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PAH sediment studies in Lake Athabasca and the Athabasca River ecosystem related to the Fort McMurray oil sands operations: sources and trends

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Abstract

The oil sands operations in northern Alberta are among the most modem in the world. However, because the operations are extensive and lie on either side of the Athabasca River, there are concerns that they will adversely affect downstream environments such as the Athabasca River, its tributaries, the Peace-Athabasca deltas and Lake Athabasca. Research and monitoring programs are now investigating hydrocarbon sources, fate, and time trends in these aquatic ecosystems. Natural hydrocarbon sources (oil sands) are numerous along the Athabasca River and its tributaries. Petrogenic hydrocarbons also are abundant in downstream lakes. Lower molecular weight compounds such as naphthalene and fluorene tend to increase in concentration from upstream sources to downstream depositional areas. There is little or no evidence of temporal trends of increasing PAH concentrations in sediment cores collected in Lake Athabasca and the Athabasca delta lakes, suggesting no or minimal impact from the oil sands operations. Some PAHs exceed interim sediment quality guidelines and some bioassay studies have shown evidence of toxicity, particularly in the Athabasca delta. However, there is no evidence that this is associated with the oil sands industry. The RAMP monitoring program will continue to assess the potential impacts of the oil sands industry on river, tributary and delta ecosystems.

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1 Introduction

1.1 General Background

Canada's oil sand resources, estimated at 28.3 billion cubic meters of recoverable bitumen and 259 billion cubic meters of in-place bitumen, are the world's largest reserve of such hydrocarbons [1, 2]. The majority of this bitumen occurs in the province of Alberta (Figure 1). The largest reserves are in the Athabasca deposit (206.7 billion cubic meters) with substantially smaller volumes in the Cold Lake (31.9 billion cubic meters) and Peace River (20.5 billion cubic meters) deposits. Surface mining of these oil sands is feasible down to depths of 75 m of overburden. Consequently, surface mining of bitumen is limited to the Athabasca deposit and then to an area roughly running between 25 - 90 km north of Fort McMurray and within 25 km of the Athabasca River and along both sides of the river. In situ extraction techniques must be used in areas where deposits lie deeper.

Bitumen is heavy, viscous and hydrogen deficient when compared to conventional crude oils [1]. Therefore, it is upgraded locally through various processes involving the creation of a slurry, the addition of naptha, separation of the bitumen froth, and thermal cracking. The final products are upgraded or synthetic crude oil. Various waste products are produced during this production including air emissions and massive volumes of water. Syncrude, which began operation in 1978, is holding 350 million cubic meters in unsettled sludge in tailings ponds. Suncor, which began operation in 1967 and has worked with newer technologies, is holding 90 million cubic meters of tailings. In 2000, Suncor removed 42.5 million m^3 of water from the Athabasca River and returned 30.5 million m^3 of water along with 24.6 tonnes of oil and grease.

1.2 Environmental concerns

While the oil sands region is in an area of relatively low population density, it also is in a region of significant ecological and human importance. Many First Nation people live along the Athabasca River including Fort McMurray, Fort McKay, and Fort Chipewyan located on the outflow from Lake Athabasca. The Athabasca River is a significant source of water to the Peace and Athabasca delta lakes, ecologically important deltas. The Peace River Delta is a protected environment, located within Wood Buffalo National Park. Lake Athabasca flows into Great Slave Lake, the headwater of the Mackenzie River.

1.3 Monitoring and Research Programs

The Regional Aquatics Monitoring Program (RAMP) is a multi-stake program involving representatives from industry, provincial and federal governments, local aboriginal groups and consultants [3, 4]. It was established in 1997 and currently is scheduled to run to 2009 although it probably will run into 2040.

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The sediment-monitoring program includes sampling in the Clearwater, Muskeg, and MacKay rivers, McLean and Fort creeks and in the Athabasca River including upstream of the tributary outflows. Samples also are collected downstream of Fort Creek and in the Athabasca delta. The sediment-monitoring program continues to expand with the increase in oil sands operations in the RAMP study area.

