

Source Investigation of the Tar Balls Deposited along the Gujarat Coast, India, Using Chemical Fingerprinting and Transport Modeling Techniques

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Supporting Information

ABSTRACT: Deposition of tar balls (TBs) along the south Gujarat coast, situated on the west coast of India (WCI), commonly occurs during the southwest monsoon season. Several offshore oil fields off the Mumbai–Gujarat coast, and refineries along the coast might be sources of oil spills/leakages and lead to the formation of TBs. To identify the sources, we collected 12 TB samples from the beaches of Gujarat (Tithal, Maroli, Umbergam, and Nargol) during 15–17 July 2012 as well as samples of crude oils, namely, Cairn, NIKO, MSC Chitra, and two at Bombay High (BH). These TBs were subject to the following multimarker approach for source identification: Diagnostic Ratios of *n*-alkanes, polycyclic aromatic hydrocarbons, pentacyclic triterpanes, compound specific isotope analysis, Principle Component Analysis and numerical simulations (hydrodynamic model coupled with particle trajectories). The chemical fingerprint results reveal that the source of the TBs is BH crude oils, and the model results confirm that the source location is BH north oil fields. This is the first study of its kind in India to use fingerprinting and transport modeling techniques for source identification of TBs.



1. INTRODUCTION

The West Coast of India is prone to receive TB deposits during the southwest monsoon season (SWM). During this season, the TB deposits frequently affect the northern part of WCI (Gujarat coast). TB is the residue of oil spill washed to seashore, which is remnant of source oil, after physical, chemical, and biological processes, called weathering in the sea. Deposition of TBs on the beaches could affect the marine ecosystem, the recreational activities, and hence the tourism. Therefore, identifying their sources is highly essential in order to find out the remedy for the cause and to mitigate the oil pollution in the region. Gujarat has the longest coastline (~1600 km) in India, and has several crude oil related industries and ports along the two gulfs—Gulf of Kachchh and Gulf of Khambhat (GoK). There are also many offshore oil fields: belonging to Cairn Energy, Niko resources, and BH oil fields. Refineries, fertilizer, chemical, and cement industries, power plants, minor and major ports, and salt works are the major industries located along the Gujarat coast; more than 10 Single Point Moorings (SPMs) are installed off Gujarat coast; Gujarat has 6 shipbuilding yards and more than 50 ports; the ports at Okha, Navlakhi, Kandla, Mandvi, and Jakhau handle a variety of cargos, especially petroleum products. In 2011–12, the ports in Gujarat handled 259 million tonnes of cargo, which

was the highest compared to previous years, indicating growth of industries and traffic. In addition to these, oil spills could also occur along the international tanker route (Figure 1a) due to tanker washes, collision, and grounding of tankers/ships; hence, oil leakages followed by TB formation may be possible, such as occurred after an oil spill accident off Mumbai on 07 August 2010 due to the collision of two ships MV Khalijia-111 and MSC Chitra causing a spill of 400 tonnes of oil. Finding the source of TBs is essential in order to mitigate oil pollution as well as TB deposition. In this context, we have carried out sampling of TBs along the Gujarat coast during July 2012 for fingerprinting.

Several studies have been carried out in order to fingerprint TB/oil spill throughout the world, but a limited number of studies are available in India. Biomarkers play a key role in environmental forensics. They are derived from the dead bodies of formerly living organisms present in the source rock of oil produced and contain the same structure of parent organic molecules. The DRs pentacyclic terpanes, *n*-alkanes, PAHs are

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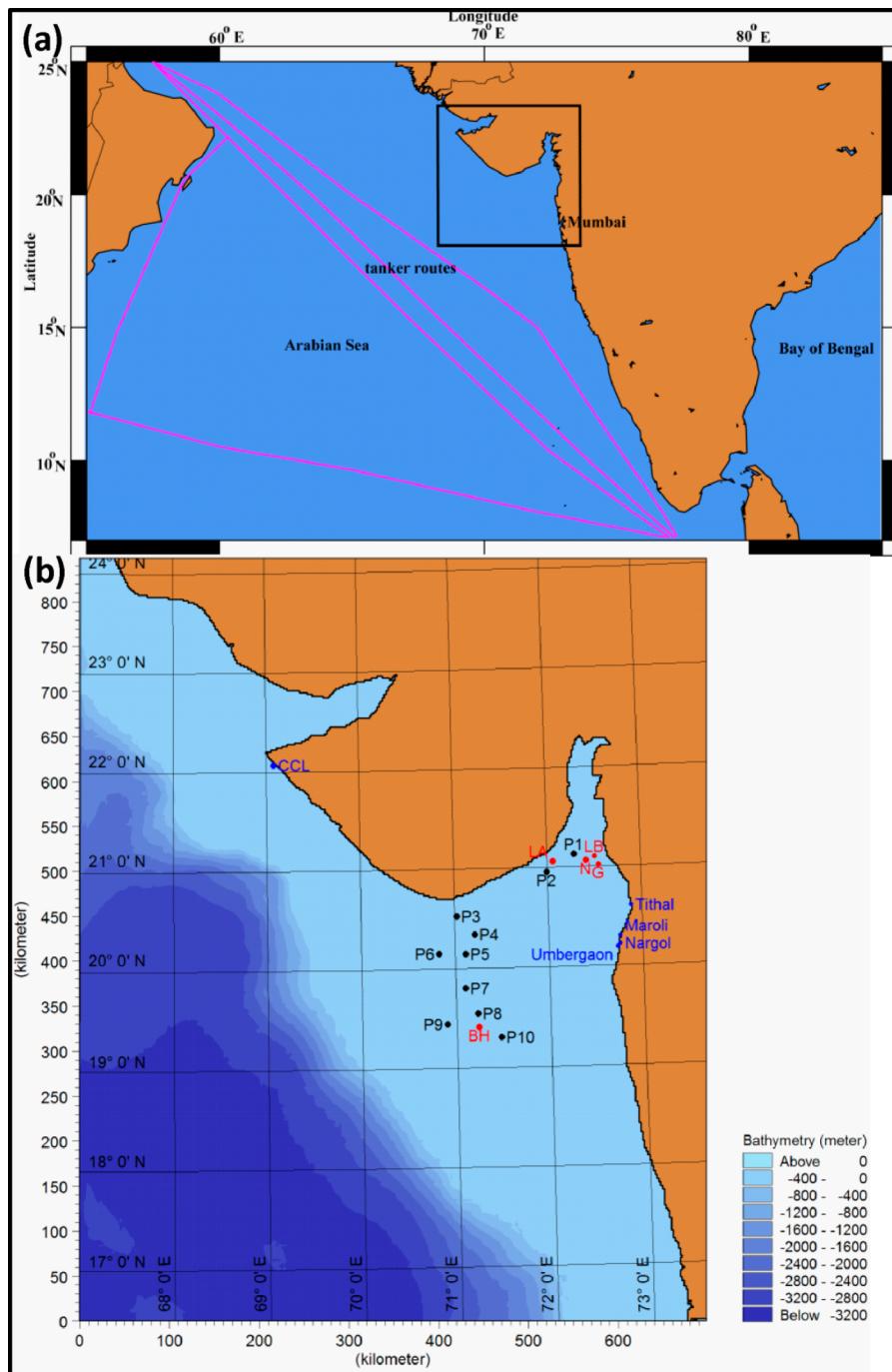


