Chapter 16

Assessing the Increase in Background Oil−Contamination Levels Along Alabama's Beaches Resulting From the Deepwater Horizon Oil Spill

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Chapter Outline

16.1 INTRODUCTION

Alabama is home to several pristine, white sandy beaches. The economy of Alabama's Gulf Coast region is intricately tied to the tourism industry associated with these beaches. The quality of these amenity beaches and the economy of the tourism industry were severely impacted by the *Deepwater Horizon* (DWH) oil spill. The DWH oil spill began when a semi-submersible rig, exploring for oil within the Macondo Prospect (Mississippi Canyon Block 252, abbreviated as MC252) owned by British Petroleum (BP), located about 120 miles southwest of Alabama exploded on April 20, 2010. This accident released about 780 million liters of light crude oil into the Gulf of Mexico (GOM) for about 3 months (until July 15, 2010, when the well was finally capped). A considerable amount of the spilled oil was transported towards the Alabama shoreline and was deposited over several amenity beaches located in between Orange Beach and Fort Morgan. The beach deposition events started in early June 2010 and continued until August 2010. The original oil spill residue that deposited on Alabama's beaches was predominantly in the form of water-in-oil emulsion, a highly viscous brownish material, commonly known as mousse.

On December 17, 2010, the Operational Science Advisory Team (OSAT), under the auspices of the DWH accident response Unified Area Command (UC), released a planning study report summarizing various sampling, monitoring, and cleanup activities planned for the region [1]. The purpose of this study was to provide federal on-scene coordinators all necessary information about the shoreline oil deposits that are amenable to removal actions under the provisions of the Clean Water Act, the Oil Pollution Act of 1990, and the National Oil and Hazardous Substances Pollution Contingency plan. The recommendations of this report were based on field data collected from sea and sub-surface monitoring assessments. The field commander of the study stated the following in the OSAT-1 report (p. 3): "based on the robust sampling

effort, the expert analysis of the data provided in this report and the decision criteria summarized above, I have determined that there is no actionable oil in the water or sediments of the deep water or offshore zones. Ongoing removal operations will continue where oil remains in nearshore sediments and shorelines." These statements, published in December 2010, indicate that within 6 months after the spill experts identified that shoreline contamination was the most serious long-term problem when compared to other offshore deep sea contamination problems. However, the extent of this shoreline problem, the time period over which it would persist, and its long-term environmental impacts were not known and hence were not addressed by the OSAT-1 study. Shortly after the release of this report, BP gave the following broad statements to the press [2]: "the scientific evidence in this report is consistent with our observations that the beaches are safe, the water is safe, and the seafood is safe." These statements were somewhat ambiguous since the OSAT-1 study clearly acknowledged that the assessment and quantitative estimation of oil remaining near shorelines and their long-term environmental impacts were beyond the scope of their efforts.

A follow-up study, the OSAT-2 report, was released on February 10, 2011 [3]. This report concluded the following (p.33): "the results of the analysis indicate that the environmental effects of the residual oil remaining after cleanup are relatively minor, especially when considered in the context of pre-spill background of shoreline oiling…" The OSAT-2 study also pointed out that oil contamination is a common problem in the GOM region due to natural petroleum seeps and anthropogenic releases from ships and other sources. These spills have resulted in establishing nonzero oil background levels for the GOM region which could vary from place to place and time to time. The OSAT-2 study was the first to mention about the importance of background oil levels. Since the OSAT-2 study, all BP oil spills related cleanup investigations began to consider the concept of "non-zero background levels," when planning their cleanup efforts. For example, the Shoreline Cleanup Completion Plan (SCCP) report, released on November 2011, considered nonzero background levels while developing their cleanup criteria and stated the following [4]: "although the highest clean-up endpoint is removal of all visible oil, this is often impossible, particularly if there is a background rate of oil deposition (e.g., natural oil seeps or shipping traffic). In these cases, a more appropriate endpoint would be cleanup of visible oil, but not exceeding the background amount." They also pointed out the National Oceanic and Atmospheric Administration's (NOAA) cleanup protocol that stated: "cleanup can be terminated when no visible oil remains on the surface, except for scattered tar balls or swash lines of minute tar balls which may occur as the sand is reworked by the waves. All tar balls or tar patties that can be removed by reasonable clean-up techniques, or that can be remobilized, should be removed. Remaining tar balls or tar patties should be at or below normal background frequency." These protocols became operational from November

2011 and, based on these cleanup criteria, the Coast Guard and BP effectively ended all the cleanup operations along the coastlines of Mississippi, Alabama, and Florida shoreline on June 10, 2013. After ending these cleanup efforts, the Coast Guard released a press statement that stated: "more than three years after the worst oil spill in U.S. history erupted in the Gulf of Mexico, the coastlines of Mississippi, Alabama and Florida have been returned to as close to pre-spill conditions as possible" [5]. Based on these available information, the working model currently assumed by policy makers and regulators is that Alabama's beaches, as of June 2013, have reached as close to natural background conditions that existed prior to the DWH oil spill. This model also implicitly assumes that Alabama's beaches always had quantifiable levels of background oil prior to the DWH oil spill. However, so far, no one has tested the validity of this broadly accepted assumption.

Over the past 5 years, it is well established that DWH oil spill residues contain various types of petroleum compounds including polycyclic aromatic hydrocarbons (PAHs), which are known to be toxic to both human and ecological systems [6−14]. Although our overall understanding of the amount of PAHs trapped in these residues has evolved considerably, several questions related to the risks posed by these residues and their eventual fate still remain unanswered [14−16]. Some of the earlier studies, which were published within months after the spill, have resulted in developing a paradigm that GOM is a highly efficient natural system full of "hydrocarbon degrading microbes" that can rapidly degrade all harmful contaminants present in the crude oil. About 3 months after capping the oil well, Kerr et al. [17] published in a note in the well-known journal *Science* where he pointed out an inter-agency study completed by the Department of the Interior and the NOAA that stated, "out of the 4.9 million barrels of oil spilled, about 75% has been cleaned up by man or Mother Nature." Statements such as these were made based on some of the early published studies that reported rapid oil biodeg-radation occurring in the GOM system. For example, Hazen et al. [18] published an article in *Science* supporting this hypothesis; their study indicated that DWH oil plumes would enrich indigenous oil-degrading bacteria which would degrade spilled "oil" within days. This study concluded: "despite the varying field and microcosm conditions, the oil half-lives are 1.2 to 6.1 days." Edwards et al. [19] later studied microbial respiration of oil in the offshore surface waters and concluded that the GOM microbial community possessed the potential to respire hydrocarbons at an unprecedented rate. General terms such as "oil degradation," "oil half-life," "oil-degrading bacteria," and "hy-drocarbon degraders" were broadly used in these articles, as opposed to mentioning specific chemicals that might be degrading rapidly. The use of these general terminologies has promoted the notion that all potentially harmful chemicals in the crude oil, including several hundreds of potentially harmful petroleum compounds and PAHs, must be degrading at a rapid first-order rate with a half-life of about 6 days. The oil half-life value of 6 days,

reported in Hazen et al. [18], implies that about 50% of the spilled oil mass will be degraded by GOM microbes within 6 days and over 75% would degrade in 12 days. Although Hazen et al. [18] used the general term "oil degradation," they did not analyze any of the toxic heavy compounds such as PAHs. Their field study primarily measured changes in alkanes observed within dissolved hydrocarbon plumes to quantify the degradation rate. However, since they described their finding using terminologies such as "oil degraders" and "oil half-lives," these studies resulted in promoting the idea that microbes were primarily responsible for degrading the oil, and also all the toxic chemicals present in the crude oil were rapidly degrading.

Later studies, such as the OSAT-2 study, were more cautious and started focusing on various classes of toxic chemicals in the crude oil, such as PAHs. However, even the OSAT-2 study had similar issues since they lumped all forms of PAHs into a single category called total PAHs (TPAHs) and only reported these values. A typical crude oil will have several PAHs and some of them have been currently classified as priority pollutants by the USEPA [12]. The OSAT-2 study primarily used laboratory data that reported total PAHs levels in DWH oil spill residues that washed along GOM shorelines and concluded: "recently collected weathered oil samples showed 86−98 percent depletion of total polycyclic aromatic hydrocarbons." During the early cleanup planning years, this conclusion further promoted the notion that all the PAHs in DWH oil were also rapidly degraded by the microbes. Recent studies have shown that most of the lower molecular weight PAHs (or light PAHs) were primarily removed by evaporation and higher molecular weight PAHs (or heavy PAHs) were transformed by photooxidation and other physico-chemical processes [14,20,21].

The OSAT-2 study also completed a modeling study and included the weathering levels estimated using computer models; these modeling studies made specific predictions for the fate of PAHs in various GOM beaches (including forecasts for some Alabama beaches). These modeling results were summarized in the report as [3]: "the simulation results for Bon Secour and Fort Pickens indicate alkanes and PAHs would degrade to approximately 15-20% of the current concentration within 2.5 to 5 years." Such statements have led to the assumption that all toxic PAHs in DWH oil spill residues will be degraded to very low levels within the first 3−5 years.

Based on the published information reviewed in the earlier sections, we have deduced the following hypotheses which are typically used to describe the current state of DWH oil spill related contamination problems in Alabama: (1) the GOM has several oil seeps and oil exploration wells; therefore, Alabama beaches always had visible levels of background oil deposited in various forms; (2) as of June 2013, Alabama's beaches have recovered and reached a minimal contamination level, which is close to the normal background level that existed prior to the DWH oil spill; and (3) the GOM system hosts highly efficient hydrocarbon degrading microbes which should have played a

FIGURE 16.1   Study area located along the Alabama shoreline extending from Perdido Bay along the Alabama−Florida border to Fort Morgan (∼50 km long).

significant role in rapidly degrading all of the toxic compounds, including PAHs, contained in the DWH crude oil. The objective of this effort is to test the validity of these hypotheses and propose an alternate set of hypotheses that better describe the current state, and also predict the future evolution patterns of the DWH oil trapped near Alabama's beaches.

16.2 STUDY AREA

Our study area includes beaches located along Alabama's GOM coastline extending from Perdido Bay in the east, located along the Florida−Alabama border, to Fort Morgan in the west (see Fig. 16.1). This shoreline is approximately 50 km (∼31 miles) long. A team of researchers from Auburn University have been sampling Alabama beaches for the past 6 years. Some of the field observations are summarized in previous studies [7,13,14,22−24]. In this chapter, we briefly review some of these studies and also other recently published studies. In addition, we will also provide additional field observations for the 2014−2016 time period.

16.3 BACKGROUND OIL LEVELS IN ALABAMA'S BEACHES PRIOR TO THE ARRIVAL OF DWH OIL SPILL

In May 2010, a background study was completed in this region by the UC, and the data are summarized in a shoreline cleanup and assessment technique (SCAT) report published in March 2011 [25]. In this study, SCAT teams surveyed 8.4 km of beaches within the City of Orange Beach and found no tar balls; however, they recovered 40 tar balls with an average size of 0.4 cm after surveying 40.5 km of beaches within the City of Gulf Shores. The overall result of this survey can be summarized as: about one small tar ball of size less than 1 cm was found within every kilometer surveyed during this study [25].

