

Oil Source Fingerprinting in Heavily Weathered Residues and Coastal Marsh SamplesEdward B. Overton^{†*}, M. Scott Miles[†], Buffy M Meyer[†], Heng Gao[†] and R. Eugene Turner[§][†]Department of Environmental Sciences, Louisiana State University, Baton Rouge, LA 70803[§]Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803

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Abstract 300015:

Oil source fingerprinting uses capillary column GC/MS analyses of a source oil and environmental oil samples to try and match the chemical composition of key indicator compounds in both samples, thus providing strong evidence that the environmental samples came from the suspected source. These environmental samples are typically not heavily weathered. However, after a major oil spill, such as the *Deepwater Horizon* Oil Spill (DHOS), oil can travel in the environment for many miles, and reside in coastal marshes and sandy beaches for months to years after the spill. This environmental resident time, and the compositional change associated with weathering process, makes oil source fingerprinting of spill residues more challenging and technically difficult. This was especially true during the DHOS because the spilled oil impacted coastal areas that had experienced chronic oiling that contributed to a high probability of background petroleum contamination due to other spill events. We have collected a large number of samples since the tragic accident in late April 2010 from near shore coastal environments, including those following storm events like Hurricane Isaac. Analytical concentration data was generated using high resolution GC/MS in selected ion monitoring mode for the saturate normal hydrocarbons (C10 to C35) and the isoprenoids, pristane and phytane, and several families of polycyclic aromatic hydrocarbons, including parent PAHs and their C1 to C4 alkyl homologs. GC/MS-SIM data was also generated for the oil biomarker compounds. Since most of the sample residues were heavily weathered, all of the light aromatic hydrocarbons, as well as the normal saturate hydrocarbons below $\sim nC_{20}$ were not present in the samples. As a result, oil source fingerprinting relied heavily on the relative composition of the recalcitrant hopanes, steranes, and triaromatic steroids biomarker compounds

(mass chromatograms 191, 217, 218, and 231). Data will be presented to demonstrate how these relative compositions were changed by weathering over a three year time frame as well as in different coastal environments.

INTRODUCTION:

The Macondo well oil spill resulting from the explosion, fire and sinking of the *Deepwater Horizon* drilling platform is the largest marine oil spill disaster ever experienced in the United States. The release of an estimated 170 to 200 million gallons of oil exposed the nation's largest and most productive marine ecosystem and wetland/estuarine environments to an unprecedented potential for environmental damage. The Louisiana, Mississippi, Alabama and northern Florida coastal environments, which comprises almost 40% of all coastal wetlands of the 48 conterminous United States, is of special concern because of the suite of environmentally and economically important services they provide to the nation. These include hurricane and storm protection, water quality enhancement, faunal support, sedimentation, carbon sequestration, major recreational and commercial fisheries, and commercially important recreational beaches. Approximately 30% of the US commercial fishery production is harvested in this region and these coastal wetlands protect oil and gas infrastructures that provide ~30 % of the oil and 12% of the natural gas to the rest of the US.

The DHOS was a release of a very large quantity of crude oil with complicated circumstances in close proximity to important ecological and economic coastal resources. The full impacts that this oil spill had on both offshore and near-shore/on-shore environments, as well as an understanding of the chemical fate of this spilled oil, are not yet fully elucidated. However, these impacts are clearly related to the changing chemical and physical composition of the oil as it moved and weathered in the coastal environments. Oil spills cause their ecological impacts through a combination of the following three primary mechanisms: 1) direct and indirect toxicity of their components and their respective routes of exposures; 2) oil coatings that causes smothering and/or loss of thermal regulation; and 3) oil component degradations that use up available dissolved oxygen. Further, degradation of significant quantities of oil may impact the ecological balance with unusual enrichment of oil-degrading bacteria and upset the normal marine microorganism populations. Other impacts, such as the effects from exposure to metabolic degradation products of oil, may be important. Additionally, some environmental damage can result from human activities associated with remedial activities.

