

**OPERATIONAL SCIENCE ADVISORY TEAM**  
**SUMMARY REPORT FOR FATE AND EFFECTS OF REMNANT OIL REMAINING**  
**IN THE BEACH ENVIRONMENT**

**ANNEX C: WEATHERING AND DEPLETION OF OIL**

**Introduction**

Annually, natural petroleum seeps release more than 17 million gallons (404,750 barrels) of oil into the Gulf of Mexico. The *Deepwater Horizon* oil spill released more than 211 million gallons (4.93 million barrels) of light, sweet crude oil into the Gulf (the term “light” refers to oil with relatively few impurities and a lower density than “heavy” oil; the term “sweet” refers to oil that is lower in sulfur content than “sour” oil). An estimated 25 percent of this volume was burned or collected, leaving the remainder available for natural attenuation or collection along shorelines. When oil is released into the environment, it weathers due to various hydrologic and chemical factors. Weathering affects both the chemical composition of the oil and its physical properties. Knowledge of the oil properties before and after weathering is needed for predicting the transport and fate of oil in various locations of the ecosystem, and also needed for the selection of various remediation alternatives. This section discusses oil weathering as the oil was transported from the wellhead to beaches and the continued weathering of oil on sandy beaches.

**Physical and Chemical Properties of Oil**

Every oil is a unique mix of compounds that contributes to or defines the oil’s physical and chemical properties, such as color and viscosity, as well as its toxic impact to exposed organisms. The highly variable chemistry of crude oil and petroleum products means that the range of compounds in the complex mixture spilled at the outset of an incident will be large. This initial oil composition, however, is not constant over time, and begins changing immediately in response to the environment where the oil is discharged. The factors of oil weathering in marine systems has been reviewed extensively (Patin 1999, ITOPF 2002, National Research Council Committee on Oil in the Sea: Inputs 2003, Shigenaka 2010) and are briefly summarized here.

Physical Properties

Physical properties affecting the fate and behavior of oil and petroleum products in the environment include viscosity, density, flash point, pour point, distillation, and interfacial tension. These properties are important to predicting oil spread, ease of collection or burning, and penetration into sediments (including beaches).

Chemical Properties and Hydrocarbon Groups

Crude oil on average has an elemental composition of 84.5 percent carbon, 13 percent hydrogen, 1.5 percent sulfur, 0.5 percent nitrogen and 0.5 percent oxygen (Fetter 1999). While oil molecules may eventually break down or metabolize into simpler compounds and support the growth of oil-degrading microorganisms that form the basis of food webs, the molecular composition of freshly spilled oil and the initial stages of decomposition are important to understand. The most commonly found hydrocarbon molecules in petroleum are alkanes (linear

or branched), cycloalkanes, monocyclic and polycyclic aromatic hydrocarbons (PAHs – as distinguished into two major groupings in Table 1), and larger, more complex chemicals such as asphaltenes and resins.

Number of rings	Analytes
2-3	Acenaphthene, Acenaphthylene, Anthracene, Biphenyl, C1-Dibenzothiophenes, C1-Fluorenes, C1-Naphthalenes, C1-Phenanthrenes/Anthracenes, C2-Dibenzothiophenes, C2-Fluorenes, C2-Naphthalenes, C2-Phenanthrenes/Anthracenes, C3-Dibenzothiophenes, C3-Fluorenes, C3-Naphthalenes, C3-Phenanthrenes/Anthracenes, C4-Dibenzothiophenes, C4-Naphthalenes, C4-Phenanthrenes/Anthracenes, Dibenzofuran, Dibenzothiophene, Fluorene, Naphthalene, Phenanthrene
4-7	Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(e)pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, C1-Chrysenes, C1-Fluoranthenes/Pyrenes, C2-Chrysenes, C2-Fluoranthenes/Pyrenes, C3-Chrysenes, C3-Fluoranthenes/Pyrenes, C4-Chrysenes, Chrysene, Dibenz(a,h)anthracene, Fluoranthene, Indeno(1,2,3-cd)pyrene, Perylene, Pyrene

Table 1. Groupings of polycyclic aromatic hydrocarbon (PAH) analytes.