Another important dataset for estimating background levels is summarized in the SCCP report, published by the UC in November 2011 [4]. According to this report, background oiling is defined as the chronic concentration

(or frequency) of oil residues or tar balls expected on a shoreline over a long period of time without an acute input such as an oil spill. Based on numerous field surveys completed between April 3, 2011, and October 7, 2011, the research team documented 680 occurrences of non-MC252 tar balls from the beaches of Louisiana, Mississippi, Alabama, and Florida [4]. These tar balls were expected to have originated from river runoff from urban areas, commercial fishing and shipping activities, offshore oil production, natural seeps, and prior spills [4]. This survey covered approximately 900 km of shoreline and took about 6 months to complete. As per our knowledge, this, by far, is the most comprehensive background study available for the GOM region. However, one of the limitations of this dataset is that the details regarding the number of tar balls collected from each individual state were not provided in this study.

A background observational study of Alabama's beaches was completed by the Auburn University team on May 9, 2010, about a month prior to the first arrival of DWH oil. During this background study the 50 km long shoreline, shown in Fig. 16.1, was surveyed by accessing various beaches located in Orange Beach, Gulf Shores State Park, Bon Secour National Wildlife Refuge and Fort Morgan regions, and visually inspecting approximately 0.5 km in either directions around these access points. The purpose of this survey was to establish background conditions of the beaches, primarily with respect to existing pre-arrival oil contamination. During this observational survey, no tar balls were found [24].

16.4 STATE OF ALABAMA'S BEACHES DURING ACTIVE OIL DEPOSITION PERIOD (FROM JUNE 2010 TO AUGUST 2010)

DWH oil started to wash on Alabama's beaches around the first week of June 2010 and continued until early August 2010. The cleanup crew used various methods to prevent oil from reaching the shoreline using various types of containment booms. Unfortunately, the nearshore containment efforts were largely ineffective and a large amount of floating oil was directly deposited onto all of the beaches located in our study area. The oil that reached Alabama's shores was a highly viscous brownish emulsion, which is commonly known as mousse. Fig. 16.2A shows a photograph taken by our team when the emulsified brownish oil was floating on water near Perdido Bay on June 11, 2010. BP mobilized a large number of cleanup workers to manually shovel the oil deposited on the beaches (see Fig. 16.2B). This manual strategy was extremely tedious but was effective and it helped to clean most of the beached oil.

Unfortunately, a substantial portion of the floating-emulsified oil that reached the Alabama shoreline interacted with suspended sand particles, which were entrained into the water column by breaking waves near sandbars and other turbulent mixing eddies, forming a mousse−sand mixture. The
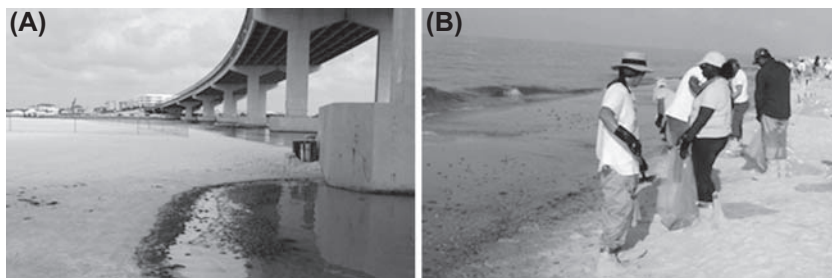
FIGURE 16.2 (A) Deepwater Horizon oil spill mousse floating on the bay under the Perdido Bay Bridge, June, 2010; (B) Cleanup crews removing the beached oil from a beach in Gulf Shores, Alabama.

density of the floating mousse was less than seawater; however, on accumulating sand particles, its density became higher than that of seawater, and the mixture started to sink. Upon reaching the sandy bottom, the oil collected more sand, forming sand−oil deposits. Fig. 16.3 shows a conceptual model, which is based on some previously published mechanisms and models [26,27], to describe the nearshore sediment−water interaction processes that resulted in submerging an unknown amount of oil along the Alabama shoreline. These sinking processes eventually formed large mats of relatively immobile oil deposits, known as submerged oil mats (SOMs).

Fig. 16.4 shows a typical SOM formed close to the shoreline. In some literature, SOMs are often referred to as "tar mats," which could be a misleading nomenclature since DWH-related SOMs contain petroleum-smelling, partially weathered crude oil, not highly weathered tar material. SOMs often break up due to the action of waves and other shoreline forces and
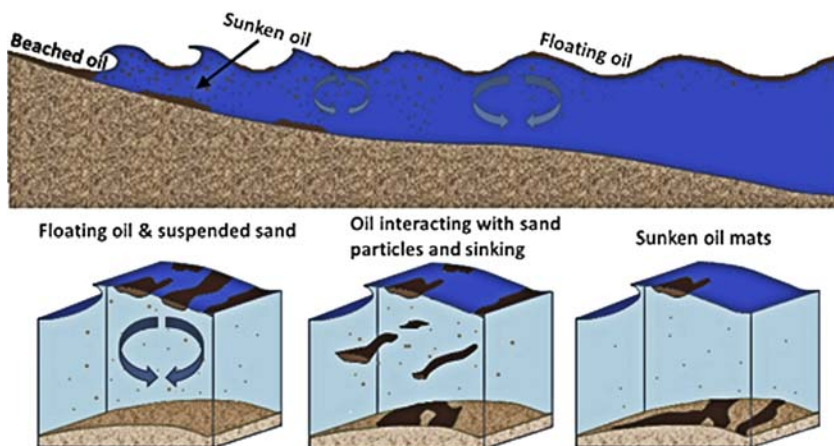

FIGURE 16.3 A conceptual schematic describing oil sinking processes near sandy beaches [26,27].
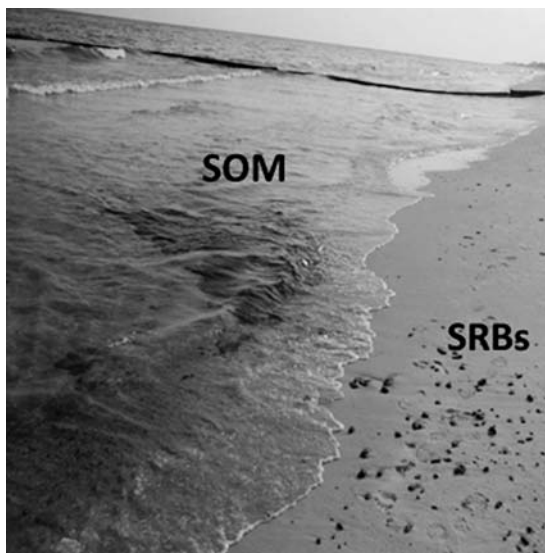
FIGURE 16.4 Typical submerged oil mats (SOMs) and the associated surface residual oil balls (SRBs) formed near sandy beaches.

form mobile oil−sand fragments known as surface residual oil balls or SRBs (see Fig. 16.4). SRBs are often referred to as "tar balls," which again could be a misleading nomenclature. In this study, we consistently use the terms SOMs and SRBs to refer to DWH oil spill−related sand−oil deposits.

16.5 STATE OF ALABAMA'S BEACHES DURING THE CLEANUP PERIOD (AUGUST 2010 TO JUNE 2013)

Between August 2010 to June 2013, BP employed various cleanup teams to actively remove beached oil. To manage the SRB (or tar ball) problem along inter-tidal zone, BP employed cleanup crews that used crab nets to manually identify and remove all beached SRBs. Locating and removing buried SOMs was a challenging task, since some of these mats were buried under several meters of sand. Occasionally, sediment migration processes and beach currents transported some SOMs to the surface and relatively close to the shoreline. When SOMs are found close to the shoreline (within about 50 m from the waterline), a long-arm excavator was used to remove the mats [28].

When the DWH oil arrived along Alabama's shoreline, most of GOM beaches were in an erosional state and this led to burial of the oil under dry beaches as the system accreted over the following months [29]. Tidal and storm currents also transported and buried a fraction of the oil directly under beaches above the waterline. These deposits trapped under dry beaches posed the risk of exposing oil spill residues to beach users. Therefore, BP employed

heavy equipment to excavate several miles of dry beaches in Orange Beach, Gulf Shores, and Fort Morgan region. The excavated sand was sieved to remove all buried sand−oil deposits. The effectiveness of these highly intrusive beach cleanup operations was reviewed in a published study [23]. This study concluded that while this cleanup process removed several large buried oil deposits, it also homogenized and distributed a fraction of the remnant oil over a larger beach volume and possibly spreading the contamination problem. Overall, it turned out to be an effective cleanup strategy that decreased the risk of exposure to larger fragments of buried oil, and spreading lead to increased dilution and possibly higher effective degradation rates [23].

During the active cleanup period, the Auburn University team completed over 15 field surveys to document the level of oil contamination in Alabama's beaches. Two types of surveys, namely observational/random sampling and observational/detailed sampling surveys, were completed and results were summarized in a published article [24]. Observations with random sampling surveys included visual observation of beach conditions and cleanup activities at various locations along the 50-km study area, and occasional collection of random SRB samples. Observations with detailed sampling efforts included all observational components along with systematic collection of SRBs from several locations. Our detailed sampling efforts employed a two- or three-member team, collecting SRBs found in the foreshore region for a fixed time period of approximately 30 min, and surveying about 0.5−1 km on either side of the sampling access point.

During these surveys, we observed large numbers of SRBs at several sites. For example, during a field survey completed on February 19, 2012, we noticed several beaches located to the west of Lagoon Pass (LP) were highly contaminated. Fig. 16.5 shows a close-up view of 15 cm × 20 cm area at one of these sites, where a penny and a quarter are used for scale, and circles are used to mark the locations of SRBs. Even within this small region, we observed 12 SRBs and therefore it was practically impossible to collect all the SRBs from these sites. In order to further quantify contamination levels, we isolated a larger area of size 50 m × 10 m and completed a rapid 10 min survey where all of our team members gathered as many SRBs as possible within this fixed time. Fig. 16.6 shows the result of this 10-min survey where we collected 70 large SRBs (3−5 cm of total weight of 550 g, a quarter is used for scale), 95 medium SRBs (2−2.5 cm, total weight of 240 g, a dime is used for scale), and 165 small SRBs (1−1.5 cm, total weight of 120 g, a penny is used for scale).

