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Research Brief: Is Submerged Deepwater Horizon Oil Degrading Offshore?

Comparison of the Chemical Signatures of Tar Mat Samples Deposited by Tropical Storm Lee in September 2011 with Oil Mousse Samples Collected in June 2010

Beginning in early June, 2010, a considerable (but unknown) amount of oil began washing onto the white sandy beaches of the northern Gulf of Mexico. Oil deposition along Alabama's shoreline was substantial, at least until about mid-July, 2010 *(1)*. The oil first arrived on the shores of Alabama predominantly as water-in-oil emulsified mousse. Figure 1 shows floating oil mousse that arrived on June 9, 2010, near Perdido Bay and the Florida-Alabama border. Our research team collected and archived samples of this floating mousse. A portion of the floating oil eventually settled to the bottom, forming what is commonly referred to as "submerged tar mats" *(2)*.

Of particular concern to many, not least of whom are the Alabama communities along this shoreline (Orange Beach, Gulf Shores, Baldwin County, and Dauphin Island), is the potential for remobilization and beach deposition of oil associated with submerged tar mats as a result of enhanced near-shore beach energy induced by large storm events. The primary reason for this concern is that oil in submerged tar mats is expected to chemically degrade more slowly than oil within the larger beach system. This concern was acknowledged by the federal government's Operational Science Advisory Team (OSAT), in their second report entitled *Summary Report for Fate and Effects of Remnant Oil in the Beach System*), although no attempt was made to determine actual submerged oil degradation rates *(2)*. Recently it has been shown that the concentrations of a subset of polycyclic aromatic hydrocarbons (PAHs) present in submerged tar mat samples collected from near-shore water off Alabama's beaches closely resembled raw crude oil collected from the MC252 (Deepwater Horizon) well *(3)*. Similar observations regarding the recalcitrance to weathering of submerged oil from past oil spills have been made at other oil spill sites *(2- 4)*.

In order to address the concerns related to tar mat mobilization by forecasted storm events, on August 29, 2011, our research team performed a limited SCUBA reconnaissance survey off the coast of Orange Beach at locations where tar mats were suspected to be present (based on earlier field work). During our survey, conducted at three different sites (each about 50 m^2) located approximately 200-300 m from the shoreline, we found no visual evidence of tar mats. However, a careful assessment of the shoreline indicated small tar balls (few millimeters to centimeters in diameter) in the swash zone over the entire length of coastline from the Florida-Alabama border to Fort Morgan, Alabama (greater than 30 miles). Our interpretation of these observations is that submerged tar mats buried off-shore of this coastline are breaking apart to yield these tar balls.

The first effects of Tropical Storm Lee began along the Alabama coast on September 2, 2011 and lingered for over two days. Our research team was present before, during, and after this storm event. The storm resulted in considerable perturbation to shoreline morphology and mobilization of sand along the shoreline. Figure 2 shows debris deposition patterns observed by our team on Orange Beach, Alabama on September 8, 2011. Immediately following the storm (and continuing today), we observed BP workers actively removing oil from shoreline areas having substantial oil impacts. Thus, the actual extent of remobilization of submerged tar mats (and subsequent beach deposition) is uncertain. BP's cleanup efforts were clearly useful to beach users and local communities. However, these activities also

Figure 1. Deepwater Horizon-related emulsified oil on Alabama's coast (June 11, 2010).

Figure 2. Post-tropical storm Lee oil and other debris deposited along Orange Beach, Alabama shoreline in September 8, 2011.

removed useful information regarding how offshore tar mats will respond to high energy storm events. It is our recommendation that future deposition events be carefully documented by local authorities before any active cleanup is initiated.

Since our research team was physically present during and after the arrival of Tropical Storm Lee, we were able to collect a number of fresh submerged tar mat samples mobilized by the storm (Figure 3). These samples provided a unique opportunity to test the prevailing hypothesis that most of the oil in submerged tar mats has been degraded. We located a number of large (tens of centimeters in diameter) tar mat samples in the surf zone at several locations along Alabama's coastline. These samples had a strong hydrocarbon odor and our visual observation indicated the sample looked very similar to fresh oil mass deposited on these beaches more than a year earlier. These samples were preserved and transported to our laboratory at Auburn University for chemical analysis.

