



Full Length Article

The photolytic behavior of diluted bitumen in simulated seawater by exposed to the natural sunlight



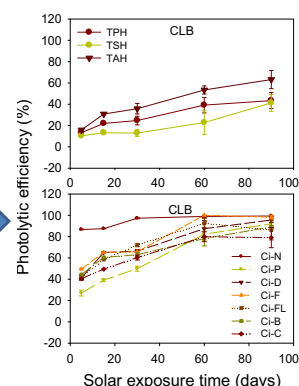
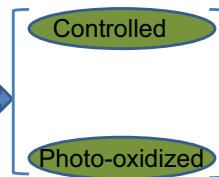
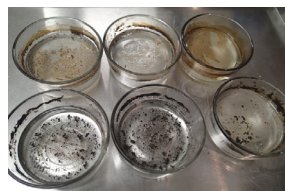
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HIGHLIGHTS

- Diluted bitumen experienced similar photolytic trends but decreased removal efficiencies compared to light crude oil.
- Aromatics were most photosensitive, followed by *n*-alkanes, then biomarkers.
- Summer exposure led to higher photolysis than winter.
- The differences of PAHs structure did not significantly affect their photolytic rates.

GRAPHICAL ABSTRACT



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ABSTRACT

Two diluted bitumen, Cold Lake Blend (CLB), Accessed Western Blend (AWB), and Alberta Sweet Mixed Blend #5 crude oil (ASMB#5), were spiked into 3.3% NaCl aqueous solution, then exposed to natural sunlight for 90 days in the winter and summer in the Northern Hemisphere (Ottawa, Canada). The effects of temperature and solar intensity on the photolytic behavior of diluted bitumen were evaluated. Simultaneously, the photolytic similarities and differences between diluted bitumen and crude oil were compared. It was found that, in all test oils, the decrease of all total petroleum hydrocarbons followed a pseudo-first-order reaction kinetic with the exposure time regardless of seasons. Aromatic fractions had the highest apparent rate constants. Similarly, the chemical fingerprinting analysis of test oils demonstrated that polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues (APAHs) were the most photosensitive compounds among the identified targets, followed by *n*-alkanes, then terpanes, and steranes. The photolytic efficiencies of the target petroleum hydrocarbons in ASMB#5 were generally higher than the two diluted bitumen. Photolysis of APAHs occurred faster in summer than in winter; however, APAHs with different number of rings and degree of alkylation did not have obvious photolytic differences. These phenomena suggest that the photolytic similarities between dilbits and conventional crude oil depend on their similar chemical structure of petroleum hydrocarbons; their differences depend on the specific oil properties. The accumulated solar irradiation intensity and temperature are the main factors contributing to their photolytic differences for winter and summer exposed oils.

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1. Introduction

The oil sands region of Alberta, estimated to contain up to 50 billion cubic meters (315 billion barrels) of bitumen, is the third largest oil reserves behind Saudi Arabia and Venezuela [1,2]. The development of oil sands industry has attracted more public concerns than ever due to the potential environmental impacts during the mining, extraction and transportation of oil sands and their associated products. It is well known that the high viscosity of bitumen has limited its transportation through pipelines. Consequently, products from oil sands industry are usually the blends of bitumen with different diluents in order to facilitate its transport through pipelines. For example, diluted bitumen (dilbit), which is diluted with 20–30% of natural gas condensates [3], is one of the main products from oil sands industry. It is noted that the composition of natural gas condensates generally ranges between 5 and 30 carbon atoms. Oil spill occurs everyday worldwide, which causes extensive damage to the ecological system, and human health [4]. Similarly, the spill of oil sands products has raised public concerns due to the potential damage to the environment. For example, the transportation of oil sands products through oil tankers and/or pipelines may cause oil spill issues to the marine environment.

While the environmental fates and impacts of conventional oil spills have been thoroughly investigated [5–7], the same cannot be said for dilbit spills. A few studies [1,8] have reported the effects of weathering on the density of dilbit, seeking to determine if dilbit would sink or float. These studies indicate that the fate of dilbit in a spill depends on the nature of the spill itself. The behaviors of dilbit have been shown to differ from conventional petroleum products (e.g., faster evaporation, more rapid mixing with sediments, and sinking of oil residues than conventional oil). Chemical dispersants have demonstrated very limited effectiveness in dispersing dilbit [1,9]. Till yet, a large unknown gap occurs for understanding the behavior, fate, impacts and remediation options for diluted bitumen spill in the environment.

Similar to conventional crude oil, dilbit is immediately subject to a variety of abiotic and biotic processes once spilled into the marine environment including evaporation, dispersion, photo-oxidation, and microbial degradation. Among these processes, photochemical degradation mediated by sunlight is an important pathway to influence their transformation and fate in the environment, especially when the oil is rich in aromatics. Since chromophores are abundant in crude oil/dilbit, many of the transformations are the result of direct photochemical processes due to absorption of light in the ultraviolet (UV) region, or by photosensitized reactions due to the presence of compounds able to absorb light in the visible region [10–12]. Generally, photo-oxidation is as important as biodegradation for conventional crude oil/fuel products in the specific environment, since these two processes act upon different components in oil; alkanes are biodegraded while aromatics tend to be photo-degraded [13,14].

