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Fate of hopane biomarkers during in-situ burning of crude oil — A laboratory-scale study

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ABSTRACT

In-situ burning (ISB) is a remediation strategy that is used for managing oil spills. ISB generates heavy residues that can submerge and negatively impact benthic environments. To track the fate of toxic contaminants in ISB residues, a conservative hopane biomarker, such as C_{30}-αβ hopane, is often used. Furthermore, diagnostic ratios of various hopanes are used for source oil identification. Use of these biomarkers assume that during ISB the quantity of C_{30}-αβ hopane will be conserved, and the diagnostic ratios of various hopanes will be stable. The objective of this study is to test the validity of these two assumptions. We conducted laboratory-scale ISB experiments using a model oil prepared from commercial C_{30}-αβ hopane standard, and a reference crude oil. Laboratory data collected under controlled burning conditions show that C_{30}-αβ hopane will not be conserved; however, the diagnostic ratios of hopanes will still remain fairly stable.

1. Introduction

During a marine oil spill event, numerous remediation methods are employed to reduce various environmental impacts (Gustitus and Clement, 2017; Han et al., 2018). One of the commonly used oil spill remediation methods is in-situ burning (ISB), also known as controlled burning (Nordvik, 1995; Ventikos et al., 2004). ISB has gained widespread acceptance since it is a relatively easy method (Wang et al., 1999) and it has the potential to rapidly remove large volumes of oil from the surface of the water (Buist, 2003; Mullin and Champ, 2003). The removal efficiency of ISB depends on oil type, oil thickness, water content, and weathering level (Lin et al., 2005). One of the disadvantages of ISB is smoke generation, which can adversely impact the health of cleanup crews and the members of the public who are exposed to the smoke (Fingas, 2014; Fingas et al., 1999; Fritt-Rasmussen et al., 2013). However, the overall advantages of this technology far outweigh some of these disadvantages (Allen and Ferek, 1993).

ISB was one of the major remediation methods that was employed during the 2010 *Deepwater Horizon* (DWH) oil spill (Perring et al., 2011). It has been estimated that a total of 411 burns were used to remove about 222,000 to 313,000 barrels of oil, which is about 5% of total oil released during the DWH spill (Schaum et al., 2010). The removal efficiency of ISB events was estimated to be about 85%, and burning yielded about 38,800 to 54,700 barrels of residues that most likely sank to the ocean bottom (Stout and Payne, 2016). The long term ecological impacts of these residues are largely unknown (Fritt-Rasmussen et al., 2015).

The physical characteristics of ISB residues are similar to those of highly weathered oil; they are viscous and dark tar-like residues, and have a higher density than the parent oil. They contain enriched amounts of asphaltenes, resins, metals, combustion-derived products, and toxic compounds such as polycyclic aromatic hydrocarbons (PAHs) (Gullett et al., 2017; Ramesh et al., 2018; Stout and Payne, 2016). Efforts to quantify the percent degradation of hazardous chemicals, such as PAHs, trapped in ISB residues require an internal recalcitrant biomarker compound. One of the most common oil spill biomarkers used for this purpose is C_{30}-αβ hopane (17α(H), 21β(H)-hopane) (Garrett et al., 2000; Jézéquel et al., 2014). Additionally, diagnostic ratios of different hopane compounds are also routinely employed to develop chemical fingerprints, which are used for source identification (Aeppli et al., 2014; Clement et al., 2017; Han and Clement, 2018; Wang et al., 2001).

While hopanes, such as C_{30}-αβ hopane, are known to be stable compounds since they are highly resistant to biochemical degradation (Prince et al., 1994), they can potentially undergo thermal degradation at higher temperatures. Prince et al. (1994) analyzed various distillation fractions of Alaska North Slope crude oil and found that the fraction collected in the range of 196 to 344 °C did not have any hopanes; this study noted that hopanes would volatilize at temperatures in excess of 344 °C (Prince et al., 1994). During ISB operations, the internal

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temperature of the slick can rise up to 350 to 500 °C and the flame temperature can reach up to 900 to 1200 °C (Buist, 2003; Mullin and Champ, 2003), and therefore these high temperature conditions could potentially impact hopane concentrations in the crude oil residues. However, the thermal degradation patterns of other hopane compounds present in crude oil at these higher ISB temperatures are largely unknown.

Despite these uncertainties, C_{30}-αβ hopane has been routinely employed as a conservative internal biomarker for characterizing ISB residues. Lin et al. (2005) measured the concentration of C_{30}-αβ hopane in pre-burn and post-burn oil spill samples while evaluating the effects of ISB on oil spill cleanup at a coastal marsh. Their data showed that several high boiling fraction compounds, including C_{30}-αβ hopane, became concentrated in the burnt residues. Stout and Payne (2016) characterized the chemical composition of floating and sunken ISB residues from the DWH oil spill and used C_{30}-αβ hopane as a conservative biomarker to quantify the apparent enrichment of PAHs. Garrett et al. (2000) used C_{30}-αβ hopane as a conservative biomarker to quantify the degradation of PAHs in a lab-scale ISB study. Jézéquel et al. (2014) used C_{30}-αβ hopane as a conservative biomarker to assess the fate of various hydrocarbons in a bench-scale ISB study. All of these investigations assume that hopanes are stable compounds and are resistant to degradation during the burning conditions.