Tar mat samples were analyzed for PAHs at our NSF-funded facility using a recently developed Agilent Technologies triple quadrupole GC/MS/MS (7000B) system. This system is equipped with a high sensitivity electron impact ionization source (EI) that improves sensitivity across the entire mass range selected in the experiments. One of the time-consuming steps in applying standard GC/MS methods to test oil contaminated sediment is the sample cleanup step. The Agilent triple quadrupole GC/MS/MS system is an excellent instrument for target compound analysis when used in the multiple reaction monitoring (MRM) mode. The triple quad system has increased selectivity that helped us to process samples rapidly with minimal cleanup. Also, our system is equipped with a back flush column that allows back-flushing of high molecular weight compounds. Back-flushing the GC column shortens run times, extends column life, reduces chemical background noise, provides consistent retention times and spectra, and keeps the MS ion source clean.

The tar mat sample was dried and was then extracted and cleaned using laboratory procedures discussed in Clement et al. *(5)*. Emulsified oil mousse samples collected on June, 11, 2010 were also prepared using similar laboratory procedures. In addition, a subsample of the tar mat sample was sequentially extracted in organic solvents to remove all oil. The

Figure 3. Submerged tar mat sample collected from surf zone immediately after Tropical Storm Lee (scale in inches; collected September 8, 2011).

remaining inorganic sand and shell materials were dried and it was estimated that the tar mat contained approximately 17% oil by mass. This is an important result which indicates that every kilogram of oil that reached the Alabama shoreline had the potential to create about 5 kg of submerged tar mat.

For the GC/MS/MS-based MRM analysis, we extracted 0.44 grams of mousse and 2.53 grams of tar mat samples using 40 ml of solvent mixtures. The final samples were spiked with four isotopically-labeled internal standards prior to analysis. All measurements were repeated at least five times to verify the reproducibility of the analytical method. Quantification of PAHs was made using calibration samples prepared from PAH standards purchased from Ultra Scientific Inc.

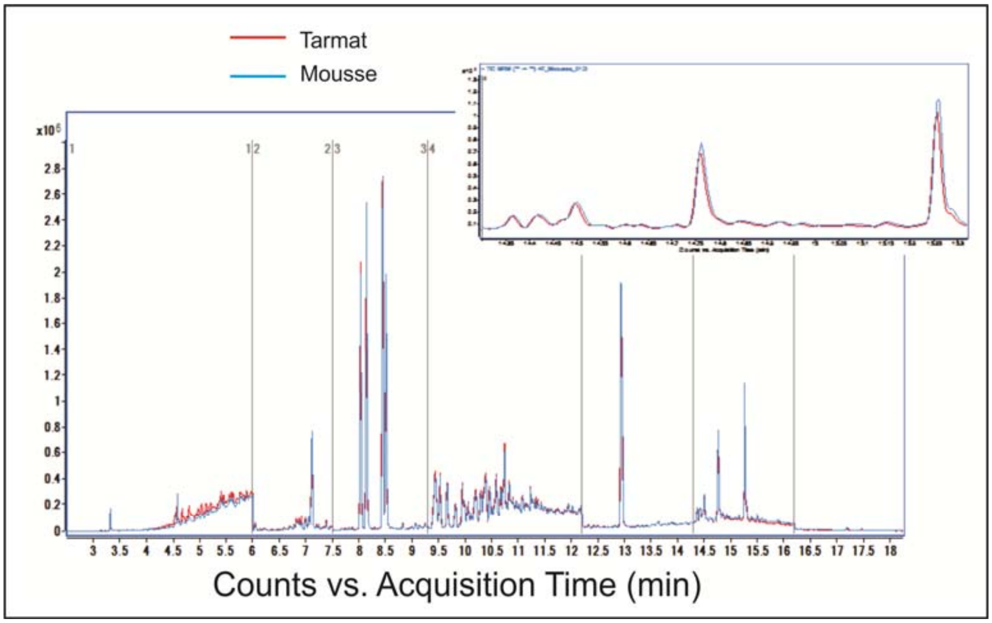

Figure 4. PAH-ion selective MRM total ion chromatogram comparing mousse sample (June, 2010) with submerged tar mat sample (September 8, 2011). Inset shows detail between approximately 14-15 minutes.

Figure 4 shows the MRM chromatogram of a mousse sample (collected on June 11, 2010) and a tar mat sample (collected on September 8, 2011). This figure shows that the chemical signatures for both samples are essentially identical. Figure 5 shows the concentrations of various PAH constituents present in the two samples. The data indicate that the concentration of various PAH compounds in both samples are remarkably similar.

