30, PAD 31) using a vertical extruder. Sediments were stored in Whirl-Pak® bags at -20°C (Saline Lake, Mariana Lake, and BM11) or 4°C (PAD 30, PAD 31).

2.2 Dating sediment cores

Each lake sediment core was ^{210}Pb dated using an Ortec High Purity Germanium Gamma Spectrometer (Advanced Measurement Technology Ink, Oak Ridge, TN, USA) at the University of Ottawa. The constant rate of supply model (Appleby et al., 1983; Appleby and Oldfield, 1978) using ScienTissiMe software (Barry's Bay, ON, Canada) determined sediment core chronologies based on excess ^{210}Pb activities. We calculated our gamma detector efficiencies based on Certified Reference Materials (312 and 385) from the International Atomic Energy Association (Vienna, Austria). Sedimentation rates (g cm^{-2} y^{-1}) are reported in Supplementary information for each lake profile (Fig.S1), as they were used to calculate parent and alkylated PAC fluxes.

2.3 PAC and Biomarker analysis

Select samples spanning the entire length of the sediment cores were analyzed from each of the five lakes for the concentration and composition of PACs and petroleum biomarkers. The

target analytes were the 16 US EPA priority polycyclic aromatic hydrocarbons, benzonaphthothiophene, and dibenzothiophene, and their respective alkylated forms (Table S1). The sediment samples we extracted (20-30 g wet weight) contained a minimum of 0.5 g total organic carbon. We used a centrifuge and diatomaceous earth (Thermo Scientific, Waltham, MA, USA) to remove water from the sediments. We then spiked samples with 100 µL of deuterated recovery mixture: Naphthalene (D_8, 99.5%), Acenaphthene (D_{10}, 99%), Phenanthrene (D_{10}, 98%), Benz[*a*]Anthracene (D_{12}, 98%), Perylene (D_{12}, 98%) and *n*-Tetracosane (D_{50}, 98%), (Cambridge Isotope Laboratories Inc. Tewksbury, MA, USA). An accelerated solvent extractor (ASE-200, Dionex Corporation, Sunnyvale, CA, USA) extracted PACs with 50:50 acetone:hexane based on US EPA method 3540C, modified for accelerated solvent extraction. We separated solvent and remaining water using liquid-liquid extraction, with a 3 x 5 mL hexane rinse. We then evaporated samples down to 2 mL under a gentle stream of nitrogen (TurboVap, Biotage, Charlotte, NC, USA) and centrifuged them to remove any remaining particulates and water. We evaporated samples down to 1 mL under a gentle stream of nitrogen and fractionated them with 6 g silica gel (Grade 644) column chromatography (Fisher S7441, Hampton, NH, USA). To separate the F1 (petroleum biomarkers) and F2 (PACs) fractions, we used 22 mL hexane and 35 mL 50:50 dichloromethane:hexane, respectively.

We evaporated the F1 fraction down to 1 mL in 2,2,4-Trimethylpentane (TMP), then spiked with a known amount of internal standard, p-Terphenyl (D_{14}, 98%). We quantified compounds using a HP 6890 gas chromatograph coupled with a HP 5973N mass selective detector (GC-MS) (Agilent Technologies, Santa Clara, CA, USA) and selective ion monitoring. We evaporated F2 samples to 3 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). We analyzed F2 samples by GC-MS following the same procedure as F1 samples. All solvents were high grade Optima® from Fisher Chemicals, except TMP (Sigma-Aldrich, Oakville, ON, Canada). We ran all F1 and F2 samples with their respective method blanks (Table S8) and were method blank corrected. PACs were subsequently recovery corrected using the deuterated standards. Mean recoveries for surrogate target compounds (+1 standard deviation) were 14.5 + 7.9 for Naphthalene (D_8, 99.5%), 23.8 + 12.7 for Acenaphthene (D_{10}, 99%), 30.2 + 15.9 for Phenanthrene (D_{10}, 98%), 50.7 + 23.3 for Benz[*a*]Anthracene (D_{12}, 98%) and 56.8 + 29.3 for Perylene (D_{12}, 98%). For petroleum biomarkers, we based our recovery corrections on *n*-Tetracosane ($C_{24}D_{50}$) in TMP (Table S9). Standard reference material (SRM) extractions (NIST 1941b) were run congruently with all samples and are presented as percent SRM recoveries in Table S9 for PAHs with certified mass fraction values. Alkylated PACs were quantified as relative response to parent PAC concentrations similar to those presented by Kelly et al. (2009).

2.4 Numerical Analyses

We used established diagnostic ratios of PACs in sediment to distinguish between pyrogenic and petrogenic PAC sources in the environment (De La Torre-Roche et al., 2009; Lima et al., 2007; Yunker et al., 2002). We considered the following PAC diagnostic ratios to discriminate between petrogenic and pyrogenic PACs: (1) fluoranthene (Fla) / pyrene (Py) ratio = Fla/(Fla+Py) and (2) indeno[1,2,3-*cd*]pyrene (IcdP) / benzo[*ghi*]perylene (BghiP) ratio = IcdP/(IcdP+BghiP) as previously described by Yunker et al. (2002), De La Torre-Roche et al. (2009) and Lima et al. (2007). Similarly, we applied diagnostic ratios for petroleum biomarkers as follows: (1) C_{21} terpane (C_{21}T) / C_{23} terpane (C_{23}T) ratio = $C_{21}T/(C_{21}T + C_{23}T)$ and (2) C_{31} (R) hopane (C_{31} (R)H) / C_{31} (S) hopane ratio (C_{31} (S)H) = C_{31} (R)H/(C_{31} (R)H + C_{31} (S)H). We

selected these petroleum biomarker diagnostic ratios to maximize differences between natural organic matter and bitumen from the Alberta oil sands (AOS) (Yang et al., 2011).