Typically, all crude oils, regardless of their source, are made up of the same types of molecular hydrocarbon structures. However, the quantities of specific hydrocarbon molecules in crude oil from a given reservoir will depend upon the reservoir's location, depth, and age. So, the same types of compounds are found in all oils, but their respective quantities will vary depending upon the source reservoir. As spilled oil moves in the marine and coastal environments, its composition, and thus physical properties, are continually changing via evaporation, dissolution, emulsification, and microbial and photo-degradation processes. However, these changes occur at different rates and some of the components in oil are degraded very slowly over a time frame of years.

Since the advent of modern GC/MS instrumentation and methodologies, the analysis of the composition of oils from various regions around the world, as well as residues from many spills, have provided insight to the fact that some components in oil and oil residues are very resistant to environmental degradation processes (Wang and Fingas 2003). The result of this insight is that oil from a given source, whether from a deposit or from a spill, has specific compositional fingerprints that are not readily changed by most environmental degradation processes and these compositional fingerprints can be used to trace the movement of oil residues through various environmental compartments until they are eventually mineralized (Roques 1994, Kennicutt 1988, Stout 2001 and 2002).

Oil source fingerprinting initially used ratios of the quantities of alkyl homologs of three and four ringed polycyclic aromatic hydrocarbons and their sulfur containing analogs (Overton 1981). The method was then expanded to include the patterns and ratios of the recalcitrant hopanes, steranes, and triaromatic steroids biomarkers (mass fragments 191, 217, 218, and 231) in oily residues collected following oil spills (Philips and Oung 1988, Wang and Fingas 1995). This concept of employing source oil fingerprinting following oil spills is currently a widely used and recognized technique (Wang and Stout 2007).

During and after the DHOS, samples of the riser oil, and many oily residue in Louisiana coastal marshes that were visually impacted by the spill were collected in the general northern Barataria Bay area. These samples have been analyzed for the following: 1) saturate alkanes from nC₁₀ to nC₃₅, and pristane and phytane; 2) two to six ringed PAHs with the two to four ringed C₁ to C₃ or C₄ alkyl homologs; and, 3) hopanes, steranes, and triaromatic steroid biomarkers. The profiles of the oil biomarkers are of particular interest because it appears as though some of the recalcitrant oil biomarkers were changing over time in Louisiana coastal wetlands. Determining such an occurrence is important so that source oil fingerprinting methodologies can be modified to accurately perform oil-spill related source identification.

MATERIALS AND METHODS:

Chemicals

Macondo well oil was collected by BP from a riser pipe from the damaged wellhead of Deepwater Horizon drilling rig in the Gulf of Mexico on May 20, 2010 and was stored at - 4 °C. Dichloromethane (DCM) (CAS no. 75-09-02) was purchased from Sigma-Aldrich (>99.9% purity). Anhydrous sodium sulfate (CAS no. 7757-82-6) was purchased from Fisher Scientific. The oil analysis standard for calibration and continuing calibrations was purchased from Absolute Standards (Lot #121004) and included n-C₁₀ through n-C₃₅ alkanes, and the parent PAHs.

Sample collection:

Surface sediments were collected from Louisiana coastal wetlands and within 10 m of the shoreline during May 2010 to June 2013. All sediment samples were collected as a composite sample of the upper 5 cm, stored in ice until delivery to the lab, and either immediately extracted or refrigerated until extraction at 4°C for no more than 14 days, as recommended by the US EPA.

Extraction procedures

The sediment samples were extracted using a modified Soxhlet extraction methodology (EPA SW-846 3540C). To be more specific, samples were homogenized and a 15 to 20-g subsample was weighted, dried with pre-cleaned anhydrous sodium sulfate, and then transferred to a Soxhlet extraction thimble. Samples were Soxhlet extracted for a minimum of 12 hours after which the solvent was concentrated, unless gross oil contamination was observed, to a final volume of 1 to 2-ml using rotary evaporation and blow-down with nitrogen gas.