Surface sediments were sampled in western Lake Athabasca, the Athabasca delta, including various river channels and lakes, Mamawai Lake and Lake St. Claire (Figure 1) as part of a Petroleum and Energy Development (PERD) research study. This study is investigating hydrocarbon composition and concentrations in the Lake Athabasca and Peace-Athabasca delta ecosystems and the possible contribution from the upstream oil sands industry. Sediment cores were collected in two delta lakes (Mamawi and Richardson) and in Lake Athabasca to infer time trends in hydrocarbon deposition.

2 Methods

RAMP sampling and analytical methods are described in detail in Golder Associates Ltd [3, 4]. In brief, sediment samples were collected with an Ekman dredge in depositional areas within each study area. Four to six replicate samples were combined to form a single composite. Only the top 3-5 cm of sediment was used in creating the composite. Samples were analyzed for the 16 target parent PAHs and for their alkylated forms. Other analyses, not presented here include metals, grain size, carbon content and organics. Hydrocarbon analyses were conducted at AXYS Analytical Services Ltd., in Sydney, British Columbia. Some sediment samples were used in toxicity testing by HydroQual, in Calgary, using the midge larvae *Chironomus tentans*, the amphipod *Hyalella azteca*, and the oligocheate *Lumbriculus variegatus*.

PERD sediment samples were collected using either an Ekman or PONAR dredge. Two to three replicates were collected per site with the upper 3-5 cm sampled. Two oil sand samples provided by Syncrude also were analyzed. Samples were analyzed for the 16 target parent PAHs and for their alkylated forms. While not reported here, samples also were analyzed for retene, dibenzofuran, perylene, alkanes, hopanes, steranes, and for grain size. All chemical analyses were performed at the Freshwater Institute. Sediment cores were collected in summer (Mamawi and Richardson Lake) in shallow waters (< 2m) by pushing a 10-cm diameter plexiglass core tube into the sediments. In Lake Athabasca, sediment cores were collected at three sites in winter by lowering the 10-cm diameter gravity corer through the ice. These samples were analyzed for PAHs. Sediment cores were dated using ^{210}Pb and ^{137}Cs techniques as described in Evans et al. [5]. Subsets of the Mamawai and Richardson Lake cores and one Athabasca core were analyzed for PAHs.

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3 Results and Discussion

3.1 Oil sands

Total PAH concentrations were high in the two oil sands samples and dominated by alkylated forms. Phenanthrenes and anthracenes were the most abundant PAHs with a mean concentration of 217,000 ng/g (98.7% in alkylated forms). Dibenzothiophenes were the next abundant with a mean concentration of 158,500 ng/g (99.9% alkylated). Fluoranthene and pyrene followed with a total mean concentration of 32,400 ng/g (94.4% alkylated). Fluorene (26,400 ng/g, 98.7% alkylated), naphthalenes (19,100 ng/g, 65.9% alkylated) and benz(a)anthracene and chrysene (9,300 ng/gm, 89.2% alkylated) also were abundant.

3.2 PAHs in surface sediments of the Athabasca River and its tributaries

Sediment samples in the Athabasca River and its tributaries were highly variable in their total PAH concentrations although the predominant PAHs were the same as those observed in the oil sands. To show general spatial patterns, concentration data for the dibenzothiophenes and naphthalenes are presented as means, combining sites within a location and years of sampling (Fig. 2). At some locations, some samples contained very high concentrations of PAHs, suggestive of oil sands inputs. For those sites, the data were grouped as low and high values.

Dibenzothiophene concentrations ranged from <100 ng/g to 25,000 ng/g (Fig. 2). Alkylated forms dominated indicating significant petrogenic sources, most likely the erosion of naturally occurring oil sands. There was no obvious north-south gradient in dibenzothiophene concentrations. In contrast, naphthalene tended to occur in higher concentrations in the northern than southern portions of the sampling area. Concentrations ranged from <100 ng/g to 10,000 ng/g. Alkylated forms dominated.