IMPLICATIONS OF THE STUDY

This study indicates that the tar mat fragments that appeared on Alabama's beaches after Tropical Storm Lee and the emulsified oil that impacted Alabama's beaches in June 2010 have essentially identical MRM total ion chromatograms (GC/MS/MS fingerprints). In addition, the concentration and relative quantity of PAHs in submerged tar mats present off Alabama's beaches today have not substantially changed from those present in the emulsified oil which arrived over a year ago. These findings are important in a number of ways. First, the results indicate that the tar mat samples are indeed related to the BP Deepwater Horizon event. Also, the data question the validity of the widely held belief that submerged oil from the Deepwater Horizon accident is substantially weathered and thus depleted of most PAHs. Also, it supports the hypothesis that submerged oil may continue to pose some level of long-term risk to near-shore ecosystems. This storm event demonstrates the potential for remobilization by similar storm events in the future. However, the magnitude of such future events cannot be determined *a priori* with any level certainty. Finally, our data questions the commonly used phrase "tar mat." The results presented here make a case that the submerged material are not highly weathered recalcitrant tars (implied by the term "tar mat.") Rather, they appear to be relatively fresh and similar to the oil that impacted Alabama's beaches in June of 2010. Hence, referring to these materials as submerged "oil mats" rather than "tar mats" is perhaps better terminology.

Disclaimer: This is not a human health assessment. The findings of this study are based on small discrete samples and have no direct relevance to human health impacts.

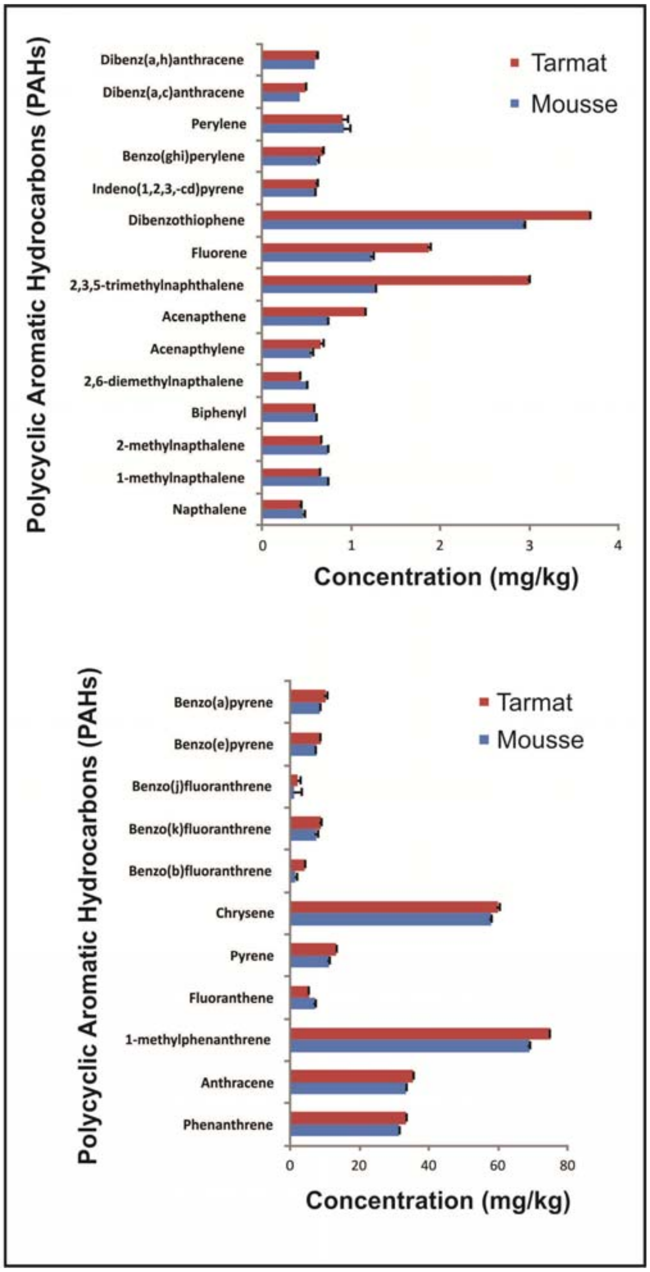

Figure 5. Comparison of PAH concentrations in mousse (June 2010) and submerged tar mat (September, 2011) samples.

AUTHORSHIP AND ACKNOWLEDGEMENT

The article was jointly authored by Dr. T. Prabhakar Clement, Feagin Chair Professor of Environmental Engineering (clement@auburn.edu), Dr. Joel S. Hayworth, Associate Research Professor of Environmental Engineering (jsh@auburn.edu), and Dr. V. Mulabagal, Research Associate. Department of Civil Engineering graduate students Yin Fang and Gerald F. John helped with the analytical work and data analysis. Undergraduate students S. Parker Ross and William Wright assisted with field work. This work was supported in part by funding received from the City of Orange Beach, Alabama, the National Science Foundation (NSF), Samuel Ginn College of Engineering, and from the Marine Environmental Sciences Consortium (MESC).

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