### Weathering of Oil and Chemistry of Deepwater Horizon Oil

Complex processes of oil transformation in the marine environment develop from the first moment the oil makes contact with seawater. As *Deepwater Horizon* oil rose up from the well and mixed with seawater, it began to separate into different fractions, which subsequently became associated with different physical locations in the nearshore and onshore beach environments. Storms and active turbulence generally speed up the dispersion of the surface slick and its fragments. A number of weathering (or decomposing) processes act on the oil. These processes are described in Table 2.

Weathering Processes	Description
Dissolution	As oil mixes with water, low molecular-weight aliphatic and aromatic hydrocarbons dissolve into the water column.
Evaporation	Within a few days following a spill, light crude oils can lose up to 75 percent of their initial volume and medium crudes up to 40 percent (Fingas 1994). Lost components of oil include lower molecular weight toxic benzene, toluene, ethyl benzene, and xylenes (BTEX) (Neff et al. 2000, ITOPF, 2002).
Photo-oxidation	The final products of photo-oxidation (hydroperoxides, phenols, carboxylic acids, ketones, aldehydes, and others) usually have increased water solubility. Experiments show that these products have increased toxicity as well. The reactions of photo-oxidation, photolysis in particular, initiate the polymerization and decomposition of the most complex molecules in oil. These reactions increase the oil's viscosity and promote the formation of solid oil aggregates.

Microbial degradation	The degree and rates of hydrocarbon biodegradation depend on the complexity of oil molecules, degree of dispersion, temperature, concentration of nutrients and oxygen, and species composition and abundance of oil-degrading microorganisms. Petroleum compounds generally degrade under aerobic conditions. Buried oil tends to be smeared over the sediments and could biodegrade provided there is sufficient moisture, nutrients, and oxygen (among others) available.
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Table 2. Marine weathering processes. Modified from (Patin 1999)

In Key Findings of the OSAT 1 report, authors concluded that:

*“Published research indicates that MC252 oil is weathering and biodegrading under natural conditions. Estimates of weathering and degradation rates vary, precluding the use of simple empirical models to assess the persistence of residual MC252 oil.”*

While published research on MC252 oil showed the expected decomposition of alkanes, the OSAT 1 report acknowledged that “the degradation rates for the complete mixture of compounds that characterize MC252 oil have not yet been determined.” (OSAT 2010). The OSAT 2 team evaluated available datasets and one new round of residual oil samples to further explore the character of weathered *Deepwater Horizon* (DWH) oil.

Supratidal buried oil and tar ball samples collected from sand beaches between October 2010 and January 2011 are substantially depleted of the light molecular weight PAHs (2-3 rings; greater than 86 percent depletion). Although the higher molecular weight PAHs (4-6 rings) have also been depleted compared to the source oil, some tar ball samples still have measureable amounts of these more persistent analytes (Figure 1). The depletion of these samples follows a bell-shaped curve, with PAH depletion ranging from 68 to 98 percent.