Figure 1. (a) International oil tanker routes in the Arabian Sea; (b) model domain indicated in (a); BH is Bombay High platform; LA, LB, and G are oil rig locations belonging to Cairn Energy (Pvt) Ltd.; N is the location of NIKO (Pvt) Ltd.; P1–P10 are locations, from where particles (TBs) are released. CCL is the location at which modeled currents are compared with observed currents.

widely used in oil fingerprinting studies. The homohopane index C_{29}/C_{30} and $\sum C_{31} - C_{35}/C_{30}$ is a more reliable source identifier for oil spill fingerprinting.^{1,2} The most used other DRs are tricyclic C_{23}/C_{24} , $C_{29}\alpha\beta/\beta$ hopane, Oleanane/ $C_{30}\alpha\beta$ hopane, T_s/T_m , and $T_s/(T_s + T_m)$.³ Recently, Mulabagal et al.⁴ have fingerprinted the TBs that are deposited along the Alabama shoreline using the DRs of hopane compounds such as T_s/T_m , $C_{29}\alpha\beta/C_{30}\alpha\beta$, $C_{31}(22S)/C_{31}(22S + 22R)$, $C_{32}(22S)/C_{32}(22S + 22R)$, $C_{33}(22S)/C_{33}(22S + 22R)$, $C_{34}(22S)/C_{34}(22S + 22R)$, and $C_{35}(22S)/C_{35}(22S + 22R)$ ratios. DRs of PAHs and *n*-alkanes, Flu/Flu+Pyr, Phe/Ant and Pr/Py, C_{17}/Pr , C_{18}/Py , and

C_{17}/C_{18} are also support tools to source identification and to estimate the rate of weathering.^{5–8} However, the results obtained by the DRs of alkanes, PAHs and hopanes may not be good enough to fingerprint the source, as ambiguities still exist, and in such cases CSIA is preferred, as it is a powerful tool to confirm the source. CSIA is widely used in marine environmental studies mainly to track the sources. The isotope ratios cannot be altered by weathering effects. For example, Macko et al.⁹ observed only 0.5‰ difference in the $\delta^{13}\text{C}$ values after 2 years of weathering. The short-term weathering processes such as evaporation and dispersion cannot affect the carbon isotope composition ($\delta^{13}\text{C}$)

values of individual *n*-alkanes.^{10,11} Though weathering causes loss of volatile compounds, $\delta^{13}\text{C}$ values of nonvolatile and semi volatile compounds are unaffected by weathering, and their isotopic ratios can be used to trace the oil spill sources.¹² Stable isotopes are resistant to decay over geological time scales and widely used for source identification and fingerprinting.¹³ Suneel et al.⁸ identified the source of TBs deposited along the Goa coast as South East Asian Crude Oil (SEACO) based on the CSIA ($\delta^{13}\text{C}$).

All the above studies are based on chemical methods. Although research work on TBs started in the 1970s, there still exists a gap in understanding their transport phenomenon on the WCI. The concentration of floating TBs in the Western Pacific from Tokyo to north of Hawaiian Island was 14 mg/m² with an average of 3.8 mg/m²,¹⁴ and these tar residues are formed due to tanker washes along the tanker route (Arabian Gulf to Japan).¹⁵ Lebreton et al.^{16,17} used a global circulation model coupled with particle-tracking to simulate the transport of floating debris. Martinez et al.¹⁸ studied the drift mechanism of floating marine debris in the Pacific Ocean. They found that floating debris accumulates to the convergence zone due to Ekman drift and geostrophic currents. Suneel et al.¹⁹ simulated trajectories of TB transport to the Goa coast using the MIKE21 hydrodynamic modeling coupled with particle analysis. In this study also, we have used the same suit of models to study the circulation pattern, and find the probable origin and trajectories of the TBs deposited on the south Gujarat coast.

The primary aim of the present study is to fingerprint the TBs that were deposited along the south Gujarat coast and to confirm the source location by using a Hydrodynamic model (HD) coupled with a Particle Analysis (PA) model. In order to fingerprint the TBs, we have used the DRs of *n*-alkanes, PAHs, pentacyclic triterpanes, in conjunction with the CSIA for 12 TB samples (collected off south Gujarat coast), and five crude oil samples (expected sources). This is probably the first study in India to identify the source of the TBs using fingerprinting, coupled with transport modeling.

