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CHEMICAL CHARACTERISTICS OF TAR-LIKE MATERIALS FOUND ON THE BEACHES ALONG THE EAST AND WEST COASTS OF INDIA IN RELATION TO THEIR SOURCE OF ORIGIN

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ONE of the categories of marine pollution which very recently concerned the authorities of National Institute of Oceanography (NIO) is oil pollution. It has been noticed that on some of the beaches along the west and east coasts of India, lumps of tar-like materials (Fig. 1) are found to be deposited at high tide levels with varying degrecs of intensity during the period June to September (South-West Monsoon)[1]. Occurrence of such tar-like materials is also reported along the beaches of Mediterranean Sea, Eastern North Atlantic[2] and Southern California beaches[3]. The existence of tar-like materials on the beaches indicate perhaps a certain amount of oil discharge or seepage occurring more or less continuously in the coastal waters since the materials represent the near end products of degradation of oil. The present paper details some information on the chemical factors of the tar-like materials in relation to their sources of origin.

FIG. 1. Tar-like materials collected from Calangute beach (Goa).

A group of scientists of Biological Oceanography Division, NIO, visited some of the beaches and collected several samples along the east and west coasts of India to investigate their intensity and probable sources with reference to beach ecological studies. For the present study, eight samples were selected from among them for analysis to ascertain their source of origin and state of degradation. Chemical analysis of the samples was done by the staff of the Indian Institute of Petroleum, Dehra Dun, on our request. Standard techniques for evaluation of the crude and its products were adopted for the analysis. Samples were analysed for water, sand, oil, total sulphur asphaltenes, waxes, and the trace elements vanadium and nickel.

The lumps are generally brownish black to black in colour having the odour of crude oil; soft to touch and having irregular shapes; the size varying from 2 mm to 8 cm, covered with sand and debris. The tar material is soluble in chloroform, benzene and insoluble in acetone and *n*-hexane. The intensity, shape, size and nature of the material in a particular location appears to be dependent on the currents, wave action and also the configuration of the beaches and the stage of degradation of the material. These features are consistent with the observations made at few beaches along the Goa coast wherein it is found that the deposition is not continuous along the vast stretches of the beach. The occurrence of the material is generally more associated with coarse sand beaches and less on fine sand beaches. The physical nature of the material reflects the extent of transformation, the oil was subjected to before reaching the beaches from offshore regions. The tar material, perhaps initially in particulate form, moving on shore by the action of currents and waves gets moulded into different shapes and sizes and picks up considerable quantities of sand and debris. The interesting feature observed is that the tar lumps are noticed during the onset of south-west monsoon when the sea becomes rough and the wave action is high. The material disappears during the post-monsoon period when the calm conditions prevail in the sea. The beaches remain clean till the next onset of monsoon. However some material is found at random on the beaches beyond the high tide mark which perhaps escaped being washed back to the sea. These lumps generally become hardened due to atmospheric exposure.

The probable sources of oil pollution found from the literature may be summarised as: (1) maritime accidents due to collision, fire, explosion or grounding which results in the release of oil either from the ships, tankers or from the cargo tanks. (2) Intentional discharge of oil or oily waste from the

pumping of bilges or from deballasting cargo tanks or from tank washings. (3) Accidental spillages while transferring fuel or cargo from ship to ship, or ship to shore, and accidental spillage resulting from the incorrect operation of valves, etc., on ship board or at oil terminals[4]. In the present context, the first type of source is eliminated as no such accidents are reported in the past or present. The third type of source is local and the contribution from that source might be occasional and considered negligible. The second type of oil pollution appears to be more probable as a continuous source of oil pollution, in the present instance, due to ever increasing ship and oil tanker traffic and this view is also substantiated by the chemical characteristics of the samples.

Before discussing the chemical characteristics of tar material it is pertinent here to mention briefly the general transformations the oil undergoes from the moment it is discharged into the sea. Spilt oil spreads quickly with an average thickness of 100 μm and depending on the wave action a viscous water-in-oil emulsion forms. During the moment it is discharged, the oil loses the lighter fractions, like volatile paraffins and aromatic hydrocarbons with the consequent increase in viscosity and density; small amount of oil may be dissolved in water and be lost. Processes of chemical oxidation and biodegradation are also operative forming various types of products including polymerised compounds, making it more viscous and denser and finally to sink as fine particles. Sometimes the water-in-oil emulsion forms into a gel-like emulsion called the "chocolate mousse" and the subsequent chemical and biological reactions are slow because of the small surface area. On reaching the shore the 'chocolate mousse' picks up sand and debris and the water evaporates leaving compact, tarry lumps, and further degardation is very slow. The tar may sometimes be waxy deposit of crude oils discharged into the sea during tank cleaning operations[4,5].