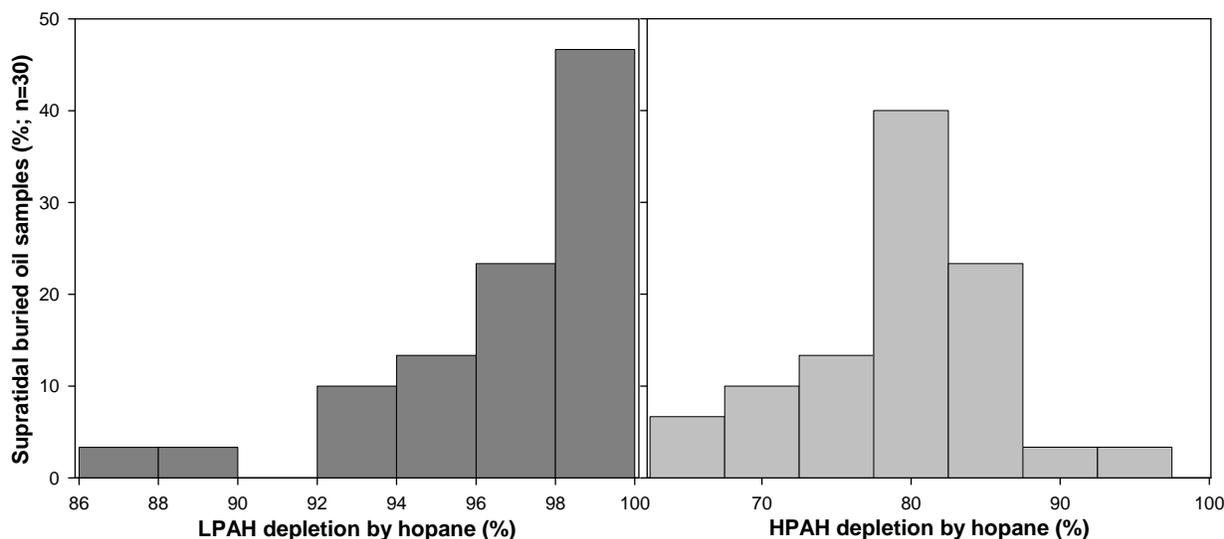


Figure 1. Depletion of low (2-3 rings) and high (4-7 rings) molecular weight PAHs (LPAH and HPAH, respectively) in supratidal buried oil tar ball samples (n = 30).

PAH depletion by hopane is calculated by:

$$(1 - ((\text{Sum PAH sample} / \text{Sum PAH source oil}) * (\text{Hopane Source oil} / \text{Hopane sample}))) * 100$$

Percent depletion of the low and high molecular weight PAHs relative to the more weather resistant hopane provides a conservative estimate of oil depletion in the sample relative to the source oil.

One sample of each of the three forms of oil was collected for chemical analysis from four representative sandy beaches impacted by the DWH oil spill: Grand Isle, Louisiana; Petit Bois, Mississippi; Bon Secour, Alabama; and Fort Pickens, Florida. This limited sampling indicates that all three forms of oil collected in Grand Isle showed similar chemical composition (TPAH range: 3,989-4,292 mg/kg oil), and are relatively less weathered (i.e., higher concentration of the lower molecular weight PAHs) than samples from the other locations (Figures 2 and 3). Of the four sites, Petit Bois had the most weathered residual oils (TPAH range: 288-415 mg/kg oil) as indicated by presence of the higher molecular weight PAHs. Submerged oil mats from Bon Secour and Fort Pickens had the highest concentrations of individual PAHs and are less weathered than the other forms of oil found within these areas. The SOM are the least weathered oil residues, and could persist in the environment in the absence of the high physical energy encountered in the wave-break zone of the beaches, where the SOM most often occur. The above comparisons indicate that weathering processes of the residual oils, even within the same areas, may vary, and that site-specific processes and dynamics will influence the fate of the residual oil.