2. EXPERIMENTAL SECTION

2.1. Sample Collection. We collected 12 TB samples from four beaches Nargao (NB1, NB2) and Umbergaon (UB1, UB2) on 15 July 2012 and Maroli (MB1, MB2), Tithal (TB1, TB2), Nargao (NB3, NB4), and Umbergaon (UB3, UB4) on 17 July 2012. Samples were collected and kept in glass bottles and stored in the laboratory refrigerator prior to the analysis. We also collected the following crude oil samples: (i) two Bombay High based crude oils. BH oil fields are located ~250 km away from the tar ball sampling points (Gujarat coast). The crude oils produced from various platforms of BH reach the Uran plant through two main pipelines—30" MUT (Mumbai High Uran Trunk) oil pipeline from the BH and 24" HUT (Heera Uran Trunk) oil pipeline from the Heera offshore Platform, (ii) two crude oil samples from Cairn and Niko oil fields, off the Gujarat coast, and (iii) one crude oil sample from the vessel MSC Chitra (MSC)—grounded after collision with MV Khalijia-III on 07 Aug 2010, off the Mumbai coast. Figure 1 shows the tar ball sampling locations and crude oil well locations.

2.2. Extraction and Chemicals. Crude oil and TB samples were weighed precisely 20 mg and 30 mg, respectively. Detailed analytical processes and fractionations are given in Supporting Information SI. 1. Authentic standards for alkanes and PAH (Sigma-Aldrich, U.S.A.) and hopane standards 17β (H) 21 α

(H)-hopane ($C_{30}17\beta\alpha$), 17 α (H)-22,29,30-trisnorhopane (Tm) (Chiron, Norway) were used.

2.3. Gas Chromatography–Mass Spectroscopy (GC–MS) Analysis. Analyses for *n*-alkane, Sterane, and Hopanes for TBs and crude oil samples were performed using a Shimadzu QP-2010 Gas Chromatograph and Mass Spectrometer interfaced with AOC-20i auto sampler. For GC–MS specifications, peaks identification and quantification, see section SI. 2, SI.

2.4. Gas Chromatography–Isotope Ratio Mass Spectroscopy (GC–IRMS). Carbon isotopic ratios of individual *n*-alkanes have been determined on Agilent 7890 A GC–C-IRMS coupled with Agilent 7000 GC–MS triple quad interfaced with oxidation–reduction reactor (980–650 °C). The specifications for GC–IRMS and quantification procedure are given in section SI. 3, SI.

2.5. Model Setup and Principal Component Analysis (PCA). The MIKE 21 HD model coupled with PA model was used to compute hydrodynamics (describing water velocities) of the model domain (67°–73.5°E and 16.5°–24.16 °N) (Figure 1b), and for generating TB trajectories. The HD model has been widely used at CSIR-NIO by researchers for simulating coastal hydrodynamics, DO-BOD, spill movement, fish and barnacle larvae transport, estimation of residence time of pollutants, sediment transport, and effluent dispersion (Babu et al.,^{20,21} Vethamony et al.,^{22,23} Grinson et al.,²⁴ Chetan et al.,²⁵ Rupali et al.,²⁶ and Samiksha et al.²⁷). The bathymetry data are generated from the combined data of MIKE-CMAP and modifiedETOPO 5.²⁸ A brief description of the models and PCA is given in the section SI. 4, SI.

3. RESULTS AND DISCUSSION

3.1. Alkane Fingerprints. The Isoprenoid alkanes, such as Pristane and Phytane, can get altered by the effect of biodegradation. Hence, the ratios C_{17}/Pr and C_{18}/Py significantly decrease when biodegradation takes place. If the samples have undergone weathering by a biodegradation process, then a hump usually appears in the GC chromatogram called Unresolved Complex Mixture (UCM). Results show that UCM is observed slightly in all TB samples (see Figure S4, SI). DRs of *n*-alkanes- Pr/Py , C_{17}/Pr , C_{18}/Py , and C_{17}/C_{18} are calculated for all the samples of TB and crude oil. The ratios of TB samples are nearly the same, suggesting that the source may be the same for all samples. The ratio of C_{17}/Pr for all the TB samples (BHM, BHH, NI, CRN, and MSC) is in the range of 0.68–0.91 (0.96, 0.94, 1.78, 1.71, and 5.97) and C_{18}/Py is in the range of 3.56–4.42 (4.81, 5.67, 9.85, 9.83, and 4.10), indicating that the samples were significantly weathered. The UCM is also present in all the TB samples. Therefore, it is prudent to state that TBs are weathered moderately in various degrees due to biodegradation. TBs derived from tanker washes are in abundance of higher molecular weight *n*-alkanes with the absence of UCM.² Therefore, the presence of UCM and lower ratios of Pr/Py when compared to unweathered crude oils suggest that the TBs had not originated from tanker washes. The Carbon Preference Index (CPI) is often used to estimate the thermal maturity of the petroleum, and it is generally 1.0 for petroleum.²⁹ The calculated CPI for all TB samples is in the range of 1.18–1.19, which shows that TBs are derived from the petroleum products. The ratios of L/H are in the range of 0.79–1.25, whereas for crude oils: BHM-1.53, BHH-1.37, NIK-1.77, CRN-3.10, MSC- 3.03 (Table S4, SI). It may be noted that L/H ratios of TBs are lower than those of crude oil because the lower molecular weight components have weathered due to evapo-

ration and biodegradation, and different ratios suggest that samples were weathered in various degrees.

