In-situ bitumen extraction associated with increased petrogenic polycyclic aromatic compounds in lake sediments from the Cold Lake heavy oil fields (Alberta, Canada)

Jennifer B. Korosi[a,ǂ], Colin A. Cooke[b,c], David C. Eickmeyer[a], Linda E. Kimpe[a], and Jules M. Blais[a*]

[a]30 Marie Curie Pvt., Department of Biology, University of Ottawa, Ottawa, Ontario, Canada, K1N 6N5
[b]Alberta Environment and Parks, 9920 108 Street, Edmonton, Alberta, Canada, T5K 2M4
[c]Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, Alberta, Canada, T6G 2E3
[ǂ]Current address: 4700 Keele St., Department of Geography, York University, Toronto, Ontario, Canada, M3J 1P3

*Corresponding author: Jules Blais: Tel.: (613) 562-5800 ext. 6650; Fax: (613) 562-5486; Email: Jules.blais@uottawa.ca

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Abstract

Most future growth in the Alberta bitumen sands will be based on thermal *in-situ* recovery technologies. To date, however, most attention on the environmental effects of bitumen recovery has focused on surface mining in the Athabasca region. Recent uncontrolled bitumen flow-to-surface incidents (FTS; appearance at the surface of bitumen emulsions from deep subsurface recovery zones) reported at the Cold Lake heavy oil fields highlight the need to better understand the potential role of *in-situ* extraction as a source of contaminants to landscapes and surface waters. We analyzed sediment cores from a lake located ~2 km away from a recent bitumen FTS incident to provide a long-term perspective on the delivery of metals, polycyclic aromatic compounds (PACs), and polychlorinated biphenyls (PCBs) to surface freshwaters, and to assess whether the onset of local *in-situ* bitumen extraction can be linked to contaminant increases in nearby lakes. An increase in alkyl PACs coincided with the onset and expansion of commercial *in-situ* bitumen extraction, and multiple lines of evidence indicate a petrogenic source for recent alkyl PAC enrichment. However, no coincident increase in vanadium (enriched in bitumen) occurred that would suggest the source of petrogenic PAC enrichment is direct input of bituminous particles. Our results show that, similar to surface mining in the Athabasca region, activities associated with *in-situ* extraction can increase the burden of petrogenic PACs in nearby lakes, but many questions still remain regarding the exact sources and pathways of PACs into the environment. Given that more than 80% of Alberta's bitumen reserves can only be accessed using *in-situ* technologies, we recommend that this be made a research priority.

Keywords: Cold Lake, Alberta; high-pressure cyclic steam stimulation; paleolimnology; metals; organic contaminants

Capsule –The concentration of petrogenic polycyclic aromatic compounds in lake sediments has increased since commercial *in-situ* bitumen extraction began at Cold Lake, Alberta, Canada

Introduction

The bituminous sands of northern Alberta and Saskatchewan (Canada) are estimated to contain 170 billion barrels of oil (Attanasi et al. 2010). Production of crude bitumen has increased steadily in recent years, with production rising from ~1×10^5 barrels of oil per day (b d^{-1}) in 1980, to 1.6×10^6 b d^{-1} in 2011. This rapid rise in production has been driven predominantly by an expansion of surface mining within the Athabasca bitumen sands region. This historical increase in production has raised concerns about potential release of contaminants to regional ecosystems, and a number of previous studies have provided compelling evidence for the release of contaminants to groundwater (Frank et al. 2014), surface water (Kelly et al. 2009, 2010) and the atmosphere (Kirk et al. 2014; Kurek et al. 2013). However, the vast majority (~80%) of bitumen sand reserves are located at depths that preclude surface mining and thus are only recoverable by *in-situ* extraction methods (Jiang et al. 2010). The process of bitumen extraction through *in-situ* technologies involves the injection of steam at high pressures through underground wells in order to heat and mobilize cold bitumen for transport to the surface. In Alberta, two main methods of *in-situ* extraction are currently used: high-pressure cyclic steam stimulation (CSS) and steam-assisted gravity drainage (SAGD) (Jiang et al. 2010). For CSS, repeated injection cycles of steam in vertical or horizontal wells are used, where steam is injected at high pressures into the bitumen deposit and allowed to soak for a period of up to several months, until bitumen viscosity is sufficiently reduced that the well can be switched to production mode and the bitumen pumped to the surface. For SAGD, steam is injected underground through a horizontal well to enable bitumen, liberated by the steam, to be pumped to the surface through a second recovery well. *In-situ* bitumen recovery volumes in Alberta exceeded those from surface mining for the first time in 2012, and contributed 55% of total bitumen production in Alberta in 2014; it is expected to reach 60% by 2024 (Alberta Energy Regulator 2015). Future growth in bitumen production will be largely achieved through continued expansion of *in-situ* recovery methods.

