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Source Identification and Fingerprinting of Tar Balls Appeared at Goa Beach

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Authors' contributions

This work was carried out in collaboration between all authors. Author KDL designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author KDL managed the literature searches, analyses of the study performed the spectroscopy analysis and author CAM collected and identified the samples and author DSR managed the experimental process and all authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Tar balls are frequently reported as indicators of extent of marine pollution owing to spill incidents. It has now been fairly established that the potential threat from operational or accidental oil spills from tankers and other oil related activities could lead to environmental pollution. The study represents the chemical analysis and source identification of tar balls appeared at Goa beach. Four tar balls samples were collected from several locations along the coast of the Goa and were analyzed for their acyclic and Poly Aromatic hydrocarbons (PAHs) by gas chromatography-mass spectrometry (GC-MS) technique. Analysis of crude oil, burnt oil and weathered oils were also included as possible sources of tar balls. Comparison was carried out between the compounds found in tar balls with that of crude oil, burnt oil and weathered oil. This study indicates that, the major source of tar balls was likely to be crude oil as evident from the fingerprints obtained from the study performed on GC-MS.

Keywords: GC-MS; poly aromatic hydrocarbons; weathered oils; tar balls.

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1. INTRODUCTION

Most concern regarding oil pollution is focused on anthropogenic sources i.e., oil extraction, transportation, and consumption. Marine seepage is due to hydrocarbon (gaseous and/or liquid phase) leakage from subsurface strata into the water column [1]. Among the most visible manifestations of marine oil in the environment is the formation and beach stranding of tar, which is the physically and chemically weathered remnant of an oil slick. Tar Balls, become the subject of great interest when it comes to the surface and spread over the shore and creating nuisance near the beaches all over the globe. Coastal tar accumulation is common on many beaches due to chronic oil emissions from natural oil seeps [2,3,4]. Tar balls are nuisance when on an amenity beach; they do not present a significant human health hazard [5]. In terms of environmental impact, they are a threat to amphibious creatures such as sea turtles, and to marine animals if ingested [6]. Tar balls are weathered petroleum residues which have been floating in the ocean and are aquatic pollutant in most environments, although they can occur naturally and as such are not always associated with oil spills [7,8,9]. Tar ball concentration and features have been used to assess the extent of oil spills and their composition can also be used to identify their sources of origin [10,11]. Tar balls may be dispersed over long distances by deep sea currents. The specific gravity of tar balls is low, and this ameliorates their environmental impact. Despite relevance to the quality of coastal life and its environmental impact, few beach studies regarding tar accumulation from natural seeps have been published [12-20]. The Indian coast of Goa is a major tourist attraction for their clear waters and coastal habitats, and is vital for fisheries and marine activities. However, the coasts are under constant threat of petroleum pollution in the form of heavy tar loads. The phenomenon of tar balls has been occurring on the coastal areas of Goa even in 1970's as per the reports of NIO (National Institute of Oceanography Goa) was usually seasonal, with high likelihood during May-October. The major appearance of tar balls on various beaches of South Goa was during the last week of July, 2005 coincidently in the same year during 21st and 22nd September, in a joint survey conducted by National Environmental Engineering Research Institute (NEERI). Pollution along the Indian coast line by tar balls is a matter of concern especially due to the fact that from the last three years, appearance of tar balls along the coast of Goa during the months of May to September has been established as a routine and sporadic oil slicks or tar balls can be seen any day as reported by Department of Tourism Goa.

Efficient and unambiguous analytical methods for the characterization of these spillages are needed in order to (1) determine defensibly the source of the oil, (2) distinguish spilled oil from background hydrocarbons and (3) evaluate the extent of impacted ecosystems in a qualitative manner.

The present study deals with the identification of the type(s) and source(s) of representative tar ball samples collected from several locations along the coast of Goa and the assessment relies upon analyzing polycyclic aromatic Hydrocarbons (PAHs). Concentrations of PAHs in environmental samples are determined mainly by chromatographic techniques; in complex mixtures, PAHs are determined by gas chromatography–mass spectrometry (GC–MS). This method is suitable for the exact and complete determination of PAHs in mixtures extracted from natural and anthropogenic materials and is used in different standard procedures. Further, the corresponding analytical data for crude oil and burnt oil from that region were also included as an attempt to find out the origin of collected tar balls and to examine the reliability of the applied weathering indicators.