Wang et al.³⁰ developed the Weathering Index (WI): WI decreases with increasing weathering of low molecular weight *n*-alkanes. We notice that WI of TB samples in various degrees (0.08–0.16). Low concentration of phytane is observed in all TB samples, and this is not because of weathering effect but may be due to source oil characteristics as all the crude oils BHM, BHH, CRN, NIK, and MSC also have the same characteristics. The ratio of Pr/Ph for TB samples is in the range of 4.22–4.77, whereas, for BHM, BHH, NI, and CRN, the ratio is 4.99, 6.03, 5.56, and 6.38, respectively, showing that ratios of TBs are much closer to the ratio of BHM; hence, the source could be BHM. The ratios of Pristane and Phytane are used as indicators of source rock depositional environment: Pr/Ph < 1 indicates anoxic environment, Pr/Ph = 1 indicates alternating oxic and anoxic conditions, whereas Pr/Ph > 1 indicates oxic condition. In the present study, Pr/Ph is >1.0 for all TB samples and crude oils, indicating that crude oils might have been derived from source rocks, deposited in oxic conditions.

3.2. PAH Fingerprints. PAHs are major constituents of crude oil (petrogenic origin), and they also form due to incomplete combustion processes of organic matter (Pyrolytic origin) biological and physicochemical alteration of organic matter that occur in sediments (diagenetic origin).¹² Methyl Phenanthrenes (MPs) such as 3, 2, 9, and 1 are useful to differentiate the crude oils. In the present study, we find that 3, 2, and 1 MPs are less abundant than the 9 MP for all tar balls and BHM and BHH crude oil samples, whereas for MSC, CRN, and NIK crudes, it is different suggesting that the source oil could be either BHM or BHH crude oil. Normally, 3, 2, and 1 MPs are less abundant than the 9 MP in crude oils, and the reverse is true in the case of heavy fuel oils.^{31,32}

The parent PAHs and their DRs such as Phe/Ant, Ant/Ant +Phe, BaA/BaA+Chr, Fth/Fth+Pyr, IcdP/IcdP+BghiP, and Fth/Pyr have been widely used for source identification.^{33,5,6,34} We have computed the same DRs for all the samples (see Table S5, SI). The results show that the ratios of MSC, CRN, and NIK are not corresponding with the TBs, whereas, the ratios of BHM are very near to those of TB samples, suggesting that the source may belong to BH crude oil. However, we cannot confirm the same only with the DRs of USEPA-16 PAHs. The alkylated PAHs and DRs of their homologue groups have been recognized as useful tools in the field of oil spill/TB fingerprint and widely used for source confirmation. In this study, the homologue groups of naphthalene, chrysene, phenanthrene, flourene, and dibenzothiophene are analyzed and the results are illustrated in Figure S5, SI. Figure S5 shows that all the TBs have identical pattern, indicating that the source might be the same. The abundance of phenanthrene and chrysene in samples relative to the others indicates that they are derived from the Bunker C fuel.²⁹ The present analysis shows that the naphthalene homologue groups are abundant in the collected samples, and the samples are neither weathered nor belonging to Bunker C fuel. The double plot ratios C2D/C2P to C3D/C3P are widely used to identify the major PAH sources in sediment, biological PAHs, combustion product PAHs, and natural petrogenic PAHs.^{35,36} In this study, we could not calculate these ratios due to technical problems, but based on the results of PAH analysis, it is possible to say that samples are derived from the petrogenic, particularly from crude oil and the source is the same for all samples.

3.3. Source Specific Biomarkers. Biomarkers are widely used in oil spill fingerprint and environmental forensic studies as they are highly resistant to weathering.^{30,37,1,2,7,8} Crude oil formed in different geological time scales unveil a unique biomarker fingerprint. Thus, the chemical analysis of biomarker plays a prominent role in fingerprinting of TBs. In this study, we used pentacyclic triterpanes (C_{29} – C_{35}) including oleanane. Pentacyclic triterpanes having large thermodynamic stability and resistant to biodegradation. Biomarkers of terpane compounds generate information in determining sources. The hopane DRs of C_{29}/C_{30} and homohopane index $\sum(C_{31}–C_{35})/C_{30}$ widely used as molecular tools to distinguish the source of petroleum. In order to fingerprint the TBs that were deposited along the Gujarat coast, we have used biomarker diagnostic indices. We found that the TB samples and crude oils (BHM, BHH, CRN, and NIK) are enriched in $C_{30}(17\alpha(H),21\beta(H)\text{-hopane})$ and their chromatograms are also apparently the same, mounting suspicion about the source of TBs—BHM, BHH, CRN, or NIK, whereas for MSC it is different. The homohopane distribution that can be used for correlation between samples,³⁸ also suggests that the MSC is quite different from all other crude oils, and TBs followed more or less the same pattern of other crude oils (Figure S6, SI). Therefore, confidently, we can state that MSC is not the source oil. The chromatograms of TBs resemble BHM (see Figures S7 and S8, SI). But a keen observation shows that Oleanane is abundant in BHM crude oil compared to other crude oils. Oleanane is a compound that is usually observed in crude oils that are produced by plant material deposited in the deltaic environment.³⁹ This specific property is therefore helpful in identifying the source of anonymous oil spills. The presence of Oleanane is an indicator of tertiary or late cretaceous source rock with terrigenous influence.⁴⁰ The samples BHM, BHH, CRN, and NIK are also abundant in Oleanane, showing that they belong to the tertiary or late cretaceous source rock. All the TB samples also contain significant amount of Oleanane, giving evidence to our suspicion. The crude oils that were produced in marine shale, carbonate, and marl source rocks have higher $C_{31}R/C_{30}$ hopane(>0.25).³⁸ All the 5 crude oils and 12 TB samples which were analyzed in this study have the ratio >0.25 (Table S6, SI), confirming that the source oils are produced in the marine shale (CRN, NIK, BHM, and BHH are produced in the marine environment in the shelf region off Gujarat). The ranges/values of different DRs for TB and crude oil samples are given in Table S6, SI. The DRs of TBs are very near to the BHM ratios. The ratios of T_s -18 α (H),21 β (H)-22, 29, 30-trisnorhopane and T_m -17 α (H),21 β (H), 22, 29, 30-trisnorhopane are indicators of maturity or source inferences of oil.⁴¹ These values show the level of maturity, and the values are more or less similar. T_m is less stable than T_s , the ratio T_s/T_m < 1 suggests a lacustrine/saline, marine evaporative or marine carbonate depositional environment.⁴²

