CHARACTERIZATION OF HOPANES IN SEDIMENT COLLECTED FROM SOUTH CHINA SEA: IDENTIFICATION OF OIL POLLUTION SOURCES

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Abstract

This study investigate the utilities and limitation of pentacyclic triterpane (hopane) including oleanane as oil pollution source identification for sediment samples collected from South China Sea and the applicability of the biomarker approach to sediments and biological samples. Norhopane, 17(α),21(β)-hopane and 17(β), 21(α)-hopane and $\sum C_{31}$-C_{35}-homohopane were found to be rich in Middle East crude oil and some of the sediment samples that were being collected in South China Sea. Some other molecular ratios of the biomarker compounds for the sediments such as Tm/Ts and Ts/Tm and n-alkane composition and distribution strongly suggest those 3 out of 27 sediment samples are derived from the Middle East petroleum. The utility of hopane as biomarker to identify the source of tar balls in Strait of Malacca is applicable for oil spill but the data is still limited for Malaysian sediments especially in South China Sea area. The use of oleanane as a biomarker is easily to be found in each sample for this study; however the concentration generally was very low for each sediment sample.

1.0 Introduction

1.1 The status of oil pollution in South China Sea prior to this study

Information from Energy Information Administration (EIA) of the US Government said that the South China Sea region is the world's second busiest international sea lane. More than half of the world's supertanker traffic passes through the region's waters. In addition, the South China Sea region contains oil and gas resources strategically located near large energy-consuming countries.

In other case, over most of the past two decades, industrial output and energy consumption has grown faster in the countries around the South China Sea than anywhere else in the world. The industrial revolution now underway will be only temporarily interrupted by the current Asian economic crisis. As a result of this economic growth, increasing urbanization, fossil fuel consumption, and regional shipping, the South China Sea has become a sink for regional environmental pollution such as crude oil.

1.2 Hopane as a biological marker

Biological markers or molecular markers are one of the most important hydrocarbons group in petroleum used for chemical fingerprinting. They are complex molecules derived from formerly living organism (Wang et al., 2007). Biomarkers found in crude oils, rocks and sediments have little or no changes in structure from their parent biochemicals, so-called biogenic precursors (e.g., steroids and terpanoids), and found living organisms.

Biomarkers are useful for chemical fingerprinting of oil spill because they retained all or most of the original parent skeleton of the original natural product, thus, testifies to the specific condition for oil generation. Wang et al. (2007) proposed that biomarkers fingerprinting has historically been used by petroleum geochemist in characterization of oils in term (1) oil-to-oil and oil-to-source rock correlation, (2) the types of precursor organic matter present in the metric, (3) effective ranking of the relative thermal stability of petroleum, (4) evaluation of migration and the degree of in-reservoir degradation based on the loss of n-alkanes, isoprenoids, aromatics, terpanes and steranes during biodegradation (5) determination of depositional environmental condition, and (6) providing the information on the age of the source of petroleum.

Hopanes are pentacyclic triterpanes commonly containing 27-35 carbon atoms in a naphthenic structure composed of four six-membered rings and one five-membered ring (Wang et al., 2007). Hopanes with the 17α(H),21β(H) configuration in the range C27 – C35 are characteristic of petroleum because of their large abundance and thermodynamic stability compared to other epimeric (ββ, αα) series. Previously, hopanes were considered to exist as three stereoisomers: 17α(H),21β(H)- Hopane, 17β(H),21β(H)-Hopane and 17β(H),21α(H)-Hopane (Peters and Moldowan, 1993; Waples and Machihara 1991)

2.0 Objectives

The general purpose of this study is mainly to identify the source of oil pollution in South China Sea that facing the East Coast of Peninsular Malaysia. Hopanes or pentacyclic triterpanes has been used as a molecular marker (Zakaria et al., 2000; Chandru et al., 2008; Peters and Moldowan, 1993; Wang et al., 2007; Peters et al., 2005) for identifying the source of oil pollution. Two objectives are aimed. The first one is the measurement of individual hopane’s concentration in selected sediments. The second objective is to determine the source of oil pollution based on hopanes ratio. By using the source identifier of hopanes, the percentage of samples (sediments) origin whether from Middle East crude oil (MECO), South East Asia crude oil (SEACO) or other origin can be calculated. As a response to the problems stated previously, the following objectives can be summarized as bellows:

1. To measure the concentration of individual hopanes in selected sediments
2. To determine the source of oil pollution based on hopanes ratio

3.0 Research methodology

3.1 Soxhlet extraction

Precisely 20 grams of sediment samples are dried by using baked anhydrous sodium sulfate until all water contents are removed. Dried sediment is put into a glass-fiber thimble and Soxhlet extracted using 300 ml of DCM for 9 hours with cycling rate of 10min/cycle. 5g activated copper is added and allow overnight to react with elemental sulfur. The solution passing funnel plugged with quartz wool, which trap the copper and copper sulfide on it. The solution is then reduced in volume to about 1 ml by using rotary evaporator.

