Identification of sources of tar balls deposited along the Goa coast, India, using fingerprinting techniques

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ABSTRACT

Deposition of tar balls along the coast of Goa, India is a common phenomenon during the southwest monsoon. Representative tar ball samples collected from various beaches of Goa and one Bombay High (BH) crude oil sample were subjected to fingerprint analysis based on diagnostic ratios of n-alkane, biomarkers of pentacyclic tri-terpanes and compound specific stable carbon isotope ($\delta^{13}C$) analysis to confirm the source. The results were compared with the published data of Middle East Crude Oil (MECO) and South East Asian Crude Oil (SEACO). The results revealed that the tar balls were from tanker-wash derived spills. The study also confirmed that the source is not the BH, but SEACO. The present study suggests that the biomarkers of alkanes and hopanes coupled with stable carbon isotope analysis act as a powerful tool for tracing the source of tar balls, particularly when the source specific biomarkers fail to distinguish the source.

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1. Introduction

Goa, situated along the central west coast of India, is one of the major global tourist destinations because of its attractive beaches with essential recreational activities. The economy of Goa primarily depends on tourism. However, the Goa coast is often under the menace of tar balls, which has become a common phenomenon during the southwest monsoon season (Dhargalkar et al., 1997). During August 2010, most of the Goa beaches were affected by tar ball deposition, whereas, in May 2011, the tar ball deposit was found only along the Mandrem beach, north Goa. This deposition attracts a huge public concern as the on-going recreational activities on beaches get seriously affected, which in turn affects the tourism industry, and the Government of India is concerned about this environmental problem. Moreover, the tar ball being a carcinogenic, it affects the marine life and tar ball pollution degrades health of the coastal waters off Goa. Therefore, tracing of the sources of these tar balls is highly important and essential. In this context, as a part of the scientific project, 'Finger-printing of oil spills and tar balls along the Indian coast', the present study has been carried out.

1.1. Recent techniques in source identification of tar balls

Several studies have been conducted worldwide for tracing the source of tar balls deposited along the beaches since 1970s. However, there is no single method that can fully fingerprint the oil spills. Fingerprint analysis mainly depends on the type of oil spilled, ambient prevailing weather and oceanographic conditions and weathering processes. Spreading and evaporation are the initial processes for weathering to start, followed by dissolution, biodegradation, photooxidation, emulsification and sedimentation, and therefore, properties of the spilled crude oil alter significantly. Pristane ($C_{19}H_{40}$) and Phytane ($C_{20}H_{42}$) are the most abundant isoprenoid compounds in oil and have been widely used for the estimation of degree of oil bio-degradation in the environment (Wang and Stout, 2007). The quantitative comparisons of the following ratios: heptadecane/pristane (C_{17}/Pr), octadecane/phytane (C_{18}/Ph), pristane/phytane (Pr/Ph) and heptadecane/octadecane (C_{17}/C_{18}) were found to be useful in identification of unknown source of tar balls as these ratios are less affected by the weathering of oil (Zafiriou et al., 1972). These ratios were used to identify the sources of tar balls deposited along the Saudi coast of Arabian Gulf after the oil spill at Nowruz oil field (Fayad, 1986). Biomarkers were established in identification of petroleum-derived contaminants in the marine environments (Bence et al., 1996; Boehm et al., 1997; Kvenvolden et al., 1995; Volkman et al., 1997; Wang et al., 1994a,b, 1999; Zakaria et al., 2000,

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2001). These biomarkers were hydrocarbon groups normally present in petroleum and its products, and are used for chemical fingerprinting because they preserve most of the carbon skeleton of the original product. The terpane and sterane biomarkers are less degradable and undergo less weathering as compared to n-alkanes and isoprenoid hydrocarbons (Volkman, 1984). The fingerprinting of terpane and steranes is a powerful tool for tracking the source of long-term weathered oil. Christensen and Tomasi (2007) reviewed the practical aspects of chemometrics for oil spill fingerprinting and provided a basis for the use of chemometric methods in tiered oil spill fingerprinting. Biomarker compounds such as isoprenoid alkanes, hopanes and polycyclicaromatic hydrocarbons (PAHs) have been proposed as molecular markers to identify the sources of oil pollution. The diagnostic ratios of alkanes, hopanes and polycyclic aromatic hydrocarbons were used to categorize the sources and weathering of tarballs deposited along the Malaysian beaches. Low molecular weight/high molecular weight ratios (L/H) of both alkanes and PAHs together are useful in categorizing the weathering effects of tar balls (Chandru et al., 2008). However, in cases such as the diagnostic ratios of biomarkers fail to distinguish the source or when different crude oils are mixed with, the normal fingerprint techniques may be ambiguous and inconclusive. In such situations, the compound specific isotope analysis will be a useful tool to identify or differentiate different samples, particularly the samples that have undergone extensive weathering, samples in which biomarker compounds such as steranes and terpanes are absent and the products having similar chromatograms (Mansuy et al., 1997; Yim et al., 2012). The δ^{13}C values of individual n-alkanes are unaffected by the weathering processes and can be used as a potential tool to identify the source of an oil spill, especially in the case of spills that have low concentration of biomarkers (Li et al., 2009). Mazeas and Budzinski (2002) studied the oil residues, oil bird feathers and tar balls that are deposited along the Atlantic coast of France after the Erika oil spill. He used alkane, PAH quantification in addition to the bulk and molecular ^{13}C/^{12}C ratio measurements. Bulk stable carbon isotopic composition confirmed the source of north Atlantic coast samples as Erika oil spill, whereas these values are higher for the samples collected along the southern part of the coast. If carbon isotopic profiles of different samples have similar appearance it shows that all the samples have come from a single source, whereas, if each sample has individual isotopic profile, that shows that they are from independent sources. Based on the carbon isotopic profiles, Mazeas and Budzinski, 2002 confirmed that oil residues deposited along the Pereire beach have the same isotopic profile as tar balls that were collected along the Salie beach. He also found that sample of Crohot beach and small tar ball sample collected from the Salie beach shows individual isotopic profiles, indicating that they have originated from independent sources. Mazeas and Budzinski, 2001 described the new analytical procedure to measure the stable carbon isotopic composition of polycyclic aromatic hydrocarbons (PAHs) in petroleum and sediments. He applied this procedure to sediment samples that are contaminated by the Erika tanker spill and confirmed that its contamination is due to the Erika oil spill. Betti et al. (2011) also provided a review of uses of isotope analysis: a tool to track the source and levels of chemical and biological contamination and tracking the organic pollutants.