The DRs of Pentacyclic triterpanes C_{29}/C_{30} and $\sum C_{31}–C_{35}/C_{35}$, called homohopane index, are reliable source identifiers.² The cross plot between the DRs C_{29}/C_{30} and $\sum C_{31}–C_{35}/C_{35}$ clearly indicate that MECO, SEACO, and MSC (red, pink, and green circles in Figure 2) do not correspond with the TBs. Nevertheless, BHM and BHH crude oils meticulously match with the TBs (black circle in Figure 2). The ranges of CRN and NIK are also very close to the TBs (orange circle in Figure 2). The Homohopane index cross plot conspicuously reveals that MECO, SEACO, and MSC crudes are not the sources for the formation of these TBs. Thus, on the basis of the DRs of alkane, PAH and pentacyclic triterpanes, the source of the TBs appears

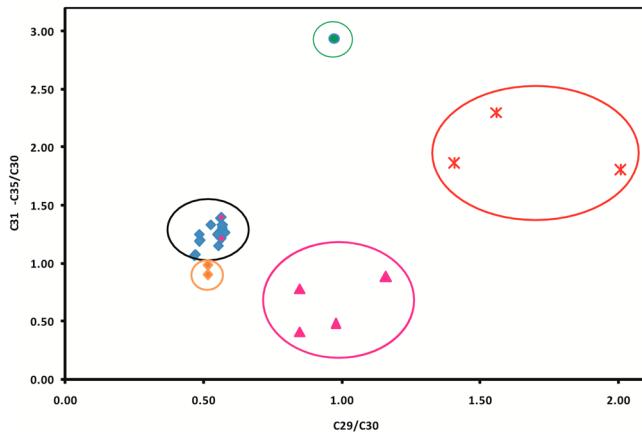


Figure 2. Cross plot of homohopane index. The red circle represents MECO, pink, SEACO; orange, CRN and NIK; green, MSC crude oil; and black circle contains TBs (blue color), BHH (pink color top), and BHM (pink color down).

to be the BH crude oils. However, the hopane DRs of CRN and NIK are close to the DRs of TBs. Therefore, in order to confirm the source of TB, we performed another diagnosis—the compound specific isotope analysis—for TB samples and crude oils.

3.4. Compound Specific Isotope Analysis (CSIA). CSIA is one of the techniques often used in the fingerprinting of spills or TBs. Macko et al.⁴³ studied the stable Nitrogen and Carbon isotope ratios and identified the sources of beach tars as natural seepage, spills in the transport, off-loading of cargo or the disposal offshore of bilge oil. Murray et al.⁴⁴ illustrated the $\delta^{13}\text{C}$ ratios for different tertiary crude oils using CSIA for *n*-alkanes. They pointed out an interesting feature in the slope of the $\delta^{13}\text{C}$ alkane line with increasing alkane size. The slope is steep in fluvio deltaic oils, whereas in most of the lacustrine, marine deltaic, and marine carbonate oils, it is shallower or flat. In the present analysis, the slope is steep and higher molecular alkanes are isotopically lighter than the lower molecular alkanes. Mansuy et al.¹⁰ confirmed that GC-IRMS is a more powerful tool to correlate the samples for the source oils. In this study, we find that $\delta^{13}\text{C}$ ratio lines of BHM and BHH are virtually identical to

each other. The CRN and NIK also apparently follow identical patterns (Figure 3).

This is because the BHM and BHH are generated from the same type of source rock and produced in the BH basin fields. Therefore, the $\delta^{13}\text{C}$ ratios are same for these two crude oils. Likewise, CRN and NIK are also produced offshore off the coast of Gujarat. The distance between these two wells is not more than 10 km; therefore, the produced crude oil characteristics of both sources can be identical. However, apparently there exists a difference between BH based crude oils and CRN and NIK crude oils. The $\delta^{13}\text{C}$ ratios of lower molecular components ($C_{15}-C_{26}$) of BH based crude oils are isotopically higher compared to those of CRN and NIK crude oils, while the $\delta^{13}\text{C}$ ratio of higher molecular components ($C_{26}-C_{35}$) are lighter, but close to each other. The case is the reverse for MSC crude oil. The $\delta^{13}\text{C}$ ratios of alkanes beyond C_{20} are isotopically heavier than TBs and BH, CRN, and NIK crude oils. Therefore, we confirm that MSC, CRN, and NIK crude oils are not the sources for the TBs deposited on the Gujarat coast. There exists a good match between BH based crude oils and the TB samples; alkane $\delta^{13}\text{C}$ ratios follow the same pattern and within the range of both the crude oils and TBs. Thus, CSIA analysis confirms that the source of the TBs is BH based crude oil (either BHM or BHH).

To confirm the source more specifically, additional PCA has been carried out. Utilizing the eigen value criterion, two factors were chosen as principal factors, which explained about 88% of the total variability in the carbon isotope data of TB samples and crude oils. The biplot between these two components is given in Figure S9, SI, which shows that MSC and CRN crude oils, to a large extent, are far away from the remaining samples, and clearly suggest that they are not the source candidates. Apparently, NIK and BH crude oils have similar characteristics. A review work by Hunt et al.⁴⁵ reveals that the combination of biomarker and stable isotope analysis can be used as a tool for source correlation in the field of petroleum geochemistry. Thus, on the basis of the triterpane and CSIA analyses, the source belongs to BH crude (either BHH or BHM), and the *n*-alkane and PAH DRs of TBs correlate with the BHM crude. In order to confirm the probable origin locations, we have simulated TB trajectories using HD model coupled with PA model.