We performed numerical and statistical analyses using the R statistical computing environment (v3.5.2). To explore the variations between both regions and between lakes' down core profiles, we conducted a principal component analysis (PCA) on the PAC data expressed as relative abundances. We normalized data using Hellinger normalization using the 'deconstand' function. We constructed the PCA biplots using the 'prcomp' function in the 'vegan' package. In order to compare temporal trends between our five study lakes, we conducted Mann-Kendall trend tests on PAC fluxes, PAC diagnostic ratios, and petroleum biomarker diagnostic ratios using the "Kendall" package.

3.0 Results and Discussion

3.1 PAC depositional history comparisons

PAC fluxes at PAD 30 and PAD 31, located near the Athabasca River terminus, are higher and exhibited greater temporal variation than at Saline Lake and the upland reference lakes (Fig. 2). Fluxes of alkylated PACs were roughly 4 to 6-fold higher than parent PAC fluxes at PAD 30 and roughly 5 to 7-fold at PAD 31, indicative of greater contributions from petrogenic sources than at the other study lakes (Fig. 2A, 2B). Temporal patterns of PAC flux correspond well with the known hydrological phases of these two lakes, which are located within ~1 km of each other on opposite banks of Mamawi Creek. PAC fluxes were moderate to high before ~1940 in PAD 30 and PAD 31, respectively, when these lakes were inundated under a high-stand of Lake Athabasca that formed during the Little Ice Age (Sinnatamby et al., 2010). PAC fluxes declined to lowest levels between ~1940 and the early to mid-1980s, when the lakes became isolated as Lake Athabasca water levels declined and Mamawi Creek was a relict, non-flowing

channel. At this time, both lakes were hydrologically closed-basins (i.e., flooding was infrequent), and supply of PACs was reduced to atmospheric deposition and erosion from their small catchments (consisting of fluvio-deltaic sediments). During the closed-drainage phase, the difference between alkylated and parent PAC fluxes was at a minimum, indicating greater relative contribution of PACs from pyrogenic sources. PAC flux increased after the mid-1980s when the Embarras Breakthrough promoted greater frequency and magnitude of flooding, as identified by marked decline of sediment carbon content and rise of sedimentation rate (Figs. 2, S1, S2).

Alkylated and parent PAC fluxes increased in the uppermost 4 cm in the core from Saline Lake (AOSR), with consistently greater increase of alkylated PACs than parent PACs (Fig. 2C). The period ~1980-2016 of rising and peak alkylated PAC flux coincided with marked rise of organic C content of sediment (Fig. S2). Such temporal change in organic carbon content identifies greater in-lake carbon production and less dilution of organic carbon content by inorganic suspended river sediment as Athabasca River levels and flood frequency declined, as has been demonstrated for other floodplain lakes in the AOSR, both upstream and downstream of Saline Lake (Klemt et al., 2020). Prior to the 1960s, parent and alkylated PAC fluxes in Saline Lake were still higher than the reference lakes (~10 ng cm^{-2} y^{-1} for parent PAC flux, and 25 ng cm^{-2} y^{-1} for alkyl PACs in Saline Lake (Fig. 2C), compared to <2 ng cm^{-2} $y^{-}$and <3 ng cm^{-2} y^{-1} for parent and alkyl PACs in reference lakes, respectively (Fig. 2D, 2E), likely the result of near surface bitumen erosion near Saline Lake. Lower contributions of petrogenic PACs prior to oil sands development in Saline Lake relative to PAD 30 and 31 farther downstream likely reflects that Athabasca River floodwaters accumulated a considerable load of eroded bitumen-rich sediment on route to the delta (Hall et al., 2012)

PACs at Mariana Lake and BM11 increased slightly in recent sediments (since the 2000s, Fig. 2). The two uppermost samples deposited at Mariana Lake after ~2013 show a marked shift towards the threshold for predominant petrogenic origin (Fig. 3E). This change could be attributed to greater traffic on Highway 63 after it was twinned to serve expanding oil sand development. At BM11, petrogenic PACs such as the alkylated naphthalenes, phenanthrenes, dibenzothiophenes, and chrysenes were mainly responsible for the slight rise (2.5cm, 2002) in alkylated PAC flux, perhaps the result of atmospheric transport associated with surface mining activity, or perhaps vehicular emissions.

3.2 Changes in PACs and petroleum biomarker composition through time

We used PAC diagnostic ratios to differentiate between pyrogenic and petrogenic endpoints (Fig. 3). We also assembled petroleum biomarker diagnostic ratio cross-plots (Fig. 4) to track shifts in petrogenic contributions in the same sediment cores based on hopanes and terpanes. The petroleum biomarker diagnostic ratios, consisting of two terpanes (C_{21} and C_{23}) and the two C_{31} hopane configurations (S and R) (Fig. 4), showed similarities with the PAC diagnostic ratios (Fig. 3). Diagnostic ratios of PACs and petroleum biomarkers generally showed that Saline Lake, PAD 30 and PAD 31 derived more from petrogenic sources than Mariana and BM11 (the two reference lakes), which were generally removed from the petrogenic space (Fig. 3, 4), as we might expect given their distance from surface bitumen and refining/upgrading activities.

