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MONITORING OF NATURAL HYDROCARBON RELEASE FROM OILSANDS DEPOSITS IN A CANADIAN RIVER BASIN

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ABSTRACT

Athabasca Oil Sands are found in the McMurray formation in the Athabasca River Basin in Northern Alberta, Canada. Monitoring studies conducted during 1998-1200, have indicated that there is a preponderance of oil sands-derived hydrocarbons, primarily PAHs, their C_{1-4} alkylated analogues, and biomarkers, in downstream sediment samples of the tributaries relative to the upstream samples. The relative composition of these hydrocarbons are diagnostic of a petrogenic source, and provides a fingerprint for characterization of biofilm samples, aquatic invertebrates, and sediments in northern rivers and tributaries. Results of GC-MS analyses of sediments, confirm that the tributaries passing through the Fort McMurray oil sands regions contain significant levels of naturally derived hydrocarbons (2-50 mg/g). Field activities in heavily impacted areas should therefore continue to emphasize the tributaries draining through oil sands deposits, as opposed to the main-stem of the Athabasca River where hydrocarbon levels are subject to dilution from high sedimentation rates.

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INTRODUCTION

The Athabasca Oil Sands are found in the McMurray formation in the Athabasca River Basin in Northern Alberta, Canada. The oilsands deposits (cohesive mixtures of fine sand, clay, bitumen and water) are estimated to contain as much as 1.7 trillion barrels of bitumen. The river basin covers approximately 42,000 square kilometres through which the Athabasca river flows along oil sands formations and transports natural hydrocarbons and sediment to downstream locations.

Many investigations have focused on the nature of effluent produced by the industry and its associated impact to biotic systems. Investigations have also been undertaken to assess the spatial distribution of these hydrocarbon contaminants, typically by determining the amount of hydrocarbon associated with deposited fluvial sediments. Natural hydrocarbon exposures, however, are evident throughout the oil sands area and studies have suggested that these outcrops may be responsible for observed biomarker responses in areas not exposed to industrial effluent. Given that the oil sands represent a natural source of hydrocarbons to the environment and with no quantification of this source, it is currently difficult to determine the true impact of oil recovery activities within a fluvial system. Monitoring of the levels of hydrocarbons released from the oilsands deposits was therefore undertaken with a primary purpose to provide an improved understanding of the nature and extent of natural hydrocarbon releases within the context of the sediment regime of the lower Athabasca River basin.

The laboratory studies reported herein, directly support the field component of the project to assess the sedimentation process, hydrology and geomorphology of several tributaries passing through oil sands deposits (i.e., Athabasca, Wabasca, Clearwater, and Steepbank) so as to identify and sample the depositional sites where released hydrocarbons and PAHs are most likely to accumulate once released to the environment. Studies of the latter included: a) application of selective extraction techniques to determine the distribution of heavy-oil in oil sands and surrounding soils; and b) development of procedures for the measurement of the distribution and migration of the target organic compounds associated with oil sands deposits to river water. It is intended that the combined field and laboratory components will serve to help quantify and

characterize the spatial distribution of natural hydrocarbon seeps in major rivers of the Athabasca and Peace river basins. This in turn will help to determine the distribution and movement of heavy oil contaminants in riverine sediments.

EXPERIMENTAL

In the fall of 1988 ten tributaries of the Athabasca river were sampled for water quality, sediment, and biofilm at both headwater and downstream locations. Following, preliminary analyses three of these tributaries, the Mckay, Steepbank and Ells rivers were selected for more detailed, longitudinal study. During 1999 spring and fall sampling periods up to twelve sites on these tributaries (as well as additional sites in the mainstem of the Athabasca) were sampled. Samples collected at some or all sites included: river water, sediment (bed material, bank material, suspended sediment) for subsequent analysis of polycyclic aromatic hydrocarbons and their alkylated derivatives.

Sediment samples were collected from selected tributaries in the Athabasca River Basin in plastic bags and stored at -40°C. Once received at the laboratory, sediments ere freeze dried. An aliquot of 2g of sample was spiked with surrogate standard, left to age for 1 hour, extracted in 20ml of dichloromethane for 1 hour. This mixture was in turn centrifuged at 15 min @ 3000rpm, the organic extract pipetted into a separatory funnel, and the extraction procedure repeated twice.

Following acid/base partitioning, the extract was dried using sodium sulphate columns and the base fraction was left to stand overnight in acid washed copper to remove elemental sulphur. The volume of the base fraction was reduced to 2ml and an aliquot of 0.5ml passed through 5% deactivated silica gel clean-up column (Grade 923 silica gel, 100 - 200 mesh, activated at 130°C for 16 hours) which was first pre-eluted with 10ml pentane. The extract was first washed with 2 x 0.5ml hexane and eluted with 10ml pentane and 15ml pentane:dichloromethane mixture (2:3). The final extract was concentrated to 1ml, solvent exchange to hexane, and 5μl of an internal standard mixture added for quantification of the analytes.

Instrumental analyses were performed using gas chromatography mass spectrometry (GC/MS) operating in the selected ion-monitoring mode. Specifically, studies were performed with a Hewlett Packard 5970 MS equipped with a 890 GC and HP 76673A autosampler. The

instrumental parameters were as follows: Injector - 250°C; Detector - 280°C; column - 0.25 mm i.d. x 30 m HP-5MS column; and temperature program: 60°C for 1 min; 25°C/min to 160°C; 3°C/min to 268°C; 12°C/min to 300°C; hold for 8 minutes. The total run time 51.6 min.

Detection was based on selected ion monitoring using the following parameters:

SIM Windows for PAH Analysis

GROUP	START TIME	m/z
1	4.00	136,128,129
2	6.00	172,
3	7.00	164,152,153,154
4	8.80	166,165
5	11.00	188,178,179
6	14.40	244,202,203
7	26.00	240,228,229
8	34.00	252,253
9	37.50	252,253,264
10	43.00	278,279,276,277

RESULTS AND DISCUSSION

A preponderance of oil sands-derived hydrocarbons, primarily PAHs, their C_{1-4} alkylated analogues, and biomarkers, were observed in downstream sediment samples of the tributaries relative to the upstream samples. The relative composition of these hydrocarbons were diagnostic of a petrogenic source (bell-shape as oppose to exponential), and provided a fingerprint for characterization of biofilm samples, aquatic invertebrates, and sediments in northern rivers and tributaries. Results of GC-MS analyses of sediments, confirmed that the tributaries passing through the Fort McMurray oil sands regions contain significant levels of naturally derived hydrocarbons (2-50 mg/g). There was evidence of extensive weathering of the petroleum fingerprints for downstream locations.

Field activities in heavily impacted areas should therefore continue to emphasize the tributaries draining through oil sands deposits, as opposed to the main-stem of the Athabasca River where hydrocarbon levels are subject to dilution from high sedimentation rates.

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REFERENCES

Headley, J.V and Conly M. 1999. Assessment of Natural and Anthropogenic Impacts of Oil Sands Contaminants Within the Northern River Basins. Progress Report for PERD Project No. 521006.