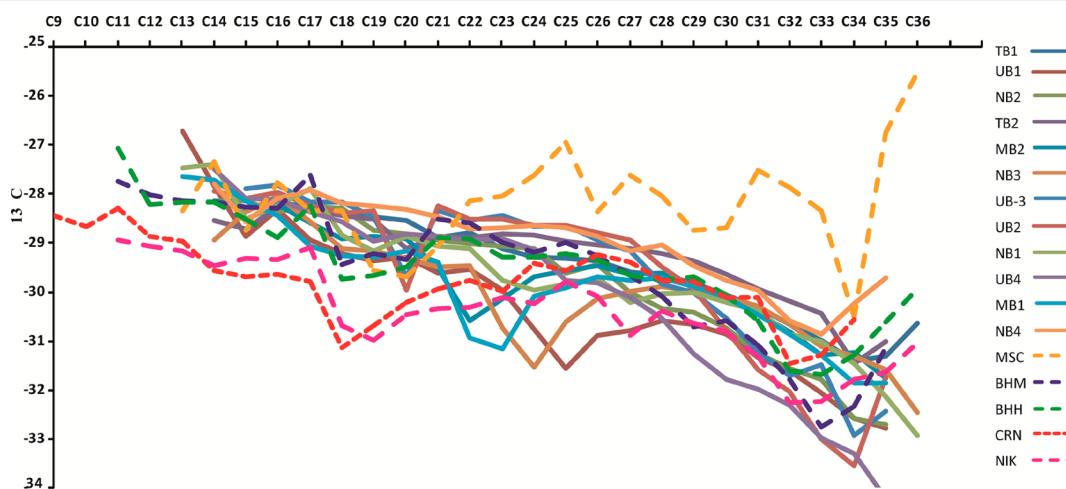


Figure 3. $\delta^{13}\text{C}$ ratios for TBs and crude oil. Dashed lines are for crude oil (red, CRN; pink, NI; blue, BHM; green, BHH; and dark yellow, MSC crude oils. Remaining lines for TB samples.

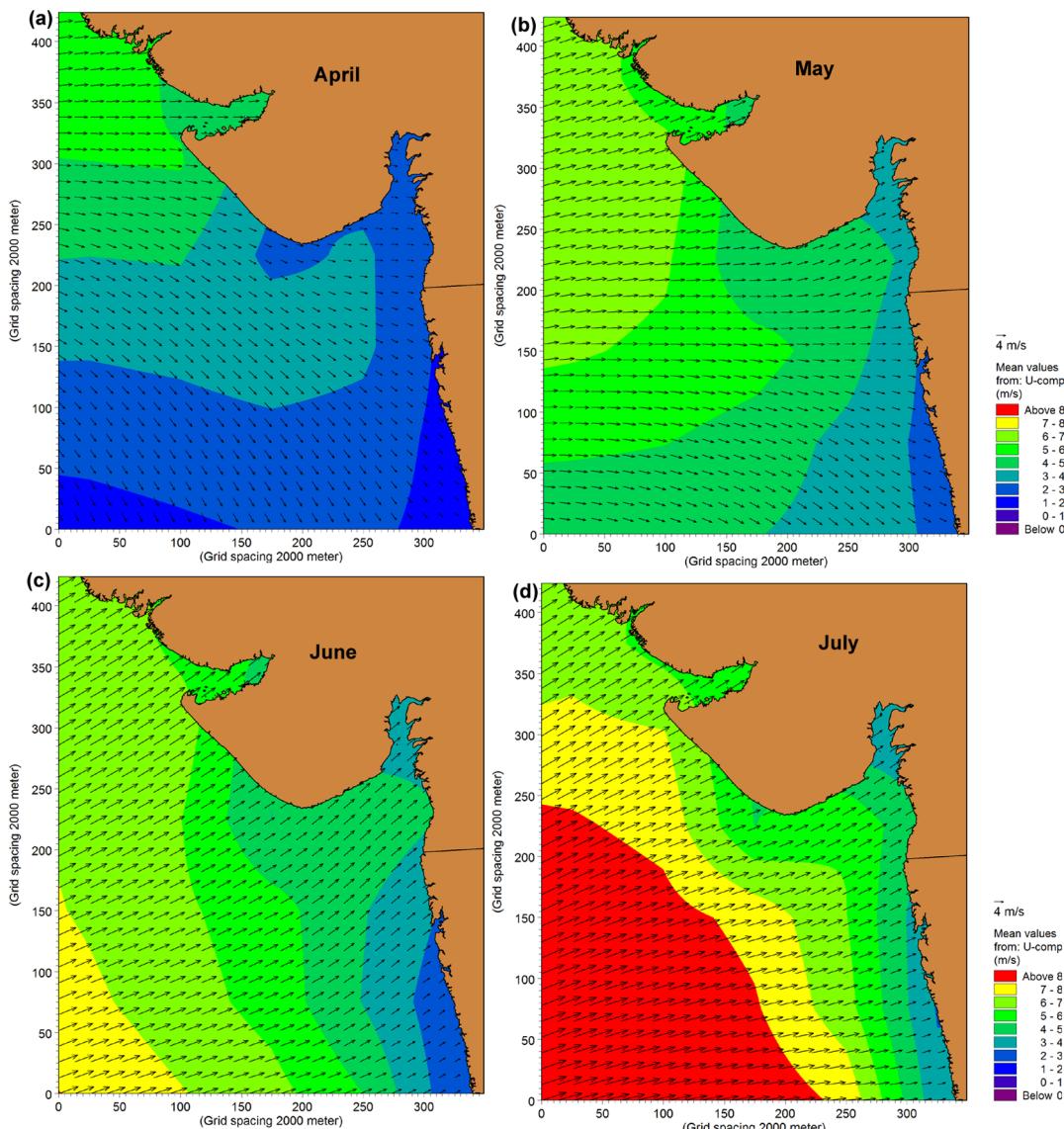


Figure 4. Typical monthly average of wind fields of: (a) April, (b) May, (c) June, and (d) July.