Fig. 16.7 shows another close-up view of the shoreline taken a year after the previous survey (on February 15, 2013), where we once again observed SRBs mixed with shells scattered all along swash zones. The figure also shows how BP managed the SRB problem by employing a cleanup crew that manually collected SRBs using crab nets. During this visit, we completed

FIGURE 16.5 Typical SRBs mixed along with shells and other debris found in the swash zone. SRB locations are marked using red dye and SRBs are also circled; a quarter and a penny are used for scale. *Photo taken near Lagoon Pass, Alabama, on February 19, 2012.*
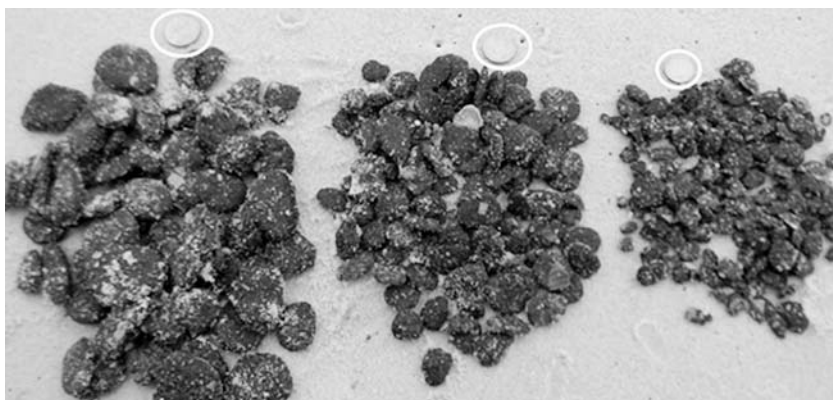
FIGURE 16.6 SRBs collected from a contaminated region of about 500 m^2 area, located to the west of Lagoon Pass on February 19, 2012 (quarter, nickel and dime are used for scale).

several 30-min sampling surveys at different locations, and the SRBs collected from LP and Bon Secour wildlife refuge are shown in Fig. 16.7. We collected a total of 130 SRBs, 2−6 cm in size, and 13 SRBs, 6−7 cm in size, with total weight of 1.5 kg from beaches located to the west of LP. We also collected 70 tar balls, 1−2 cm in size, and 260 tar balls, 2−4 cm in size, with a total weight of 1.6 kg from the Mobile Street beach, which is located within Bon Secour wildlife refuge. These datasets are good examples of the level of oil contamination observed by our team during the active cleanup period, which officially ended on June 10, 2013.

FIGURE 16.7 (A) SRBs mixed with shells deposited along a swash zone at Gulf Shores, Alabama, on February 15, 2013; (B) BP cleanup crews removing SRBs using crab nets; and (C) SRBs collected from Lagoon Pass and Bon Secour (Mobile Street) beaches during February 2013 survey.

16.6 STATE OF ALABAMA'S BEACHES DURING POST-CLEANUP PERIOD (2013−14)
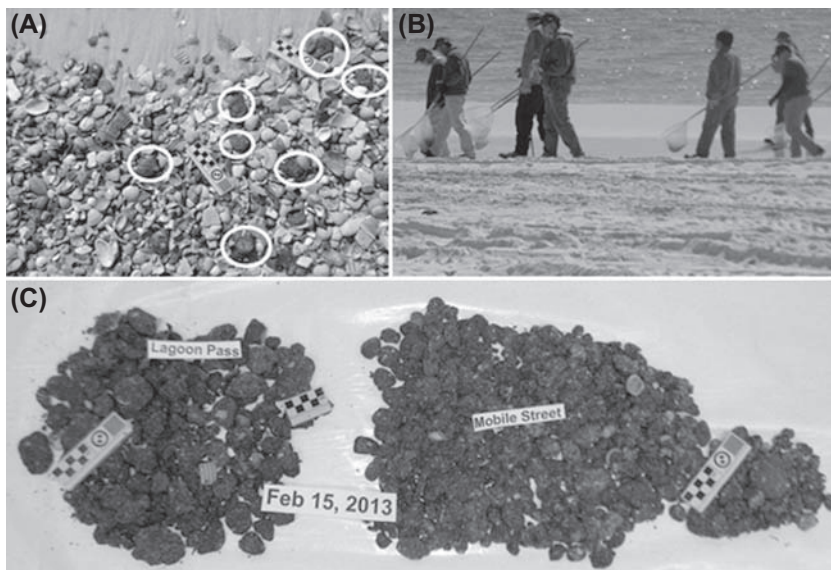
Between June 2013 and December 2014, a total of four detailed sampling surveys were completed in this region. This first post-cleanup survey was conducted on June 7, 2013, immediately after BP terminated all of its active cleanup operations for Alabama's beaches. The second, third, and fourth surveys were completed on October 9, 2013, January 26, 2014, and August 16, 2014, respectively, and the details of these surveys are discussed in our published study [24]. Table 16.1 provides the weights and numbers of SRBs collected from various sampling points during August 2014. This was a rapid survey where the team spent 30 min at each of the four sampling points and collected a total 190 SRBs weighing about 750 grams (g) from beaches located in the Orange Beach, Gulf Shores, Bon Secour, and Fort Morgan regions.

16.7 POST-CLEANUP SURVEYS COMPLETED FROM 2015 TO 2016

During 2015, our team completed two detailed sampling surveys. In addition to these two surveys, we also completed several observational surveys and a well-focused, event-specific survey at an excavation site near LP. The first

TABLE 16.1 Details of SRBs Collected During August 2014 Survey

Sampling Date	Location	Weight (g)	Number
August 16, 2014	Fort Morgan	214	58
	Bon Secour	167	42
	Gulf Shores	223	53
	Orange Beach	145	36

detailed survey was conducted on April 30, 2015, and the second survey was completed on November 11, 2015. Table 16.2 summarizes the details including the size distribution of SRBs collected during these two surveys. As shown in the table, during our April 2015 survey, we recovered SRBs with a total weight of about 1900 g; and during November 2015 survey we collected about 2300 g of SRBs.

TABLE 16.2 Details of SRBs Collected During April 2015, November 2015, and January 2016 Surveys

			Size Distribution (cm)		
Sampling Date	Location	Weight (g)	1–2	2–5	>5
April 30, 2015	Fort Morgan (Gulf side)	516	–	130	7
	Fort Morgan (bay side)	444	–	80	13
	Bon Secour (Mobile St.)	325	85	23	–
	Gulf Shores (Lagoon Pass)	125	–	55	–
	Orange Beach	337	100	78	–
November 11, 2015	Fort Morgan (Gulf side)	836	102	107	9
	Bon Secour (Mobile St.)	330	70	38	–
	Gulf Shores (Lagoon Pass)	685	84	91	5
	Orange Beach	152	32	48	–
January 30, 2016	Fort Morgan	1310	96	126	11
	Gulf Shores (Lagoon Pass)	1120	45	53	14
	Orange Beach	98	14	12	–

Between June, 3 and June 15, 2015, we completed an event-based survey that focused on sampling a relatively small region of about 100 m × 200 m area located to the west of LP. This survey was initiated when an excavation project aimed to remove sand deposits accumulated near the LP inlet inadvertently mobilized SRBs trapped under the sand bed. Fig. 16.8A and B compares the mouth of the LP before and after the excavation effort. Fig. 16.8C and D shows various stages of the project where sand deposits were removed using a long-arm excavator and the excavated sand was stored near the inlet. This excavation project provided a unique opportunity to access oil-contamination levels buried under sand deposits accumulated near the shoreline. This survey was jointly completed by Alabama Department of Environmental Management (ADEM) and Auburn University. The ADEM team started sampling the excavated sand starting from June 3, 2015, and they continued to collect samples on a daily basis until June 13 and the Auburn team completed their sampling effort on June 15, 2015. Typical surveys included inspecting the beaches and the excavated sand for about 2 h and collecting the SRBs. Table 16.3 summarizes the SRBs collected during over the entire survey period, and Fig. 16.9A and C shows the SRBs collected during these 12 days. Fig. 16.9D shows a typical buried SRB trapped under the excavated sand. A total of about 10 kg of SRBs were collected over 12 days of sampling.
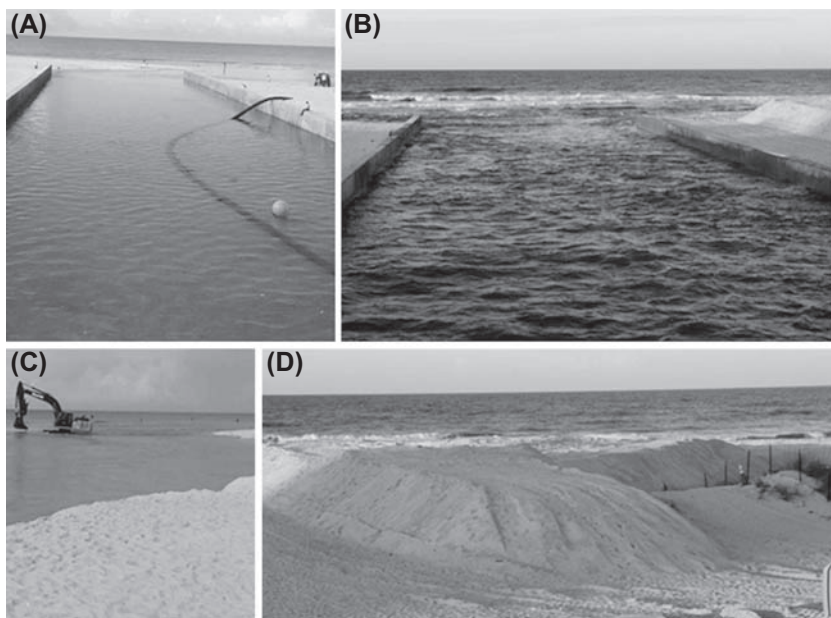
FIGURE 16.8 Stages of the excavation project completed at the mouth of Lagoon Pass in June 2015: (A) inlet before excavation; (B) inlet after excavation; (C) long-arm excavator removing sand from the inlet; and (D) excavated sand deposits.

TABLE 16.3 Details of SRBs Collected During the Excavation Project Completed Near the Lagoon Pass Inlet in June 2015	
Date	Weight (g)
June 3, 2015	1932
June 4, 2015	1261
June 5, 2015	1179
June 6, 2015	1016
June 7, 2015	930
June 8, 2015	898
June 9, 2015	626
June 10, 2015	544
June 11, 2015	644
June 12, 2015	767
June 13, 2015	200
June 15, 2015	244

FIGURE 16.9   SRBs collected near Lagoon Pass during the excavation project (the figures show beached as well as buried SRB samples collected from the site from June 3 to June 15, 2015). The figure also shows partially exposed SRBs buried in sand.

FIGURE 16.10 SRBs collected from Lagoon Pass and Fort Morgan during January 2016 survey.