3.3 PAHs in the Athabasca River, delta, and lake ecosystems

Mean concentrations for various PAHs were graphed to summarize general patterns in concentration over the entire RAMP and PERD study areas (Fig. 3). Tributary samples were separated into "high" sites (HT) which contained oil sands and "low sites" (LT) which were less impacted by oil sands inputs. The Athabasca River was divided into sites upstream (ARU) of Fort Creek and downstream including the Athabasca River Delta (ARD) channel sites.

Athabasca River sediments tended to have PAH concentrations intermediate between high and low tributary sites. This suggests rapid dilution of oil sands PAHs in the sediments of the Athabasca River. In addition, a significant fraction of the PAHs observed in Athabasca River sediments probably originated from upstream sources. The annual suspended sediment

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load at Fort McMurray has been estimated at 5.63 kilotonnes [6]. While the majority is carried downstream to Lake Athabasca and delta, some particulates become part of the depositional areas of the Athabasca River. PAH concentrations in the RAMP sediments generally were similar to those observed in previous sampling of the Athabasca and Peace rivers [7].

There was a weak tendency for naphthalene and fluorene to increase in concentration from the main body of the Athabasca River (ARU) to the Athabasca River Delta channels (ARD) while the converse was observed for fluoranthene/pyrene and benzo(a)anthracene/chrysene. Naphthalene and fluorene concentrations tended to be higher in lakes in the Athabasca delta (AD), the Peace Delta (PD), western Lake Athabasca (LA), and the outflow channels from Lake Athabasca than the mainstem Athabasca River. This pattern was less pronounced for higher molecular weight PAHs.

3.4 Interim Sediment Quality Guidelines and sediment toxicity

Interim Sediment Quality Guidelines (ISQG) have been developed for relatively few PAHs and mainly for the parent compounds [8]. There is no guideline for dibenzothiophene. These guideline values were compared with sediment data reported for 46 RAMP samples and for 27 surface PERD samples. Some manipulations of the RAMP data were performed. RAMP does not report 2-methylnaphthalene but C1-naphthalene. In the PERD samples, approximately 50% of the C1-naphthalene is 2-methylnaphthalene. This figure was used to estimate 2- methylnaphthalene concentrations in RAMP samples. Similarly, RAMP reports benzo(a)anthracene and chrysene as a sum. Therefore, a ratio of 1:3, as observed in the PERD samples, was used to estimate the individual parent concentrations in RAMP samples.

Several of the RAMP samples exceeded ISQG concentrations (Table 1), especially for chrysene, benzo(a)anthracene, phenanthrene, and 2-methylnaphthalene. Concentrations in most samples were only slightly above ISQG's although some sediment samples collected in Donald Creek, McLean Creek, and upstream of Fort Creek were high and approached Probable Effects Values (862 ng/gm for chrysene and 782 ng/gm for benzo(a)anthracene. PERD study area exceedences were primarily for naphthalene and 2-methylnaphthalene. The Fort Chipewyan sample was slightly enriched with fluoranthene and pyrene.

Sediment toxicity studies under the RAMP program have shown high survivorship of (>80%) of *C. tenans, H. tentans,* and *L. variegatus* in Athabasca River and tributary samples [3, 4]. Lower values were associated with *C. tentans* (42%) and *H. azteca* (72%) survivorship and *L. variegatus* (62%) growth in a 1999 Athabasca River delta sample. *L. variegatus* growth also was low (53-58%) in 2000 in two delta samples. Samples were silty clays in both years. The reason for this reduced growth and survivorship is unknown. Toxicity testing often yields variable results.

