



Forensic source differentiation of petrogenic, pyrogenic, and biogenic hydrocarbons in Canadian oil sands environmental samples



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HIGHLIGHTS

- Characterized hydrocarbons (HCs) in various oil sands impacted environmental samples.
- Investigated the distribution patterns of oil PAHs/biomarkers from the study sites.
- HC were attributed to four sources: petrogenic, biogenic, pyrogenic, and light fuels.
- HC in snow were due to oil sands particulates associated with mining activities.

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ABSTRACT

To facilitate monitoring efforts, a forensic chemical fingerprinting methodology has been applied to characterize and differentiate pyrogenic (combustion derived) and biogenic (organism derived) hydrocarbons from petrogenic (petroleum derived) hydrocarbons in environmental samples from the Canadian oil sands region. Between 2009 and 2012, hundreds of oil sands environmental samples including water (snowmelt water, river water, and tailings pond water) and sediments (from river beds and tailings ponds) have been analyzed. These samples were taken from sites where assessments of wild fish health, invertebrate communities, toxicology and detailed chemistry are being conducted as part of the Canada-Alberta Joint Oil Sands Monitoring Plan (JOSMP). This study describes the distribution patterns and potential sources of PAHs from these integrated JOSMP study sites, and findings will be linked to responses in laboratory bioassays and in wild organisms collected from these same sites. It was determined that hydrocarbons in Athabasca River sediments and waters were most likely from four sources: (1) petrogenic heavy oil sands bitumen; (2) biogenic compounds; (3) petrogenic hydrocarbons of other lighter fuel oils; and (4) pyrogenic PAHs. PAHs and biomarkers detected in snowmelt water samples collected near mining operations imply that these materials are derived from oil sands particulates (from open pit mines, stacks and coke piles).

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1. Introduction

Oil sands are a type of deposit of bitumen, the heaviest and thickest form of petroleum. In its raw state, bitumen is a mixture of extremely complex organic liquids that are highly viscous, black, sticky, asphalt-like, and entirely soluble in carbon disulfide. The two largest-known global sources of naturally occurring bitumen (in Alberta and Venezuela) each contain more petroleum than the

entire proven conventional oil reserves of the Persian Gulf [1]. Most of the Canadian oil sands reserves (estimated to hold 1.7 trillion barrels of crude oil) are located in three major deposits in northern Alberta (Athabasca, Cold Lake, and Peace River) [2]. Oil sands production, including raw bitumen production and upgraded synthetic crude oil, currently makes up just over half of western Canada's total crude oil production [3]. It is expected to grow from over 1.8 million barrel/day (b/d) in 2012 to approximately 4.5 million b/d in 2025 following current trends [4]. The Alberta oil sands consist of bitumen (10–12%), sand (~83–85%) and water (~4–5%). The typical API (American Petroleum Institute) gravity of Alberta Athabasca oil sands bitumen is 8–10 API^o. To produce crude oil, bitumen in the oil

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sands is generally extracted with hot water and upgraded by heat, pressure, and catalysts. Generally, oil sands bitumen is rich in heteroatoms (N, S and O), contains a high percentage of asphaltenes and resins, and the hydrocarbon content is estimated to be 35–45% [5,6].

As global demand for energy keeps growing and conventional crude oil reserves on land are approaching depletion, the production of off-shore reserves and heavy oils such as Alberta oil sands have been steadily increasing. Undoubtedly, increasing mining, production, transportation and usage of the oil sands has driven rapid economic growth in Alberta. However, this rapid growth of production of the Alberta oil sands has become a concern due to possible impacts of the oil sands mining activities on water and air quality, the health of aquatic biota, soil and ecological systems, and on the environment as a whole [7]. For example, the mining, extraction and production of oil sands consume water resources, emit greenhouse gas, and result in large tailings ponds containing oil sands-affected process waters. Recent studies by Kelly et al. [8,9] suggest that for over a decade, oil sands mining and processing has been contributing metals and PAHs to the Athabasca River. Also, some earlier studies by the EC [10–12] provided preliminary characterization and source assessment of PAHs in tributary sediments of the Athabasca River and lake ecosystems.

Petroleum hydrocarbons (PHC or TPH) are ubiquitous constituents in the environment. In addition to petrogenic hydrocarbons, there are two other potential sources of hydrocarbons to the oil sands region: (1) naturally occurring biogenic organic compounds (BOC), formed in situ through biological process; and (2) “pyrogenic PAHs”, generated from natural forest fires spread through air transport, and combustion of fossil fuel, organic material or waste. Current monitoring for PHC in soil and sediments is conducted typically in Canada by the Canadian Council of Ministers of the Environment (CCME) Tier 1 method [13]. This method does not distinguish between biogenic, pyrogenic and petrogenic inputs. It will be necessary to distinguish between naturally occurring BOC in environmental samples from anthropogenically introduced oil sands hydrocarbons. Under the new JOSMP [14], it indicates that the suite of analyses are being conducted as part of a large program to address sources, fate, distribution and effects of oil sands related chemical compounds on riverine ecosystem. Therefore, it is important to characterize and differentiate PHC, BOC and pyrogenic hydrocarbons in oil sands contaminated environmental samples.

