



Fate of oxygenated intermediates in solar irradiated diluted bitumen mixed with saltwater[☆]



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ABSTRACT

Two types of diluted bitumen (dilbit) and a light crude oil spiked onto the surface of saltwater were irradiated with natural solar light in Ottawa to assess the impact of sunlight to the fate of oxygenated intermediates. Oxygenated components, including carbonyl polycyclic aromatic hydrocarbons (PAHs) and acidic polar fractions (naphthenic acid fraction compounds, NAFCs), were identified after periods of solar exposure under both winter and summer conditions. Carbonyl PAHs and NAFCs were formed in both seasons; however, light crude and summer irradiation produced higher abundance of them than dilbits and winter exposure. The formed NAFCs were abundant with the congeners containing a heteroatom of oxygen only (O_0 species), accompanied by the minor amounts of sulfur- and nitrogen-containing acids. The produced O_0 species were predominant with the congeners with light molecular weight, high degree of saturation and heavy oxygen numbers. For both carbonyl PAHs and NAFCs, their abundance continually increased throughout the period of winter exposure. In the summer, some carbonyl PAHs and all O_0 species increased during the early exposure period; then they decreased with continued exposure for most oils, illustrating their transitional nature. Oxygenated intermediates thus appear to have been created through the photo-oxidation of non-to medium-polar petroleum hydrocarbons or the intermediates of aldehydes or ketones (O_1). Oil properties, the duration of exposure, exposure season and the chemical structure of these intermediates are critical factors controlling their fate through photo-oxidation. The observed chemical changes highlight the effects of sunlight on the potential behavior, fate and impact of spilled oil, with the creation of new resin group compounds and the reduction of aromatics and saturates. These results also imply that the ecological effects of spilled oil, after ageing in sunlight, depend on the specific oil involved and the environmental conditions.

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1. Introduction

Diluted bitumen (dilbit) is an oil sand product produced by the mixture of 20–30% light condensates in bitumen (Crosby et al., 2013). Its environmental fate and behavior has drawn extensive attention from environmental chemists. As with conventional crude oils, once spilled into the marine environment, dilbit immediately begins to undergo a variety of physical, chemical and biological processes, such as evaporation, dispersion, photo-oxidation and microbial degradation. Among these processes, photochemical degradation caused by the adsorption of photons

from sunlight represents an important pathway influencing the transformation and fate of oil components in the environment.

Oil fingerprinting technology uses gas chromatography (GC) or gas chromatography-mass spectrometry (GC-MS) to characterize the components of petroleum hydrocarbons and evaluate the ratios of selected 'diagnostic' compounds. This technology has been used extensively to investigate the photolytic fate of GC-detectable petroleum hydrocarbons resulting from the irradiation of conventional crude oil or diluted bitumen (D'Auria et al., 2008; Radovic et al., 2014; Wang et al., 2016; Yang et al., 2016). It has been shown that abiotic and biotic weathering processes produce oxygenated transformation products that account for 60–80% of extractable material (Aeppli et al., 2012). Photo-oxidation most likely enhances the dispersion of oil spills by transforming the oil into more water-soluble oxygenated components (King et al., 2014;

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Ray et al., 2014; Wang et al., 2016). A very large discrepancy exists between the abundance of the conventional GC-detected petroleum hydrocarbons (e.g., PAHs) and the associated biological response. This suggested that unidentified compounds—and not only PAHs—are responsible for the adverse biological responses (Halton et al., 2010; Incardona et al., 2013). Studies have concluded that after photo-oxidation, oil has more adverse effects on algae, bacteria, marine invertebrates and fish (Maki et al., 2001; Halton et al., 2010) relative to the original oil that had not been aged by sunlight.

GC-based techniques are limited to compounds having the volatility below ca. 400 °C. Therefore, only some petroleum hydrocarbons (e.g., the GC-detectable petroleum hydrocarbons (TPH), *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs) and their alkylated congeners (APAHs), and some petroleum biomarkers) can be analyzed using GC-based techniques (D'Auria et al., 2008; D'Auria et al., 2009; John et al., 2016; Yang et al., 2016). Other than the GC-detected targets, most of newly formed oxygenated intermediates produced through biodegradation/photo-oxidation have a low volatility and high polarity due to the addition of oxygen. If the profile of these oxygenated components in both raw petroleum products and weathered oils (e.g., from an oil spill) can be measured, it would be possible to gauge the extent of weathering that has occurred and, in part, confirm the mechanisms causing this weathering. Studying the variability of these oxygenated components within petroleum mixtures will provide a better understanding of the environmental weathering processes that have occurred over time, and thus, a better understanding of the fate and behavior of oil spill events.