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Table 1. Interim Sediment Quality Guidelines (ISQG) and the number of RAMP (n = 46) and PERD (n = 27) exceeding this guideline. The range in exceedence concentrations is shown in parentheses. * Fort Chipewyan Harbor. See text for further explanation.

Compound	ISQG	RAMP	PERD
Naphthalene	34.6	0	5 (35-77)
2-Methlynaphthalene	20.2	7 (22-33)	19 (20-92)
Fluorene	21.2	0	0
Phenanthrene	41.9	3 (45-58)	0
Anthracene	46.9	0	0
Fluoranthene	111	0	1 (131)*
Pyrene	53.0	0	1 (118)*
Benz(a)anthracene	31.7	5 (48-300)	0
Chrysene	57.1	5 (142-900)	0

Occasional studies using upstream Athabasca River sediments have reported very low survivorship (0-29%) and growth (0-53%) of *L. variegatus*. Sands generally dominate these sites, a poor habitat for *L. variegatus*.

3.5 Sediment cores

There was little evidence from the sediment cores of a temporal increase in PAH concentrations, which could be related to the oil sands industry. Data are presented for only the Richardson and Lake Athabasca cores and then for two time periods. In general most PAHs occurred in higher concentrations in the sediment core slices from the 1950s than in recent times. The reasons for this are unclear. Only phenanthrene and anthracene in the Richardson Lake core showed evidence of higher concentrations in recent times.

Table 2. Concentrations of selected PAHs (parent and alkylated forms) at two depths (time periods) for a core collected in Richardson Lake and Lake Athabasca. Units are ng/gm dry weight.

Compound	Richardson Lake		Lake Athabasca	
	1998	1950	1998	1957
Naphthalenes	153	365	464	722
Fluorenes	125	125	71	141
Dibenzothiophenes	225	220	77	107
Phenanthrene/anthracene	681	456	267	362
Fluoranthene/pyrene	253	200	137	214
Benzo(a)anthracene/chrysene	205	159	237	305
Benzo(a)pyrene	4	5	6	16

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4 Conclusions

Sediments in the Athabasca River, its tributaries, downstream deltas and western Lake Athabasca are dominated by petrogenic PAHs. Lower molecular weight compounds tend to increase in concentration from upstream sources to downstream depositional areas. On occasion, some PAHs, particularly 2-methylnaphthalene, exceed ISQGs. Some bioassay studies have shown evidence of toxicity, particularly in the Athabasca delta. However, there is no evidence of impacts from the oil sands operations on hydrocarbon distributions and sediment toxicity. RAMP will continue to assess the potential impacts of the oil sands industry on aquatic ecosystems.