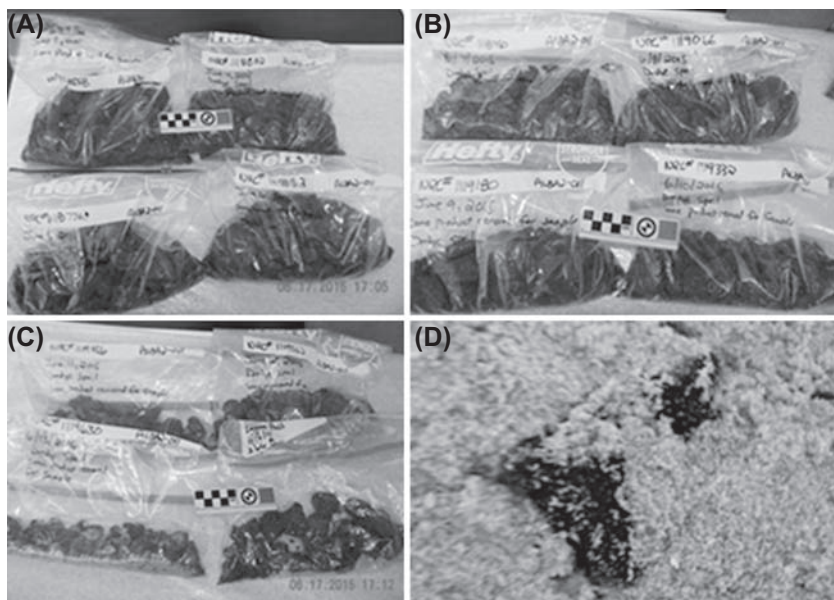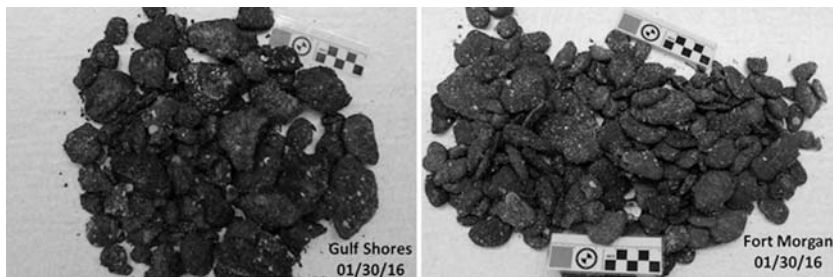The most recent SRB survey was completed by our team on January 30, 2016. This survey included collection of SRBs from three locations including Fort Morgan, Gulf Shores (LP), and Orange Beach. Fig. 16.10 shows the pictures of SRBs collected during this survey and Table 16.2 summarizes the weight and size characteristics of these SRBs. Interestingly, the SRB activity levels observed during this survey near LP and in Fort Morgan were some of highest levels observed by our team over the previous 2.5 years (since the termination of shoreline cleanup efforts in June 2013). The Fort Morgan bayside beach had a considerable amount of SRBs. Although the SRB activity in LP was not as high as it was in Fort Morgan, the average size of SRBs collected from the LP area were relatively large (6 SRBs were over 7 cm long). Comparison of SRBs samples collected from LP (Gulf Shores) in February 2013 with the samples collected in January 2016 (compare Figs. 16.7 and 16.10) indicate that the SRB deposition pattern has not changed over the past 3 years.

16.8 LABORATORY STUDIES: CHEMICAL CHARACTERIZATION OF DWH OIL SPILL RESIDUES

One of the first challenges in understanding the impacts of the DWH oil spill on Alabama's beach systems is identifying whether these SRBs originated from the MC-252 oil. The focus of our earlier studies was to address this problem by using various types of chemical fingerprinting techniques [13,14,30]. In these published studies, we have analyzed several DWH-SRBs and compared them against various types of crude oils and tar balls and concluded that DWH-SRBs have unique hopane and sterane fingerprints, and they also have relatively high concentration of heavy PAHs such as chrysene and alkylated chrysenes. Furthermore, they also have unique physical characteristics—unlike traditional tar balls, which are rigid, highly weathered, rubbery objects with little or no sand, the DWH-SRBs are brownish, fragile, and sticky containing considerable amount of sand. All the field samples discussed in previous sections matched these unique physical characteristics. In the following section, we provide detailed fingerprinting data for a selected set of samples collected from Alabama's beaches.

Our past studies, as well as several other published studies, have shown that DWH SRBs contain various hazardous chemicals, including PAHs that are toxic to both human and ecological systems [7,8,11,31,32]. Recently, Dubansky et al. [33] conducted toxicity experiments using DWH oil−contaminated sediments and found upregulation of cytochrome P4501 A protein in the gills, liver, intestines, and kidneys of killifish (an abundant, nonmigratory baitfish). Also, laboratory exposures of killifish embryos to these contaminated sediments resulted in developmental abnormalities. The study concluded that these data are predictive of potential population-level impacts when killifish are exposed to oiled sediments present along the northern GOM coast.

PAHs are some of the most important groups of toxic environmental compounds present in crude oil [10], and these organic compounds have two or more fused aromatic rings. Due to their mutagenic and carcinogenic properties [6,9], PAHs are classified as hazardous compounds. Well over 100 PAHs have been identified in crude oil and currently 16 of them are classified as priority pollutants by the USEPA [12]. Many PAHs found in crude oil are highly recalcitrant in natural environments and they can persist in oil-contaminated sediments for a long time. For examples, higher molecular weight PAHs at concentration levels nearly the same as the levels found in the original oil were measured in the residues of *Arrow* oil spill (occurred in Nova Scotia, Canada in 1970) collected 20 years after the accident [34].

As discussed in the field sampling section, since the first arrival of ocean-weathered mousse on Alabama's beaches in June, 2010, our team has been continuously collecting and archiving various types of DWH oil spill residues found along Alabama's beaches. In the section below, we present the details of a chemical characterization dataset published in one of our recent field studies [14].

16.8.1 Material and Chemical Characterization Methods

16.8.1.1 Samples

DWH source crude (MC252 oil) was supplied by BP and is referred to as DWH oil. A number of ocean-weathered, first arrival oil spill samples were collected from various beaches in Alabama. We used a floating mousse sample recovered near Orange Beach (see Fig. 16.2A) on June 11, 2010, as the reference for ocean-weathered oil spill (OWO) sample. Details of SRB sampling locations used in this study are shown in Fig. 16.1. Temporal variations in target PAHs were assessed by sampling SRBs from LP at six different times: September 8, 2011 (LP1), February 19, 2012 (LP2), September 02, 2012 (LP3), February 15, 2013 (LP4), June 14, 2013 (LP5), and August 01, 2014 (LP6). Additionally, we also prepared a laboratory-weathered oil sample (LWO) by evaporating a small quantity (triplicates using 0.79, 0.80, and 0.80 g of oil) of DWH reference crude oil in a dark fume hood for a period of 6 days. Evaporation is one of the major weathering processes experienced by an oil spill and therefore we prepared this reference sample.

16.8.1.2 Materials

The organic solvents used in this study were of analytical grade or higher. The solvents, silica gel (60−200 μm), and anhydrous sodium sulfate (ACS grade) were purchased from VWR International (Suwanee, GA). All hopane standards were purchased from Chiron, Trondheim, Norway. PAH standard mixtures consisting of 27 PAHs (naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, 1-methylphenanthrene, anthracene, dibenzothiophene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*j*)fluoranthene, benzo(*k*)fluoranthene, benzo(*e*)pyrene, benzo(*a*)pyrene, perylene, dibenz(*a,c*) anthracene, dibenz(*a,h*)anthracene, indeno(1,2,3,-*cd*)pyrene and benzo(*ghi*) perylene) were purchased from Agilent Technologies, Wilmington, DE. A mixture of four surrogate standards (SS) including naphthalene-d_8, acenaphthalene-d_{10}, phenanthrene-d_{10}, and benzo(a)pyrene-d_{12} were purchased from Ultra Scientific Analytical Solutions (North Kingstown, RI). Internal standard (IS) *p*-terphenyl-d_{14} (purity 98.5%) was purchased from AccuStandard (New Haven, CT). Chromatographic separation of various PAH compounds was achieved using a J&W DB-EUPAH (Agilent Technologies) column (20 m × 180 μm × 0.14 μm). The back flush setup used Agilent Technologies inert fused silica column (0.7 m × 150 μm × 0 μm; 450°C). Prior to use, activated silica gel was prepared according to an established protocol [35]. Silica gel was serially rinsed three times with 250 mL acetone, hexane, and dichloromethane, and then left to dry for 12 h in a fume hood. After drying, silica gel was heated in an oven at 40−50°C for 8 h and then activated at 180°C for 20 h. Anhydrous sodium sulfate was purified by heating at 400°C for 4 h and then cooled and stored in tightly sealed glass containers.

16.8.1.3 Oil Percentage Levels in Field Samples

About 1 g of the homogenized oil spill sample was extracted using 10 mL of dichloromethane. The extraction step was repeated four times, and the remaining solid residues in the vial was dried and weighed. The average values of oil content determined were: 17%, 24%, 22%, 15%, 17%, and 16% for LP1 to LP6 samples, and 12%, 12%, and 12% for OB, BS, and FM samples, respectively. The average standard deviation of these estimates was 0.9%.

16.8.1.4 Analytical and Quantitation Methods
16.8.1.4.1 Column Fractionation

Column chromatographic fractionation was performed following an approach modified from a published procedure [35]. A glass column (250 mm × 10 mm) was plugged with glass wool at the bottom, and then packed with 3 g of activated silica gel and topped with 1 g of anhydrous sodium sulfate. The chromatographic column was charged with 20 mL of hexane and the eluent was

discarded. About 12 mg of oil or 25 mg of mousse sample was weighed in a vial, spiked with four surrogate standards, and mixed with 1 mL of hexane. The entire mixture was transferred to the column, and the vial was sequentially washed with 2 mL of hexane (with 1 mL in each step); contents from sequential washing were also transferred to the column. For SRB samples, about 25 mg oil-equivalent sample was used, and the weight was adjusted based on the oil content (e.g., 147 mg of LP1, having 17% oil content yields 25 mg of oil). About 12 mL of hexane was added to the column to elute aliphatic hydrocarbon fractions, and this hexane fraction was labeled as F1. Then 15 mL of solvent containing a mixture of 50% hexane and 50% dichloromethane was used to elute the aromatic hydrocarbon fraction, and this fraction was labeled as F2. The F1 and F2 fractions were concentrated under a gentle stream of nitrogen and required amount of solvent was added to adjust the final sample volume to 10 mL. 1 mL of the adjusted F1 and F2 samples were spiked with $C_{30}\beta\beta$-hopane ($17\beta(H),21\beta(H)$-hopane) and p-terphenyl-d_{14}, respectively, prior to chemical analysis. All the samples were prepared in duplicate and analyzed in triplicate.