At PAD 30, Fla/(Fla+Py) shifted from pyrogenic to petrogenic signatures in sediments deposited after ~1975 (10.5cm), though IcdP/(IcdP+BghiP) ratios remained relatively unchanged in that core (Fig. 3A). PAC diagnostic ratios in PAD 31 were similar to PAD 30 (Fig. 3B). Petroleum biomarkers captured the closed-drainage phase at PAD 30 (~1940-1980) as a rise in

C21/C23 ratio, indicating a shift from a bituminous source to natural organic matter. Following the Embarras Breakthrough (10 cm), C21/C23 ratio dropped markedly to values more typical of sediment deposited before the closed drainage phase, capturing a return to influx of river sediment with higher bitumen content (Fig. 4A). Petroleum biomarkers in PAD 31 showed petrogenic contributions throughout the stratigraphy (Fig. 4B). Evans et al. (2016) likewise 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). We observed similar trends in our study lakes: decreased Fla/[Fla+Py] ratio indicated increased petrogenic sources in the PAD after 1980 (Fig. 3A, 3B), which coincided with increased flooding promoted by the Embarras Breakthrough (post-1982) as captured by marked decline of organic carbon content and rising sedimentation rate (Figs. S1, S2). This shift to more petrogenic hydrocarbons in sediment also occurred during a period of rapid expansion of upstream oilsands extraction, upgrading, and refining, which may have contributed to the petrogenic hydrocarbon increase at this time. During the prior closed-drainage (non-flooding) phase, PAC signatures in the PAD more closely resembled pyrogenic emissions likely from forest fires (Hall et al., 2012; Jautzy et al., 2015b, 2015a). In summary, these results indicated increasing contributions from petrogenic sources in PAD lakes since the 1980s based on PAC diagnostic ratios (Fig. 3A, 3B), and petroleum biomarker diagnostic ratios (Fig. 4A, 4B), coeval with increased flux of sediment and PACs, and declines in carbon content at that time (Fig. 2A, 2B, S1, S2).

At Saline Lake, PAC diagnostic ratios provided a record of oil sands mining operations, as evidenced by a shift to more petrogenic sources since the early 1980s, marking a rise of bitumen mining in the region (CAPP, 2018) (Fig. 3C). Likewise, petroleum biomarker ratios in Saline Lake showed consistently strong petrogenic contributions throughout the core, (Table 1,

295 Fig. 4C). Large petrogenic contributions to Saline Lake based on PAC diagnostic ratios (Fig. 3C)
296 and petroleum biomarkers (Fig. 4C) likely explained the substantial elevated PAC fluxes to that
297 lake (Fig. 2C). PAC diagnostic ratios in BM11 shifted slightly towards petrogenic sources for
298 PAC and petroleum biomarker diagnostic ratios (Fig. 3D, 3D), however petrogenic contributions
299 to BM11 throughout its history were minimal. Similarly, in Mariana Lake, Fla/Py ratios
300 decreased after ~2010 (Fig. 3E), indicating an increasing petrogenic signal in recent sediments,
301 though petrogenic contributions prior to that time were minimal. Petroleum biomarker diagnostic
302 ratios corroborated these results with a marked decline in the C21/C23 ratio after ~2013 (Fig.
303 4E). In 2008, the convenience store and gas station closed to allow an additional lane on nearby
304 highway 63. Increased vehicle traffic along the highway may have added petrogenic
305 hydrocarbons to Mariana Lake, shifting both PAC and biomarker diagnostic ratios (Fig. 3E, 4E).
306 Furthermore, alkylated PAC fluxes to Mariana Lake increased in 2013, further indicating
307 increased petrogenic contributions at that time (Fig. 2E).

308 We used the Mann-Kendall test to determine whether sources and fluxes of PACs and the
309 two petroleum biomarkers in Fig. 4 changed through their respective cores (Table 1, Table S7).
310 Diagnostic ratios with negative τ values, suggest a shift from pyrogenic to petrogenic PAC
311 (Fla/Py and IcdP/BghiP) sources (Ravindra et al., 2008; Thienpont et al., 2017). Similarly,
312 negative τ values, suggest a shift from natural OM to bituminous sources (C_{21}/C_{23} and
313 $C_{31}(R)/C_{31}(S)$. In the AOSR and PAD lakes, PAC and petroleum biomarker diagnostic ratios had
314 statistically negative τ values ($p<0.05$), thus supporting a shift from pyrogenic to petrogenic
315 sources, except for PAD 30 (IcdP/BghiP, C_{21}/C_{23} and $C_{31}(R)/C_{31}(S)$) (Table 1). Shifts from
316 pyrogenic to petrogenic sources were identified by both PAC ratios at Saline Lake (AOSR) and
317 coincided with the onset of mining activities (1970s) and reduced Athabasca River influence (as

318 detected by increased sediment carbon content). Similar shifts in PAD 30 and PAD 31 are
319 attributable to increased flooding that increased the flow of natural bitumen sources into the low-
320 lying areas of the PAD, as a result of the Embarras Breakthrough. Interestingly, PAC diagnostic
321 ratios in Mariana Lake shifted later (mid 1990s IcdP/BghiP and 2010s Fla/Py, respectively) than
322 oilsands-affected sites. Petroleum biomarker diagnostic ratios, however, shifted earlier (early
323 1970s C_{21}/C_{23} and $C_{31}(R)/C_{31}(S)$), possibly caused by vehicle traffic and the nearby gas station.
324 Zielinska et al. (2004) analysed different gasoline and diesel sources for hopanes and steranes,
325 showing higher proportions of petroleum biomarkers in higher emitting vehicles (likely oil
326 burning) for both fuel types. In Saline Lake and BM11, ∑parent and ∑alkylated PACs had
327 statistically positive τ values (Table 1), indicating an increase in PAC flux towards the top of the
328 sediment core. We attribute the near surface PACs increase in Saline Lake to industrial
329 development of the oilsands due to increased parent and alkylated benzonaphthothiophenes and
330 dibenzothiophenes, PACs commonly associated with oil sands developments (Fig. 5) (Kurek et
331 al., 2013; Zhang et al., 2015). In BM11, prevailing winds may have transported PACs (ECCC,
332 2019) across the oil sands, resulting in near surface PAC flux increases in recent years (2000s).
333 Significant increases ($p<0.05$) in some of the BM11 petroleum biomarkers ratios (Table S7) may
334 also be attributable to atmospheric deposition. In Mariana Lake, the τ value was significantly
335 positive for all but the ΣParent PACs, indicating increased deposition (Table 1, Fig. 2E), likely
336 from increased vehicle traffic on highway 63 since that time. PACs are released from several
337 traffic related sources, especially exhaust, tire wear, motor lubricants, road surface wear and
338 brake linings. Based on these emissions, roads and traffic are estimated to release 990-3900 μg
339 per vehicle kilometers of PACs, primarily from diesel passenger vehicles and light commercial
340 vehicles (<3.5 tons) based on a study in Sweden (Markiewicz et al., 2017). Analysis of diesel