2. MATERIALS AND METHODS

2.1 Sampling of Tar Balls

Four tar balls as samples were collected from the Goa beaches (India) viz; Colva, Betalbatim and Velsao in South Goa on 30th and 31st August, 2010, as the tar balls appearance was major on these beaches. The tar ball samples were collected from entire stretch of affected beaches and also covered the various types of its formation viz; smaller size or bigger size of tar balls as well as slick formation. The tar ball samples were collected by hand using clean plastic gloves, kept in clean aluminum foil and glass bottles and stored frozen before analysis. They measured from 4 to 7 cm, and weighed 10-35 g and were loaded with variable amounts of sand and debris. Individual samples of crude oil (Crude oil is a complex mixture of volatile and nonvolatile hydrocarbon compounds ranging from light aliphatic and aromatic compounds (volatile) to heavy and viscous oils) and burnt oil (used petroleum-based oil) were also used for the study as a reference and were collected from nearby sources ships. The collected crude oil sample was kept in the open Petri-plate for 10 days for exposing it to the open atmosphere. The weathered crude oil (Weathered crude or "mousse" is crude petroleum that has lost most of its volatile components and has mixed with sea water and organic matter) samples thus obtained after removal of volatile contents was taken as weathered crude oil [A]. Artificially weathered sample [B] was formed when crude oil was weathered in simulated sea water conditions (by aerating crude oil and collected sea water in open glass jar in laboratory) for a period of 10 days and then these weathered samples were used for the further extraction and analysis. Weathering (physicochemical) processes have changed the appearance of these residual spilled oils to varying degrees. Details on sampling locations and nature of samples were presented in Table 1 and Fig. 1.

Table 1. Sampling location of collected tar ball samples

Sr. no	Location	Latitude/Longitude	Sample
1	Colva Beach	$15^0$16'57.82'' N $73^0$55'03.29'' E	Composite of tar balls/slicks occurred at the beach
2	Betalbatim Beach	$15^0$17'57.57'' N $73^0$54'45.95'' E	Composite of mostly oil slicks with associated sand
3	Velsao Beach	$15^0$21'35.10'' N $73^0$53'21.68'' E	Composite of mostly oil slicks with associated sand
4	Colava Beach	$15^0$16'57.82'' N $73^0$55'03.29'' E	Only typical tar balls (composite)

2.2 Solvent Extraction of Tar Balls

Selection of solvent mixture was based on its ability to solubilize /extract contents of tar balls to its maximum extent such as dichloromethane and n-hexane (DCM: n-hexane) (9:1 v: v). Two gram sample was taken in thimble and extracted in solvent mixture using Soxhelt - Extraction assembly [21]. The extract was concentrated to 25 ml and then passed through the Silica gel column to retain oil and grease material, followed by anhydrous sodium sulfate column to remove the traces of moistures if any. The extract was concentrated to approximately 5 ml using rotary evaporator, other samples of burnt oil and crude oil and weathered crude oil [A] and weathered crude oil [B] were also extracted in the same way as that for tar balls [22]. The extracted samples were subjected to fingerprinting of various organic compounds on the gas chromatograph-mass spectrometry (GC-MS) [23,24]. Solvents and chemicals used in the study were from Merck Specialties Pvt. Ltd Mumbai (India).

2.3 Analysis of PAHs

Qualitative analysis of the samples viz; tar balls, crude oil, burnt oil, weathered crude oil [A] and weathered crude oil [B] was performed on the extracts obtained by using solvent matrices and following the extraction method. Extracted samples were analyzed on GC-MS for the characterization of the organic compounds likely to be present in the tar ball samples and for source apportionment. In the present study complete fingerprint of extracted sample is required to develop, following techniques of separation, identification based on retention time and further confirmation of the identified compounds against the standard library as provided with GC-MS have been used.

The GC-MS instrument, Varian GC-450 and MS-240, USA, was used with the column DB-5, 30m, 0.25mm I.D., 0.25 micron film thickness for the characterization of the various compounds in the tar ball samples. The GC-MS monitor depicting confirmation of identified compounds through inbuilt mass spectral library NIST 08, USA, The standard used for the GC-MS was of Dr. Ehrenstorfer. The analysis was carried under the following analytical conditions: temperature program, oven temperature, 60-270ºC with raise in 15ºC min-1; and injection temperature, 270ºC; carrier gas, helium; flow rate, 1 ml/min; column, DB-5; detector, mass spectrometer; mass range scanned, 50-1000 amu, respectively [23,24].