4. MODELING: HYDRODYNAMICS AND PARTICLE TRACKING

The Indian Ocean experiences seasonal reversal of winds—SWM during June to September and northeast monsoon (NEM) during November to February. SWM is the stronger and during this season, strong winds prevail over the Arabian Sea (AS), and directly hit WCI. The reversal of wind pattern builds up the circulation in the north Indian Ocean. Therefore, surface currents in the AS are due to combined effect of wind driven Ekman drift and geostrophic currents.⁴⁶ In order to understand the circulation and particle transport, we performed four experiments during April, May, June, and July.

In the numerical experiment, particles weighing 5 g were released at probable locations. We find that TBs deposited along the Gujarat coast during 15–17 July 2012 were in the range of 2–4 cm diameter. According to Sontro et al.⁴⁷ TBs of 3 cm in diameter and 0.405 cm in thickness would contain a mass of approximately 5.96g. On the basis of this calculation, TBs of mass 5g should have a diameter of 2.516 cm; this value reasonably matches with the range of diameter of the TBs deposited along the Gujarat coast.

4.1. Winds and Currents in the Domain. The monthly averages of ECMWF winds used in the study depicts that the weak northwesterlies prevail in April, moderate westerlies in May and strong southwesterlies in June and July (Figure 4) matches with the earlier study.⁴⁸ These winds were given as input to the MIKE21 HD to simulate hydrodynamics.

The West India Coastal Current (WICC), which is instigated due to the remote forcing, plays a major role in the AS circulation pattern.⁴⁶ The current flows like a jet in the vicinity of continental slope. The U and V velocity components of the currents obtained from the HD model were calculated for monthly averages while the tidal currents are being eliminated (see SI Figure S10). SI Figure S10 depicts that significant WICC flows equatorward along the continental slope during April to July. As a whole, the currents on the shelf are stronger and flow toward the southeast, while the currents beyond the continental slope are weaker. We find that currents are stronger in the GoK (mouth to head); magnitudes of zonal components are smaller as tidal currents are removed by averaging. Tidal currents play a significant role in the circulation pattern off GoK, a macro-tidal regime, where tide range exceeds 7.0 m.

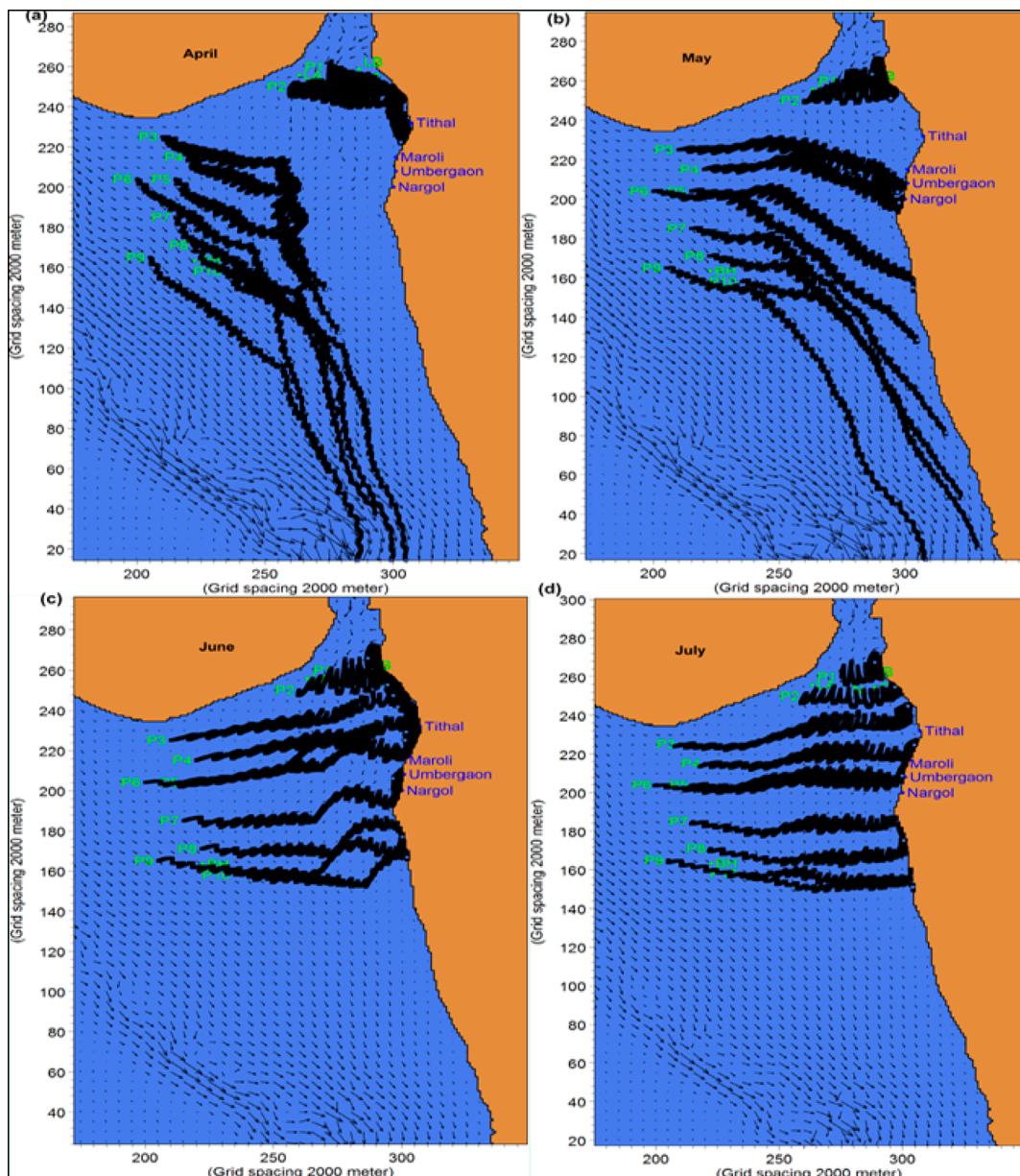


Figure 5. Trajectories of TBs obtained from the PA model for (a) April, (b) May, (c) June, and (d) July.