exhaust from urban buses showed higher ∑alkyl PACs than ∑parent PAC in all samples, with high contributions from alkylated phenanthrenes and naphthalenes (Casal et al., 2014). The primary classes of sulfur containing compounds in diesel fuels are benzothiophenes and dibenzothiophenes, which have increased through time in Mariana Lake (Wang et al., 2003). Additionally, the analysis of sulfate emissions in both gasoline and diesel vehicles showed significant increases in cold temperatures for gasoline vehicles, while diesel emissions showed no change (Zielinska et al., 2004). Expansion of the oilsands industry may have also contributed indirectly to increased vehicular PAC emissions reaching Mariana Lake.

3.4 Multivariate analysis of lake sediment cores

We performed principal components analysis (PCA) for the proportional abundances of parent PACs, alkylated PACs, and petroleum biomarkers in sediments to visualize stratigraphic changes in these hydrocarbons (Fig. 5, S3-4). The first two PCA axes (axis 1 and axis 2 respectively) explained 92% of the total variance in parent PACs in Saline Lake (Fig. 5), with high positive axis 1 scores for the petrogenic benzonaphthothiophene (BNT) and dibenzothiophene (DBT). We observed a clear transition toward petrogenic hydrocarbons in Saline Lake, progressing toward higher axis 1 scores by the 1980s (Fig. 5). This transition toward increasing petrogenic contributions (higher axis 1 scores) in Saline Lake sediments coincided with increased PAC flux to this lake and marked rise in carbon content of the sediment (Fig. 2C), and also corroborated the PAC diagnostic ratios (Fig. 3C) and the petroleum biomarkers (Fig. 4C), both of which recorded increasing petrogenic contributions to sediments at that time. When we consider these independent lines of evidence together, our study showed a remarkable consistency of interpretation among proxies of petrogenic emissions. Furthermore, a PCA for the proportional abundance of the alkylated PACs explained 98% of the total variance

364 in the first two axes (Fig. 5), and tracked a shift in the Saline Lake stratigraphy toward the
365 petrogenic alkylated (C1-C4) BNTs and DBTs by the early 1980s, consistent with the parent
366 PACs in Fig. 5.

367 **4.0 Conclusions**

368 We showed evidence of increased PAC fluxes in a floodplain lake within the AOSR and
369 two floodplain lakes in the PAD since ~ 1980. Increased river flooding at PAD 30 and PAD 31
370 have likely contributed to PAC increases at these lakes which challenges our ability to assess the
371 impacts of oil sands mining activity there. At Saline Lake (AOSR), we observed a pronounced
372 rise in petrogenic hydrocarbon fluxes since 1970, which tracked the expansion of bitumen
373 extraction, upgrading, and refining in the AOSR. Among all sites considered in this study,
374 petrogenic sources are most evident closer to the surface mining and upgrading activities in the
375 AOSR. We observed clear shifts from pre-industrial pyrogenic PACs (likely from forest fires) to
376 petrogenic PACs in sediment profiles in most of our sites (Mariana Lake, Saline Lake, PAD 30,
377 PAD 31). Likewise, petroleum biomarkers in the PAD and AOSR tracked a shift to petrogenic
378 sources in more recent sediments of most lakes. We used novel petroleum biomarker diagnostic
379 ratios to provide strong evidence of changes in petrogenic contributions to lake sediment.
380 Alkylated PAC concentrations in reference lakes increased in recent (>2010) sediments in
381 conjunction with diagnostic ratios, indicating increased petrogenic contributions in these recent
382 sediments. PAC fluxes in reference lakes were upwards of three orders of magnitude lower than
383 lakes in the AOSR and the PAD, demonstrating a clear difference in PAC deposition across these
384 regions. We recommend future studies to consider petroleum biomarkers when interpreting
385 petrogenic contributions in lake sediment profiles, even outside of petroleum-rich areas.

386

CRediT Author Statement

Salat Alexandre: conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing – original draft, visualization. Eickmeyer David: methodology, software, validation, formal analysis, resources, writing – review & editing. Kimpe Linda: methodology, software, validation, resources, project administration. Hall Roland: resources, writing – review & editing. Wolfe Brent: resources, writing – review & editing. Mundy Lukas: conceptualization, resources, writing – review & editing, funding acquisition. Trudeau Vance: writing – review & editing, funding acquisition. Blais Jules: conceptualization, methodology, validation, investigation, resources, writing – review & editing, visualization, supervision, project administration, funding acquisition.

Acknowledgments

This work was funded by a Natural Sciences and Engineering Research Council (NSERC) Strategic Partnership Grant STPGP 463041-14 awarded to VLT and JMB. Support was also provided by the Oil Sands Monitoring Program; this work is a contribution to that Program but does not necessarily reflect the position of the Program. The authors thank P. Thomas for help in project development, J.Rodriguez-Gil for help with statistical analysis and C. Casey for help with study map creation.

Table 1

Result of Mann-Kendall trend test: p-value (p), and rank correlation coefficient (τ) of sum parent and alkylated PAC fluxes, PAC diagnostic ratios (Fla/Py = Fla/(Fla+Py) and (IcdP/BghiP = IcdP/(IcdP+BghiP)), petroleum biomarker diagnostic ratios (C_{21}/C_{23} = $C_{21}/(C_{21}+C_{23})$) and ($C_{31}(R)/C_{31}(S)$ = $C_{31}(R)/(C_{31}(R)+C_{31}(S))$. Bold font denotes statistical significance, α = 0.05.

