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Distribution and Biodegradation Potential of Buried Oil on a Coastal Headland Beach

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ABSTRACT 300129:

Buried and surface MC252 oil from the intertidal on a coastal headland beach was sampled using a randomized block methodology. Weathering indices contrasting alkylated 3- (phenanthrenes) and 4-ring (chrysene) PAH concentrations were computed based on analyses of these samples. Buried oil was detected at a frequency of 18% and, of those samples, 29% had indices indistinguishable from oil sampled near the wellhead indicating that PAH weathering was not occurring. These samples with persistent PAHs were associated with one or more conditions in the beach profile: located at or near the depth of the water table, nearest to the shoreline, or within a thicker oil mat deposit. Surface oil samples, consisting of oil:sand aggregates recently washed in by the surf, had a higher percentage (81%) of oil with weathering indices indicating persistence. These observations, coupled with measurements of biogeochemical analyses on the beach from other studies, suggest that insufficient oxygen in the nearshore environment of these coastal headlands creates conditions for PAH persistence over time frames of years to decades.

INTRODUCTION:

Coastal headland beach environments along the Louisiana Gulf coast were disproportionately impacted by shoreline oiling during the *Deepwater Horizon* spill. These coastal headlands consist of several distinct microenvironments: subtidal, intertidal and supratidal zones on the beach and mudflat, marsh and mangrove environments in the area adjacent to the beach. These systems are extremely dynamic, with sand and mud reworking by waves, tides and storm surge overwash resulting in intermittently changing elevation and position of the sands (McBride et al., 1992). Crude oil reached the Louisiana shoreline primarily in the form of a water-in-oil emulsion resulting in formation of several unique oil forms including small aggregates of oil, sand and shell termed surface residue balls (SRBs) (Urbano et al., 2013) and larger agglomerations of oil, sand and shell termed submerged oil mats (SOMs). Storm-driven processes have resulted in stratified layers of oil, oiled sands and clean sands on coastal headland beach systems resulting in a mixture of surface and buried oil deposits. Previous studies have examined the distribution and fate of oil stranded on the supratidal portion of the beach environment (Elango et al., 2014; Lemelle et al., 2014; Urbano et al., 2013), but little information on the distribution and fate of oil in the intertidal is available.

Buried oil on beaches is produced by two primary mechanisms: penetration of oil through the sands (Vandermeulen et al., 1979) and changes in beach morphodynamics driven by storms and tides (Bernabeu et al., 2006; Gonzalez et al., 2009). Physicochemical weathering processes (e.g., evaporation, dissolution, photodegradation and dispersion), biological processes (e.g., biodegradation), affect unburied or surface oil deposited in the intertidal zone. These processes are particularly effective on oil deposited in the middle to upper portions of this zone (Short et al., 2007; Taylor and Reimer, 2008), since it receives the maximum tidal flushing and wave action (Taylor and Reimer, 2008). The degree to which dissipation or degradation will take place is dependent on the energy levels at the shoreline and the types of substrates present on the beach (Taylor and Reimer, 2008). In some low energy settings, sediments in the water column can mobilize stranded oil through oil-fines interactions (OFI) or oil-mineral aggregate (OMA) interaction (Owens, 1999; Taylor and Reimer, 2008). For buried oil, weathering rates can be considerably reduced (Short et al., 2007; Short et al., 2006; Taylor and Reimer, 2008).

Intrinsic and enhanced biodegradation of buried crude oil has been investigated in a number of beach types (Pontes et al., 2013; Roling et al., 2004; Roling et al., 2002). Important factors affecting subsurface oil biodegradation include limited nutrient availability to sustain oil biodegradation and low oxygen availability (Short et al., 2007). Site-specific issues affecting potential for biodegradation of buried oil include the emulsified nature of the oil deposits, the presence of a confining clay layer with elevated organic matter underlying the beach sands, and low dissolved oxygen concentrations in beach groundwater (OSAT-II, 2011). In addition, weathering at sea has reduced concentrations of more biodegradable lower ring PAHs leaving a mixture of alkylated 3- and 4-ring compounds with lower susceptibility to further physical and biological weathering processes (Urbano et al., 2013). In the supratidal beach environment, biodegradation of PAHs in surface deposited SRBs proceeded over a time frame of months to a year to produce a very biodegraded profile, despite suboptimal moisture and nutrient conditions (Elango et al., 2014).