3. RESULTS AND DISCUSSION

An assessment of the degradation and weathering trends of tar ball samples can be illustrated by qualitative and quantitative aspects of the GC fingerprints [25,26]. GC-MS results for the analysis of the tar balls, crude oil, and weathered oil [A] and weathered oil [B] was as follows:

3.1 Tar Balls

An assessment of the degradation and weathering trends of tar ball samples can be illustrated by qualitative and quantitative aspects of the GC fingerprints [25,26]. In the tar balls, it was found that different type's saturated and unsaturated alkanes ranging from the C10 to C20 and substituted with the side chain containing alkyl groups i.e. some of lower alkyl groups such as methyl, ethyl etc., along with other functional groups such as hydroxyl groups are present. Following compounds such as Naphthalene; Anthracene; Pyrene; Fluorene; Phenanthrene; Acenaphthylene; chrysene etc. are found in the tar balls. On review of Table 2.1, it was observed that most of the compounds detected in tar balls (samples 1 to 4) were the Naphthalene based derivatives which are substituted with alkyl groups, such as Naphthalene 1 methyl; Naphthalene 1, 6, dimethyl; 9H- Fluorene 1–methyl; 4, 6, 8-tri methyl Azulene; 9H-Fluorene, 2 methyl; Pyrene 2, 5 dihydro; Phenanthrene 2, 7 dimethyl etc. Total ion chromatograms have been depicted in Figs. 2-5.

Table 2.1 PAHs identified in Tar ball samples

Sr. no.	Compounds	Tar balls			
		Samples			
		1	2	3	4
1	Anthracene	√	√	√	√
2	Acenaphthylene			√	
3	Chrysene				√
4	9H Fluorene, 2 methyl		√		
5	9H Fluorene, 9 methyl	√	√		
6	Naphthalene	√	√	√	
7	Naphthalene, 2 – methyl			√	
8	Naphthalene 1,2,3,4 – tetrahydro – 1,6,dimethyl – 4 (1-methylethyl)				√
9	Naphthalene 1,3, dimethyl			√	√
10	Naphthalene 1,5, dimethyl				√
11	Naphthalene 1,6, 7 trimethyl	√	√	√	√
12	Naphthalene 1,6 , dimethyl		√	√	√
13	Naphthalene 1 ethyl			√	
14	Naphthalene 1,2,3,4 – tetrahydro – 1,6,dimethyl – 4 (1-ethyl)	√			
15	Naphthalene 1,4 dimethyl	√	√		
16	Naphthalene 2, (methyl ethyl)	√			
17	Naphthalene 1 Propyl		√		
18	Naphthalene 1,2,3,4 – tetrahydro – 1,6,dimethyl – 4 (1-methyl)	√	√	√	
19	Naphthalene 2, ethenyl	√	√		
20	Naphthalene 1,4 – dihydro 2,5,8 trimethyl				√
21	Naphthalene 1,4 dimethyl				√
22	Phenanthrene, 2,7 dimethyl				√
23	Phenanthrene 2, 7 dimethyl		√	√	
24	Phenanthrene 2,3, 5 trimethyl				√
25	Pyrene 4,5, dihydro	√			
26	Pyrene 2,5, dihydro				√

Further to identify the source of these tar balls, the likely sources such as crude oil, weathered crude oil, burnt oil etc were analyzed to obtain the fingerprints and matched with those of compounds identified from tar balls.

3.2 Crude Oil

Crude Oil or Petroleum is simply unprocessed oil found deep beneath the earth's surface. Overall properties of crude oils are dependent upon their chemical composition and structure. Generally all crude oils were made up of hydrocarbon compounds. The main hydrocarbons found in crude oil were Aliphatic, Alicyclics, and Polycyclic Aromatic Hydrocarbons (PAH).The samples of crude oil after fingerprinting had shown the presence of the monaromatic and polyaromatic compounds such as Naphthalene; biphenyl; Anthracene; Undecane and also some of them are substituted with alkyl groups such as 2-methyl; Benzene 1,2,3,4- tetra methyl; 1,1'-biphenyl; 3 methyl; 9H Fluorene, 9 Methyl;

Naphthalene 2 methyl; Naphthalene 2 ethyl results are depicted in Table 2.2. Total ion chromatogram has been depicted in Fig. 6.