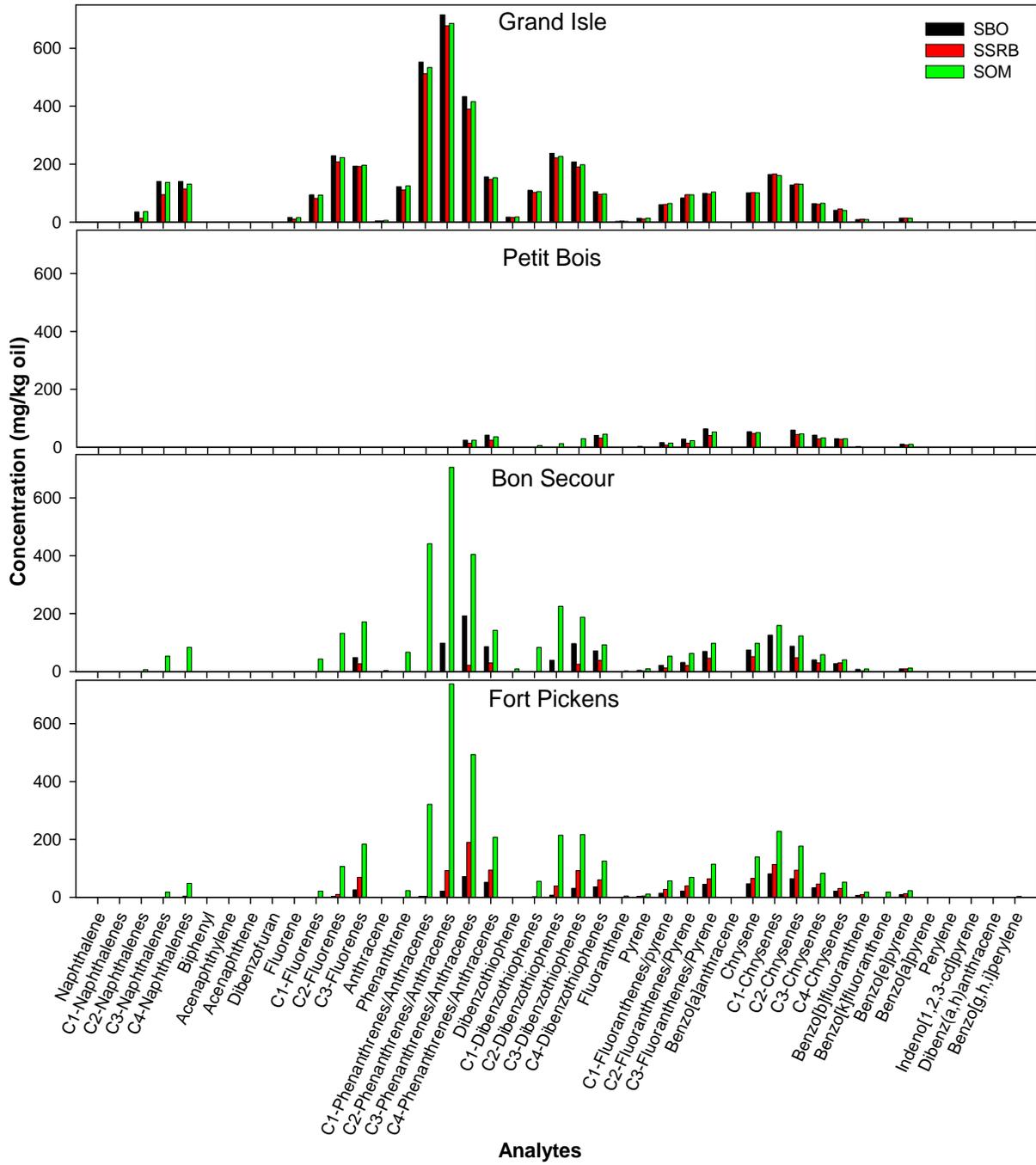


Figure 2. Comparison of the PAH composition of the three forms of residual oil found within representative beach habitats for each of the four States. Submerged oil mats= SOM; small surface residue balls= SSRB; supratidal buried oil= SBO.