The objective of this study was to understand the distribution and compositional changes of crude oil in the intertidal environment of Fourchon Beach, LA located west of the Mississippi delta in Lafourche Parish, LA. In particular, the compositional changes in buried oil due to biodegradation were of interest. Detailed measurements of the chemical composition of the oil deposited on the surface and subsurface of the beach were conducted between months 9-15 (February 2011-August 2011) after oil reached the shoreline (May 2010). A randomized block sampling approach was used to assess the presence and composition of surface and subsurface oil. Ratios of PAHs susceptible to biodegradation to more recalcitrant PAHs and hopanes were used to infer weathering processes occurring in samples of the buried and surface oil. Understanding the compositional changes of MC252 crude oil across coastal headlands impacted by the *Deepwater Horizon* spill and dynamics of oil contamination in these microenvironments is critical to establishing a rate of recovery.

METHODS:

Study site

Fourchon Beach is the westernmost 9-mile segment of the 13.8 mile Caminada Headlands, comprised of this Fourchon Beach and Elmer's Island. It is located in Port Fourchon, LA approximately 100 miles south of New Orleans, LA. Fourchon Beach is owned by the Edward J. Wisner Donation, a land trust, and is closed to the public. Clean-up has been conducted at the beach since 2010 and segments continue under active response three years after the spill reached the shoreline in May 2010. For operational clean-up purposes, the beach was divided into 9 zones, approximately 1 mile in length each, numbered 1-9 running east to west by Incident Command (**Figure 1**). These zones were used as arbitrary blocks and at least one segment of each zone was sampled (with the exception of one closed for archaeological purposes) using the procedures described below.

Sampling procedures

A randomized block sampling procedure was used to collect surface and subsurface samples for oiling during this period. First, one of the nine zones was randomly selected for sampling (**Figure 1**). A segment of that zone was then selected randomly and a grid was established 80 m along the shoreline and whatever distance was required to reach the beach crest at the tidal conditions prevalent during sampling. Typically, this distance was ~25 m. Within that 80 m x ~25 m grid, 16 sample locations were selected using a random number table. To insure that an even distribution of locations was selected normal and parallel to the shoreline, blocks were established to distribute the samples along the shoreline (0-20 m, 20-40 m, 40-60 m, 60-80 m). Additionally, four blocks were established between the water and the beach crest. At each of the 16 locations, a 1 x 1 m square was placed and any surface samples were collected for analysis. Following surface sample collection, a test pit was dug to the underlying clay layer or the saturated water layer of the beach, whichever was reached first. Each test pit was observed for the presence of oil and samples were collected during the digging process. In addition to the samples obtained from the test pits, oil washing up in the surf within 0.5-1 meter of the sampled shoreline was also collected to determine the mass and quality of oil washing ashore on the sampling day tidal cycle. No effort was made to time the visits around low or high tides, therefore, the ambient tidal conditions during sampling were another random variable.

Oil extraction and analysis

Samples were extracted using hexane:acetone and analyzed using GC-MS using methods detailed in Urbano et al. (2010). Quantitation was performed using selected ion monitoring (SIM) mode with deuterated PAHs as internal standards. Daily quality control included blanks and continuing calibration standards for analytes.

Weathering ratios

Because of the variability in the amount of oil in samples and within the aggregate type of samples present at the site, ratios of measured compounds were used to detect patterns of compositional change driven by biodegradation and other weathering processes. Similar indices have been used to study weathering processes in previous spills (Hayes and Michel, 1999; Wang et al., 1998). Four ratios were used to draw conclusions about the PAHs present in the samples.

a. **ΣPAH/hopane index.** This index is defined as the ratio of the following concentrations:

$$\frac{\Sigma(C_1, C_{2,}C_3 - PHEN, C_{1,}\ C_{2,}C_3 - CHRYS)}{C30 - hopane}$$