GC/MS instrumentation

Chemical analyses were performed using an Agilent 7890A Gas Chromatograph (GC) (Santa Clara, CA) equipped with an Agilent 5975C inert XL mass selective detector (MSD) and fitted with a 5% diphenyl/95% dimethyl polysiloxane high resolution capillary column (Phenomenex Zebron, 30 m long, 250 μ m diameter and 0.25 μ m thick film). The GC injection temperature was set at 280°C and only high-temperature, low thermal-bleed septa were used in the GC inlet. The carrier gas was ultrahigh purity helium (Air Liquide, Houston, TX) at a constant flow rate of 1 ml min⁻¹. The injection port was set at 280 °C, run in splitless mode and was fitted with a single tapered deactivated borosilicate liner. The oven temperature program was as follows: the initial temperature was set to 60 °C and was held for 3 minutes; the temperature was then increased to 280 °C at a rate of 5 °C min⁻¹ and held for 3 minutes. The oven was then heated from 280 °C to 300 °C at a rate of 1.5 °C min⁻¹ and held at 300 °C for two minutes.

The MSD was operated in the selective ion monitoring (SIM) mode to ensure low level detection of the target constituents associated with crude oil in sediment samples. In addition to detection of the saturate hydrocarbons (SIM ion 57) and the PAHs (SIM ions 128, 166, 178 184, 202, 228, 234 252, 276, and 278), the C1 to C4 alkyl homologs of the two to four ringed PAHs, and the hopanes, steranes, and triaromatic steroids biomarkers (SIM ions 191, 217, 218, and 231) were acquired. During the 2010 time frame, extracts were only analyzed for the hopanes and steranes biomarker ions (SIM ions 191 and 217); thereafter, the full suite of oil biomarker ions were used for biomarker fingerprinting.

RESULTS AND DISCUSSION:

Figure 1 shows the SIM ion chromatograms for the fresh MC252 Riser oil and a weathered oily residue collected from northern Barataria Bay. The figure begins with the examination of the SIM ion 57 profile (n-alkanes and isoprenoids) that reveals significant weathering of the oily residue detected has occurred. The profiles thereafter in the figure compare the oil biomarkers from fresh MC252 and the oil residue in the sediment sample; and, as expected, the profiles of the hopanes and steranes of the weathered oil are nearly identical to those from the MC252 Riser oil. The red dots in Figure 1 indicate particular groups of biomarker peaks (compounds) that are typically used for source fingerprinting.