4.2. Trajectories from the PA Model. Utilizing the above-described winds and currents, PA model has been run for April, May, June, and July in order to understand the forcing mechanism of TB transport during 15–17 July 2012 along the Tithal, Maroli, Umbergaon, and Nargol beaches off south Gujarat.

4.2.1. April and May Simulations. We have used a 2D model to calculate depth averaged currents, the entire water column was assumed as one layer. It has been assumed in the model that the tar ball particles are neutrally buoyant at the sea surface. Particles were released at 10 predetermined locations on 2 April 2012. Only the particles P1 and P2 landed on to the coast between Tithal and Maroli, while the remaining 8 particles found their direction toward the south, without being washed on to the coast (Figure 5a). Overall, the trajectories of the particles were toward the south. This is because, during April, the winds are toward the southeast (Figure 4) and wind driven mean currents are toward

the southeast. Therefore, the resultant trajectories of the particles are toward the south–southeast.

Unlike in April, the trajectories during May have slightly deviated in an anticlockwise direction from south–southeast to southeast, as shown in Figure 5b. Since the particles P1 and P2 were near to the coast, they were the first to reach the coast as well. However, the locations where they were washed up are not our interest (no TB deposition). Subsequently, particles P3 and P4 reached Umbergaon and Nargol beaches, respectively, and regions around P3 and P4 may be the probable areas for the origin of the TB formation (it may be noted that there are a few BH wells in this region).

4.2.3. June and July Simulations. The particle trajectories during June and July are entirely different from April and May trajectories. June simulation (Figure 5c) shows that initially a few particles traveled toward east and directly reached the coast, while some of them turned toward northeast and then toward southeast (because of local tide effect) and finally landed on the

coast. Particles P4, P5, P6, and P7 landed along the coastal stretch between Tithal and Nargol after 17, 18, 20, and 18 days of release, respectively. During June, under the influence of winds (southwesterly) and currents (toward southeast), the TB particles take a resultant direction toward east–northeast.

In July, the winds and currents are stronger than in June, while the direction is the same. Particles P4, P5, and P6 precisely landed along the coastal stretch of Tithal, Maroli, and Umbergaon. The rest of the particles—P1 and P2 landed far north of Tithal, and, P7, P8, P9, and P10 landed far south of the Nargol (region not of interest to us). Particles P4, P5, and P6 traveled for 15, 18, and 21 days to reach the coast (10th, 13th, and 17th July 2012, respectively), and this reasonably matches with the TB depositions that occurred during 15–17 July 2012 along the beaches of Tithal, Maroli, Umbergaon, and Nargol.

On the basis of the four months simulations, we can state that TB particles start moving from the region of origin during late May/June, and take a turn toward either east or northeast (particle trajectories during April to July shift in anticlockwise direction, Figure 5) and reach the coast. During April to July, the mean surface current pattern in the domain is unchanging, and it is in the southeast direction (see SI Figure S10,). However, the winds change their direction: such as northwesterly in April, westerlies in May, and southwesterlies in June and July. Therefore, the shift of trajectories from April to July must be primarily due to the influence of winds. The width of the continental shelf is maximum off GoK (250 km), and it decreases toward the south. This wider shelf (~250 km) has less than 200 m depth, and is dominated by tidal currents and winds. A small influence of large-scale wind driven currents is also expected off GoK.⁴⁹ Therefore, the effect of open ocean currents is less in this region. Thus, winds, tidal currents played a major role together with the minor contribution of wind driven currents in the transportation of TBs to the south Gujarat coast during July 2012. BH is the leading offshore oil field in India, and is situated approximately 160 km west-northwest off Mumbai in the AS (Figure 1b). It has more than 110 well platforms.⁵⁰ BH is divided into two blocks as BH North (BHN) and BH South (BHS). The crude oil produced from the BHN is pumped to Uran terminal through the MUT pipeline (see SI Figure S11). The particles at P3, P4, P5, and P6 locations are very near to the BHN platform.

The DRs of *n*-alkanes, PAHs, triterpanes, CSIA, and PCA confirm that the source of the TBs is BH oil, and the transport model results confirm that the probable source locations are in the vicinity of BHN oil fields. Therefore, we can confidently state that the TBs deposited along the beaches of Tithal, Maroli, Umbergaon, and Nargol during 15–17 July 2012 were of BHM origin. But, the question is, whether it is the operational spill in the BH oil fields or natural seepage from the BH basin is the culprit. Detailed research has to be conducted to answer this question, and we have just initiated this work.

ASSOCIATED CONTENT

Supporting Information

Brief description of GC–MS (section SI. 2); the consistency check performed for the GC–MS (Figure S1); and data for the same (Table S1). Information on GC–IRMS and its calibration (SI. 3, and Table S2). Calibration curves used for quantification of alkane, PAHs, and hopanes (Figure S2). The comparison of HD model results with the measured currents (Figure S3); presence of UCM in TB samples (Figure S4); and the distribution of PAH and hopane compounds (Figures S5 and S6). The hopane chromatograms for the TBs and crude oil

samples (Figures S7 and S8) and the compound name of the peaks shown in Figures S7 and S8 (Table S3). The monthly means of HD currents from Apr–July 2012(Figure S10). The DRs of *n*-alkanes, PAHs, hopanes (Tables S4, S5, and S6). Locations of BH oil fields and pipelines (Figure S11). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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