By normalizing the concentrations of the three dominant groups of PAHs to the poorly biodegradable C30-hopane, declines in the ratio occur as the more-biodegradable PAHs disappear from the mixture.

b. Alkylated phenanthrenes/chrysene index

$$\frac{100 * \Sigma(C_1, C_{2,} C_3 - PHEN)}{\Sigma(C_1, C_{2,} C_3 - CHRYS) + \Sigma(C_1, C_{2,} C_3 - PHEN)}$$

The alkylated 3-ring PAHs are more subject to weathering processes such as biodegradation than the alkylated 4-ring PAHs, therefore declines in the ratio of the sum of alkylated phenanthrenes (C1-C4 PHEN) to the sum of the alkylated chrysenes (C1-C3 CHRYS) will indicate the weathering of 3-ring PAHs relative to the more recalcitrant 4-ring PAHs.

c. C2-phenanthrenes/C2 chrysenes and C3-phenanthrenes/C3 chrysenes

Another facet of the weathering response is the relative degradation of two sets of alkylated PAHs, the C2-substituted phenanthrenes and chrysenes and the C3-substituted phenanthrenes and chrysenes. Lower alkylated compounds will have more rapid biodegradation than higher alkylated congeners. Declines in these ratios will result from biodegradation or other weathering reactions which change this ratio.

RESULTS /DISCUSSION:

Subsurface oil detection and chemical composition

Subsurface oil was detected at a frequency of 18.8% across all segments sampled (**Table 1**). The segment with the most frequent detection was 50% for a segment sampled in Zone 3 on 5/5/11. The lowest frequency was no subsurface oil detected in a segment in Zone 6 on 3/31/11 and Zone 2 on 6/14/11. The form of oil detected included buried oil:sand aggregates (i.e., SRBs), stained sands, oiled shell hash, and at a lower frequency, contiguous layers of oil mat. Across the fifteen, 80 m segments sampled, 70 samples were collected for PAH and alkane analysis and weathering ratios. From those samples, 55 had concentrations significant enough to conclude that MC252 oil was present based on 191 m/z ion chromatograms, detections of petrogenic PAHs known to be present in this crude oil and visual and photographic evidence of the oil in the test pits. In some cases, multiple samples were taken for pits with oil at different depths.

Two sets of indices computed from measured PAH concentrations were used to examine relative weathering in the subsurface samples. First, the alkylated phenanthrene to chrysene index and the ΣPAH/hopane ratio were plotted in **Figure 2**. Relatively unbiodegraded sample profiles lie at the top right of the plot and samples with more biodegraded profiles lie near the origin. A subset of samples (N=16) showed no evidence of biodegradation and had PAH concentrations similar to the oil initially reaching the shoreline (Diercks et al., 2010; Urbano et al., 2013). The remaining samples exhibited some evidence of PAH weathering including a significant number near the origin, representing samples that had lost much of their alkylated phenanthrenes. Samples were arbitrarily divided into two groups of samples, those with C30-hopane concentrations indicative of less than 1% MC252 and those with hopane concentrations indicative of greater than 1% MC252. These concentrations were calibrated based on previous measurements of C30-hopane and total C in aggregates on the supratidal (Elango et al., 2014).

The presence of higher and lower percentages of oil in the sample did not appear to be an important factor in the presence or absence of a weathered oil profile.

The geological setting of these 16 samples is of interest and a description of each is in **Table 2**. This is based on the written and photographic records from the test pits. Three factors were used to classify the samples: the proximity of the samples to the shoreline, the presence or absence of a contiguous oil mat, and the proximity of the sample to the water table. Each of these factors is associated with low oxygen conditions at this beach, which we hypothesize as being important to explain PAH persistence in the subsurface. Twelve of the 16 samples were present in larger oil mat deposits, with 7 of the 16 samples at or below the water table. Five of the samples were located in the block closest to the shoreline. These were higher frequencies than the dataset as a whole, suggesting they may be important classifiers for PAH persistence. Even though sampling was conducted during spring and early summer when cold fronts and tropical storms are uncommon to substantially rework the beach sands, the residence time of the oil in the subsurface was unknown, providing an additional source of variability to the weathering data.