Most investigations into the potential for environmental degradation resulting from development in the Alberta bitumen sands have focused on surface mining in the Athabasca. However, the environmental concerns associated with *in-situ* bitumen extraction are distinct from those associated with surface mining. In contrast to surface mining of bitumen, *in-situ* extraction does not generate large volumes of tailings. In addition, while surface mining requires large quantities of fresh water (Sauchyn et al. 2015), *in-situ* technologies can make use of non-potable groundwater to generate steam. Identified environmental risks posed by *in-situ* development include: habitat fragmentation of the boreal forest (Schneider and Dyer 2006), fossil fuel emissions from steam generation and gas flaring, pipeline leaks, and the potential for uncontrolled (vertical) release of bitumen from the bitumen sand reservoir to surface environments, i.e., flow-to-surface (FTS) incidents. CSS enhanced bitumen recovery methods have previously been shown to cause significant ground deformation, with up to 30 cm of upward ground displacement occurring over 1-month injection cycles (Samsonov and Czarnogorska 2014; Stancliffe and van der Kooij 2001). Improperly sealed wellbores and natural faults and fractures in the bedrock provide pathways for bitumen to flow upwards to the surface (Alberta Energy Regulator 2014). Indeed, in May and June, 2013, four uncontrolled bitumen FTS incidents were discovered at the Canadian Natural Resources Ltd. (CNRL)

Primrose East and Primrose South operations in the Cold Lake *in-situ* bitumen fields of Alberta. A particularly large incident occurred beneath an unnamed water body at site 9-21, where bitumen oozed to the surface for a period of several months before the flow was eventually stopped. The waterbody was subsequently drained and the basal sediments excavated and disposed of as part of the remediation effort. This FTS event follows a similar event at Primrose East in 2009 that was implicated in contamination of regional groundwater aquifers (Alberta Energy Regulator 2016). Naturally occurring geological features at Primrose Lake may have made this region particularly susceptible to bitumen FTS incidents (Alberta Energy Regulator 2014).

Confounding the concerns raised about the safety of *in-situ* bitumen extraction technologies is a lack of long-term environmental monitoring. Lake sediments integrate environmental information from a range of spatial and temporal scales, and thus offer a natural archive that can be analyzed to overcome the absence of long-term monitoring data. A growing body of scientific literature has demonstrated the effectiveness of lake sediment cores (paleolimnology) for reconstructing temporal contaminant deposition histories and identifying the spatial extent of contaminant deposition near surface mining operations in the Athabasca region of northeastern Alberta (Hall et al. 2012; Jautzy et al. 2013; Kurek et al. 2013); however, similar efforts related to *in-situ* bitumen extraction are limited to just two studies, both within the southern region of the Cold Lake bitumen sands region (Korosi et al. 2013; Skierszkan et al. 2013). Integrating a paleolimnological analysis of metals and polycyclic aromatic compounds (PACs) in two lakes with a spatial assessment in soils and spruce needles showed that *in-situ* bitumen extraction likely caused localized PAC contamination, although the sources of contamination were unclear (Korosi et al. 2013; Skierszkan et al. 2013). Analysis of PACs in moose and wolf scat south of Fort McMurray similarly showed evidence of increased wildlife exposure to petrogenic PACs near intensive *in-situ* drilling operations (Lundin et al. 2015). Collectively, these studies demonstrate the pressing need to better quantify and characterize contaminant release to the environment near *in-situ* drilling wells.

The primary objective of this study is to assess the potential for the release of environmental contaminants due to *in-situ* bitumen extraction. We focus here in the Cold Lake *in-situ* development, where no surface mining of bitumen occurs, and specifically on a potential contamination hotspot: the CNRL Primrose South operation that was the site of a large bitumen FTS incident in 2013. We reconstructed historical trends in PACs, bitumen-associated metals, and industrial pollution markers [polychlorinated biphenyls (PCBs), mercury(Hg)] deposited over the past several hundred years from duplicate sediment cores collected from a small, unnamed lake referred to as “Lake 12-26”, located ~2 km northeast of the 2013 FTS incident at site 9-21 (Fig. 1). We hypothesized that, given the region’s known vulnerability to bitumen FTS incidents, lake sediment cores from this site would show a strong signal of enrichment in petrogenic PACs and bitumen-associated metals consistent with the onset of bitumen extraction by high-pressure CSS. Our study provides a historical context that is necessary for evaluating *in-situ* bitumen extraction as a source of environmental contaminants in a region both vulnerable to environmental degradation from *in-situ* drilling operations and lacking in long-term monitoring data.