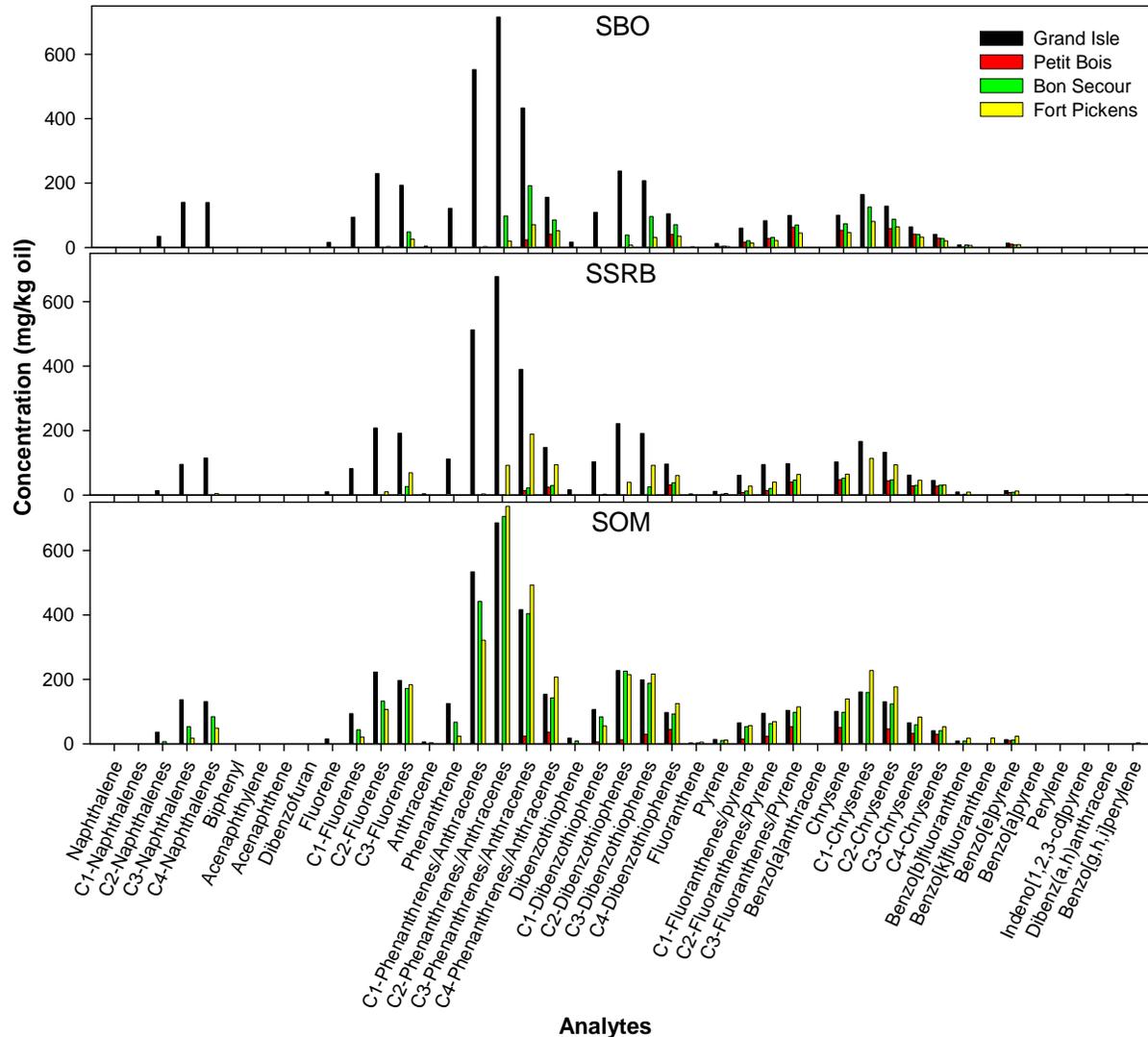


Figure 3. Comparison of the PAH composition of the three forms of residual oil found across representative beach habitats for each of the four States. Submerged oil mats= SOM; small surface residue balls= SSRB; supratidal buried oil= SBO.