Another set of weathering indices was computed by comparing individual congeners of the more biodegradable 3-ring phenanthrenes and chrysenes. Nearly all of the points plot below a 45-degree reference line suggesting that C2-phenanthrenes weather prior to the C3-phenanthrenes. For both categories of samples, the values of the indices ranged from near the origin (more weathered samples) to near the values observed in oil near the wellhead (**Figure 3**). This continuum in the value of these indices suggests that a wide range of biogeochemical conditions developed in the subsurface allowing for partial weathering of the 3 ring phenanthrenes. A significant percentage of the buried samples (16/55 = 29%) showed no evidence of weathering.

To determine if samples were changing over the time frame of the study, the alkylated phenanthrene to chrysene ratio was plotted over time (**Figure 4**). No temporal trend was observed in the data suggesting that differences in setting within the intertidal were more important than time since the spill. At any given location and time, samples covering a wide range of weathering indices could be sampled in the subsurface on Fourchon Beach.

Surface oil

Surface oil was detected in 9.5% of the randomly selected plots. At 9 of the 15 segments, surveys of oil in the surf were successful at collecting samples for analysis in quantities as high as 1 kg over the 80 m distance. The form of oil detected in the shoreline surveys was consistently a higher oil content aggregate, smaller and more rounded than many of the SRBs encountered in the intertidal sands. This was confirmed by C30-hopane concentrations that indicated MC252 concentrations in the aggregates were greater than 5-10%.

For comparison purposes, the same weathering indices used for the subsurface oil was used for the surface oil (**Figures 2 and 3**). The plot of the alkylated phenanthrene to chrysene ratio and the ΣPAH/hopane ratio shows that most of the surface sampled oil was not weathered relative to the oil near the wellhead (**Figure 2**). Of the 21 samples, only four showed any evidence of weathering. Similarly, when the C2/C3 ratios were calculated as above, the same 4 - 5 samples had evidence of partial weathering of the phenanthrenes but, again, most were untransformed (**Figure 3**). The source of this surface oil is unknown, but we hypothesize that it originated from subtidal oil mats, which have continued to erode and deposit oil on the beach to the present day. Other possibilities include alongshore transport of SRBs or another oil form from other locations. Regardless of the identity of the source, the quality of the surface oil suggests that oil similar in quality of the original oil reaching the shoreline continued to move into the intertidal in the year after the spill.

Biogeochemical conditions and comparison with supratidal biodegradation rates

Previous studies have shown persistence of buried oil in a number of settings and oil types ((Bernabeu et al., 2010; Boehm et al., 2008; Short et al., 2007; Teal et al., 1978). The absence of sufficient oxygen has been implicated as a cause of persistence in crude oil in buried crude oil (Short et al., 2007). Three additional pieces of data support the hypothesis that oxygen limitations were important for the persistence of buried oil. We have measured oxygen concentrations across several profiles in the beach tidal groundwater and every concentration has been <0.5 mg/L, even in water 15 cm below the surf zone (data not shown). These are consistent with measurement of 0.4 mg/L in beach groundwater at adjacent Grand Isle, LA during the OSAT-II study (OSAT-II, 2011). Finally, microelectrode measurements in SRBs incubated in the laboratory in aerated seawater showed readily depleted oxygen in the aggregate (Urbano et al., 2013). Other biogeochemical parameters measured at this location included nutrient concentrations, salinity and the presence of PAH degrading populations (Urbano et al., 2013; Elango et al., 2014). Three-ring PAHs (phenanthrenes and dibenzothiophenes) readily degraded in the supratidal zone of this beach over the same time frame. At these locations, weathering indices demonstrated a response consistent with biodegradation, despite suboptimal moisture and nutrient conditions in the supratidal.

The weathering observed in the buried oil samples was consistent with biodegradation considering the patterns observed and the mass transfer limitations on other weathering processes (i.e., evaporation, dissolution, dispersion, photodegradation) for buried oil. In the intertidal, moisture and nutrient conditions have been mitigated, but oxygen levels may be slowing or altogether preventing degradation of phenanthrenes if samples are below the water table or present in mat deposits where oxygen demand is high.