The objective of this study is to test the following two hypotheses: a) the internal biomarker C_{30}-αβ hopane will remain as a conservative compound during the ISB process, and b) the characteristic hopane diagnostic ratios will remain stable and hence it can be used for fingerprinting ISB residues. We conducted two sets of controlled burning experiments using a model oil containing pure C_{30}-αβ hopane and a reference crude oil collected during the DWH oil spill event to test the validity of these two hypotheses. In order to enhance the burning efficiency of oil in all our laboratory-scale ISB experiments, hexane was used as a burning aid.

2. Experimental methods

2.1. Materials

MC252 crude oil (released during DWH accident) was supplied by British Petroleum (BP). Since only a limited amount of MC252 crude oil was available in our laboratory, all the oil on water burning experiments, which required relatively large amount of oil, were conducted using MC252 surrogate oil supplied by AECOM (Fort Collins, CO, USA). This oil had similar physio-chemical characteristics as the MC252 oil and hence was identified as a surrogate to the original MC252 source crude oil (Pelz et al., 2012); in this study we referred to it as Surrogate Oil. The organic solvents dichloromethane and hexane used in this study were of analytical grade or higher. The solvents, silica gel (60–200 μm), and anhydrous sodium sulfate (ACS grade) were purchased from VWR International (Suwanee, GA). All hopane standards were purchased from Chiron (Trondheim, Norway). Chromatographic separation of various hydrocarbons was achieved using a J&W DB-EUPAH (Agilent Technologies) column (20 m × 180 μm × 0.14 μm).

2.2. Design of in-situ burning experiments

The burning experiments were designed to be conducted within a laboratory hood which offered a controlled environment. For safety reasons, when burning the oil, the experiments were designed to have a smaller flame and generated minimum fumes and smoke that can be contained within the laboratory hood. In order to achieve higher degradation of oil in these laboratory setups, similar to that of a real world ISB event in the open ocean, the oil was relit several times. In order to enhance oil burning efficiency, we used hexane whenever the combustion ceased.

2.2.1. Model oil experiment

The model oil containing 200 ng/mL of C_{30}-αβ hopane was prepared using hexane as the solvent. 1 mL of the model oil, which contained 200 ng of C_{30}-αβ hopane, was added into an aluminum dish. The sample was lit in a fume hood using a kitchen lighter and the residue remaining after combustion was designated as the 1-burn sample. Typical combustion time for a burn ranged from 25 to 35 s. For preparing 2, 4, 8 and 16-burn samples, an additional 1 mL of hexane was added to the aluminum dish and mixed thoroughly with the residues of the previous burn, and then the sample was reignited. After the appropriate number of burns had been completed, the ISB residues in the aluminum dish were extracted using hexane, concentrated under a gentle stream of nitrogen and reconstituted to a total volume of 1 mL using hexane. The pre-burn (control) and post-burn solutions were spiked with C_{30}-ββ hopane (IS) prior to GC/MS analysis. The 2, 8 and 16-burn experiments were completed in triplicates, and all GC/MS analyses were completed in duplicates.

2.2.2. Crude oil experiment

Literature data show that the concentration of C_{30}-αβ hopane in fresh MC252 oil is about 50 mg/kg-oil (Mulabagal et al., 2013; Schantz and Kucklick, 2011). We took about 200 mg of MC252 oil and dissolved it in 5 mL of dichloromethane to prepare a solution containing crude oil concentration of 40 mg/mL. 100 μL of this solution was transferred into an aluminum dish, which resulted in an estimated C_{30}-αβ hopane mass of about 200 ng in the dish, which is similar to that of the hopane content used in our model oil. Similar to the model-oil experiment, 1 mL of hexane was added to the aluminum dish and the contents were mixed and then lit sequentially to prepare 1, 2, 4, 8 and 16 burn samples. Small scale crude oil burning experiments are expected to have lower efficiency (van Gelderen et al., 2017), however addition of hexane helped to maintain sustained combustion and increased the overall burning efficiency. The post-burn residues in the aluminum dish were extracted using dichloromethane and the contents were transferred to a vial. 100 μL of pre-burn crude oil solution was also taken in a separate vial and was used as the control sample. The residual amount of dichloromethane solvent present in all the ISB samples was removed by evaporation under gentle stream of nitrogen prior to the sample cleanup step.

2.2.2.1. Column fractionation and sample cleanup procedure. Column chromatographic fractionation for the crude oil was performed using an approach outlined in previous studies (John et al., 2016; Wang et al., 1994). A glass column (250 mm × 10 mm) was plugged with glass wool at the bottom, and then packed with 3 g of activated silica gel and topped with 1 g of anhydrous sodium sulfate. The chromatographic column was charged with 20 mL of hexane and the eluent was discarded. The control or ISB residue samples in the vials were sequentially extracted three times, using 1 mL hexane at each time, and the contents were transferred to the column. About 12 mL of hexane was added to the column to elute all aliphatic hydrocarbons. The eluent was then concentrated under gentle stream of nitrogen, adjusted to 1 mL using hexane, and was then spiked with C_{30}-ββ hopane (IS) prior to GC/MS analysis. All GC/MS analyses were completed in duplicates.

2.3. Burning oil on water surface

Under field conditions, spilled oil is typically collected using a boom and burnt over the ocean water. In order to test the efficiency of hopanes degradation processes under more realistic field conditions, we designed a laboratory experiment where the crude oil was burnt over water. Due to limited availability of the MC252 source crude oil, this burning experiment was conducted using the Surrogate Oil. About 10 g of Surrogate Oil was dissolved in a solvent mixture of hexane and dichloromethane (4:1) and diluted to 25 mL, yielding oil concentration of