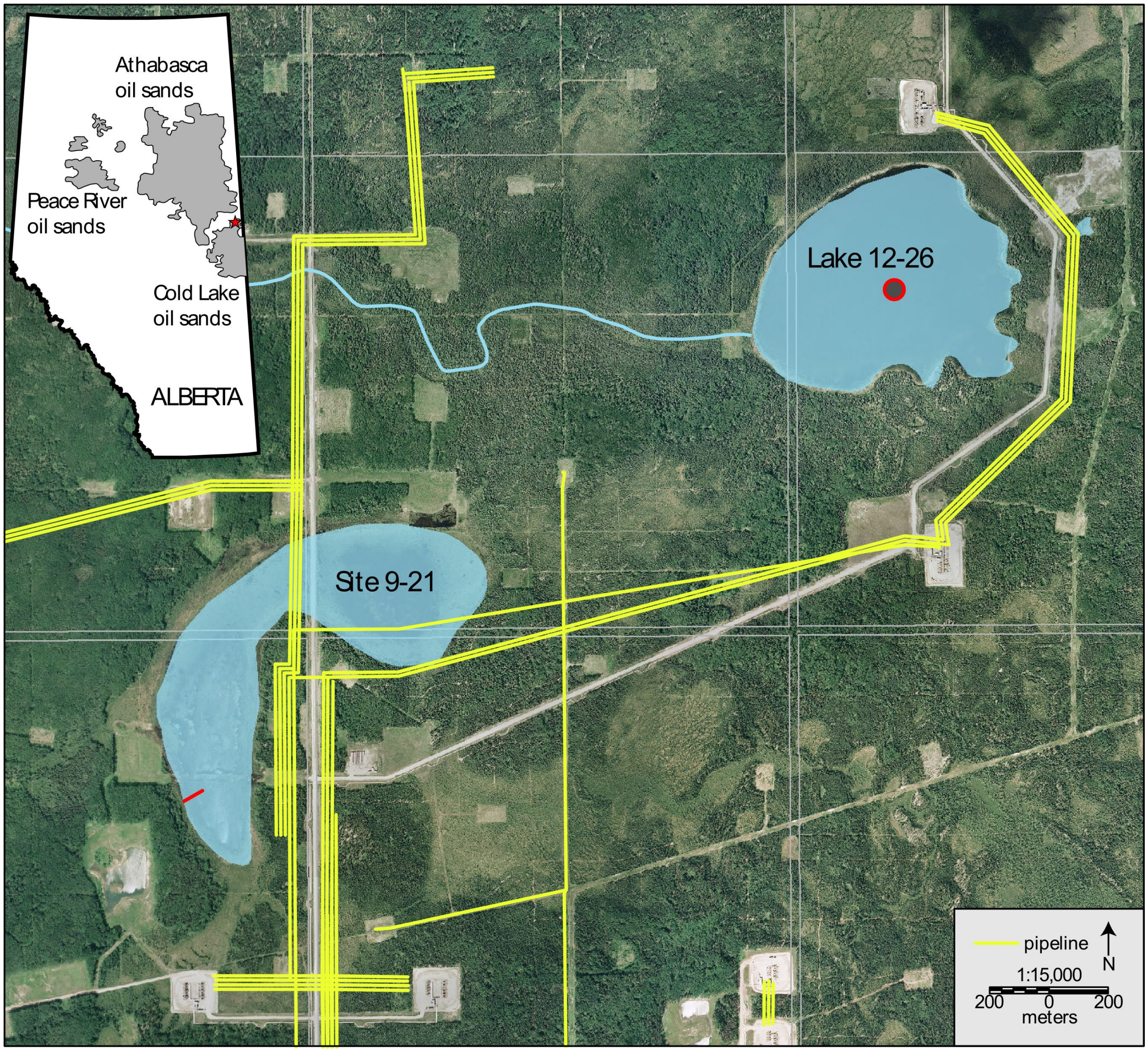

Fig. 1. Map showing the location of Lake 12-26 at the Primrose Lake development in the Cold Lake bituminous sands region, relative to site 9-21 where a large bitumen flow-to surface incident occurred in 2013. The red line marks where bitumen was observed flowing into the lake from the subsurface. Inset shows the location of the Cold Lake bitumen sands deposits within Alberta. The waterbody at site 9-21 was drained following the bitumen FTS incident, and its sediments excavated and disposed of. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Study Site Description

The Cold Lake bitumen sands region is located in the boreal forest of northern Alberta, approximately 300 km northeast of the city of Edmonton and 300 km southeast of surface mining operations in the Athabasca region. Bitumen at Cold Lake is produced primarily from the Lower Cretaceous Clearwater Formation, located ~400 m below ground. Commercial bitumen production by high-pressure CSS began in the mid-1980s following pilot projects conducted in the 1960s and 1970s. Pilot testing of SAGD began in the 1990s, and commercial bitumen production by SAGD commenced in 2006 (Jiang et al. 2010). There are four major operators in the Cold Lake bitumen sands region: Imperial Oil Ltd., CNRL, Shell, and Husky. Lake 12-26 (54˚49'50.3898", -110˚30'32.6658) is located in CNRL's Primrose South production area on the Cold Lake Air Weapons Range, in the northern part of the Cold Lake *in-situ* development. Development at the Primrose Lake project area began in 1980, and the site was acquired and expanded by CNRL in 2000. Bitumen extraction at Primrose South is conducted using high-pressure CSS.

