ACCESS NUMBER: 30470

STUDY TITLE: University Research Initiative on the Effects of Offshore Petroleum Development in the Gulf of Mexico

REPORT TITLE: Characterization of Chronic Sources and Impacts of Tar Along the Louisiana Coast

CONTRACT NUMBER: 14-35-0001-30470

SPONSORING OCS REGION: Gulf of Mexico

APPLICABLE PLANNING AREA: Central Gulf of Mexico

FISCAL YEARS OF PROJECT FUNDING: 1992, 1993

COMPLETION DATE OF REPORT: June 1993

COST: FY92: $ 0; FY 93: $48,102

CUMULATIVE PROJECT COST: $48,102

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KEY WORDS: Tar balls, pelagic tar, hydrocarbons, source-fingerprinting, PAH, source indexes, morphological classification, Louisiana beaches, tar ball weathering, aromatic, Paraffinic, bimodal wax

BACKGROUND: At the current rate of oil transportation in the Gulf of Mexico, when oil spills occur, it is not a simple case of petroleum found upon the shores originated from the spill incident. Stranded oil and tar balls are frequently deposited along the southern coast of Louisiana, without the cause and effect relationship of a reported petroleum release. Many potential sources of accidental or illegal discharges exist. The petroleum transportation off Louisiana shores range in the millions of barrels, with the Louisiana Offshore Oil Port (LOOP) receiving more than 200 million barrels per year. Also contributing to this transportation system are the Outer Continental Shelf production activities, transporting 98% of their production by pipeline and 2% by barge. Illegal bilge cleaning and dumping and oil seeps may also add to the tar along Louisiana beaches. The distribution, frequency, and composition of this stranded oil was assessed at nine study sites, covering an approximate range of 200 miles along the Louisiana coastline.

OBJECTIVES: The overall goal is to develop a baseline estimate of the chronic oiling of Louisiana Beaches. We hope that this preliminary survey will provide a better understanding of coastal impacts related to oil production and transportation in the Gulf of Mexico. The objectives for this study are:

1. 1.Assess the abundance, distribution, and composition of stranded oil and tar at 9 stations along the South Louisiana coast.

2. 2.To investigate tar balls collected for specific source-biomarkers and source-indexes by a detailed GC/MS source-fingerprint technique to identify related sources. The questions we are attempting to address are: What are the sources of the stranded oil and tar found upon the beaches? Are they primarily small unrelated events, or are they chronic discharges from identifiable sources?

Description: Nine study sites were selected in the spring of 1992 along the southern coast of Louisiana. These stations were 50 meter wide, running parallel to the beach face and covering the distance between Grand Isle on the east to Martin's Beach on the west, approximately 200 miles. The stations were sampled in the spring and fall for petroleum deposition. The samples found within the stations were removed and taken to LSU for morphological characterizations and GC/MS analysis.

SIGNIFICANT CONCLUSIONS: There existed an extreme difference in petroleum distribution, with 9.6 tar balls per 50 meter station in the east compared to 40 tar balls per station for the west. The samples collected from these stations were analyzed by detailed GC/MS and compared for similarities using a source-fingerprinting data synthesis process. The data indicates a wide range of petroleum sources with unweathered high paraffin heavy oil and weathered oil with a bimodal wax component as the most abundant. The latter are generally associated with bunker and crude oil washings or sludge discharges and represented 26% of the tar balls analyzed. An assessment by detailed GC/MS characterization and source fingerprinting, utilizing selective ion monitoring (SIM) was completed for 124 of the 528 samples collected. The results indicated 18 sources with multiple occurrences and 47 unrelated sources of which 55% of the samples were sourced from the 18 multiple sources and 45% were from the unrelated sources.

STUDY RESULTS: There was no statistical difference between the Spring and Summer periods, indicating a constant deposition and removal of petroleum. The visual appearance of the petroleum was 80% black and pliable, with 10% brown and the remaining 10% various colors of petroleum products. The gross number of tar balls for the various stations and average weight distribution per meter indicated greater petroleum abundance for the western stations. A total of 480 samples were collected in the west compared to 48 in the east and can be expressed as 40 tar balls/station in the west compared to 9.6 tar balls/station in the east. Between the backshore and foreshore beach zones, there were more tar balls collected in the upper beach region than the lower with 18.8 backshore tar balls/station compared to 12.2 foreshore tar balls/station. A total of 4416.42 g were collected in west compared to 627.65 g in the

east during the Spring 1992 sampling period. A similar trend was observed during the Summer 1992; 4573.6 g in the west compared to 125.2 g collected in the east. In comparison to other shoreline studies within the Gulf of Mexico, the concentration of tar balls along the Louisiana coast were low. The range of stranded tar as reported in g/m for the Wider Gulf of Mexico Region was 0 to 4366.61 g/m (the highest value was reported in Discovery Bay, Jamaica by Jones, 1990); during our study, the quantity of tar collected ranged from 0.53 to 47.77 g/m. If the estimated threshold concentration of 100 g/m is considered a good guide in determining the degradation of beaches for tourist purposes, the beaches studied were below a level of social-economic concern. Although, any stranded oil on a beach is aesthetically unpleasant, and the presence of oil reduces the value placed on that beach as a resource.

Of the 118 samples analyzed by detailed GC/MS, 32% were indicative of high pour point, heavy oils (most likely bunker or heavy heating oils), closely followed by tanker washings or sludge discharges at 26%. Therefore, greater than 50% of the samples collected can be associated with transportation activities. The persistence of the spilled heavy petroleum oils, enriched with asphaltene and high molecular weight residuum hydrocarbon components was considered greater than for many crude oils and light refined petroleum products. Often, light oils spilled in the marine environment spread very thin on the water's surface and disperse by natural processes, such as storms, never forming tar balls. Heavy oils, which are more viscous and less effected by physical processes persist longer. Microbial degradation, the ultimate fate of most tar balls in the marine environment, is limited by the available surface area of the petroleum and by the recalcitrant petroleum constituents.

Source-fingerprinting by manual comparison of the available GC/MS data was effective in identifying 66 different sources from a sample population of 118. Cluster plot analyses are effective in screening a large population of GC/MS data to determine which samples may be related. The possible matches would then require conformation by a qualitative comparison of all chromatographic data. Mathematical, or statistical, techniques were limited by the lack of replication and range in index values. The use of statistical principal component analyses may provide a higher degree of separation of suspected sources. More work is required to fully develop a statistical approach to source-fingerprinting.

Several of the sources appear to be derived from the discharge of tanker washings containing crude oil and high molecular weight paraffins. Biomarker signatures typical of Middle East and Alaskan North Slope crudes have been identified in the tar balls analyzed. This is not surprising since approximately 30% and 8%, respectively, of the crude oils transported into the Northern Gulf of Mexico are from these two sources.

STUDY PRODUCTS: Henry, C.B., P.O.Roberts and E.B. Overton. 1993. Characterization of Chronic Sources and Impacts of Tar along the Louisiana Coast. A final report submitted by Louisiana Universities Marine Consortium to the U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico Region OCS

Office, New Orleans, LA. Contract No. 14-35-0001-30470 OCS study MMS 93-0046. 64 pp.

Roberts, P.O., C.B. Henry, and E.B. Overton. 1993. Source Targeting Tar Balls Along The Southern Louisiana Coastline. International Oil Spill Conference Proceedings. Tampa, Florida. p: 891. (Abstract only.)

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