Oxygenated PAHs are a class of photoproducts. These include PAH ketones and PAH quinones, formed through the photo-transformation of PAHs, which may be subjected to further mineralization or degradation. These products are more toxic than their parent compounds (Mallakin et al., 1999). The other major polar photoproducts are naphthenic acid fraction compounds (NAFCs), which contain a diverse family of carboxylic acids and other acid-extractable organic compounds having varied structures (e.g., aromatic, adamantane or diamondoid structures) and different species (such as sulfur- and nitrogen-containing compounds and multiple oxygenated acids) (Rowland et al., 2011). NAFCs have been reported as the principal toxicants in oil sands processed waters (OSPW) (Clemente and Fedorak, 2005; Frank et al., 2008, 2009; Vanderveen et al., 2017). Due to their complex composition and limited availability of authentic standards, identifying and quantifying NAFCs is quite limited using conventional identification technology. Currently, some advanced analytical techniques have characterized polar and nonvolatile compounds produced through photochemical transformation (Headley et al., 2011; Islam et al., 2013; Ray et al., 2014; Vaughan et al., 2016), biodegradation (Hughes et al., 2007), natural weathering (Lemkau et al., 2014), or found in some crude oils (Stanford et al., 2007) and aqueous matrices (Brunswick et al., 2015). Ultrahigh resolution electrospray ionization in negative mode (ESI⁻) Orbitrap mass spectrometry (ESI⁻) Orbitrap MS) has been shown to be suitable for the characterization of naphthenic acids with monocarboxylic acid (*O*₂-NAs) and NAFCs in Athabasca Basin OSPW (Headley et al., 2012). Therefore, this technique could be used to identify and quantify NAFCs within solar irradiated petroleum oils, and to evaluate the fate and behavior of NAFCs produced through photo-oxidation at a molecular level.

This study is an extension of our earlier work (Yang et al., 2016) where two diluted bitumen oils, Cold Lake Blend (CLB) and Accessed Western Blend (AWB), and one conventional light crude oil (Alberta Sweet Mixed Blend, ASMB), were spiked onto the surface of saltwater and irradiated with natural solar light (Ottawa,

Canada, 45.4°N) over the winter and summer seasons. AWB was not tested over winter as it has similar physicochemical properties as CLB. GC and GC/MS analysis was used to assess the variation of TPH, alkanes, aliphatic petroleum biomarkers, and APAHs through photo-oxidation. We showed that the chemical structure of petroleum hydrocarbons controlled the photolysis of different chemical groups in the dilbits and ASMB (Yang et al., 2016). Specifically, aromatic hydrocarbons were photo-oxidized the fastest, followed by *n*-alkanes and then the weathering-resistant biomarker steranes and terpanes. Oil properties, temperature and solar intensity were other factors affecting the rate of photolysis for these petroleum hydrocarbons. However, this previous work did not investigate the fate and behavior of intermediates generated through photo-oxidation. As aged brine tends to be more toxic due to the higher polarity and bioavailability of these oxygenated intermediates compared to PAHs (Maki et al., 2001; Halton et al., 2010), it is important to study their fate and behavior related to photo-oxidation to improve our understanding of the environmental implications of photo-oxidized diluted bitumen.

Solar irradiated samples collected at pre-determined time points were run through the appropriate pre-treatment procedures, analyzed by GC-MS for carbonyl PAHs and by high performance liquid chromatography-ultrahigh resolution Orbitrap mass spectrometry combined with electrospray ionization in negative mode (HPLC-HRMS) for NAFCs. The chemical composition of representative carbonyl PAHs and NAFCs produced through photo-oxidation was investigated. This study provides a molecular snapshot of the compositional changes of oxygenated components in dilbits at different solar exposure times and for different seasons (different solar irradiance intensities and environmental temperature). It is important to note that, as of yet, no certified reference materials for identifying and quantifying NAFCs exist due to their extremely complex chemical composition. Average mass spectra were generated to identify NAFCs based on the elemental composition of each sample. Therefore, all values reported in this study must be regarded as being semi-quantified as the reported results represent the relative abundance normalized to the response of the internal standard for each injection.

2. Materials and methods

Most of the chemicals and standards were supplied by Sigma-Aldrich (Bellefonte, PA, USA) and Sigma-Aldrich (Oakville, ON, Canada). A summary is as follows: the LC/MS purity chemicals include acetic acid, formic acid and ammonium acetate; HPLC grade solvents include methanol, isopropanol and acetonitrile; deuterated carbonyl PAHs include [²H₆] 1,4-naphthoquinone (1,4-naphthoquinone-*d*₆), and [²H₈] 9-fluorenone (9-fluorenone-*d*₈); deuterated fatty acids include [²H₁₅] caprylic acid (C8:0-*d*₁₅), [²H₂] palmitic acid- (C16:0-*d*₂), and [²H₂₇] myristic acid (C14:0-*d*₂₇); ten carbonyl PAH standards include 1-indanone, 1,4-naphthoquinone, acenaphthenequinone, 9-fluorenone, peinaaphthenone, anthraquinone, 9, 10-phenanthrenequinone, 2-ethyl anthraquinone, benzo [*a*]fluorenone, and 5, 12-naphthacenequinone. All other solvents used are of the highest purity and obtained from Caledon (Georgetown, ON, Canada). Ultra-pure water was prepared in-house from a Milli-Q water purification system (Millipore, Billerica, MA, USA). Silica gel (100–200 mesh) was supplied by Spectrum Chemicals (Gardena, CA, USA).

2.1. Exposure experiments

Stock solutions of the CLB and AWB dilbits and one representative light crude oil (ASMB) were prepared by dissolving in hexane and several drops of dichloromethane (DCM) to 150 mg/mL. The

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