Materials and Methods

A sample of the bitumen emulsion at site 9-21 was collected in a sterilized glass jar, and shipped to the University of Ottawa for analysis of PAC composition. An archived bitumen sample from the Cold Lake bitumen sands region was also provided by Environment Canada. Duplicate sediment cores were obtained from the center of Lake 12-26 in March 2014 using a gravity corer, and sectioned into 0.5 cm intervals using a vertical extruder. Sediment intervals were placed into sterile glass jars and shipped frozen to the University of Ottawa for analysis. Duplicate, independently dated sediment cores from Lake 12-26 were used to reconstruct the deposition history of three classes of contaminants: metals (core A), PCBs, and PACs (core B). To establish a chronology in both sediment cores, select intervals were freeze-dried and ^{210}Pb and ^{226}Ra activities were measured using an Ortec High Purity Germanium Gamma Spectrometer (Oak Ridge, TN, USA). Certified Reference Materials obtained from the International Atomic Energy Association (Vienna, Austria) were used for efficiency corrections, and results were analyzed using ScienTissiME software (Barry's Bay, ON, Canada). The constant rate of supply model was used to establish a chronology based on unsupported ^{210}Pb activities (Appleby and Oldfield 1978). The ^{137}Cs, a radioisotope produced from atmospheric nuclear bomb testing, was used as an independent chronostratigraphic marker (see Supplementary Information for dating results).

Freeze-dried sediment samples and Marine Sediment Certified Reference Materials from the National Research Council of Ottawa (MESS-3) were analyzed for total mercury using an automatic mercury analyzer based on thermal decomposition, dual step gold amalgamation and detection via cold-vapor atomic absorption using an Sp-3D mercury analyzer (Nippon Instrument Corp). Approximately 0.5 g of freeze-dried sediment was shipped to SGS Minerals Services in Lakefield, Ontario, a Canadian Association for Laboratory Accreditation Inc. accredited facility, for metals analysis. Analysis of total organic carbon (TOC) was conducted at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa) following the procedure described in Korosi et al. (2013). PACs and PCBs were extracted using US EPA Method 3540C modified for accelerated solvent extraction. Sulfur was removed using the tetrabutylammonium sulfite reaction from US EPA Method 3660B. Clean up with US EPA Method 3630C was adapted for use on 6 mL (1g) Supelclean™ LC-Si solid-phase extraction cartridges, with PCB and PAC fractions collected separately, and reduced to 1 mL. PACs and PCBs were analyzed on a DB-5MS 30 m x 0.25 μm x 250 μm column following methods outlined in Korosi et al. (2016). Additional methods, as well as the full suite of PCB and PAC compounds analyzed and quantified, are provided in the supplementary information. Laboratory procedure for the extraction and analysis of PACs in the bitumen emulsion collected from site 9-21 and the Cold Lake bitumen sample followed methods described in Yang et al. (2011).

We conducted a principal components analysis (PCA) on the total concentration (ng·g $^{-1}$ DW) of individual targeted PAC compounds (Table S1) and C1-C4 dibenzothiophenes analyzed in the sediment core from Lake 12-26 using the vegan package for the R software environment. Highly correlated variables identified using Spearman Rank correlations were removed prior to analysis. The Pyrogenic Index (PI) was calculated using the following formula, modified from Wang et al. (2014):

PI = ∑("other" 3-6 ring EPA PAHs)* / ∑(5 alkylated PAC homologues)**

*Includes acenaphthylene, acenaphthene, anthracene, fluoranthene, pyrene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene

**C0-C4 naphthalene, C0 phenanthrene, C1-C4 phenanthrene/anthracene, C0-C3 dibenzothiophene, C0-C3 fluorene, C0 chrysene, C1-C3 benz[a]anthracene/chrysene

Results and Discussion

Reconstruction of historical contaminant trends in Lake 12-26

Metals

We investigated historical trends in the concentrations and sedimentary fluxes of metals known to be enriched in bitumen [vanadium (V), nickel (Ni), molybdenum (Mo); Shotyk et al. 2014] or petroleum products in general [V, Ni, zinc (Zn), and tin (Sn); Magaw et al. 2001]. We normalized the concentration of metals to aluminum (Al), in order to account for mineralogical effects on metal accumulation in lake sediments (Ho et al. 2012; Wickland et al. 2012). Contrary to our initial hypothesis, there was no strong increase in the normalized concentration of V, Zn, and Mo after local *in-situ* drilling operations began (Fig. 2a). In contrast, Ni concentrations (normalized to Al) increased after approximately 1985, consistent with the onset of *in-situ* drilling operations, while Sn was below detection limit in the deeper sediment intervals, and showed a steady increase in concentration after approximately 1960. Sn is slightly enriched in bitumen, although to a lesser extent than V, Ni, and Zn (Magaw et al. 2001), and also has many industrial uses, such as a constituent in solder. Low background sources of tin in the sediments of Lake 12-26, in contrast to V, Ni, Zn, and Mo, likely account for its clear signal of recent enrichment. The timing of increase in Sn occurs ~20 years prior to the onset of commercial *in-situ* production of bitumen extraction, but is consistent with the beginning of industrial development for pilot projects in the Cold Lake bitumen sands, as well as the operational history of the Cold Lake Air Weapons Range (on which the Primrose Lake *in-situ* development is located), which began fighter pilot training operations in the 1950s. This could indicate an industrial source, rather than a petrogenic one. In contrast to the other metals mentioned, Hg concentrations first increased during the early 20th century, rising from ~20 to 70 $ng \cdot g^{-1}$ DW. These concentrations are typical of regional lake sediments (Neville et al. 2014).