3.2 Fractionation

The sample is pipetted onto the top of 5% H_2O deactivated silica column chromatography (1 cm i.d x 9 cm length). The stopcock is opened to permit the extract to penetrate the silica surface, and then the stopcock is closed. Hydrocarbon ranging from n-alkanes to PAHs with 7 rings eluted with 20 ml of DCM/hexane (1:3 vol/vol). The solution is then reduced in volume to about 1 ml by using rotary evaporator and then pipette on the top of fully activated silica gel column chromatography (0.47 cm i.d x 18 cm length). 4 ml of HPLC grade of n-hexane where respectively, 0.4 ml, 0.3 ml, 0.3 ml, 0.5 ml and 0.5 ml series of HPLC grade of n-hexane has been used to wash the flask. The washed is transferred onto the column in order to fractionate hopane components. Remaining 2 ml of n-hexane has been use to elute the hopane components that remained in the column.

3.3 Drying and pre-injection steps

The fraction is evaporated using rotary evaporator to 0.5 ml and transferred into a 1.5 ml glass ampoule vial. The target compounds were concentrated to a few milliliters using rotary evaporator followed by gentle nitrogen blow down to remove interfering of H_2 and CO_2.The vials contained hopane sample were re-dissolved in 50 µl of isooctane solution for subsequent instrumental analysis. Hopanes analysis will be done by using quadrupole mass spectrometer integrated with gas chromatography (GCMS) with scan mode. Before injecting the sample, 10 ppm of an external standard mixture of 17(β), 21(α)-norhopane, 17(α), 21(β)-hopane, 17(β), 21(α)-hopane and IIS (17 (β), 21(β)-hopane) has been injected to the GCMS machine. Procedure blank and the standards were run together with the samples (once for batch) for all the steps of analytical procedure to achieve the quality control and quality assurance of the analysis throughout the whole procedures.

4.0 Result and discussion

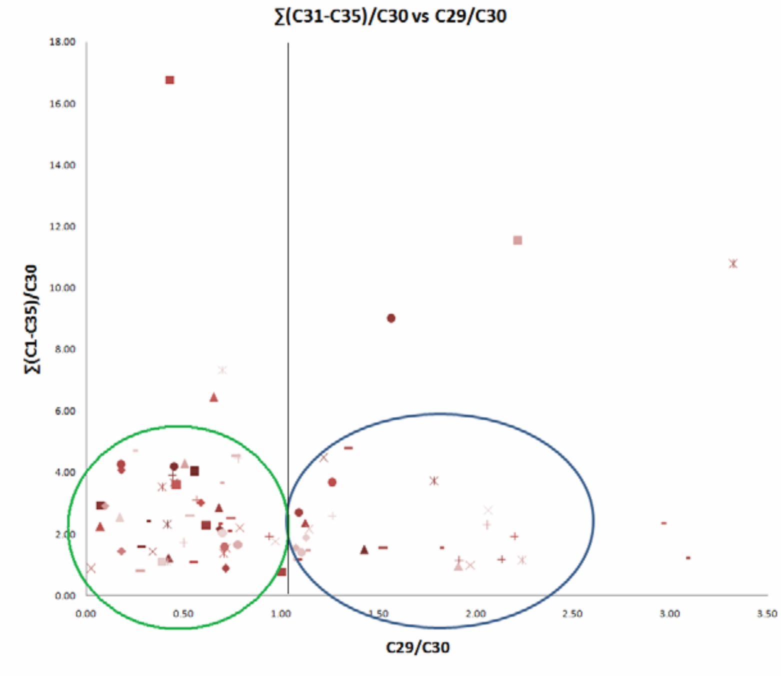

Figure 1: Correlation chart of

5.0 Significant of findings

Environmental problems are global issue around the world. Identifying spilled oil origins using sediments and linking them to a known source are extremely important in settling questions of environmental impact and legal liabilities for both government agencies and the oil and gas industry. No comprehensive study has been carried out in the area chosen so far. If the findings of this study met the above stated objectives, the research will be significant where it is pioneering in the area of South China Sea facing East Coast of Peninsula Malaysia. This study is also preliminary to characterize the core sediment samples. Then, the finding is used to fingerprint oil spill, especially in South China Sea. The fingerprinting and data interpretation techniques discussed include recognition of distribution patterns of petroleum hydrocarbons.