Very recently, Jautzy et al. [15] reported century-long source apportionment of PAHs in Athabasca oil sands region lakes using compound-specific carbon isotope signatures. Furthermore, several novel approaches have been used to characterize and/or quantify mining-related “naphthenic acids” in the Athabasca oil sands region [16–22]. This paper focuses on the PAH and biomarker distribution patterns and potential sources for various oil sands environmental samples. These results will be used to aid in the interpretation of potential effects in laboratory organisms and wild organisms exposed to these same groups of samples. A forensic chemical fingerprinting methodology using gas chromatography–mass spectrometry (GC–MS) and gas chromatography–flame ionization detection (GC–FID) was applied to characterize and differentiate pyrogenic and biogenic from petrogenic hydrocarbons in oil sands environmental matrices. The characterized target hydrocarbons included hydrocarbon groups (such as PHC and UCM, unresolved complex mixture of hydrocarbons), *n*-alkanes, the oil-characteristic alkylated PAH homologous series and other EPA priority unsubstituted PAHs, biomarker tritopenta-cyclic terpanes and steranes, and bicyclic sesquiterpanes. Furthermore, numerous indicators of target petroleum hydrocarbons were quantitatively determined and applied for differentiation and indication of the presence or absence of PHC, pyrogenic and/or BOC compounds in oil sands environmental samples.

2. Experimental

2.1. Chemicals and materials

All solvents used were obtained at the highest purity available without further purification. Silica gel (100–200 mesh, 150 Å, pore 1.2 cm²/g, active surface 320 m²/g) was obtained from Sigma–Aldrich Canada (Oakville, ON, Canada). Silica gel and sodium sulfate were sequentially rinsed with acetone, dichloromethane (DCM) and hexane three times by each solvent, respectively, and completely dried in the fume hood at room temperature. The pre-cleaned silica gel and sodium sulfate were then activated at 180–200 °C for 20 h in a shallow tray that was loosely covered with aluminum foil. All glassware was rinsed successively with methanol, DCM, and hexane three times prior to use.

Normal alkane calibration standards and PAH calibration certified standard mixtures were purchased from Restek (Bellefonte, PA, USA) and Aldrich (St. Louis, MO, USA), respectively. Deuterated internal and surrogate PAH standards were purchased from Supelco (Bellefonte, PA, USA). Biomarker terpane and sterane standards were obtained from Chiron (Trondheim, Norway).

For quality assurance and quality control (QA/QC) purposes, Prudhoe Bay crude oil (13.1% weathered) was used as a reference oil [23].

2.2. Sample collection and preparation

Fig. 1 shows the site map for various oil sands water, snowmelt water and sediment samples collection. All samples collected are from sites where wild fish, invertebrate communities, toxicology and detailed chemistry of other oil sands related contaminants (such as naphthenic acids and metals) are being assessed. Water and sediment samples were collected from the Athabasca River and its tributaries (Steeptank, Ells, Firebag Rivers) in upper, middle, and lower reaches during September in the years 2009–2012.

Surface water and sediment: surface water samples were collected in 20 L stainless steel containers, sediments in plastic buckets lined with food grade polypropylene bags. All samples were refrigerated (4 °C) from collection and during shipment to Burlington, ON. Sediment samples were collected from edgewater by shovel and stored in polypropylene bags in 20 L pails. Prior to subsampling, sediments were thoroughly homogenized with a motorized stainless mixer to ensure homogeneity. Subsampling into amber glass bottles was conducted in Burlington under refrigeration and samples were shipped on ice packs to Ottawa for analyses.

Tailings pond samples: samples were collected by boat using a 2 L stainless steel dipping pan from pond surfaces into 20 L stainless steel containers. All samples were refrigerated (4 °C) from collection and during shipment to Burlington ON. Subsampling into amber glass bottles was conducted in Burlington under refrigeration and samples were shipped on ice packs to Ottawa for analyses.

Snow samples: snow samples were collected by stainless steel shovel into 20 L plastic totes lined with food grade polypropylene bags. Totes were kept frozen and shipped to Burlington at –20 °C. At subsampling, totes from each site were pooled in rainbarrels lined with food grade polypropylene bags until fully thawed. Samples were then stirred prior to subsampling into amber glass bottles, and then shipped to Ottawa. Upon arrival, all samples were stored at 4 °C until extraction. Snow water filtration was conducted at the ESTS Oil Research laboratory of Ottawa. Snow samples were collected during March of 2010, 2011 and 2012. In 2010, snow sample locations included three sites north of Fort McMurray (AR-6, AR-15, and ST-2), one site just upstream (south) on the Athabasca of Fort McMurray and the confluence of the Clearwater River (AR-1), and one southern reference location outside of the McMurray oil sands

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