When corrected for sedimentation rates (to estimate an annual flux of metals to lake sediments), an increasing trend was observed for V, Ni, Zn, and Mo since ~1985, but especially in the two uppermost surface sediment intervals deposited after 2006 (Fig. 2b). However, this recent increase is within the range of down-core variability. For example, V, Ni, Zn, and Mo flux actually peak during the mid-20th century. Similar increases in flux in the uppermost two sediment intervals were also observed for redox-sensitive elements like manganese, iron, and arsenic (Supplementary Information). The long-term, post-1900 increase in flux of total mercury we observed is consistent with the previous paleolimnological investigation of Hilda Lake and

Ethel Lake, in the southern region of the Cold Lake bitumen sands region (Skierszkan et al. 2013).

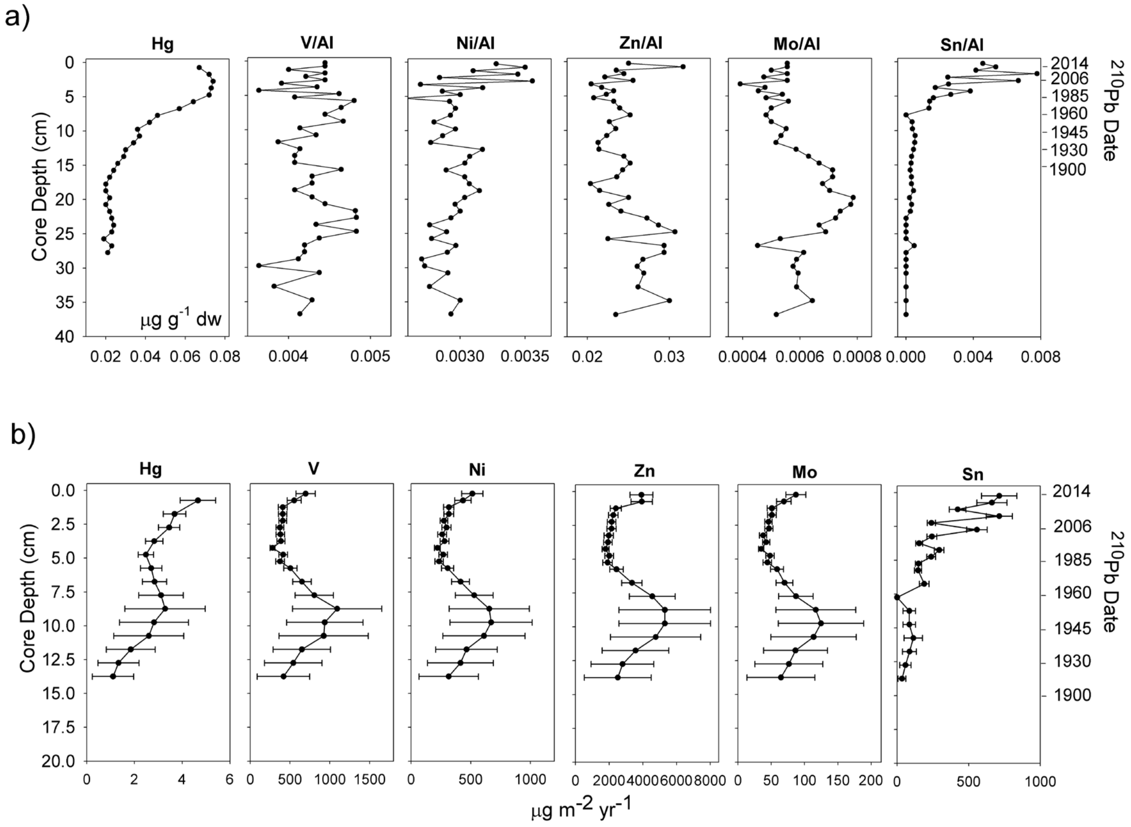

Fig. 2. a) Total concentrations normalized to Al (except Hg, shown in mg g^{-1} dry weight) and b) sedimentary flux rates of bitumen-associated metals and Hg over time in a sediment core from Lake 12-26. The ^{210}Pb dates are shown on the right. Flux rates were not calculated below the horizon of unsupported ^{210}Pb activity, as associated errors for inferred date and sedimentation rate are large.

Polychlorinated biphenyls

PCBs were first detected in the sediments of Lake 12-26 after 1950, and concentrations and sedimentary flux increased to 4 ng·g^{-1} DW and 258 ng·m^{-2}·yr^{-1} by 2000 (Fig. 3a). The post-1950 increase in PCBs may be related to the onset of operations on the Cold Lake Air Weapons Range, or the initial growth of the Cold Lake bitumen sands for pilot projects in the 1960s and 1970s. Primrose Lake is also located ~300 km east (in the direction of the prevailing winds) of the Swan Hills Treatment Centre, where the majority of Canada's high-concentration PCB wastes are treated. The Swan Hills Treatment Centre commenced operations in 1987, coincident with the increase in sedimentary PCB loading we describe. The treatment centre is an important point source of PCBs (Blais et al. 2003), and a notable fugitive emission episode occurred at the treatment centre in 1996 following a transformer furnace malfunction.

