CrossMark

Sources of polycyclic aromatic hydrocarbons (PAHs) to northwestern Saskatchewan lakes east of the Athabasca oil sands

Jason M.E. Ahad [a,*], Josué J. Jautzy [b], Brian F. Cumming [c], Biplob Das [d], Kathleen R. Laird [c], Hamed Sanei [e]

[a] Geological Survey of Canada, Natural Resources Canada, Québec, QC G1K 9A9, Canada
[b] INRS Eau Terre Environnement, Québec, QC G1K 9A9, Canada
[c] Paleoecological Environmental Assessment & Research Lab (PEARL), Dept. of Biology, Queen's University, Kingston, ON K7L 3N6, Canada
[d] Saskatchewan Ministry of Environment, Regina, SK S4S 5W6, Canada
[e] Geological Survey of Canada, Natural Resources Canada, Calgary, AB T2L 2A7, Canada

ARTICLE INFO

ABSTRACT

The past several decades have witnessed a significant expansion of mining activities in the Athabasca oil sands region, raising concerns about their impact on the surrounding boreal forest ecosystem. To better understand the extent to which distal sites are impacted by oil sands-derived airborne contaminants, we examine sources of polycyclic aromatic hydrocarbons (PAHs) in surface sediments and dated sediment cores from Saskatchewan lakes situated ~100–220 km east–northeast of the main area of bitumen mining activities. The concentrations and fluxes of both parent and alkylated PAHs are low and show considerable variability over the past 70–100 years. Small yet discernible increases in PAH concentrations and fluxes occurred over the past 30 years, a trend which coincides with the rapid growth in bitumen production. However, several lines of evidence point to wildfires as the principal source of PAHs to these lakes: (1) the significant co-variations in most cores between retene (1-methyl-7-isopropyl phenanthrene) and other groups of parent and alkylated PAHs, (2) the similarity in compound specific $\delta^{13}C$ signatures of the parent PAHs phenanthrene and pyrene in recently deposited surficial sediments and those corresponding to time intervals considerably pre-dating the large scale development of the oil sands and (3) the discernible up-core increases in the proportion of refractory carbon (i.e., char) in Rock-Eval 6 data. The collective evidence points to softwood combustion from boreal forest fires as the principal source of retene in sediments and the general increase in forest fire activity in this region over the past several decades as the source of refractory carbon. Mining activities associated with the Athabasca oil sands are thus not considered a major source of PAHs to these lakes.

1. Introduction

The rapid growth in oil sands mining activities in the Athabasca region of northern Alberta, Canada, poses an increasing risk to the surrounding boreal forest ecosystem. One of the major concerns is the atmospheric transport of polycyclic aromatic hydrocarbons (PAHs), a group of organic contaminants that are toxic to a range of aquatic wildlife (Newsted and Giesy, 1987; Colavecchia et al., 2004) and are suspected or known carcinogens (Boffetta et al., 1997; Boström et al., 2002). Naturally present in bitumen, PAHs are also released into the environment through the incomplete combustion of organic matter, including modern biomass and fossil fuels, and via diagenetic processes.

In northern Alberta and Saskatchewan, where forest fires are a common occurrence (Larsen, 1997; Stocks et al., 2002), an understanding of historical PAH deposition is essential to evaluate potential inputs from mining activities. This historic evaluation should extend prior to 1967, when large scale industrial development of the Athabasca oil sands (AOS) began (Schindler, 2010). Unfortunately, however, routine monitoring of PAHs in ambient air in the region only began in late 2010. Other approaches to investigate natural background variability and temporal trends are therefore required.

As noted by the Federal Oil Sands Advisory Panel (Dowdeswell et al., 2010), sedimentary records found in lakes provide an excellent opportunity to assess baseline, pre-impact conditions and post-impact trajectories in the AOS region. A recent study by Kurek et al. (2013) reported significant up-core increases in PAH concentrations and fluxes in six lakes situated 6–90 km away from the centre of AOS mining activities, with the clearest trends found

in lakes located ⩽ 25 km the operations. Jautzy et al. (2013) utilised compound specific carbon isotope signatures and molecular diagnostic ratios and demonstrated an increasingly large input of petroleum derived (i.e., petrogenic) PAHs over the past 30 years in two lakes located 40 km and 55 km east of the main area of mining activities. The petrogenic source was attributed to the deposition of bitumen in dust particles associated with wind erosion from open pit mines. Studabaker et al. (2012) also suggested mine dust as an important source for airborne PAHs in the AOS region. The Kurek et al. (2013), Jautzy et al. (2013) and Studabaker et al. (2012) studies were in agreement with a previous investigation by Kelly et al. (2009) that showed substantial loadings of airborne particulates containing PAHs to snowpack within an approximately 50 km radius from the centre of the oil sands mining operations. Particulate deposition exponentially declined at sites > 50 km distant, in agreement with Hall et al. (2012) who found no evidence for a recent increase in atmospherically transported PAHs to the Athabasca Delta, situated ∼220 km north of the city of Fort McMurray, Alberta. Nevertheless, further research is needed to refine and quantify the contributions of the different mining and non-mining related inputs (Ahad et al., 2014; Cho et al., 2014; Parajulee and Wania, 2014a,b; Wang et al., 2014) and to better understand the geographic extent and potential impact of PAHs associated with oil sands mining activities in areas further afield from operations.