Lake	∑Parent		∑Alkyl		Fla/Py		IcdP/BghiP		C_{21}/C_{23}		$C_{31}(R)/C_{31}(S)$	
	τ	p	τ	P	τ	p	τ	p	τ	p	τ	p
BM11	0.60	**0.01**	0.53	**0.03**	-0.66	**0.01**	-0.78	**1.1E-03**	-0.64	**0.01**	-0.62	**0.01**
Mariana	0.38	0.06	0.54	**0.01**	-0.91	**7.2E-06**	-0.91	**7.2E-06**	-0.87	**4.4E-05**	-0.85	**7.3E-05**
Saline	0.82	**1.3E-03**	0.78	**2.4E-03**	-1.00	**2.6E-05**	-0.89	**1.9E-04**	-0.67	**0.01**	-0.62	**0.01**
PAD 30	0.62	0.07	0.62	0.07	-0.82	**1.3E-03**	-0.47	0.07	0.32	0.24	0.04	0.93
PAD 31	0.07	0.90	0.50	0.11	-0.56	**0.03**	-0.64	**0.01**	-0.57	**0.03**	-0.51	**0.05**

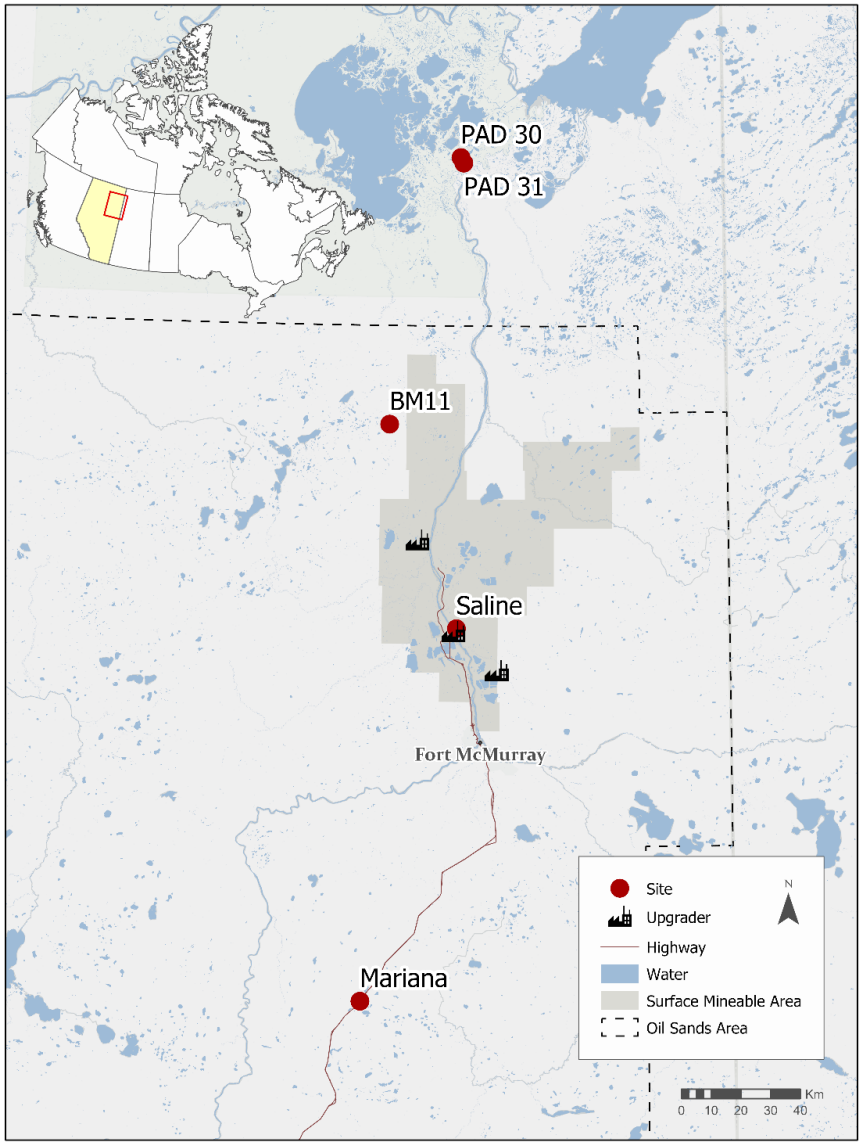

Fig.1. Map of study region, identifying sampling locations in the Athabasca oil sands region: Saline Lake (57°04'41.81" N, 111°31'20.43" W), BM11 (57°41'35.97" N, 111°54'26.08" W), and Mariana Lake (55°57'02.35" N, 112°01'34.97" W), and sampling location in the Peace Athabasca Delta: PAD 30 (58°29'59.72" N, 111°30'59.65" W) and PAD 31 (58°28'58.28" N, 111°30'08.52" W). Map inset of Canada shows the study location outlined in red.