Polycyclic aromatic compounds

We observed a sustained, long-term decrease in the concentration and flux of unsubstituted PACs from a subsurface peak at a core depth of 15 cm (~1900 to present), decreasing from ~200 $ng \cdot g^{-1}$ DW and 13 $\mu g \cdot m^{-2} \cdot yr^{-1}$ at 15 cm, to 85 $ng \cdot g^{-1}$ DW and 5 $\mu g \cdot m^{-2} \cdot yr^{-1}$ in the surface sediments (Fig. 3a). The main compounds driving this trend are acenaphthene, fluorene, fluoranthene, and anthracene. A similar pattern was observed for the alkyl PACs, until a reversal of this trend occurred after ~1985, when alkyl PACs increased from 265 $ng \cdot g^{-1}$ DW and 16 $\mu g \cdot m^{-2} \cdot yr^{-1}$ to 850 $ng \cdot g^{-1}$ DW and 49 $\mu g \cdot m^{-2} \cdot yr^{-1}$ (Fig. 3a). The timing of increase in alkyl PACs in Lake 12-26 occurs later than our industrial pollution markers (Hg post-1900, PCBs and Sn post-1950), and is consistent with the onset of commercial bitumen extraction in the 1980s. The highest concentrations and flux rates of alkyl PACs were recorded in the uppermost two sediment intervals, deposited after 2005. The compound contributing most to the increase in alkyl PACs was C2 naphthalene, which increased from an average of ~25 $ng \cdot g^{-1}$ DW for the time period of approximately 1900 to 1985, to an average of 170 $ng \cdot g^{-1}$ DW after 1985 (Fig. 3b). Post-1985 increases in C2 and C3 fluorene, C2 phenanthrene/anthracene, and C1 and C4 dibenzothiophene were also evident (Fig. 3b).

There are multiple sources (both natural and anthropogenic) and pathways by which PACs can enter the aquatic environment. At the Primrose Lake *in-situ* development, potential anthropogenic sources of pyrogenic PACs include emissions from road and air traffic, or fossil fuel combustion from steam generation and other industrial activities. Wildfires are an important natural source of pyrogenic PACs to regional freshwaters in boreal ecosystems like Primrose Lake (Ahad et al. 2015). For example, during the summer of 2015, one year after the sediment cores used in this study were collected, a forest fire disrupted *in-situ* drilling operations at Primrose Lake. In May, 2016, a large forest fire disrupted surface mining operations in the Athabasca bitumen sands region, and caused the evacuation of the town of Fort McMurray. Anthropogenic sources of petrogenic PACs could include industrial waste releases associated with *in-situ* activities, such as pipeline leaks, oil spills, or processed water releases, in addition to bitumen FTS seeps.