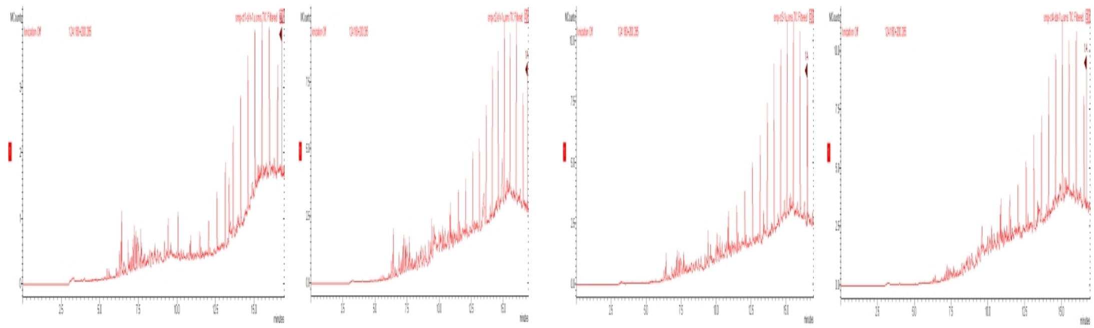
Table 2.2. Identification of PAHs in all reference oils

Sr. no.	Compounds	Biomarkers (Reference oil)			
		Crude oil	Weathered crude oil – A	Weathered crude oil – B	Burnt Oil
1	Anthracene		√	√	
2	Naphthalene	√	√	√	√
3	Naphthalene, 2 – methyl	√	√	√	√
4	Naphthalene 1,2,3,4 – teteahydro – 1,6,dimethyl – 4 (1-methylethyl)		√	√	
5	Naphthalene 1,3, dimethyl		√		
6	Naphthalene 1,5, dimethyl		√		
7	Naphthalene 1,6, 7 trimethyl		√	√	√
8	Naphthalene 1,6 , dimethyl	√			
9	Naphthalene 1 ethyl			√	√

Fig. 1. Sampling Locations of collected tar balls

3.3 Weathered Crude Oil [A]

Weathering processes eventually created a tar ball that was hard and crusty on the outside and soft and gooey inside. These droplets may also result in the creation of a secondary slick or thin film on the surface of the water Sample .Weathered crude oil sample was also extracted with the use of solvent (DCM:n-hexane) matrices the results have been depicted in Table 2.2. Total ion chromatogram has been presented in Fig. 7.



(2) (3) (4) (5)

Figs. 2-5. Total Ion Chromatogram of tar ball samples

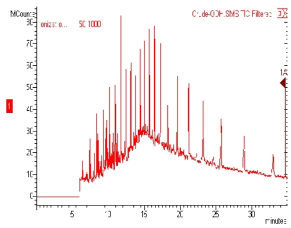
3.4 Weathered Crude Oil [B]

Sample of weathered crude oil (B) has been extracted with the use of solvent (DCM: n-hexane) matrices and the results showed the presence of different aromatic compound substituted with the different alkyl groups such as Anthracene; 1, 1, Biphyenyl; 3-methyl; Benz(a) Azulene; Benzene 1,2,4 triethyl; Naphthalene; Naphthalene 1,2,3,4–teteahydro–1,6,dimethyl–4 (1-methylethyl),Naphthalene 1,6,7 trimethyl; 9H- Fluorene 9-ol; 1,4,5,8, tetra methyl Naphthalene; 1,8 dimethyl Naphthalene etc, results are depicted in Table 2.2.Ttal ion chromatogram has been presented in Fig. 8.

3.5 Burnt Oil

Extracted samples of burnt oil have shown the presence of different compounds such as Benz(a) Anthracene; 1-1 Biphenyl 3 methyl; 1,2 Biphenyl 2 methyl; 1,1'- biphenyl; 4,4' Dimethyl; Naphthalene 1 methyl; Naphthalene 1 ethyl; Naphthalene 1,5, dimethyl; Naphthalene 1, 7, dimethyl etc. Results have been depicted in Table 2.2. Total ion chromatogram has been presented in Fig. 9.