Chemical analysis of tar materials strongly suggests that the source material is crude oil. As per the report of analysis the pollutant contains hydrocarbons (indicated by wax content), sulphur and trace metals (Table I). The concentration levels

TABLE I

Characterisitcs of the tarry lumps found on the Indian beaches

Charecteristics	Location of sample							
	West cost				East coast			
	Vijay-durga Lat. 16° 20′ N.	Devgarh Lat. 16° 00′ N.	Calan-gute Lat. 15° 30′ N.	Coonda-pur Lat. 13° 20′ N.	Pulicat Lat. 13° 15′ N.	Covalam Lat. 12° 30′ N.	Pt. Cali-mere Lat. 10° 10′ N.	Mimisal Lat. 9° 20′ N.
Water %	3·3	4·3	3·0	1·0	0·7	1·6	2·2	1·2
Sand %	12·0	24·9	16·2	38·0	39·3	40·2	16·0	35·0
Oil %	84·7	71·8	80·8	61·0	60·0	58·2	81·8	63·8
Total sulphur % weight	0·60	1·5	2·58	1·3	0·77	2·3	1·96	2·06
Asphaltenes % weight	4·66	3·48	2·0	2·19	7·33	5·46	4·45	4·9
Wax content % weight	17·5	6·68	*	19·2	26·0	7·0	*	*
Wax congealing point °C	59·0	71·0	*	71·0	*	67·0	*	*
Vanadium ppm	60	200	*	220	*	150	*	*
Nickel ppm	Not detected	100	*	60	*	100	*	*

* Not analysed.

and characteristics of the constituents of tar materials indicate that the source of crude oil to be "Aghajari" crude oil (imported crude). From Table I, it can be seen that the concentration of the constituents show certain degree of variability suggesting that the material is in different stages of degradation on the beaches. There is a general inverse relationship between the water % and the sand % and direct relation between water content and oil. These features reflect on the relative freshness of the samples. Broadly, it may be said that the east coast samples are in more weathered condition than the west coast samples. The general high asphaltene % in east coast substantiates the above view. The vanadium and nickel concentrations do not indicate relative stages of degradation excepting that the general high concentration of the samples analysed, were subjected to significant weathering; normally concentration of the trace

elements are less in the fresh crude than the weathered product. The apparent concentration of trace elements in the weathered coumpound will be increased due to evaporation of volatiles and due to the processes of chemical transformation of the original crude. The high content of sulphur, asphaltenes also indicate that the crude oil washings discharged into the sea, have been weathered in course of time. The high wax content of some of the samples suggests that the probable source is the residue left in tanker compartments of the oil tankers[6].

Increased incidences of discharge from the oil tankers appear to be all the more plausible in view of the increased oil tanker traffic that feed the Indian refineries. Petroleum tankers take aboard substantial quantities of water ballast into cargo tanks after discharging their cargo. Such ballast will be contaminated by the cargo, was of black oil (crude or fuel oil) will be unfit for discharging into the harbour water, the next loading port and in view of this the cargo compartment must be washed clean during the ballast voyage in order to enable them to hold clean water from the sea for safe discharge at the loading terminal[6]. Thus the cleaning operations of the tankers might be active immediately on their return voyage. The abundant occurrence of tar materials on the beaches along central west coast of India where refineries are not situated, lends itself support to the deduction that the source of origin might be oil tankers discharging their tank washings during their return voyage from Bombay port.

The physical and chemical effects of oil on marine organisms are said to be as diverse and complex as the nature of its numerous components and products. Toxicities induced may be direct or indirect. Indirectly it affects the marine organisms by limiting oxygen exchange of the surface or by coating the gills of fishes and other gill breathing animals. Direct absorption or ingestion of toxic constituents like volatile paraffins, olefins and aromatics is hazardous to organisms causing functional alterations and affecting their normal behaviour patterns. It is also observed that certain aromatic constituents of oil are carcinogenic which may reach human system indirectly through consumption of affected organism[7,8]. Crude oil contains relatively high concentration of nickel which is more toxic of the heavy metals and is a cumulative type of inhibitor that can build in an area of frequented oil pollution[9]. The above-mentioned ill-effects of oil pollution are only few among many and it may be mentioned that in general, the knowledge on the toxicity of the oil, its constituents and products is at present quite meagre. Fortunately, majority of the toxic constituents are water soluble and volatile and so they are quickly dispersed and lost. Unless the oil spill is extensive and continuous it may not pose an immediate threat to the marine life.

The present levels of concentration of tarry lumps found on Indian beaches do not suggest hitherto, any alarming oil pollution, hazardous to marine life excepting that this may have undesirable effects at some recreation spots. In India the oil pollution is now believed to be in the initial stages. However, in the long run the possibility of increasing concentration of the tarry lumps is envisaged and reckoning the extent of oil pollution based on the concentration of these materials, it may perhaps assume dangerous proportions affecting marine living resources and recreation centres. Therefore, it is imperative that concentrated studies on the probable sources of oil, and its physico-chemical nature, the modes of chemical and biodegradations and the toxic effects at different stages of transformation must be pursued to take effective preventive measures.

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