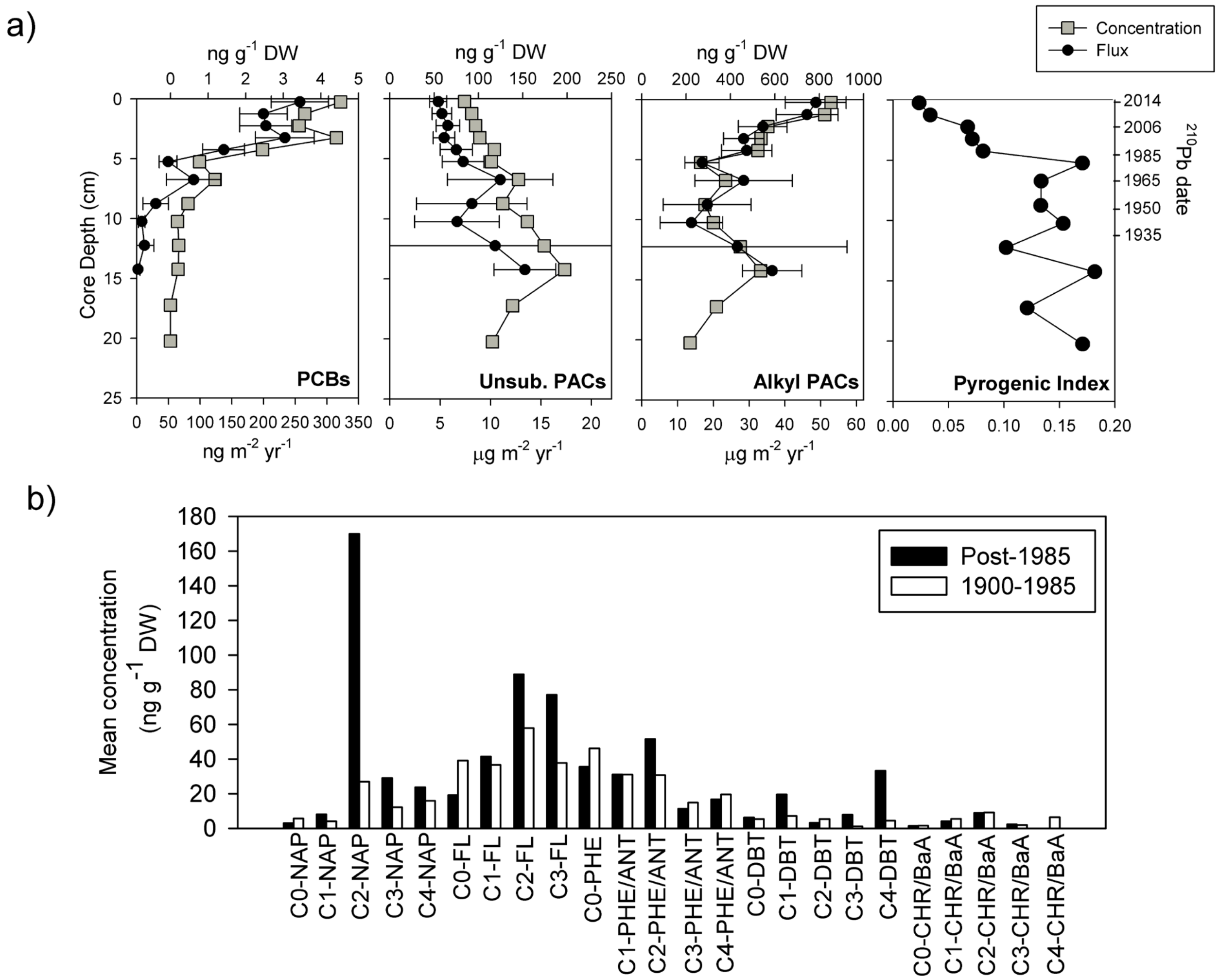

Fig. 3. a) Total concentrations and fluxes of polychlorinated biphenyls (PCBs), unsubstituted and alkyl polycyclic aromatic compounds (PACs), and the pyrogenic index (Wang et al., 2014) of PACs over time in a sediment core from Lake 12-26. The ^{210}Pb dates are shown on the right. Flux rates were not calculated below the horizon of unsupported ^{210}Pb activity, as associated errors for inferred date and sedimentation rate are large; b) Bar graphs comparing the mean concentration of the five target petroleum-characteristic alkyl PAC series deposited between 1900 and 1985 (core depth 5-15 cm), and after the onset of bitumen sands development (post-1985, core depth 0-5 cm).

Potential sources of alkyl PAC enrichment in Lake 12-26

Our observation of an increase in alkyl PACs in Lake 12-26, but not unsubstituted PACs, is a clear indication of a petrogenic source, as alkylated homologues are more abundant than the unsubstituted compounds in petroleum products (Stogiannidis and Laane 2015). PACs indicative of fossil fuel combustion, such as fluoranthene, chrysene, pyrene, and benzo[a]pyrene (Pereira et al. 1999; Yunker et al. 2002), were either absent or present only in low concentrations in Lake

12-26. We calculated the PI (Wang et al. 2014), to visualize temporal changes in the predominance of petrogenic versus pyrogenic PAC sources to Lake 12-26. Previous studies have shown that light petroleum products have a PI ratio <0.01, heavy oils and fuels 0.02-0.05, and that the value of this ratio increases as the proportion of pyrogenic PACs increases (Wang et al. 1999, 2014). In Lake 12-26, prior to 1985, the PI ranged from 0.1 to 0.2 (Fig. 3a). After 1985, the PI decreased to 0.02 in the surface interval, indicating an increase of petrogenic inputs. Down-core changes in the diagnostic ratios of select alkyl and unsubstituted PACs (Supplementary Information) also indicated a shift towards predominantly petrogenic PAC sources to Lake 12-26 after 1985. In particular, we observed a decrease in the ratio of retene to total alkyl PACs after the onset of oil sands operations at Primrose Lake, suggesting that boreal forest fires are not the source of recent alkyl PAC enrichment (Ahad et al. 2015).

The multiple lines of evidence described above provide strong support for a petrogenic source of recent alkyl PAC enrichment in Lake 12-26. We conducted a PCA on our stratigraphic profile of targeted PAC compounds (listed in Supplementary Table S1) and alkyl dibenzothiophenes in Lake 12-26 to visualize compositional changes in PAC composition through time. We then compared down-core changes in PCA axes scores to the Primrose Lake bitumen seep and Cold Lake bitumen, plotted as passive samples. The resulting PCA biplot showed that a compositional shift towards alkyl PACs occurred after regional bitumen sands development began in 1985, followed by a later shift towards a greater predominance of 2-methylphenanthrene, 3-methylphenanthrene, and C1 dibenzothiophene as development intensified after 2000 (Fig. 4). Sediment intervals deposited after 2000 (the top 3 cm) plotted proximal to the Primrose Lake bitumen sample in PCA ordination space (Fig. 4), showing that the PAC composition in Lake 12-26 sediments in recent years has become more similar to the composition of the bitumen that seeped into the waterbody at site 9-21. However, direct input of high volumes of bituminous particles into Lake 12-26 is unlikely, given the lack of increase in vanadium and other trace metals abundant in bitumen (Shotyk et al. 2014), as well as the strong increase in C2 naphthalene, which is generally depleted in bitumen, although it was present in our Cold Lake bitumen samples. C2 naphthalene showed the largest magnitude of increase of all PACs examined in this study, and is abundant in light diesel fuels, or the diluent used to dilute the bitumen so that it can be transported in pipelines (Wang et al. 2014). This may suggest that the primary pathway of petrogenic PACs into Lake 12-26 is related to pipeline leaks, processed water releases, or oil spills, although further work is needed to resolve this.