16.8.1.4.2 Determination of PAHs Depletion Levels

Organic compounds in crude oil will weather concurrently; therefore, it is important to use a conservative marker to normalize the concentration of contaminants measured in environmental samples [36]. We used $C_{30}\alpha\beta$-hopane as the conservative marker. Hopane response in the original crude oil source sample was quantified by first computing a ratio H_{oil}, which is the peak area of $C_{30}\alpha\beta$-hopane in crude oil (normalized to the oil weight) to the peak area of the IS $C_{30}\beta\beta$-hopane. We also estimated another hopane ratio $H_{weathered}$, which is the peak area of $C_{30}\alpha\beta$-hopane in a weathered oil spill sample (normalized to oil weights) to the peak area of the IS $C_{30}\beta\beta$-hopane. These ratios were used to compute the hopane normalizing factor, $H_{oil}/H_{weathered}$, which was then used to estimate the degree of weathering for a target PAH using the following formula [21,36]:

$$\text{Actual \% depletion of PAH} = (1 - \frac{\text{PAH in weatherd sample}}{\text{PAH in reference oil}} \times \frac{H_{oil}}{H_{weathered}}) \times 100 \qquad (16.1)$$

Concentrations of PAHs and the responses of biomarker compounds were quantified using an Agilent 7890 gas chromatograph coupled with an Agilent 7000B triple quadrupole (QqQ) mass spectrometer, fitted with an electron ionization (EI) source and a collision cell.

16.8.1.4.3 Analytical Methods

The F1 fraction was analyzed for hopanes and steranes using a GC/MS procedure performed in selected ion monitoring (SIM) mode. The F2 fraction

was analyzed for five parent PAHs (naphthalene, phenanthrene, dibenzothiophene, fluorene, chrysene) and their 18 alkylated homologs using a SIM method. In addition, the F2 fraction was analyzed for 17 additional parent PAHs using a GC/MS/MS procedure performed in multiple reaction monitoring mode. Further details about these analytical procedures are given in Yin et al. [14].

16.8.2 Chemical Characterization Results

16.8.2.1 Source Identification

Field samples were analyzed first to confirm their origin. In terms of physical characteristics, all the samples matched DWH SRB characteristics described in previous studies [3,30]: they were all brownish, sticky material with considerable amount of sand, and had a strong petroleum odor. To compare their chemical fingerprints, we first analyzed hopane and sterane signatures (shape of their chromatograms) using the approaches described in Mulabagal et al. [30] (results not shown). In the environmental forensic literature, it has been well established that source-specific diagnostic ratios of certain groups of hopanes will vary from one oil to another [37−39]. Mulabagal et al. [30] established that fresh and weathered DWH oil can be distinguished from other oils by two source-specific hopane ratios, namely T_s/T_m and C_{29}/C_{30}. Fig. 16.11 shows the T_s/T_m and C_{29}/C_{30} hopane ratios of various oil spill samples collected from June 2010 to August 2014, and compares them with the ratios measured for the DWH reference oil. The data show T_s/T_m and C_{29}/C_{30} values vary from 0.92 to 0.98 and 0.36 to 0.40, respectively. The T_s/T_m and C_{29}/C_{30} ratios of various SRB samples match the ratios of DWH reference oil (see Fig. 16.11); also, the hopane data are consistent with the data reported in Mulabagal et al. [30].
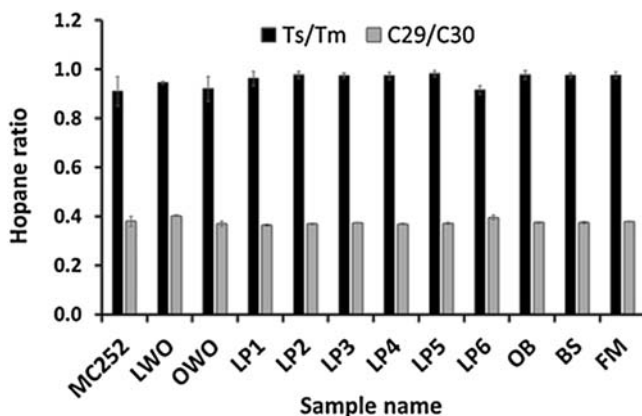

FIGURE 16.11 Comparison of hopane diagnostic ratios in the MC252 source oil and SRB samples. *(Yin F, John GF, Hayworth JS, Clement TP. Long-term monitoring data to describe the fate of polycyclic aromatic hydrocarbons in deepwater horizon oil submerged off Alabama's beaches. Science of The Total Environment 2015;508:46−56. http://dx.doi.org/10.1016/j.scitotenv. 2014.10.105.)*

16.8.2.2 Comparison of PAHs Measured in DWH Oil, Laboratory Weathered DWH Oil (LWO), and Ocean-Weathered DWH Oil

To quantify the effects of open-water weathering processes including evaporation, dissolution, photooxidation, and biochemical reactions, we compared PAH concentrations measured in the source oil with PAHs in LWO and OWO samples. DWH source oil contains high levels of volatile hydrocarbons; hence we postulated that evaporation should have removed a considerable amount of PAHs and other organics while the oil was in the open ocean [8,30]. To estimate the effects of evaporation on weathering, we monitored the changes in the mass of the LWO sample for 6 days, and these results are summarized in Fig. 16.12. The data show that within 5 h about 33% of the oil mass was volatilized, and within a day about 39% of the oil mass was removed. The rate of evaporation declined considerably after about 12 h; and after 6 days of evaporation, about 44% of the total oil mass was removed from the system. The average standard deviation of the weathering data was 0.7%.

The concentrations of 22 parent PAHs and 18 alkylated PAH homologs measured in the original source oil are summarized in Table 16.4. The total amount of target PAHs measured was 16,115 mg/kg oil. PAHs in the source oil were predominantly lower molecular weight compounds (two and three ring), mostly naphthalene and its alkylated homologs, which accounted for about 68% of the total PAH mass. Phenanthrene and its alkylated homologs contributed 18%, followed by fluorene and its alkylated homologs which contributed another 8%. Higher molecular weight (four−to six rings) PAHs accounted for only 0.5% of the total target PAHs in the source oil. Although their relative percentage is low, several of these higher molecular weight PAHs

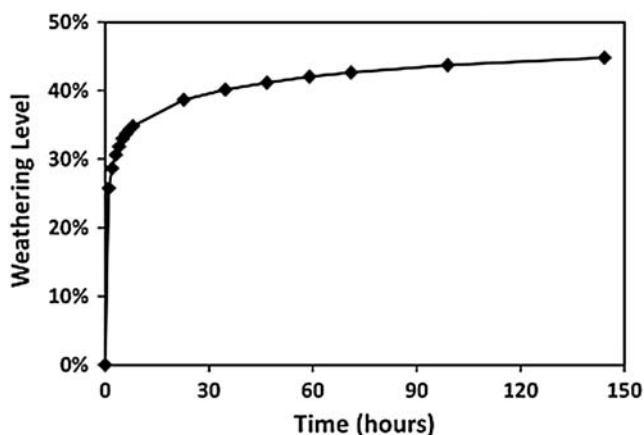**FIGURE 16.12** Temporal changes in weathering levels in the LWO sample (weathering is due to mass removal via evaporation). *(Yin F, John GF, Hayworth JS, Clement TP. Long-term monitoring data to describe the fate of polycyclic aromatic hydrocarbons in deepwater horizon oil submerged off Alabama's beaches. Science of The Total Environment 2015;508:46−56.* http://dx.doi.org/10.1016/j.scitotenv.2014.10.105.*)*

TABLE 16.4 Concentration (Average ±SD) of PAHs (mg/kg-Oil) in DWH Oil, LWO, and OWO Samples

Compound	DWH	LWO	Depletion of PAHs in LWO (%)	OWO	Depletion of PAHs in OWO (%)
C_0-naphthalene	712 ± 3	DL	100	DL	100
C_1-naphthalenes	2405 ± 3	1.3 ± 0.3	100	DL	100
C_2-naphthalenes	3335 ± 5	89 ± 2	99	0.70 ± 0.09	100
C_3-naphthalenes	2445 ± 6	1293 ± 9	72	8 ± 1	100
C_4-naphthalenes	2031 ± 8	2358 ± 29	39	37 ± 5	99
C_0-phenanthrene	297 ± 1	474 ± 8	16	28 ± 3	94
C_1-phenanthrenes	849 ± 4	1561 ± 6	3	285 ± 8	80
C_2-phenanthrenes	853 ± 6	1687 ± 4	0	437 ± 3	70
C_3-phenanthrenes	601 ± 3	1166 ± 3	0	281 ± 1	73
C_4-phenanthrenes	330 ± 1	649 ± 7	0	152 ± 9	73
C_0-dibenzothiophene	45 ± 1	65 ± 1	23	2.7 ± 0.3	96
C_1-dibenzothiophenes	70 ± 1	125 ± 1	6	16 ± 2	87
C_2-dibenzothiophenes	101 ± 1	187 ± 1	3	43 ± 4	75
C_3-dibenzothiophenes	69 ± 1	132 ± 1	0	36 ± 3	69
C_0-fluorene	123 ± 1	77 ± 0.4	67	0.58 ± 0.03	100
C_1-fluorenes	384 ± 7	514 ± 8	29	17 ± 2	97
C_2-fluorenes	409 ± 5	709 ± 5	9	42 ± 3	94
C_3-fluorenes	368 ± 3	675 ± 9	3	72 ± 8	89
C_0-chrysene	49 ± 1	95 ± 1	0	46 ± 4	45
C_1-chrysenes	92 ± 4	182 ± 1	0	63 ± 4	60
C_2-chrysenes	105 ± 1	220 ± 2	0	44 ± 2	76
C_3-chrysenes	72 ± 1	157 ± 3	0	17.3 ± 0.8	86
C_4-chrysenes	36 ± 1	83 ± 2	0	7.7 ± 0.5	88
Biphenyl	175 ± 2	DL	100	DL	100
Acenaphthylene	5.2 ± 0.7	1.4 ± 0.1	86	DL	100
Acenaphthene	58 ± 2	33 ± 1	71	DL	100

TABLE 16.4 Concentration (Average ±SD) of PAHs (mg/kg-Oil) in DWH Oil, LWO, and OWO Samples—cont'd

Compound	DWH	LWO	Depletion of PAHs in LWO (%)	OWO	Depletion of PAHs in OWO (%)
Anthracene	5.4 ± 0.4	11 ± 1	0	1.0 ± 0.1	89
Fluoranthene	6.2 ± 0.4	13 ± 1	0	3.9 ± 0.7	63
Pyrene	17 ± 2	35 ± 2	0	6.8 ± 0.6	77
Benzo(*a*)anthracene	9.7 ± 0.9	19 ± 1	0	0.35 ± 0.05	98
Benzo(*b*)fluoranthene	8 ± 1	20 ± 1	0	6.4 ± 0.7	55
Benzo(*k*)fluoranthene	2.8 ± 0.6	6.1 ± 0.1	0	1.5 ± 0.3	68
Benzo(*j*)fluoranthene	2.5 ± 0.1	4.9 ± 0.3	0	0.90 ± 0.07	79
Benzo(*e*)pyrene	13 ± 1	27 ± 1	0	8 ± 1	64
Benzo(*a*)pyrene	2.3 ± 0.2	3.9 ± 0.4	11	0.36 ± 0.05	91
Perylene	1.5 ± 0.2	2.5 ± 0.2	9	0.26 ± 0.02	90
Dibenz(*a,c*)anthracene	6 ± 1	13 ± 1	0	0.5 ± 0.1	95
Dibenz(*a,h*)anthracene	3.0 ± 0.8	5.8 ± 0.4	0	0.8 ± 0.3	84
Indeno(1,2,3,-*cd*)pyrene	1.4 ± 0.5	2.7 ± 0.6	3	0.6 ± 0.2	75
Benzo(*ghi*)perylene	5 ± 1	9.8 ± 0.7	1	1.9 ± 0.5	78
Total PAHs	16,115	12,718	58	1714	94

Depletion levels were computed using Eq. (16.1). *DL*, below detection limit.