The implication of these results for beach response is that intertidal, buried oil higher in the beach profile can undergo weathering reactions for PAHs that will contribute to recovery. However, persistent oil may be present in these systems if it is below the water table on the beach, trapped in the subtidal or associated with thicker deposits where oxygen limitations are common. This strongly implicates aerobic microbial processes as important fate processes for buried oil but confirmation of this can only be obtained in controlled laboratory studies where weathering reactions can be observed in the absence of bacteria.

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Table 1. Locations and detection frequency of sampled beach segments organized by operational zone.

Zone	Date Sampled	Reference Coordinate	Surface Oil Detection†	Subsurface Oil Detection†
1	6/21/11	N29°09.047 W90°06.755	1/16	4/16
1	6/21/11	N29°09.133 W90°06.646	4/16	1/16
1	8/4/11	N29°09.292 W90°06.396	2/16	5/16
2	6/13/11	N29°08.747 W90°07.219	3/16	7/16
2	6/14/11	N29°08.784 W90°07.176	1/16	0/16
2	6/14/11	N29°08.896 W90°06.982	6/16	2/16
3	4/14/11	N29°08.630, W90°07.409	3/16	4/16
3	5/5/11	N29°08.660, W90°10.510	2/16	8/16
6	3/31/11	N29°06.760, W90°07.380	0/16	0/16
7	8/2/11	N29°06.157 W90°11.268	0/16	
7	8/2/11	N29°06.258 W90°11.108	0/16	4/16
7	6/20/11	N29°06.377 W90°10.988	0/16	4/16
8	2/21/11	N29°06.072, W90°11.398	1/16	2/16
9	3/15/11	N29°05.205 W90°13.352	0/16	1/16
9	3/1/11	N29°05.537 W90°12.637	0/16	3/16
Total			23/240 = 9.5%	45/240=18.8%

†# of sites with detected oil/# of sites sampled

Table 2. Characteristics of 16 subsurface samples showing no biodegradation

Sample[1]	Date	At or below water table?[2]	Oil mat?[3]	Near shoreline?[4]
A'C (2-15), 8	2/22/11		1-1.5	✓
B'B (35-12), 9	3/1/11		1-1.5	
C'C (57-13), 9	3/1/11		1-1.5	
D'C (62-14), 9	3/1/11		1-1.5	
D'D (71-23),9	3/1/11		1-1.5	
A'A (9-5), 3	4/13/11		2.5	✓
B'B (39-12), 3	4/13/11	✓	1-1.5	
C'B (44-11), 3	4/13/11			
A'D(76-3), 5	4/20/11	✓		✓
A'D (18-19).3	5/5/11	✓	2.5	✓
C'C (49-10), 3	5/5/11	✓	4.0	
D'B (72-6), 3	5/5/11		1-1.5	
C'A (19-7), 2	6/13/11	✓	2.5	
A'C (54-1), 2	6/13/11	✓		✓
B'A (1-7), 1	6/21/11	✓	5	
D'A (15-8), 7	8/2/11			

[1] Sample block designation (i.e., A'C), coordinates on grid (y-x) in meters and operational zone (1-9)

[2] Samples located within 4 cm of the water table during sampling

[3] Samples consisted of contiguous oil layer with thickness in cm indicated

[4] Sample located in the A' block at the shoreline (Figure 1)