The above results indicate the sources of emerging tar balls i.e. weathering of crude oil, degradation, evaporation, dispersion, emulsification and decomposition of most of the compounds that had removed or changed their chemical composition by leaving oil and grease and naptha or asphalt based compounds which converted into the shape of tar balls. Apart from this, the other likely sources could be burnt oil and heavy oil deposition from the ships and waste materials which are produced from the cleanup process (i.e. machinery etc.). So from the fingerprinting of the tar ball samples and crude oil and other samples, the correlation was made as presented in the Table 2.2. Only Naphthalene based derivatives are present with a very low concentration level of other compounds found in crude oil. As the oil contains both aliphatic and aromatic compounds, but it was found that the aliphatic compounds do not remain in the atmosphere for that longer time, the other aromatic compounds which were obtained were mostly substituted compounds. In general, tar balls accumulate at a faster rate or remain longer time on all beaches during the summer and following months; however some factors such as prevailing winds and currents combined with more quiescent wave conditions favor the accumulation and preservation of tar balls on the beach during the summer and following months. In contrast, winter storms, with greater wave action remove beach sand and other materials, and stormy seas tend to break up oil that might weather into tar balls.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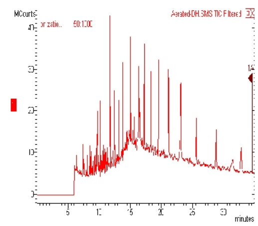
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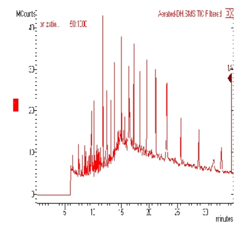
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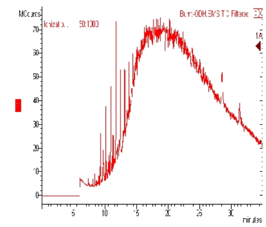
(9)

Figs. 6 -9. Total Ion Chromatograms of Crude oil, weathered crude oil (A), weathered crude oil (B) and Burnt oil

4. CONCLUSION

GC techniques have proved to be effective for the study of the composition and source assignment of tar balls. The study includes collection of tar balls along the Goa Coast from different locations. After proper preservation and using selected extraction procedures, analysis of different derivatives of hydrocarbons was carried out through proper instrumentation (GC-MS). Table 3 shows the comparison of components observed in Tar ball with that of crude oil, burnt oil and weathered oil [A] and weathered oil [B]. The study indicated that, the major source of tar balls is likely to be weathered crude oil and crude oil as evident from the fingerprints of most of its components viz. Anthracene; Naphthalene; Naphthalene; 2 – methyl; Naphthalene 1,2,3,4 – tetrahydro – 1,6,dimethyl – 4 (1-methylethyl); Naphthalene 1,3, dimethyl; Naphthalene 1,5, dimethyl; Naphthalene 1,6, 7 trimethyl; Naphthalene 1,6, dimethyl; Naphthalene 1 ethyl, were found to be similar with that of Tar balls. Maximum Naphthalene based derivatives are observed in the tar balls which were formed from the greasy and asphaltic materials due to weathering effects.

While assigning the source to crude oil, possible routes for introduction of crude oil in sea were also found to be the potential sources. Minor contribution to composition of tar ball was also assigned to waste clean materials used for machinery equipment installed on the vessels / ships and also the bilge water generated during the process of cleaning (vessels platform / floor) containing oil and greasy materials. Though the source may appear minor at the point generation, but could because of its persistent existence and nature may contribute immensely. The shift towards shore though slow may likely to contribute to formation of tar balls in coastal areas. All these wastes and spilled materials containing oil and grease periodically undergo changes through weathering effects (dispersion, dissolution, emulsification, evaporation and decomposition) depending on the marine environment and sea conditions and take the shape of tar balls which travel with waves and currents and other meteorological conditions prevailing due to monsoon setup in the offshore area. It is also observed that, the composition of the tar ball is related to the availability of maximum greasy and asphaltic materials.

Table 3. Comparison between tar balls and reference oil samples

Sr. no.	Compounds	Crude oil	Weathered crude oil - A	Weathered crude oil - B	Burnt oil	Tar balls			
						Samples			
						1	2	3	4
1	Anthracene		√	√		√	√	√	√
2	Naphthalene	√	√	√	√	√	√	√	
3	Naphthalene, 1-methyl	√	√	√	√				
4	Naphthalene, 2 – methyl	√	√	√	√			√	
5	Naphthalene 1,2,3,4 – teteahydro – 1,6,dimethyl – 4 (1-methylethyl)		√	√					√
6	Naphthalene 2 ethyl	√	√	√	√				
7	Naphthalene, 1, 8, dimethyle		√	√					
8	Naphthalene 1,3, dimethyl		√					√	√
9	Naphthalene 1,5, dimethyl		√						√
10	Naphthalene 1,6, 7 trimethyl		√	√	√	√	√	√	√
11	Naphthalene 1 ethyl			√	√			√	

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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