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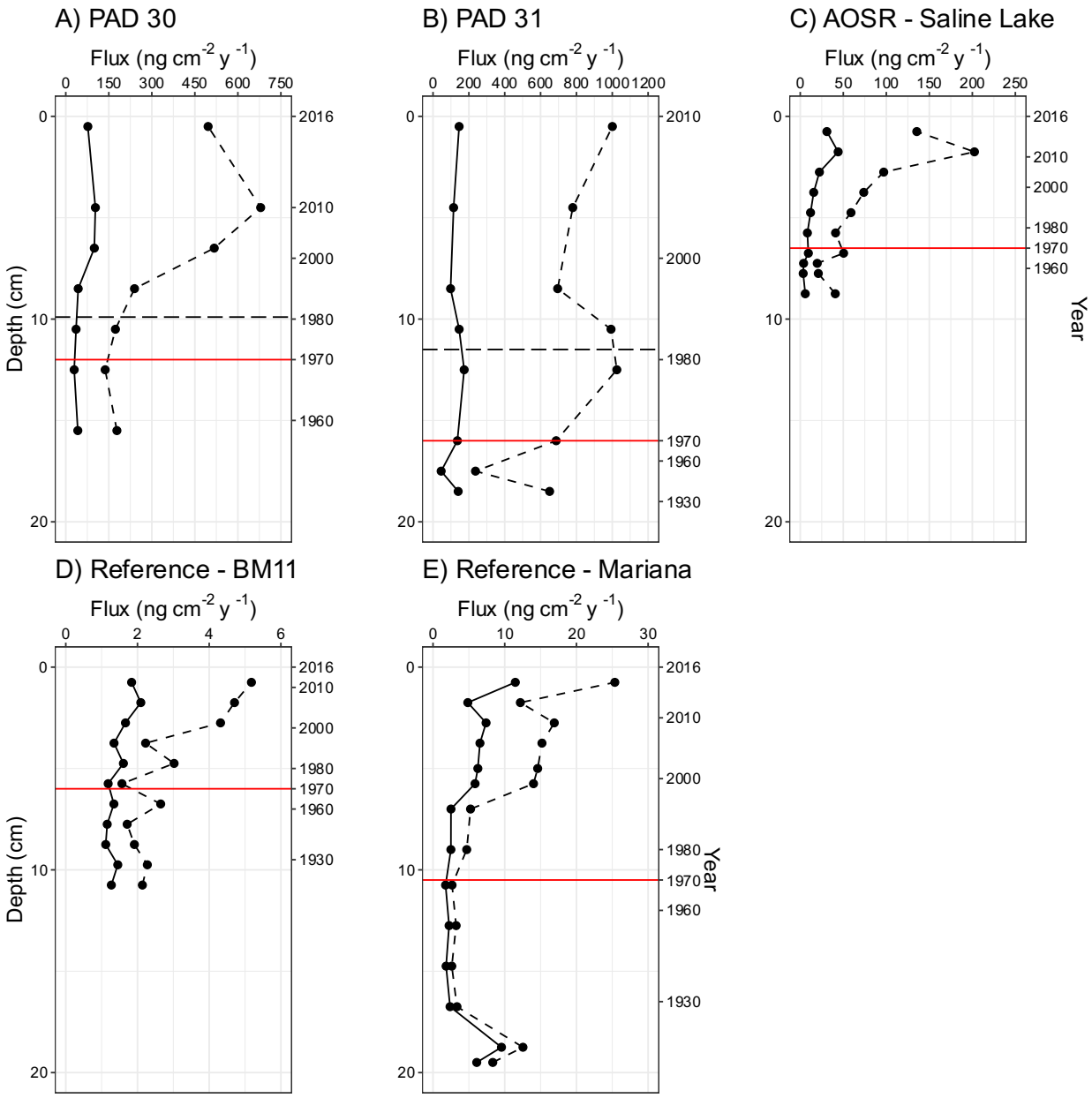

Fig.2. Line plot of PAC flux (ng cm^{-2} y^{-1}) versus depth (cm) for each lake down core. Depth is shown on the left y-axis and the corresponding date (year) is shown on the right y-axis. Solid lines represent parent PACs and the dashed line represents alkylated PACs. Red line indicates the beginning of oil sands production (1970). Horizontal black hatched line indicates the Embarras Breakthrough (1982) in the Peace Athabasca Delta.