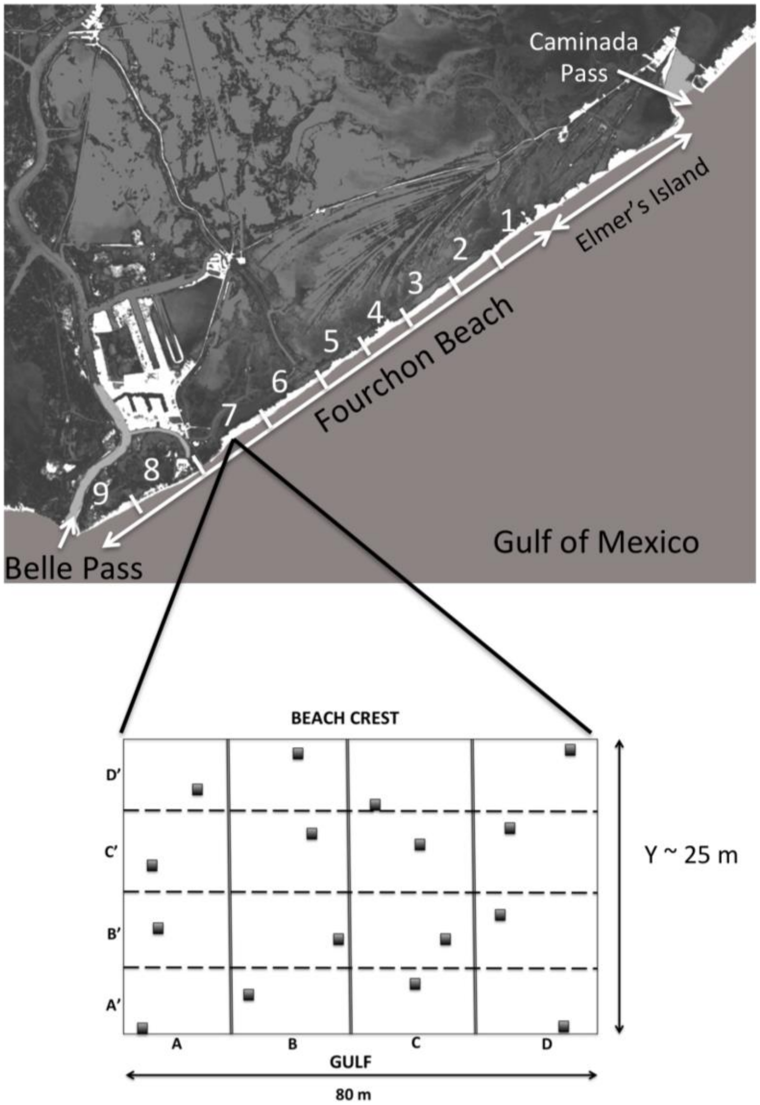


Figure 1. Fourchon Beach with operational clean-up zones 1-9 and diagram of typical randomized block sampling approach