(such as benzo(*a*)pyrene, chrysene and chrysene homologs) are known to be highly toxic compounds [40−43].

Table 16.4 also shows the concentrations of various parent PAHs and their alkylated homologs measured in the LWO sample. The total amount of PAHs measured was 12,718 mg/kg-oil. Since the original amount of PAHs in source oil was 16,115 mg/kg-oil, the apparent percentage loss of PAH mass was 21%. However, as discussed in our methods section (see Section 16.8.1.4.2), to quantify the true percentage depletion level (or net weathering level), the measured concentrations must be normalized to a conservative species [36]. In

this study we used hopane responses and estimated the value of the hopane normalization factor ($H_{oil}/H_{weathered}$) for LWO as 0.53. Using Eq. (16.1), the true loss of PAHs in the LWO sample after 6 days of evaporation was 58%. These results indicate that evaporation must have removed a considerable amount of PAHs when the spilled oil was transported over the open ocean. The percentage depletion levels of individual PAHs in the LWO sample are summarized in Table 16.4. The data show that lower molecular weight PAHs (such as naphthalene and its alkylated homologs) will be rapidly removed by the evaporation processes; however, higher molecular weight PAHs (3 or more rings) will be fully conserved. For example, the 2-ring parent naphthalene level dropped from 712 mg/kg-oil to below detection limit, while the 4-ring parent chrysene concentration increased in the weathered sample from 49 mg/kg-oil to 95 mg/kg-oil. The concentrating effect observed here is due to changes in the overall oil mass. When chrysene concentrations were normalized using the hopane normalization factor for the sample (i.e., $H_{oil}/$ $H_{weathered}$ value of 0.53), the actual percentage depletion was zero; chrysene was unaffected by evaporation. Overall, the data shown in Table 16.4 indicate that the evaporation process preferentially removed several light PAHs including naphthalenes, parent fluorene, biphenyl, acenaphthylene, and acenaphthene, while evaporation concentrated various heavy PAHs.

The ocean-weathered oil, which first arrived along the Alabama shoreline traveled over 120 miles, continuously weathering over open GOM water. In addition to evaporation, the OWO sample would have been influenced by other natural weathering processes such as chemical dissolution, photodegradation, and biodegradation. In this study, we used the OWO sample to quantify the combined effects of all natural open-water weathering processes. Table 16.4 shows the concentrations of parent PAHs and alkylated PAHs measured in the OWO sample. The total amount of PAHs measured was 1714 mg/kg-oil. The true percentage depletion level, computed after hopane normalization (using the estimated value of $H_{oil}/H_{weathered} = 0.58$), was 94%. This depletion level was substantially higher than the net weathering level estimated for the LWO sample, which was only 58%. The OWO sample data show that both light PAHs as well as some heavy PAHs were weathered in the open-water environment. As expected, light parent naphthalene and its alkylated homologs decreased to nearly zero. Heavy PAHs did not show the concentration effects observed in the LWO sample. For example, the 4-ring parent chrysene concentration decreased from 49 mg/kg-oil in the source oil to 46 mg/kg-oil in the OWO sample; after hopane normalization, the true percentage depletion level for chrysene was estimated to be 45%. This depletion level was distinctly different from the conservative concentration effect for chrysene (i.e., 0% depletion) observed in the LWO sample. These results indicate that in addition to evaporation, other ocean-scale weathering processes played an important role in transforming chrysene (and also other PAHs), while the spilled oil was transported over the open ocean from the well head to Alabama's beaches.

16.8.2.3 Temporal Distribution of Target PAHs in SRBs

As pointed out in OSAT-2 [3], in the vicinity of the shoreline, a portion of ocean-weathered oil interacted with sediment particles and were buried as SOMs. These SOMs were later fragmented by nearshore forces to form SRBs. Both SOMs and SRBs were discontinuously buried and uncovered as they evolve; they can be conceptually viewed as oil spill residues buried in a partially closed sediment system (as compared to the open-ocean system discussed above). To understand the temporal evolution of various PAHs in this partially closed system, we compared the PAH depletion levels in six different SRB samples collected at a location near LP in Gulf Shores, Alabama, over a 4-year period. The PAH concentrations reported here are measured in the residual oil extracted from the SRBs. The measured concentration data are summarized in Table 16.5. The data show that the total PAHs measured in the six SRB samples are 2,382, 2,047, 1,892, 2,206, 2013, and 1533 mg/kg-oil for LP1, LP2, LP3, LP4, LP5, and LP6, respectively. The hopane normalization factors for various samples are estimated to be: 0.48 for LP1, 0.53 for LP2, 0.59 for LP3, 0.40 for LP4, 0.44 for LP5, and 0.52 for LP6. Using these factors, the true percentage depletion levels of PAHs were estimated to be 93% for LP1, 93% for LP2, 93% for LP3, 95% for LP4, 95% for LP5, and 95% for LP6. These data indicate that once open-ocean weathered oil was trapped within the partially closed sediment system (SOMs or SRBs), PAH weathering rates slowed down considerably. In the section below we provide additional data to explore how individual PAH concentrations in SRBs have evolved over the past 4 years.

The percentage depletion levels for selected parent PAHs and alkylated PAHs were computed and the results are summarized in Table 16.5. We have organized the PAHs data into six distinct groups based on their structural properties. Group-1 includes C_0-C_4 alkylated phenanthrenes; Group-2, C_0-C_3 alkylated dibenzothiophenes; Group-3, C_0-C_3 alkylated fluorenes; Group-4, C_0-C_4 alkylated chrysenes; Group-5, various benzo-compounds (benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*j*) fluoranthene, benzo(*e*)pyrene, benzo(*a*)pyrene, and benzo(*ghi*)perylene); and Group-6, all other compounds (anthracene, fluoranthene, pyrene, perylene, dibenz(*a,c*)anthracene, dibenz(*a,h*)anthracene and indeno(1,2,3,-*cd*)pyrene). Note naphthalene and its alkylated homologs, biphenyl, acenaphthylene, and acenaphthene, were not considered since these compounds were predominantly removed by ocean-scale weathering processes and hence were low or undetectable (refer to first arrival OWO sample data in Table 16.4).

Fig. 16.13 shows the temporal changes in all six groups of PAHs measured in the SRB samples recovered from LP. Fig. 16.13A presents temporal variations in the depletion levels of C_0-C_4 alkylated phenanthrenes. The percentage depletion levels for C_0-phenanthrene measured in various SRBs collected over 4 years ranged from 95% to 99%. These results, compared to results reported for the OWO sample (see Table 16.4), which experienced only

TABLE 16.5 Concentration (Average ±SD) of PAHs Measured in SRB Samples

Compound	Temporal Samples					
	LP1	LP2	LP3	LP4	LP5	LP6
C_0-naphthalene	DL	DL	DL	DL	DL	DL
C_1-naphthalenes	DL	DL	DL	DL	DL	DL
C_2-naphthalenes	0.88 ± 0.06	0.59 ± 0.03	0.58 ± 0.07	1.1 ± 0.1	1.05 ± 0.08	0.85 ± 0.06
C_3-naphthalenes	9 ± 1	4.0 ± 0.6	5.5 ± 0.3	12.0 ± 0.3	13.7 ± 0.7	10.1 ± 0.2
C_4-naphthalenes	47 ± 7	25 ± 4	32 ± 2	61 ± 2	64 ± 1	59 ± 2
C_0-phenanthrene	32.6 ± 0.3	23.6 ± 0.4	24.5 ± 0.8	10.2 ± 0.3	9.1 ± 0.8	3.0 ± 0.2
C_1-phenanthrenes	346 ± 4	292 ± 5	276 ± 9	183 ± 7	131 ± 2	32 ± 3
C_2-phenanthrenes	601 ± 8	521 ± 5	472 ± 12	517 ± 4	445 ± 2	286 ± 13
C_3-phenanthrenes	403 ± 54	353 ± 5	318 ± 10	412 ± 4	390 ± 2	339 ± 12
C_4-phenanthrenes	233 ± 2	207 ± 4	185 ± 6	253 ± 9	232 ± 1	215 ± 7
C_0-dibenzothiophene	2.8 ± 0.4	2.4 ± 0.3	2.7 ± 0.2	4.7 ± 0.2	7.7 ± 0.1	2.4 ± 0.5
C_1-dibenzothiophenes	19 ± 2	16 ± 2	16 ± 1	15.2 ± 0.4	15.8 ± 0.3	6.3 ± 0.5
C_2-dibenzothiophenes	57 ± 7	51 ± 6	48 ± 3	62 ± 2	62 ± 1	40 ± 1

C_3-dibenzothiophenes	51 ± 7	46 ± 5	43 ± 3	59 ± 2	57 ± 2	45 ± 1
C_0-fluorene	0.60 ± 0.05	0.41 ± 0.04	0.50 ± 0.03	0.66 ± 0.03	1.27 ± 0.04	0.45 ± 0.05
C_1-fluorenes	23 ± 3	18 ± 2	21 ± 2	23.7 ± 0.8	25 ± 1	15 ± 2
C_2-fluorenes	62 ± 9	59 ± 7	62 ± 5	80 ± 3	85 ± 3	53 ± 4
C_3-fluorenes	105 ± 12	101 ± 12	99 ± 8	141 ± 5	141 ± 2	117 ± 7
C_0-chrysene	65 ± 8	59 ± 6	53 ± 4	75 ± 2	67 ± 1	60 ± 2
C_1-chrysenes	90 ± 12	82 ± 8	74 ± 6	109 ± 4	96 ± 1	90 ± 2
C_2-chrysenes	67 ± 9	61 ± 6	55 ± 5	82 ± 3	72 ± 1	69 ± 1
C_3-chrysenes	28 ± 4	25 ± 3	24 ± 3	35 ± 2	33 ± 2	30 ± 1
C_4-chrysenes	13 ± 2	11 ± 1	10 ± 1	16.0 ± 0.7	15 ± 1	13.0 ± 0.5
Biphenyl	DL	DL	DL	DL	DL	DL
Acenaphthylene	DL	DL	DL	DL	DL	DL
Acenaphthene	DL	DL	DL	DL	DL	DL
Anthracene	1.4 ± 0.2	1.2 ± 0.2	1.3 ± 0.1	1.57 ± 0.08	1.72 ± 0.09	1.18 ± 0.04
Fluoranthene	5.3 ± 0.6	4.5 ± 0.5	4.1 ± 0.4	5.7 ± 0.2	5.4 ± 0.5	4.5 ± 0.2
Pyrene	10 ± 1	9 ± 1	8.0 ± 0.7	11.3 ± 0.3	11.1 ± 0.1	9.5 ± 0.5
Benzo(*a*)anthracene	0.58 ± 0.07	0.50 ± 0.05	0.46 ± 0.05	0.64 ± 0.03	0.60 ± 0.04	0.67 ± 0.05