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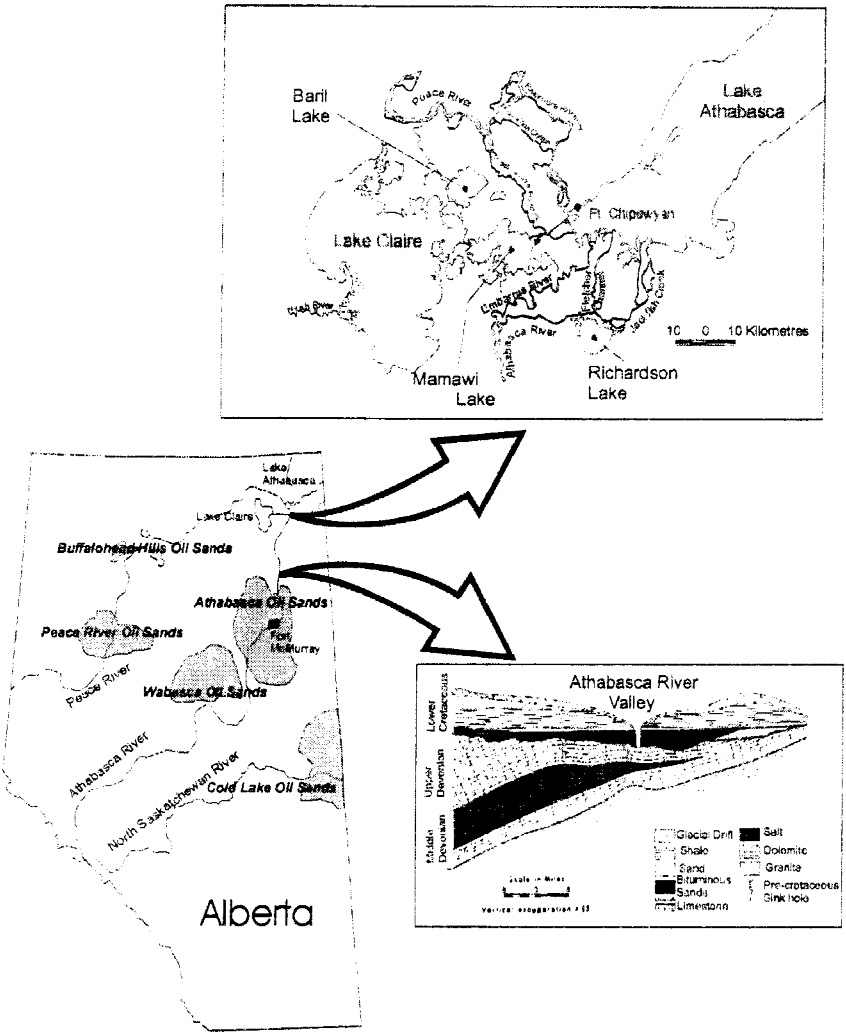

Figure 1. Map showing the province of Alberta and location of major oil sands deposits. Also shown is the Peace-Athabasca River Delta and western Lake Athabasca (upper right) and a geological cross section (lower right) through the Athabasca oil sands and river valley. Modified from Oil Sands Reclamation Network (2002).

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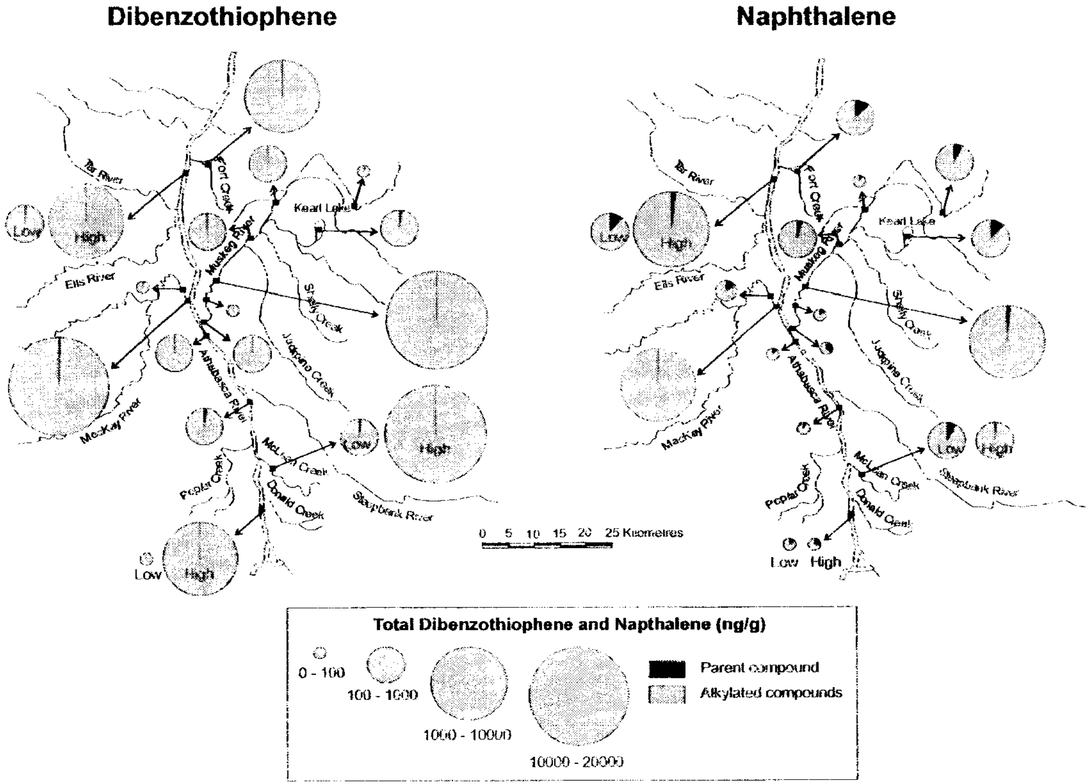