The present study primarily aims at applying the fingerprint techniques, such as diagnostic ratios of alkanes and triterpanes coupled with compound specific isotope analysis, on the tar balls that are deposited along the Goa coast, in an attempt to identify the source of tar balls. The results are compared with the available MECO and SEACO database and the results of BH sample analysis. This is the first study on fingerprinting of tar balls in the coastal waters of India.

2. Methodology

2.1. Sample collection

Altogether six tar ball samples, representing five locations on Goa beaches and one BH Crude oil – assuming it as the possible source, were used for analysis in the present study. Four tar ball samples were collected from Candolim and Calangute beaches in the north Goa and Colva and Benaulim beaches in the south Goa, whereas, two samples were collected from the Mandrem beach in the north Goa. Fig. 1a shows the international tanker route and the location of BH. Fig. 1b shows the location of tar balls sampling along the Goa coast during 30–31 August 2010 and on 20 May 2011, and the closest tanker route across the Arabian Sea. Tar ball samples were collected by hand using plastic hand gloves, packed with aluminum foil and kept in labeled zip lock bags, and transferred to the laboratory for further analysis.

2.2. Chemicals

Authentic standards for alkanes and PAH were purchased from Sigma Aldrich, USA, and hopane standard 17β(H)21α(H)-hopane (C$_{30}$17β) was purchased from Chiron, Norway. A 100–200 mesh silica gel was baked at 400 °C for 4 h, cooled, then activated at 200 °C overnight and deactivated with 5% of distilled water. Organic solvents were distilled in glass before use. All glassware were washed with detergents and tap water and then rinsed with methanol, acetone and hexane.

2.3. Extraction and fractionation

BH crude oil and the collected tar ball samples were precisely weighed as 22.5 mg and 35 mg, respectively and dissolved in excess n-hexane and transferred to 5% H$_2$O deactivated silica gel column (1 cm i.dx 9 cm). Hydrocarbons ranging from alkanes to PAH were eluted with 20 mL of DCM/hexane (1:3 v/v); 5 gm of activated copper was added to the collected elute and allowed to stand overnight to react with sulfur. Then the copper was removed and the sample was subjected to roto-evaporation to decrease the volume to 2 mL. The sample was then transferred to the fully activated silica gel column (0.47 cm i.d × 18 cm). Two fractions were eluted. The first fraction was eluted with 4 mL of hexane containing the aliphatic and alicyclic hydrocarbons (aliphatic hydrocarbon fraction). The second fraction was eluted with 16 mL of hexane/DCM (3:1, v/v) containing the higher molecular weight PAHs (Aromatic Fraction). These two fractions were evaporated to dryness under the nitrogen blow down and rinsed with DCM HPLC grade and transferred to 1.5 mL ampule, and added with 200 µL isooctane for further GC–MS analysis.

2.4. Gas Chromatography–Mass Spectroscopy (GC/MS) analysis

Analyses for n-alkane, PAHc and hopanes were performed on a Shimadzu QP5050A Gas Chromatograph and Mass Spectrometer with a Shimadzu AOC-20i autosampler. A 30 m × 0.25 mm id (0.25 µm film thickness) fused silica capillary column was used. The carrier gas used was helium (1 mL/min). The injector and detector temperatures were set to 230 °C and 300 °C, respectively for alkane and PAH analysis, whereas, they were 300 °C and 230 °C for hopane analysis. The oven temperature program for alkane and PAHs was: 2 min hold at 70 °C; ramp to 150 °C at 30 °C/min; and ramp to 310 °C at 4 °C /min and finally a 15 min hold at 310 °C. The oven temperature program for hopane analysis was 2 min hold at 5 °C; ramp to 300 °C at 6 °C/min; and finally a 15 min hold at 300 °C.