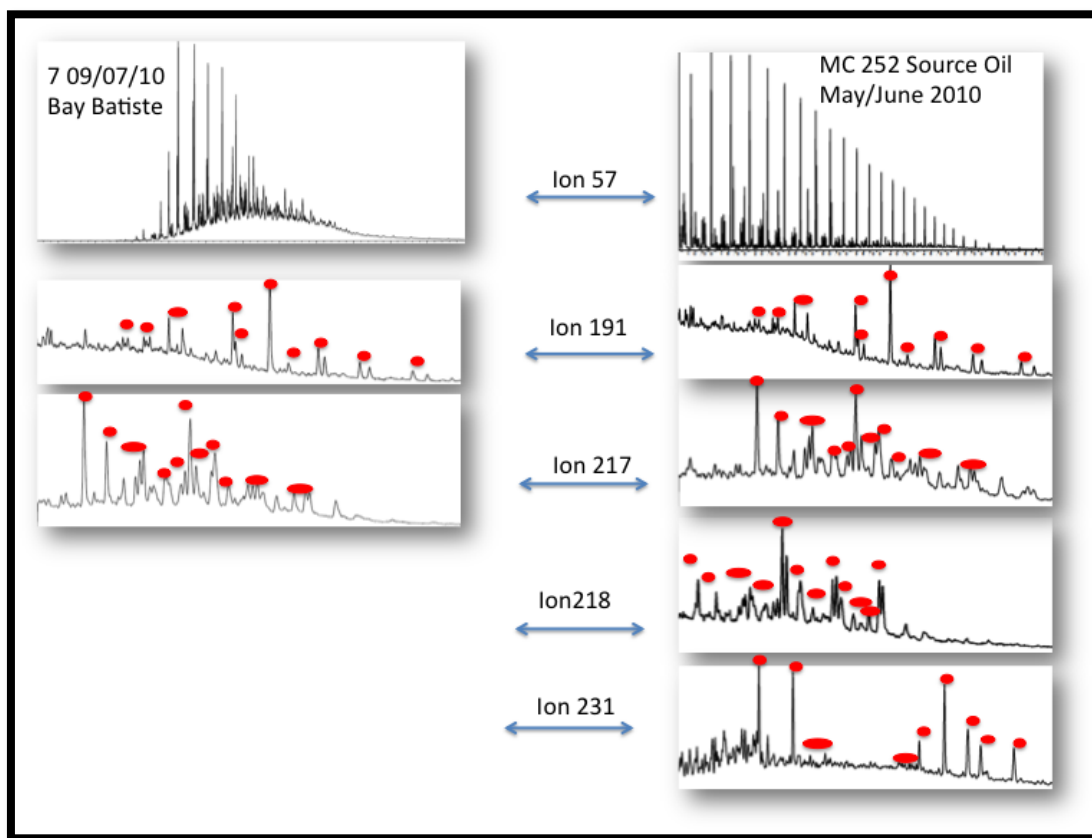


Figure 1: Ion chromatograms for the saturates (m/z 57) and hopanes and steranes biomarker compounds in the MC252 Riser Oil and a residue collected in September 2010 from a heavily oil marsh in northern Bay Batiste.

Figure 2 shows profiles of samples with oily residues collected from impacted areas (in general, northern Barataria Bay; specifically Wilkerson Bay and Bay Jimmy) one year after the spill. The saturate profiles at the top of the figure suggest that these samples were heavily weathered with no resemblance to the normal alkane distribution seen in un-weathered oil. In fact, the samples contained normal background hydrocarbons in addition to hydrocarbons from an oily residue. Again, careful examination of the oil biomarker profiles indicated very modest differences in the between sediment samples collected one year after the spill compared to un-weathered MC252 Riser oil.

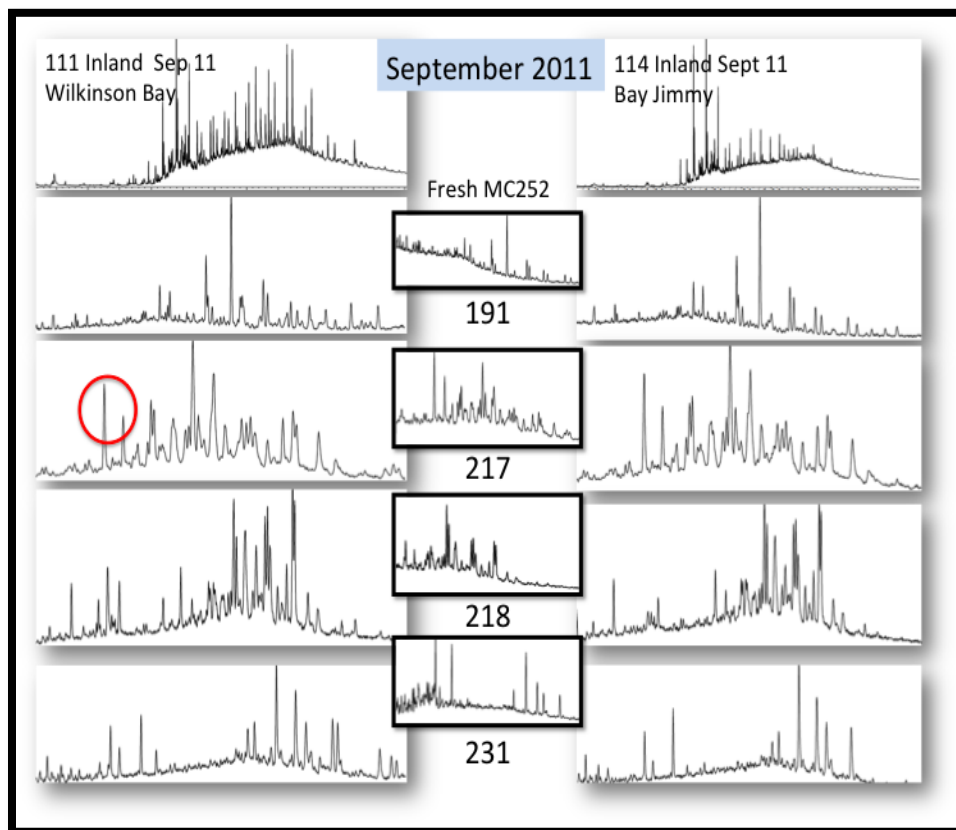


Figure 2: Ion chromatograms of two oily residues collected from visually impacted areas in northern Barataria Bay. The biomarker profiles of the un-weathered MC252 Riser oil are shown for comparisons.