Continued

TABLE 16.5 Concentration (Average ±SD) of PAHs Measured in SRB Samples—cont'd

Compound	Temporal Samples					
	LP1	LP2	LP3	LP4	LP5	LP6
Benzo(*b*)fluoranthene	9 ± 1	8.3 ± 0.9	7.6 ± 0.7	11.1 ± 0.2	9.75 ± 0.01	8.8 ± 0.1
Benzo(*k*)fluoranthene	2.2 ± 0.3	1.9 ± 0.3	1.7 ± 0.2	2.37 ± 0.08	2.16 ± 0.04	2.0 ± 0.1
Benzo(*j*)fluoranthene	1.3 ± 0.2	1.1 ± 0.2	1.01 ± 0.07	1.5 ± 0.1	1.4 ± 0.1	1.2 ± 0.1
Benzo(*e*)pyrene	11 ± 1	10 ± 1	9.4 ± 0.9	13.6 ± 0.3	12.0 ± 0.1	11.4 ± 0.2
Benzo(*a*)pyrene	0.44 ± 0.02	0.38 ± 0.02	0.39 ± 0.04	0.44 ± 0.05	0.46 ± 0.06	0.48 ± 0.04
Perylene	0.34 ± 0.03	0.28 ± 0.02	0.27 ± 0.02	0.34 ± 0.03	0.34 ± 0.01	0.28 ± 0.02
Dibenz(*a,c*)anthracene	0.73 ± 0.06	0.57 ± 0.07	0.54 ± 0.07	0.71 ± 0.06	0.69 ± 0.04	0.84 ± 0.07
Dibenz(*a,h*)anthracene	1.2 ± 0.2	1.0 ± 0.3	0.9 ± 0.1	1.10 ± 0.08	1.04 ± 0.06	0.8 ± 0.2
Indeno(1,2,3,-*cd*)pyrene	0.9 ± 0.1	0.7 ± 0.1	0.59 ± 0.08	0.8 ± 0.2	0.71 ± 0.08	0.6 ± 0.1
Benzo(*ghi*)perylene	2.9 ± 0.4	2.5 ± 0.3	2.3 ± 0.2	3.3 ± 0.1	2.89 ± 0.05	2.9 ± 0.1
Total PAHs	2382	2047	1892	2206	2013	1533

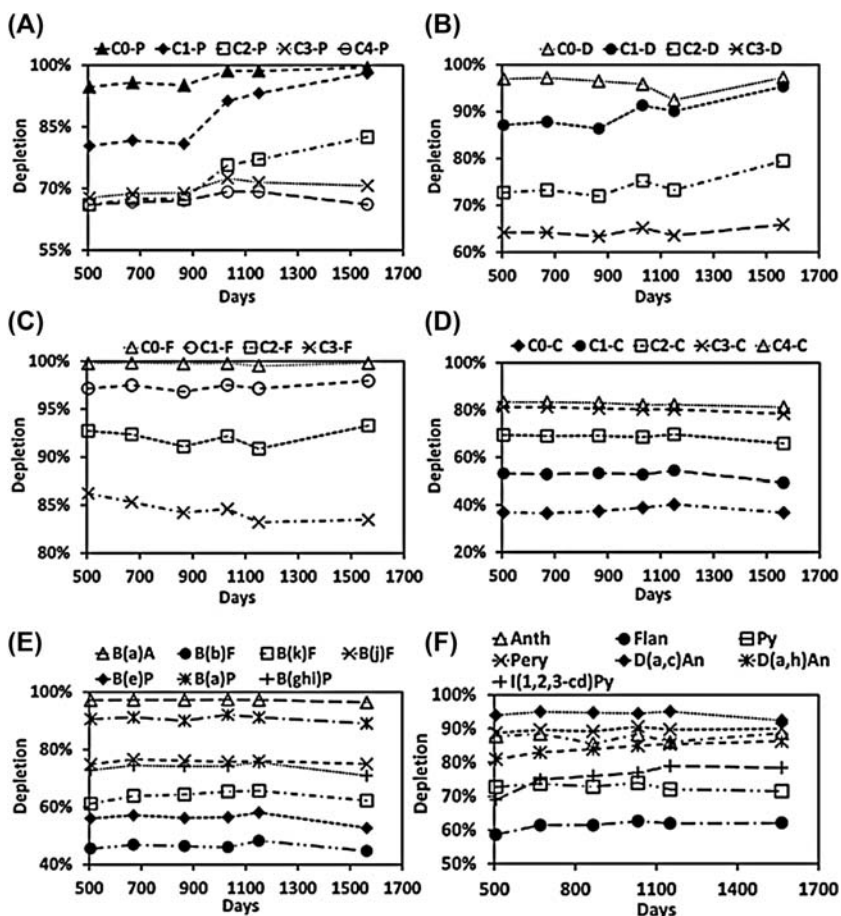Values are reported in mg/kg-oil. *DL*, below detection limit.

FIGURE 16.13 Temporal variations in the percentage depletion levels of the six groups of parent PAHs and alkylated PAHs (days indicate elapsed time since the DWH accident). *(Yin F, John GF, Hayworth JS, Clement TP. Long-term monitoring data to describe the fate of polycyclic aromatic hydrocarbons in deepwater horizon oil submerged off Alabama's beaches. Science of The Total Environment 2015;508:46−56. http://dx.doi.org/10.1016/j.scitotenv.2014.10.105.)*

about a month of open-ocean weathering, indicate that the C_0-phenanthrene weathering rate decreased once the oil was trapped within SOMs/SRBs. Fig. 16.13A also shows that similar to parent phenantherene, rates of degradation of C_1, C_2, C_3, and C_4 alkylated phenanthrenes in SRBs have also slowed down when compared to open-ocean weathering rates. The C_1 depletion levels ranged from 80 to 98% and C_2 levels ranged from 66 to 83% over the past 4 years, and they continue to degrade at a reduced rate. The C_3 depletion levels ranged from 68 to 72% and C_4 levels ranged from 66 to 69%, and these levels appear to be fairly stable. Furthermore, the net loss of various phenantherenes appears to decrease with the level of alkylation, indicating a trend where the net depletion for $C_0 > C_1 > C_2 > C_3 > C_4$.

The temporal evolution of C_0-C_3 alkylated dibenzothiophenes are shown in Fig. 16.13B, and the temporal changes in C_0-C_3 alkylated fluorenes are shown in Fig. 16.13C. In both cases, the level of weathering is high for parent PAHs when compared to their alkylated homologs. For C_0-dibenzothiophenes, the removal levels ranged from 92 to 97%; this removal level was higher than those observed for C_1-dibenzothiophenes (86−95%), followed by C_2-dibenzothiophenes (72−79%) and C_3-dibenzothiophenes (63−66%). For fluorenes, C_0-fluorene weathered by almost 100%, followed by C_1-fluorenes (97−98%), C_2-fluorenes (91−93%), and C_3-fluorenes (83−86%). Weathering rates for both dibenzothiophenes and fluorenes appear to have slowed once the oil was trapped in SRBs. For both dibenzothiophene and fluorene compounds, the overall loss appears to decrease with alkylation levels with a trend of $C_0 > C_1 > C_2 > C_3$, which is identical to the trend observed for phenantherenes.

The temporal evolution of C_0-C_4 alkylated chrysenes are shown in Fig. 16.13D. Interestingly, the overall removal trend for chrysene homologs is: $C_4 > C_3 > C_2 > C_1 > C_0$, which is opposite the trend observed for phenantherenes, dibenzothiophenes, and fluorenes. The highly alkylated C_4-chrysenes were the most weathered species (81−83%), followed by C_3-chrysenes (78−81%), C_2-chrysenes (66−70%), and C_1-chrysenes (49−54%). The least degraded compound in this group is the C_0-chrysene, which was degraded only by about 37−40%. When these weathering levels are compared with the levels measured for the OWO sample (which weathered for about 30 days in the open ocean), it is clear that the weathering of chrysene and its alkylated homologs have essentially stopped once the oil was trapped in SRBs. Previous laboratory-scale experiments have shown that the rate of photo-degradation of chrysenes in crude oil increases with increased alkylation when the oil is exposed to ultraviolet light [44]. This could explain why higher alkylated chrysene homologs are degraded more than the lower alkylated chrysenes in OWO and SRB samples. These data also suggest that chrysene weathering was predominantly due to abiotic processes rather than biological processes. A recent study, which was completed to differentiate the roles of photooxidation and biodegradation in the weathering of floating crude oil, has shown that photooxidation was indeed one of the dominant mechanisms that weathered heavy PAHs when the oil was floating over the ocean [20].

The temporal evolution of various benzo-compounds in Group-5 are shown in Fig. 16.13E. These data show that benzo(*a*)anthracene weathered by about 96−97%, benzo(*a*)pyrene by about 89−92%, benzo(*j*)fluoranthene by about 75−77%, benzo(*ghi*)perylene by about 71−76%, benzo(*k*)fluoranthene by about 61−66%, benzo(*e*)pyrene by about 53−58%, and benzo(*b*)fluoranthene by about 45−48%. The trend lines shown in Fig. 16.13E are almost horizontal, indicating that little weathering has occurred over the past 4 years.

The temporal evolution of Group-6 PAHs are shown in Fig. 16.13F. The data show that dibenz(*a,c*)anthracene weathered by about 92−95%, perylene by about 89−91%, anthracene by about 86−89%, dibenz(*a,h*)anthracene by about

81−86%, indeno(1,2,3,-*cd*)pyrene by about 69−79%, pyrene by about 72−74%, and fluoranthene by about 59−63%. Again, the trend lines are almost horizontal indicating little or no additional weathering has occurred over the past 4 years.

16.9 DISCUSSION

As per our knowledge, currently there are no published studies available in the peer-reviewed literature that document any major oil spill (other than the DWH spill), which has occurred within 100−200 km away from the Alabama shoreline in the past three decades. Also, although GOM has several natural oil seeps, all known oil seeps are located well over 200−300 km away from the Alabama shoreline [45] and there is no published record of any beach contamination problem due to these natural seeps.