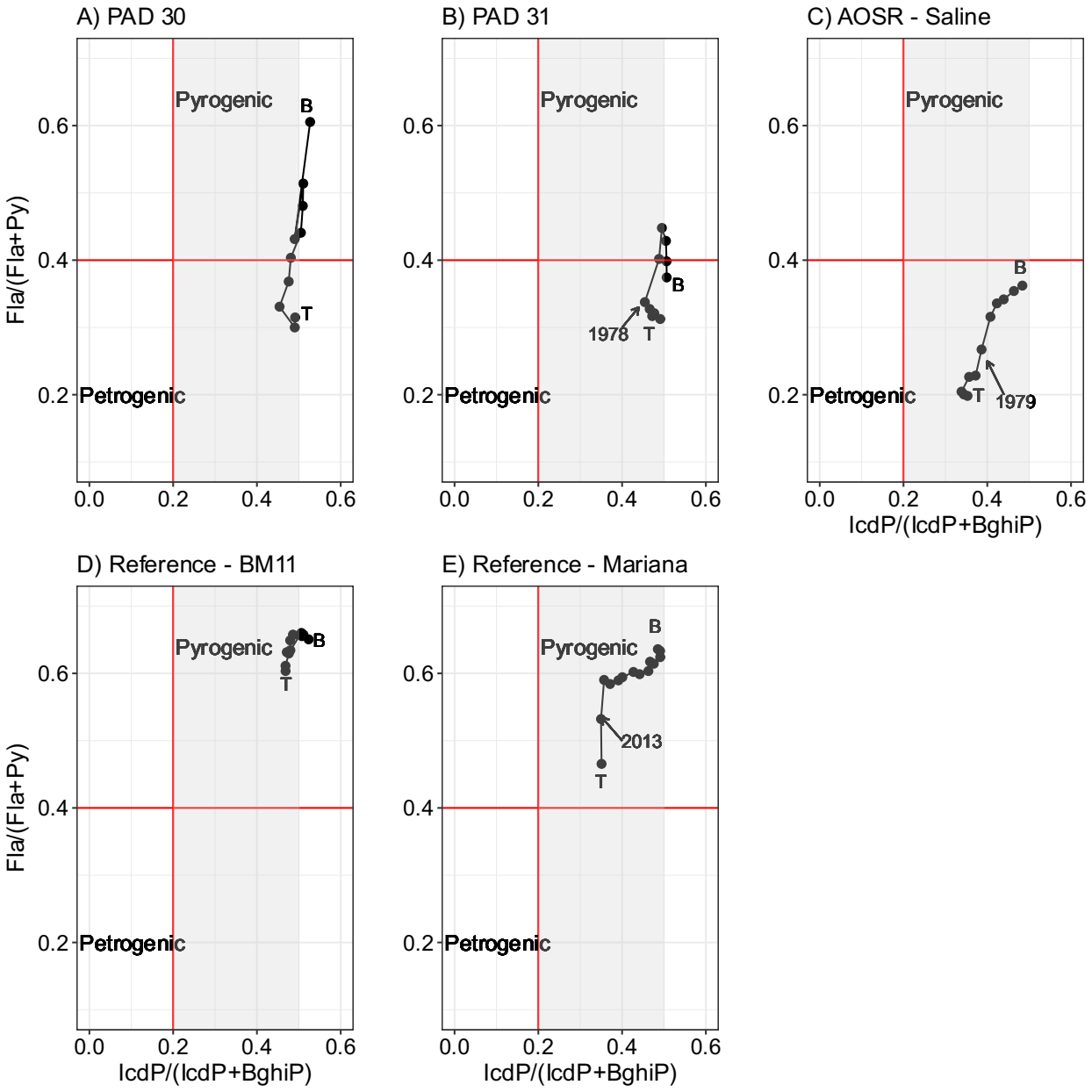

Fig.3. Plots showing PAC source apportionment of lake sediment cores from the five study sites in relation to the PAC diagnostic ratios fluoranthene/pyrene, (Fla/(Fla+Py), and indeno[1,2,3-*cd*]pyrene / benzo[*ghi*]perylene, (IcdP/(IcdP + BghiP)). Data points are connected to show the sequence of sediment deposition. (B) indicates the bottom of each core (time before industrial development) and (T) indicates the top of the core (most recent sediment, deposited during industrial development). Red lines indicate separations from petrogenic and pyrogenic space. Grey shaded area represent the petroleum combustion zone for IcdP/(IcdP + BghiP).