Figure 3 shows typical data collected in September 2012 from heavily impacted areas in Bay Batiste. The sample “8 RET” has very similar biomarker profiles as MC252 oil; yet, in sample “9 RET”, the biomarker profiles are significantly changed from the source oil. In fact, using conventional thought, this sample would be declared as a non-match with the MC252 source oil. Many samples from the same general geographical location documented as heavily impacted by the *Deepwater Horizon* disaster had biomarker profiles similar to “9 RET”. However, it seems unlikely that this oily residue originates from anything other than MC252 oil. We believe this sample and others with similar oil biomarker profiles illustrate how these normally recalcitrant-to-weathering compounds are being degraded in Louisiana’s coastal marshes.

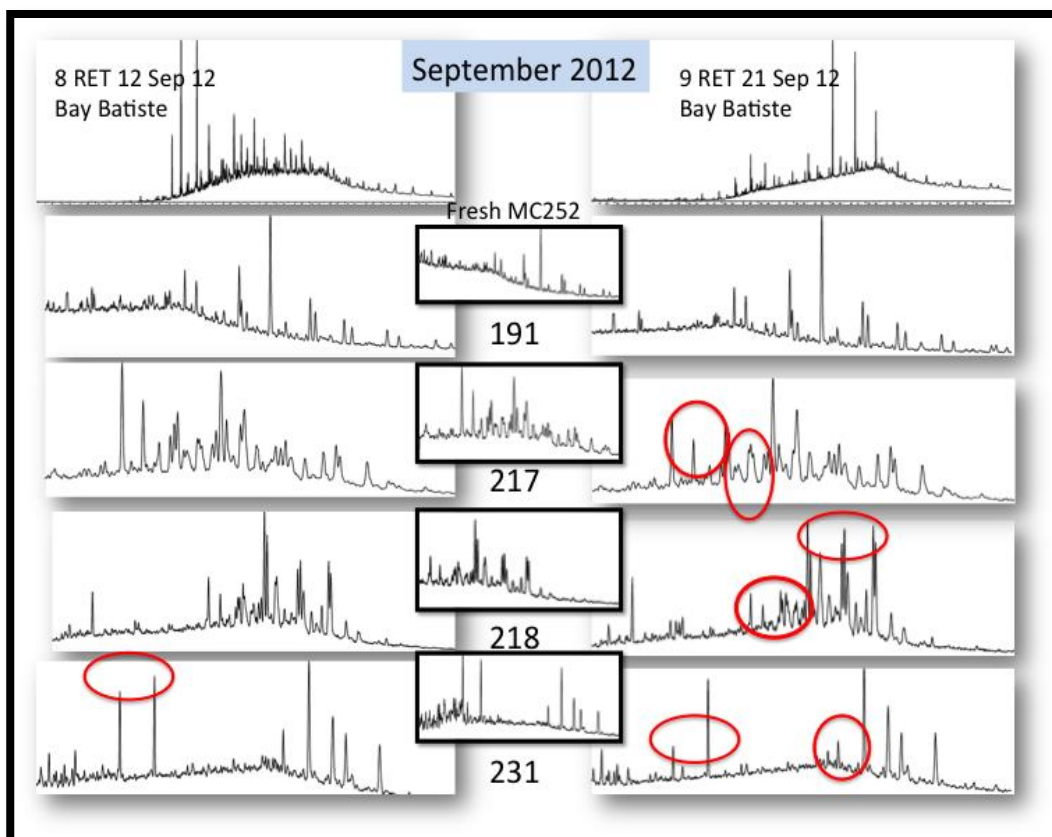


Figure 3: Biomarker ion profiles of heavily weathered oily residues collected from visually impacted areas of Bay Baptiste in September 2012.