In this study, we report concentrations and deposition fluxes of 15 Environmental Protection Agency (EPA) priority PAHs, retene, perylene, coronene, dibenzothiophene and several alkylated PAH groups in dated sediment cores from four Saskatchewan lakes situated 100–190 km east to east–northeast of the main area of oil sands mining operations. Compound specific carbon isotope signatures ($\delta^{13}C$) and Rock-Eval 6 analyses are used to provide insight into PAH sources. A previous investigation in these lakes by Laird et al. (2013) found no consistent trends in the concentration or flux of total or individual priority pollutant elements (PPEs) including lead, mercury, copper, zinc and vanadium. To the best of our knowledge, this is the first paleolimnological study to address potential cross-boundary atmospheric transport of oil sands mining-related organic contaminants in northern Canada.

2. Materials and methods

2.1. Study sites

Parent and alkylated PAHs were determined in four Saskatchewan lakes chosen from among the ten previously described by Laird et al. (2013). The lakes were selected based on a water chemistry survey of 259 headwater lakes sampled during 2007–2008 within ∼ 300 km of Fort McMurray (Scott et al., 2010). The initial criteria for lake selection targeted relatively shallow, small headwater lakes (4–15 m depth with lake surface areas < 200 ha) with relatively undisturbed catchments that were identified as being sensitive or very sensitive to acid deposition. The lakes examined here (Fig. 1) were chosen to cover a range of distances east to east–northeast of the main centre of AOS mining operations: 100 km (Lake 8D and Lake 10W), 130 km (Lake 10G) and 190 km (Lake 13C). Lakes 8D, 10W and 10G are located on the Boreal plain, Mid-Boreal Upland ecoregion, whereas Lake 13C is located on the Boreal Shield, Churchill River Upland ecoregion (Laird et al., 2013). In addition, surface (0–2 cm) and deep core (28–40 cm) sediments from Lake 10M (105 km east), also located on the Boreal plain, were collected in September 2010 and were only used here for compound specific $\delta^{13}C$ characterisation. Further details on this lake are provided elsewhere (Stanners, 2014). Sediments from deeper sections (10–16 cm) of a core from Lake 12D (220 km

east–northeast), located on the Boreal Shield (Laird et al., 2013), were also used just for $\delta^{13}C$ analyses. The prevailing winds in this region are in general from the southwest and southeast.

Sediment cores from lakes 8D, 10W, 10G and 13C were collected in March 2010 using a Glew gravity corer with a 7.6 cm internal diameter core tube. One core was taken for PAH analysis and a separate core was used for age determination and measurements of diatoms, chrysophytes, mercury and other metals (Laird et al., 2013). The two cores were located within 10 m of each other and were cored near the centre of each lake. The core used for PAH analysis was sectioned into 1 cm intervals between 0 cm and 10 cm, and every 2 cm for the deeper intervals. The number of samples presented varies among sites because the range of time represented by the sediment intervals varied due to differences in the sedimentation rate between lakes. Full details on radiometric dating and age models for these lakes are provided by Laird et al. (2013). Unsupported ^{210}Pb activities were used to estimate the chronology of the cores using the constant rate of supply (CRS) model (Appleby and Oldfield, 1978).

2.2. Analysis of PAHs

Freeze dried or oven dried (50 °C for 48 h) sediments were homogenised with a mortar and pestle and solvent extracted with 1:1 acetone:hexane (Optima grade, Fisher Scientific, Ottawa, ON, Canada) using a Microwave Accelerated Reaction System (MARS, CEM Corporation, Matthews, NC, USA). Each sample was spiked with an internal surrogate mixture containing 5α-cholestane and m-terphenyl (Sigma–Aldrich, Oakville, ON, Canada) prior to extraction. The extracts were gravity filtered using pre-combusted (450 °C for 4 h) glass fibre filters and elemental sulfur was removed by the addition of activated copper. The extracts were evaporated to ∼ 0.5 ml under ultrahigh purity N_2 and passed through a chromatographic column packed with fully activated (pre-combusted at 450 °C for 4 h) silica (70–230 mesh, Silicycle, Québec, Canada). The top of the column was covered with ∼ 0.5 g anhydrous sodium sulfate to remove any residual water. The extracts were separated into the following three fractions: F1 (hexane), F2 (hexane:dichloromethane) and F3 (methanol). The aromatic fraction containing PAHs (F2) was further purified by column chromatography using 3% deactivated Al_2O_3 (Fisher Scientific).

PAHs were analysed using GC–MS in selected ion monitoring (SIM) mode and concentrations were determined using the following external standards: retene (1-methyl-7-isopropyl phenanthrene), coronene, perylene and dibenzothiophene (Sigma–Aldrich); 16 EPA Priority PAH mixture, 2-methylanthracene, 9,10-dimethylanthracene, 1-methylnaphthalene, 1-methylphenanthrene and 1-methylfluorene (Anachemia Science, Saint-Pierre, QC, Canada). Concentrations of alkylated PAHs were determined using the closest external standard available and identified with at least two different ions. The following GC temperature program was used for analysis: 70 °C (hold 2 min), increase to 290 °C at 8 °C/min (hold 8 min), increase to 310 °C at 10 °C/min (hold 10 min). Naphthalene was excluded from the total PAHs due to low recoveries and a lack of reproducibility between replicate samples. The following PAHs were quantified and are reported here: the parent PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b/j/k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene and dibenzothiophene), retene, perylene, coronene and five alkylated PAH groups: C_1–C_2 fluorenes (Flu), C_1–C_4 dibenzothiophenes (DBT), C_1–C_4 phenanthrenes/anthracenes (Phe), C_1–C_4 fluoranthenes/pyrenes (Fla), C_1–C_3 chrysenes/benz[a]anthracenes (Chy). The sum of the alkylated PAH groups not including retene are reported as $\sum PAH_{alk}$, and the sum of the parent PAH groups as $\sum PAH_{parent}$. The limits