One study has reported that the densities and viscosities of one representative dilbit, Cold Lake Blend (CLB) in water, increased with the extension of UV exposure [8]. Another report demonstrated that the densities of dilbits floating on the seawater surface did not alter significantly after photo-oxidation; however, the pH of the seawater decreased and a crust was formed in the surface of oil slick [1]. Analyzing the variation of chemical composition of dilbits after photo-oxidation is crucial to address the photolytic similarities and differences between diluted bitumen and crude oil.

The purpose of this study is to investigate the photolytic behavior of dilbits in different seasons (e.g., summer and winter) with varied temperature and solar intensity, and compare the photolytic properties of diluted bitumen and crude oil. Herein, two dilbits

(CLB and Accessed Western Blend (AWB)), and Albert Sweet Mixed Blend #5 crude oil (ASMB#5) were spiked into the simulated seawater, then exposed to the natural sunlight in summer in the Northern Hemisphere (Ottawa, Canada). Similarly, CLB and ASMB#5 were exposed in the winter sunlight in Ottawa. Different parameters including total petroleum hydrocarbons (TPH), total saturated hydrocarbons (TSH), total aromatic hydrocarbons (TAH), representative alkanes and petroleum biomarkers, and polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues (APAHs) were analyzed at pre-determined time points. Their photolytic efficiencies were studied to evaluate the photolytic behavior of different oils in the simulated marine system at molecular level. The comparison of winter and summer solar exposure serves to elucidate the importance of photo-oxidation process under specific environmental conditions. This study will supply scientific support for appropriate remediation technologies in the event of oil spill in the marine environment.

2. Experimental

2.1. Chemicals and materials

All solvents used were the highest purity (Caledon, Canada). Silica gel (100–200 mesh) was supplied by Spectrum Chemicals (Gardena, CA, USA). Silica gel, sodium sulfate and glass wool were sequentially rinsed with acetone, hexane and dichloromethane (DCM) three times each, then completely dried in the fume hood. The dried silica gel and sodium sulfate were then activated at 180 °C for 20 h in a shallow tray that was loosely covered with aluminum foil. All glassware was rinsed successively with acetone, hexane and DCM three times prior to use.

Normal alkane calibration standards from $n\text{-C}_9$ to $n\text{-C}_{40}$, 5 α -androstane, *o*-terphenyl, petroleum biomarker standards, PAH calibration certified standard mixtures, and 1-octadecanol were purchased from Restek (Bellefonte, PA, USA), Chiron (Trondheim, Norway), the National Institute of Standards and Technology (NIST, Gaithersburg, MD USA), and Sigma-Aldrich (Oakville, Canada), respectively. Deuterated standards, including deuterated internal and surrogate PAH standards ($[^2\text{H}_{14}]$ terphenyl (terphenyl- d_{14}), $[^2\text{H}_8]$ naphthalene, $[^2\text{H}_{10}]$ acenaphthene (acenaphthene- d_{10}), $[^2\text{H}_{10}]$ phenanthrene (phenanthrene- d_{10}), $[^2\text{H}_{12}]$ benz[a]anthracene (benz[a]anthracene- d_{12}), and $[^2\text{H}_{12}]$ perylene (perylene- d_{12})), deuterated oxygenated PAHs ($[^2\text{H}_6]$ 1,4-naphthoquinone (1,4-naphthoquinone- d_6), and $[^2\text{H}_8]$ 9-fluorenone (9-fluorenone- d_8)), and deuterated fatty acids ($[^2\text{H}_{15}]$ caprylic acid (C8:0- d_{15}), $[^2\text{H}_2]$ palmitic acid (C16:0- d_2), $[^2\text{H}_{27}]$ myristic acid (C14:0- d_{27}), were purchased from Supelco (Bellefonte, PA, USA) and Sigma-Aldrich (Oakville, Canada). It is noted that deuterated carbonyl PAHs and fatty acids were spiked for analysis of carbonyl PAHs and polar acid extractable components (Data not shown here).

2.2. Exposure experiments

Dilbits, CLB and AWB, and one representative crude oil (ASMB#5), were diluted by hexane with a small amount of dichloromethane (DCM) to 150 mg/mL. The detailed information for the used oils is presented in Section 3.1.

Solar exposures were conducted by pouring 250 mL of artificial brine into a 20-cm (i.d.) \times 10-cm (height) glass reactor. The artificial brine was prepared by dissolving 0.33% (mass/mass) of sodium chloride into ultra pure water (with a pH of 7, 18.2 M Ω of resistivity, 0.01 $\mu\text{g/mL}$ of TOC, and undetectable cations, anions and total dissolved solids). Two (2.00) mL of the fuel mixture (Section 2.2) was spiked into the surface of the homemade brine. Water samples

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