One of the earliest available oil spill related tar ball studies, which was completed closer to the Alabama shoreline, was done by Romero et al. [46]. This study included the Panhandle region of Florida. This field study was completed in between 1979 and 1980 and it included northwestern Florida beaches that are close to Alabama. This baseline study was motivated by the possibility that the 1979 Ixtoc blowout, which occurred in the southern Bay of Campeche, Mexico, might have increased the tar ball activity level along Florida's beaches. One of the key conclusions from the study was that it is rare to find oil contamination or tar balls in the Panhandle region [46]. Furthermore, even when they were found, the levels were extremely low. An average annual value of four tar balls per site was found at each of the following four monitoring points (all located within the Panhandle region): Carrabelle, St. Joe State Park, St. Andrews State Park, and Santa Rosa Island. The values measured at northern Florida beaches were some of the lowest values recorded in this statewide, yearlong survey. Based on the field data the study made the following conclusion about Florida's Panhandle beaches located close to Alabama [46]: "the beaches of the northeast (i.e., Panhandle beaches) and entire west coast (of Florida) are quite pristine with many of them having no observable tar balls."

Based on background tar ball data reported in various publications [4,25,46] and based on our own observation of Alabama's beaches over the past 6 years, we derive an average background oiling level (i.e., non-DWH oil level) for Alabama's beaches. Our best estimate for background tar ball activity is about 2−4 highly weathered tar balls (each weighing about 0.5−1 g) deposited along a kilometer of shoreline over a year (here shoreline refers to the ∼10 m wide swash zone, where shells and other marine debris are constantly deposited). Based on these values, the background level for Alabama beaches prior to the DWH oil spill is estimated to be about 1−2 g of oil per kilometer of shoreline per year (g/km/year). This is both spatially and temporally averaged long-term estimate. Also, for some pristine Alabama beaches (e.g., beaches along the City of Orange Beach) where no tar balls were

found during the pre-oil spill surveys completed by the Unified Command [25] and by our team [24] the background estimate could be almost close to zero.

All of the SRB datasets for Alabama's beaches collected by our team since June 2010 show that the oiling levels are several orders of magnitude higher than the estimated background level. For example, during our recent January 2016 survey we collected 98 g of SRBs from Orange Beach, 1120 g from Lagoon Pass, 1310 g from Fort Morgan beaches—all collected by surveying about half a kilometer of shoreline ($\sim$500-m long and $\sim$10-m wide swash zone) for about an hour. It is likely that these beaches have the propensity to deposit these levels of SRBs within a week or even within a day. For example, the daily sampling survey completed during the Lagoon Pass excavation project did reveal that the system has the potential to deposit considerable amount of SRBs on a daily basis. In order to derive an estimate for current SRB deposition rates, we assumed that the SRBs collected on January 30, 2016, were deposited over a period of month (this perhaps is a conservative assumption since the continuous monitoring data shown in Fig. 16.9 indicate that SRBs can be rapidly replenished within a relatively short period). Based on this assumption, we have estimated that the current background oil levels as: 0.24×10^4 g/km/year for Orange Beach, 2.7×10^4 g/km/year for Gulf Shores, and 3.1×10^4 g/km/year for Fort Morgan beaches. These values are about 3 or 4 orders of magnitude higher than the background levels estimated for the time prior to the DWH oil spill (which was $\sim$2 g/km/year). We acknowledge that this is a preliminary, first-order estimate to quantify the increase in oil levels along Alabama's beaches that resulted from the DWH oil spill. As per our knowledge, this is the first attempt to objectively quantify this increase, and currently there are no other data available even to make orders of magnitude estimates. We certainly acknowledge that these estimates will have considerable uncertainty due to seasonal and spatial variations in SRB deposition patterns, and therefore more field studies are needed to fully understand both temporal and spatial variations in these values.

In our laboratory dataset, we have compiled the concentrations of 22 parent PAHs and 18 alkylated PAH homologs present in different types of DWH oil spill samples. We have analyzed four types of samples, namely the original DWH oil, a week-old laboratory-weathered oil, first arrival oil mousse, and several shoreline-weathered SRB samples collected from Alabama beaches over a 4-year period (2000−14). Our results show that low molecular weight PAHs were the dominant group of PAHs in the source crude (MC-252 oil). When the oil was allowed to evaporate under laboratory conditions, about 58% of PAH compounds were removed within 6 days, and most of the evaporated PAHs were low molecular weight volatile compounds. Several high molecular weight PAHs (e.g., parent chrysene) concentrated like a conservative biomarker in the laboratory-evaporated sample. The PAH levels measured in the ocean-weathered sample indicated that both light as well as several of the

heavy PAHs have weathered in the open-ocean environment. The depletion levels of all light PAHs and their alkylated homologs were close to 100%. The percentage depletion level for the 4-ring parent chrysene, for example, in the ocean-weathered sample was 45%, which was substantially higher than the close to 0% depletion of chrysene observed in the laboratory-evaporated sample. Similar trends were also observed for several other heavy PAHs. These results indicate that in addition to evaporation, other physicochemical weathering processes, such as photo-oxidation, dissolution, and biochemical reactions have played a significant role in removing PAHs when the oil was floating over the open ocean. Interestingly, all of these weathering processes have slowed down significantly (or even ceased in some cases, e.g., chrysene) once the oil was buried within the partially closed nearshore beach environment. The 4-year temporal dataset for PAHs measured in SRB samples collected near Lagoon Pass supports this "slowing down" hypothesis.

These chemical data, when combined with the conceptual framework for physical evolution of DWH oil spill residues and their potential toxic effects discussed in recent published studies [22,24,32,33,47], suggest the likelihood that these SRBs have the potential to pose long-term ecological risks to GOM beaches for several years. Although questions related to the spatial and temporal extents of this problem (i.e., how widespread are the SRB/SOM contaminated areas, and how long would they last) cannot not be fully answered at this time, it is highly likely that the organisms which live in or frequent the DWH oil−contaminated beaches are being exposed to several toxic heavy PAHs trapped in these residues. The long-term ecological consequences of these exposures are currently unknown.

16.10 CONCLUSIONS

The MC252 tar balls (or DWH tar balls) contain brownish, sticky, petroleum smelling, relatively unweathered oil mixed with considerable amount of sand. There is no past record for the presence of oil spill residues with such physical characteristics washing along Alabama's beaches prior to the 2010 DWH accident. While the oil released from the GOM's natural seeps, ships, or exploration wells has the potential to form traditional tar balls (black, rubbery, and weathered with little or no sand), it is extremely rare to find these tar balls on Alabama's beaches. Based on available background data, we estimated the historic background oil level for the Alabama shoreline, prior to the DWH accident, was about 2 g/km/year. The current background oil level can be about thousand times higher than this historic background value. Using our recent January 2016 monitoring dataset, we estimated the current background oil levels as: 0.24×10^4, 2.7×10^4, and 3.1×10^4 g/km/year for Orange Beach, Gulf Shores, and Fort Morgan beaches, respectively.

Our laboratory data show that several higher molecular weight PAHs, such as chrysene and its alkylated homologs, trapped in submerged DWH oil spill

residues are degrading at a rate slower than the rates initially occurred when the oil was weathering over the open ocean. Therefore, unless there is substantial dispersion due to physical disintegration (i.e., SRBs are broken apart by physical forces), these PAHs will remain trapped in submerged SRBs.

Based on above results we derive the following set of conclusions, which can also serve as a revised set of hypotheses, that describe the present state of Alabama's beaches and also predict the future evolution patterns of the DWH oil trapped within this environment. They are: (1) the current background oil−contamination levels are much higher than the relatively low (in some cases, negligible) background levels that existed prior to the DWH oil spill; (2) virtually all of the visible oil spill residues currently deposited along the Alabama shoreline in the form of fragile, brownish, sticky tar balls and tar patties should have originated from the DWH oil spill; and (3) several higher molecular weight PAHs, such as chrysene and its alkylated homologs, trapped in DWH oil spill residues are degrading at a much slower rate than they were prior to the oil being submerged near the shoreline; also, it is highly likely that these contaminants will remain in the nearshore environment for an extended period of time.

This study exclusively focused on Alabama beaches located between Perdido Bay and Fort Morgan; therefore, these hypotheses primarily describe our understanding of this region. More studies are needed to test and extend the validity of these hypotheses to other GOM beach systems. Currently, monitoring data are not available to track the on-going changes in background oil levels occurring along the Alabama shoreline. Also, there are no rational methods available for objectively quantifying the value of the background oil level. Future research efforts should conduct organized field surveys to capture both temporal and spatial variations in oil deposition levels. Furthermore, these studies should focus on developing rational metrics that can help quantify changes in background oil levels and track its seasonal variations. Finally, the biological and ecological implications of the increases in background oil levels that resulted from the DWH oil spill are not clear at this stage, and more biological studies are needed to understand these implications.

LIST OF ABBREVIATIONS

Anth Anthracene
B(a)A Benzo(*a*)anthracene
B(a)P Benzo(*a*)pyrene
B(b)F Benzo(*b*)fluoranthene
B(e)P Benzo(*e*)pyrene
B(ghi)P Benzo(*ghi*)perylene
B(j)F Benzo(*j*)fluoranthene
B(k)F Benzo(*k*)fluoranthene
BP British Petroleum

BS Bon Secour National Wildlife Refuge
C_0-C C_0-chrysene
C_0-D C_0-dibenzothiophene
C_0-F C_0-fluorene
C_0-P C_0-phenanthrene
C_1-C C_1-chrysenes
C_1-D C_1-dibenzothiophenes
C_1-F C_1-fluorenes
C_1-P C_1-phenanthrenes
C_2-C C_2-chrysenes
C_2-D C_2-dibenzothiophenes
C_2-F C_2-fluorenes
C_2-P C_2-phenanthrenes
C_3-C C_3-chrysenes
C_3-D C_3-dibenzothiophenes
C_3-F C_3-fluorenes
C_3-P C_3-phenanthrenes
C_4-C C_4-chrysenes
C_4-P C_4-phenanthrenes
CE Collision energy
D(a,c)An Dibenz(*a,c*)Anthracene
D(a,h)An Dibenz(*a,h*)Anthracene
DL Below detection limit
DWH Deepwater Horizon
EI Electron ionization
Flan Fluoranthene
FM Fort Morgan
GOM Gulf of Mexico
I(1,2,3-cd)Py Indeno(1,2,3,-*cd*)pyrene
IS Internal standard
LOD Limit of detection
LOQ Limit of quantitation
LP Lagoon Pass
LWO Laboratory-weathered oil samples
MC252 Mississippi Canyon Block 252
MRM Multiple-reaction monitoring
OB Orange Beach
OWO Ocean-weathered DWH oil
PAHs Polycyclic aromatic hydrocarbons
Pery Perylene
Py Pyrene
RRF Relative response factor
SD Standard deviation
SIM Single-ion monitoring
SOMs Submerged oil mats
SRBs Surface residual oil balls
SS Surrogate standard
TS Time segment

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