All of these various weathering processes begin transforming the original source product into a mixture with different physical and chemical characteristics, and thus, different toxicities. For example, Neff et al. (2000) found that artificially weathering different oils changed their chemical composition and their relative toxicities. They identified the monocyclic (mononuclear) aromatic hydrocarbons as the most acutely toxic fraction of the oils tested. However, with weathering, the proportion of monocyclic aromatic hydrocarbons decreased and the contribution of PAHs (which are a much smaller component of fresh oil) became the primary fraction contributing to toxicity. Oil toxicity and the compounds contributing to toxicity therefore change during weathering and over time, and weathering does not cease once oil reaches shorelines. The oil addressed in OSAT 2, supratidal buried oil, SSRBs, and submerged oil mats, continues to be influenced by weathering processes, as described below (Table 3).

Weathering Drivers	Supratidal buried oil	Small surface residue balls (SSRBs)	Submerged oil mats
Wind (northwestern winds)	Will expose buried oil, which will facilitate further weathering.	Will continue to erode SSRB surfaces.	May cover submerged oil mats preventing further erosion of its surface.
Storms (tropical storms and hurricanes)	Will expose and move buried oil, potentially deeper, resulting in slower decomposition, or potentially back into nearshore conditions of active degradation.	Will provide moisture to increase microbial degradation; will redistribute and either expose oil to weathering processes or cover or limit processes due to sand cover.	May facilitate the redistribution of residual oil (i.e., smaller mats, tar balls).
Photo-oxidation	Will not occur.	Sand coating will restrict the rate of this process (Winters et al. 1985).	Sand coatings, turbid water will restrict the rate of this process (Winters et al. 1985).
Microbial degradation	Limited by moisture and nutrients.	Sand coating will restrict the rate of this process.	Coarse sand (AL and FL) will ensure that pore water in the unsaturated zone has sufficient oxygen. Surf zone turbulence and movement may help keep oxygen levels high, but sand coating will inhibit exchange/degradation.

Table 3. Shoreline weathering processes.

Rates of weathering are driven as much by environmental factors as the potential of oil to degrade (Atlas 1981). In the intertidal zones, oil persistence has been attributed to differences in beach erosion and accretion processes, as related to beach geomorphology, and wave, tide and storm dynamics. That is, high energy shorelines will see more rapid breakdown of buried oil, while low energy beaches risk slower decomposition and greater potential for transport to groundwater (Bernabeu et al. 2006, Bernabeu et al. 2009). Marine bacteria continue to metabolize and degrade oil in this low energy beach zone.

Several studies have documented the persistence of oil residue constituents in nearshore habitats. A few years after the *IXTOC* oil spill, samples of seagrass growing within oil mats contained 6 times more aliphatics (predominantly C12-C19 and above) and at least 15 times more aromatics than those samples collected from areas without visible oil (Baca, 1982). Culbertson, et al., (2007) found that several decades after the 1969 *Florida* barge spill in Buzzards Bay, MA, moderately degraded oil residue remained 8-20 cm below the surface. Volatile and more water-soluble compounds, n-alkanes, and acyclic isoprenoids were depleted, but alkyl cyclohexanes, alkylbenzenes, and PAHs, as well as many other unresolved complex mixtures (UCM; n-C10 to

n-C26 alkanes), still persist. Long-term studies on the persistence of oil residues from the 1970 tanker *Arrow* spill found substantial quantities of the weathered oil in the form of stratified layers within the sediments (Lee et al. 2003). Asphalt pavements, oil mats, and traces of sheen and residual oil are still present along the shoreline and within the sediment. Although all of the alkanes, iso-alkanes and the more water soluble aromatics ( $K_{ow} < 4$ ) (octanol:water coefficient; low values indicate that the compound is very water soluble) were depleted from sediment samples, high molecular weight alkyl PAH homologues (chrysenes) and biomarker compounds (triterpanes- C25, C28 and C29, steranes and hopanes-C30) still remain in the sediments.