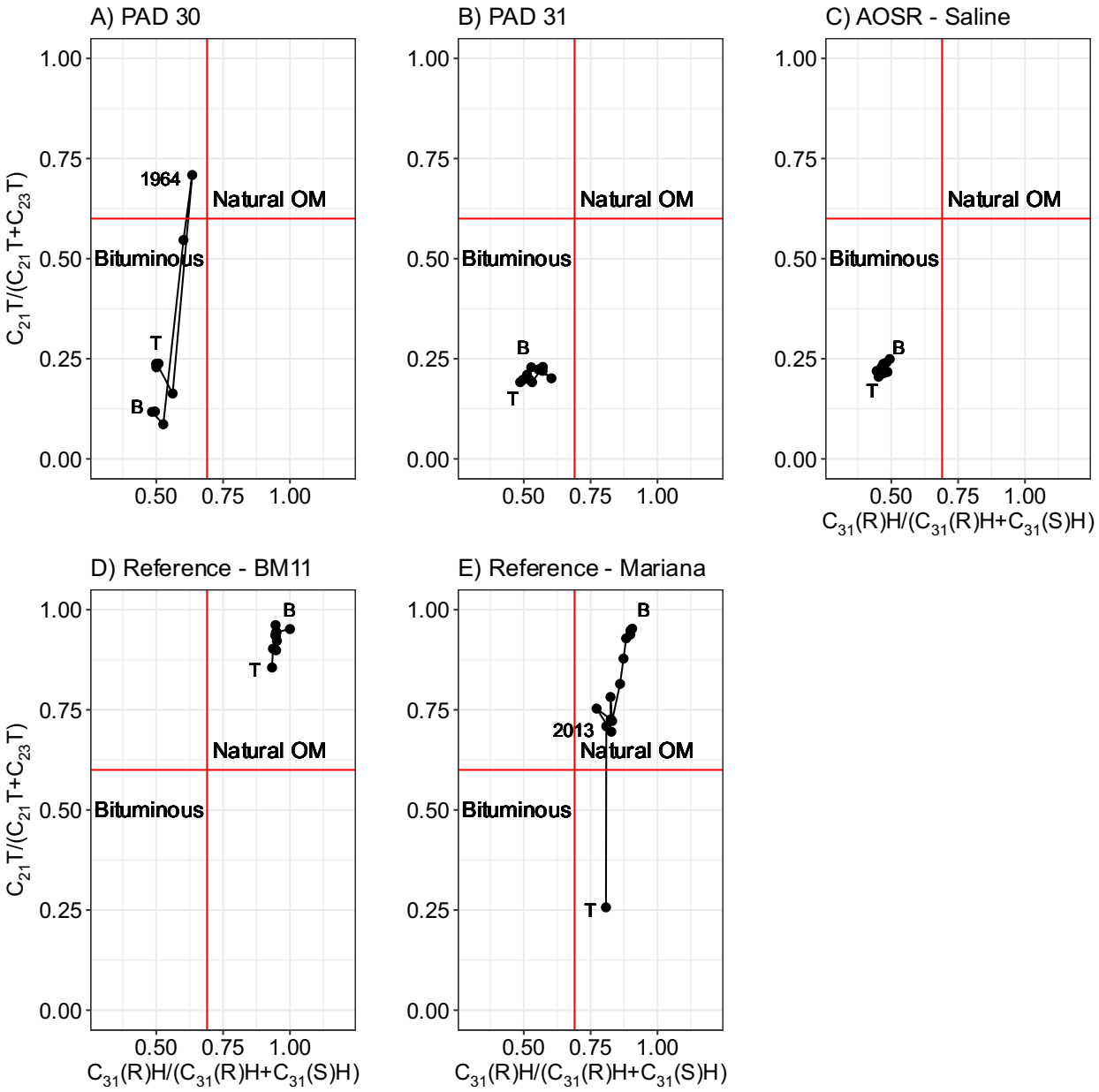

Fig.4. Plots showing petroleum biomarker source apportionment of lake sediment cores from the five study sites in relation to the petroleum biomarker diagnostic ratios C_{21} T/C_{23} T, ($C_{21}T/(C_{21}T+C_{23}T)$, and $C_{31}(R)H/C_{31}(S)H$, ($C_{31}(R)H/(C_{31}(R)H+C_{31}(S)H)$). Data points are connected to show the sequence of sediment deposition. (B) indicates the bottom of each core (time before industrial development) and (T) indicates the top of the core (most recent sediment, deposited during industrial development). Red lines indicate separations from bituminous and natural OM space.

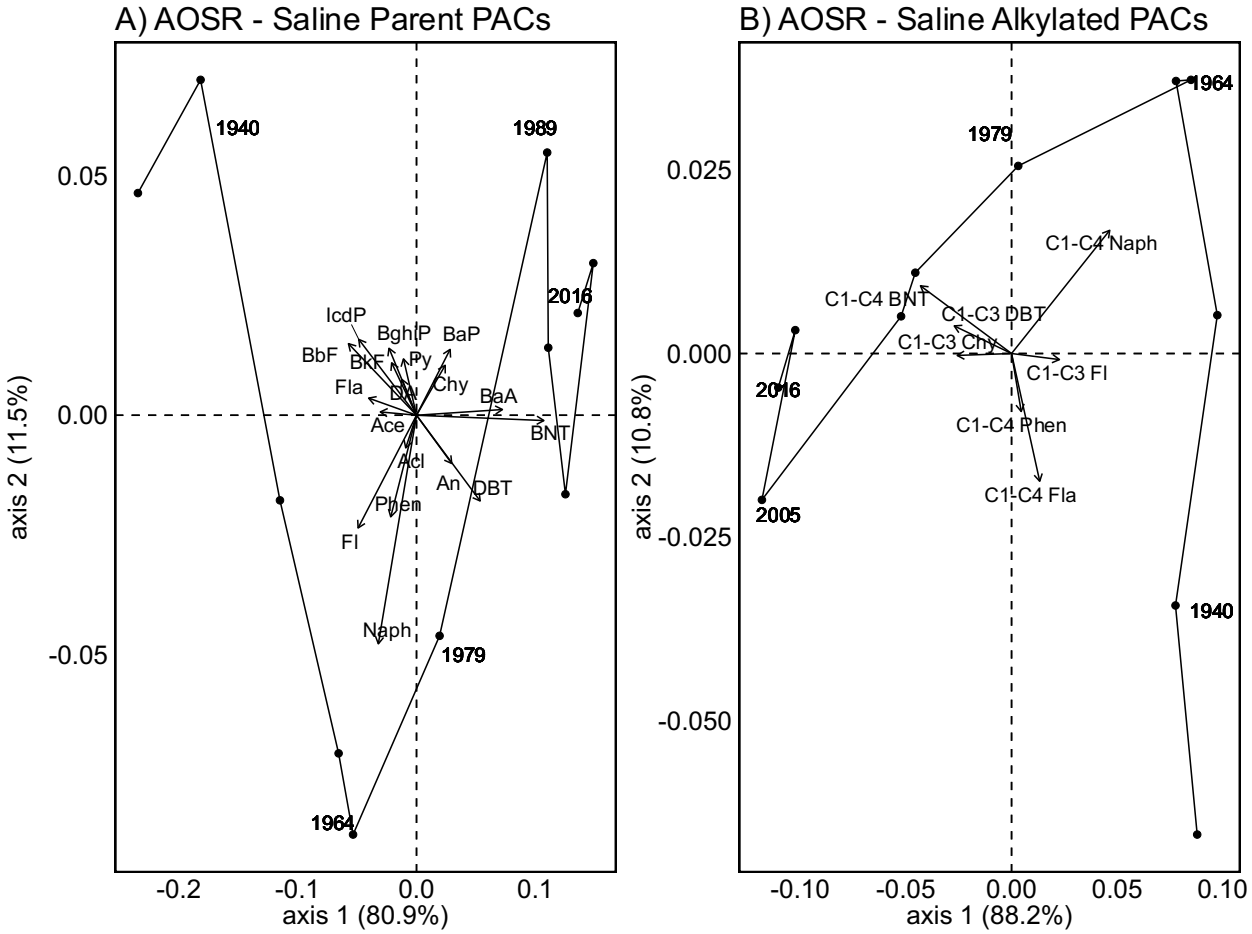

Fig.5. Ordination plot of principal components for parent PACs (A) and alkylated PACs (B) in intervals of the Saline Lake sediment core to visualize compositional changes through time. Each biplot shows sample scores and parent PACs as explanatory variables. Vectors indicate the contribution of explanatory variables in black. A list of all parent PACs are as follows: Ace: Acenaphthene, Acl: Acenaphthylene, BaA: Benz[*a*]anthracene, BaP: Benzo[*a*]pyrene, BbF: Benzo[*b*]fluoranthene, BghiP: Benzo[*ghi*]perylene, BkF: Benzo[*k*]fluoranthene, BNT: Benzonaphthothiophene, Chy: Chrysene and triphenylene, DA: Dibenz[*a,h*]anthracene, DBT: Dibenzothiophene, Fla: Fluoranthene, Fl: Fluorene, IcdP: Indeno[1,2,3-*cd*]pyrene, Naph: Naphthalene, Phen: Phenanthrene, Py: Pyrene.

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