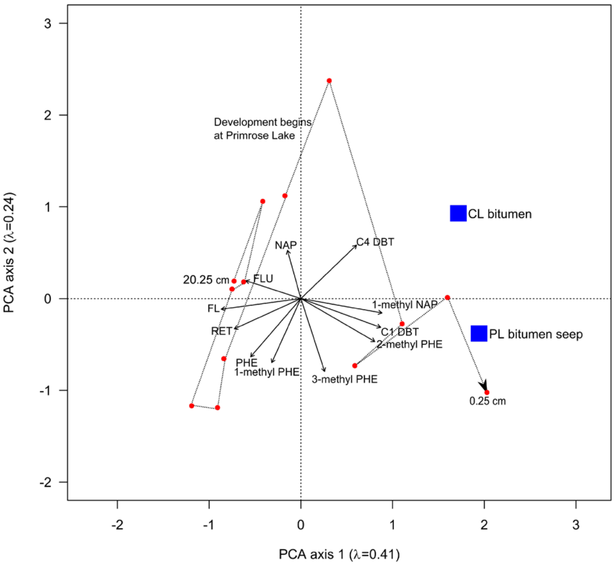

Fig. 4 – Biplot showing changes in principal components analysis (PCA) axis 1 and 2 scores through time for targeted polycyclic aromatic compounds in sediment intervals (points connected by dotted lines) in the core collected from Lake 12-26. The bottom (20.25 cm – pre-industrial) and surface (0.25 cm –representing present-day conditions) sediment intervals are identified. Cold Lake bitumen (CL bitumen) and the Primrose Lake bitumen seep (PL bitumen) are plotted passively. NAP = naphthalene, FL = fluorene, FLU = fluoranthene, RET = retene, PHE = phenanthrene, DBT = dibenzothiophene.

Regional contamination trends associated with in-situ *bitumen extraction*

This study complements two previous spatial and paleolimnological investigations into metals and PACs in the southern region of the Cold Lake bitumen sands region (Korosi et al. 2013; Skierszkan et al. 2013). Based on the collective results of our study and these previous investigations, a picture of environmental contamination around *in-situ* developments is beginning to emerge that is distinct from the Athabasca bitumen sands region. In the Athabasca region, metals and PACs are enriched in a bullseye pattern for a 20 km radius around major mining and oil production facilities (Kelly et al. 2009, 2010; Kirk et al. 2014; Landis et al. 2012; Shotyk et al. 2014), and increased deposition of airborne PACs consistent with the timing of development was evident in sediment cores collected from lakes up to 90 km downwind of Athabasca operations (Kurek et al. 2014). Petcoke dust has recently been identified as the major source of environmental contamination in the Athabasca region (Zhang et al. 2016), and fugitive dust from exposed bitumen, tailings sand, and haul road and overburden components are additional sources (Jautzy et al. 2013; Landis et al. 2012). These major sources of environmental contaminants are absent in the Cold Lake bitumen sands region, perhaps providing an explanation for why metals do not appear to be an important environmental contaminant around *in-situ* drilling wells at Cold Lake, and PAC concentrations in the environment remain comparably lower and compositionally distinct from the Athabasca. Even in the absence of fugitive dust, tailings ponds, and upgraders/refineries, localized PAC contamination is still evident in the Cold Lake region, just without the predictable bullseye pattern that could be used to select for priority monitoring sites.

Reconstructions of contaminant histories in three study lakes in the Cold Lake bitumen sands region [Hilda Lake and Ethel Lake (Korosi et al. 2013, Skierszkan et al. 2013), Lake 12-

26; this study)] revealed that PAC enrichment occurred after ~1985 consistent with the onset of *in-situ* bitumen sands development in Hilda Lake and Lake 12-26, but not in Ethel Lake. The compositional PAC changes differed between Hilda Lake and Lake 12-26, indicating that there are multiple sources of PACs to regional aquatic ecosystems near *in-situ* drilling operations that need to be resolved. In Hilda Lake, acenaphthylene showed a strong increase in sediments deposited after 1985, despite acenaphthylene being absent in the Cold Lake bitumen samples analyzed in this study. In contrast, we observed a clear increase in C2 naphthalene in Lake 12-26 after 1985, as well as a general shift in the overall composition of PACs in Lake 12-26 to become more similar to the PAC composition in Cold Lake bitumen. This strongly implicates activities associated with recent *in-situ* development as contributing to the recent increase in the concentration and flux of alkyl PACs in this lake.

The recent bitumen FTS incident at drilling pad 9-21, located 2 km southwest of Lake 12-26, is a dramatic example of localized PAC contamination. We show, based on the sediment core profile from Lake 12-26, that *in-situ* bitumen extraction may also be contributing petrogenic PACs to the environment over the longer-term through other pathways, outside of the recent and widely reported bitumen FTS incidents. The results summarized above highlight the need for future research to better characterize the sources and pathways of PACs to aquatic ecosystems near *in-situ* drilling operations, similar to the extensive contaminant diagnostic efforts that have been (and continue to be) conducted in the Athabasca bitumen sands region (Jautzy et al. 2013; Landis et al. 2012; Zhang et al. 2016).

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