In March 1978, the tanker *Amoco Cadiz* spilled large quantities of crude oil when it landed near the beaches of Brittany, France. Vandermeulen et al. (1979) observed that the spilled oil transformed or weathered into different fractions that impacted and penetrated the beaches differently. They categorized the oil states as oil sheens, early mousse, and late mousse. Oil sheens covered large areas of water and were deposited over the complete tidal range of the shore during ebb tides. In some locations, sheen oil readily penetrated into porous sediments. Mousse, on the other hand, penetrated only slightly into porous sediments. Early mousse readily clung to marsh grasses and became buried with subsequent sand deposits. Late mousse accumulated sand, increasing its density and was deposited in less energetic subtidal zones. Hydrocarbons were measured using a spectrofluorimetric method and were not separated into different fractions, i.e., aliphatic and aromatic compounds. Two types of beach oiling were observed: (1) low level homogenous oiling of the sand column; and (2) burial of discrete high oil concentration layers. In some locations, up to four distinct oil layers were observed. The authors suggest that sheen oil was more likely to percolate through the sandy beaches while mousse was the major component of the buried layers of oil. Oil buried in this manner became immobile until the onset of winter storms and associated beach erosion.

Two basic mechanisms for subsurface pollution of beaches are penetration, or downward percolation (leaching) of oil, and burial, by way of beach dynamics. Geologic factors such as grain size, burrows and “bubble sand” can influence persistence of oil in beaches (Hayes et al. 1993). Influences of mangrove root systems on oxygen levels can also lead to persistence of oil along shorelines (Corredor et al. 1990). Distinct stratification of buried oil layers indicates that storm events, most notably Hurricane Alex, have shifted sands on Gulf beaches and have buried oils. Results of the Shoreline Cleanup and Assessment Technique (SCAT) surveys in the four-State Gulf coast region show that oil layers can be found deeper than 1 meter below the surface of sand beaches. Although biodegradation is found to occur even at the base of dunes on sandy beaches (Daniels et al. 1995), buried oil can be persistent because degradation slows with increasing depth and decreasing aerobic activity (Teal et. al, 1978, Hayes et al., 1993, Burns et al. 1994, Li and Boufadel, 2010; Boufadel et al., 2010). Oxygen limitation should not occur in the unsaturated zone of sandy beaches due to the presence of air in the interstices of the sediments. Moisture availability could be limiting if it reaches low values (less than 10 percent of the porosity). However, a study by Fallgren et al. (2010) showed that the microbial activity at 30 percent of the porosity is higher than observed for saturation at 70 and 90 percent. In some cases, weathering may result in significant chronic toxicity (Carls et al., 2003, Peterson et al. 2003, Bernabeu, et. al 2009), because weathering depletes oil residues of the lower molecular weight and more acutely toxic PAHs (i.e., naphthalenes), while enriching oil residues with the higher molecular weight and more chronically toxic PAHs (i.e., chrysene). Samples collected in

2001 and 2005 from sand beaches impacted by the 1989 *Exxon Valdez* oil spill contained well-preserved n-alkanes and PAHs, and semi-liquid oil, highly adhesive on contact with dry surfaces (Short et al., 2007). Abundant organic matter and soil texture (Pereshki et al. 2000) are important in natural degradation. In supratidal water-limited environments, continuous wetting of the sediments would play a critical role in the ultimate breakdown of oil.

The degree and rate of weathering of Deepwater *Horizon* oil is still uncertain. Better understanding of the degradation processes of oil in the environment is still needed. A team from Temple University through the Interagency Alternative Technology Assessment Program (IATAP) studied oil degradation using the model BIOMARUN. The U.S. Geological Survey provided a second modeling study using the SEAM3D platform. The objective for these models was to provide temporal and compositional estimates of degradation processes. These models are described in the following annexes of the OSAT 2 report. The predictions of these models should be validated by a long term monitoring program that can be conducted through the Natural Resource Damage Assessment process or other research or compliance programs.

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