Figure 4 shows the oil biomarker profiles of two additional sediment samples collected in 2012 from Bay Batiste. Again, the profiles are significantly different from the MC252 source oil but are nearly identical to each other. We believe this demonstrates the possible progression of weathering changes on the profiles of the hopanes, steranes, and triaromatic biomarkers in MC252 oil in coastal Louisiana environments over the course of three years. Interestingly, in all of the profiles shown in Figures 1 through 4, the 191 ion profile of the hopanes remains virtually unchanged. Clearly, not all oil biomarkers weathered at the same rate over this three year interval.

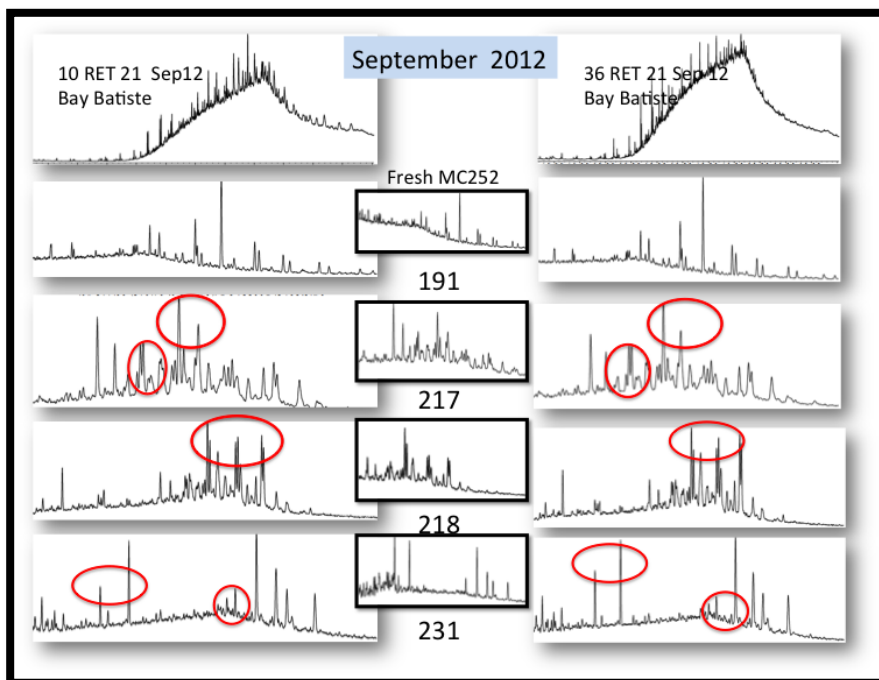


Figure 4: Biomarker ion profiles of heavily weathered oily residues collected from visually impacted areas in Bay Baptiste in September 2012.

CONCLUSION AND FUTURE STUDY:

Source oil fingerprinting is a highly useful and reliable environmental forensics technique that can match oily environmental residues to a potential source oil. However, it is normally used when comparing fairly fresh spilled oil to suspected sources. The hopanes, steranes, and triaromatic steroids oil biomarkers detected by GC/MS analytical methodology during normal oil spill situations are generally not degraded by weathering so selected ratios in these ion chromatograms remain nearly unchanged compared to the source oil. However, data presented in Figures 2, 3 and 4 provide evidence that extensive weathering can cause changes in some of these normally recalcitrant compounds. Environmental weathering is a complex process that includes evaporation, dissolution, photo-degradation and various routes of microbial change (aerobic and anaerobic, sulfate and nitrate degradations). Additionally, some relatively unweathered mousse residues that were buried in coastal wetlands are getting redistributed by erosion events and these undergo additional microbial aerobic degradation. The next step is to see if we can determine why some oil biomarker profiles seems unaffected by weathering and

other oil biomarker profiles are significantly altered in a marsh environment. Clearly oil degradation processes in marsh environments are highly complex due to different chemical events (e.g. aerobic and anaerobic conditions, different mineral contents) and physical events such as continuous tidal washing and high energy storm events.

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