Figure 2. Dibenzothiophene and naphthalene concentrations in Athabasca River and tributary sediments, 1998-2002. For sites in which multiple years and/or locations were sampled, sites are separated into high (oil sands inputs) and low sites.

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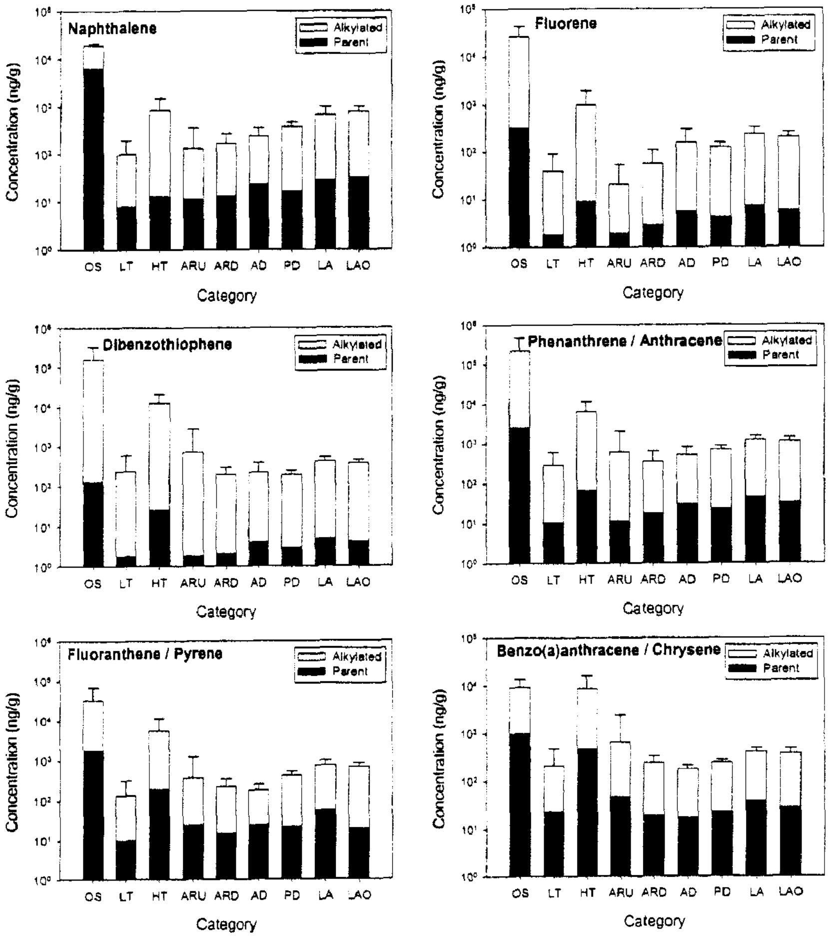

Figure 3. Mean concentration (and standard deviation) of selected PAHs in oil sands (OS), low site Athabasca tributaries (LT), high site Athabasca tributaries (HT), the Athabasca River to Fort Creek (ARU), the Athabasca River and delta channels downstream of Fort Creek (ARD), Athabasca delta lakes (AD), Peace Delta lakes (PD), Lake Athabasca (LA), and outflow channels from Lake Athabasca (LAO).