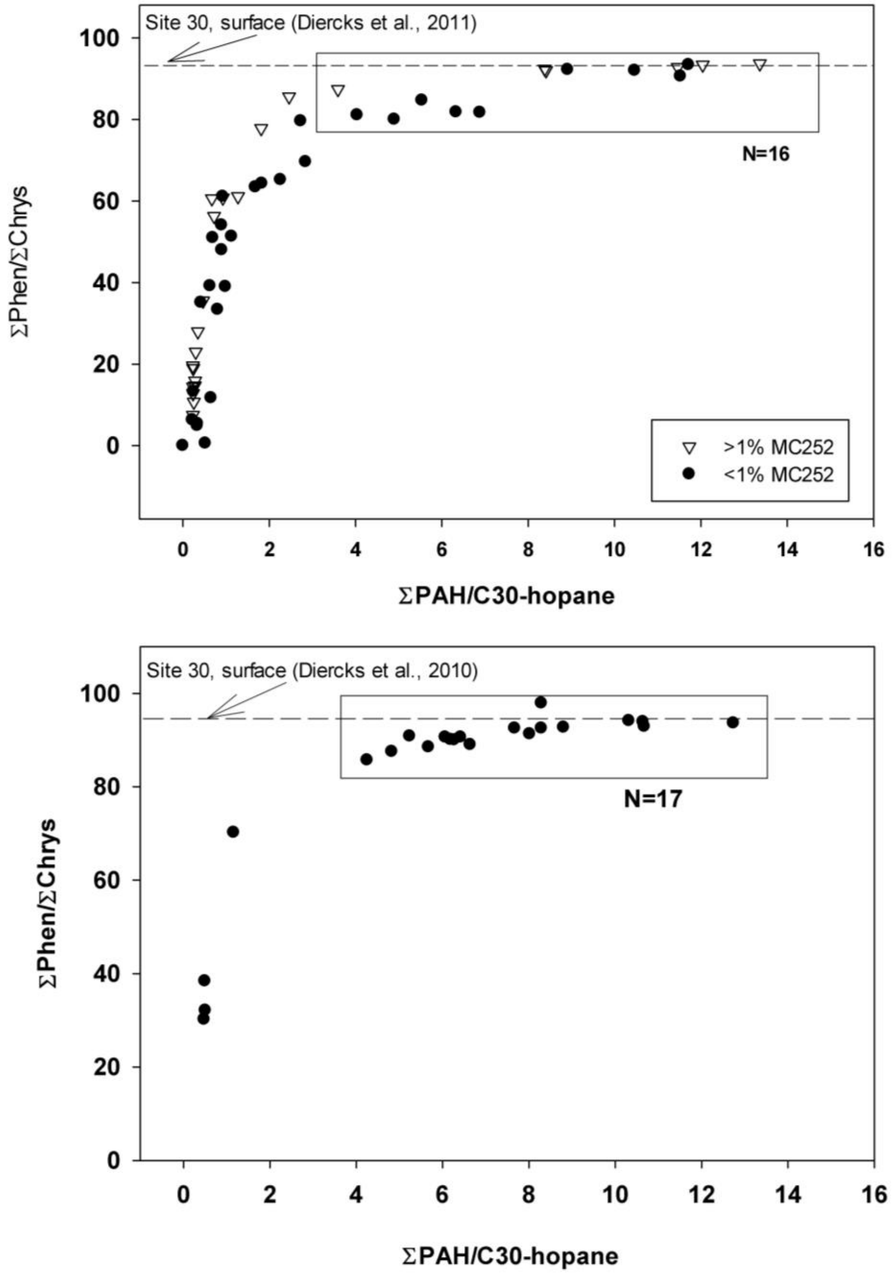
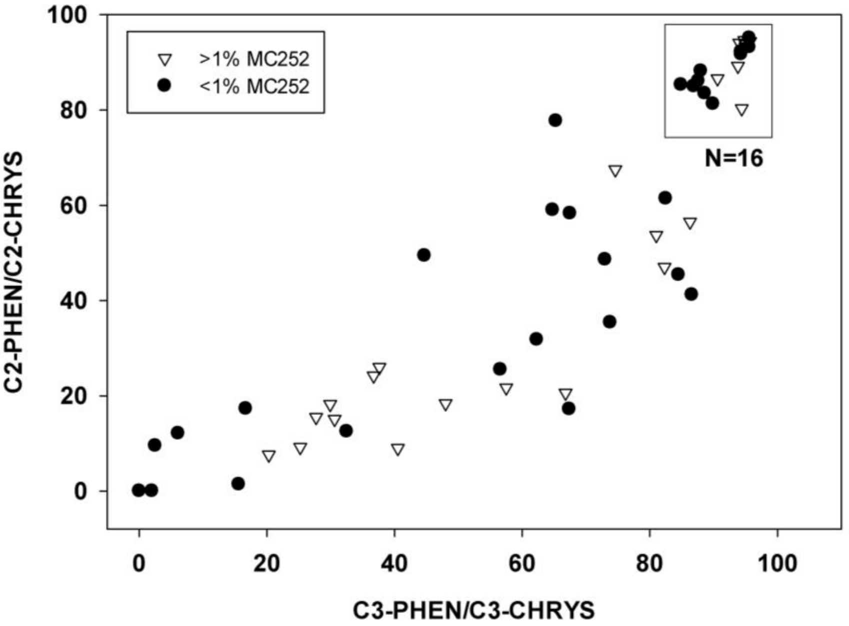


Figure 2. Weathering indices for subsurface oil (above) and surface oil (below). Reference line for the alkylated phenanthrene to chrysene weathering index for surface oil near wellhead (~100 miles away) (Diercks et al., 2010) included for comparison. Subsurface locations classified as having greater than (triangles) or less than (circles) 1% MC252 oil in the sample. Numbered samples in subsurface (N=16) and surface (N=17) graphs represent unweathered samples.



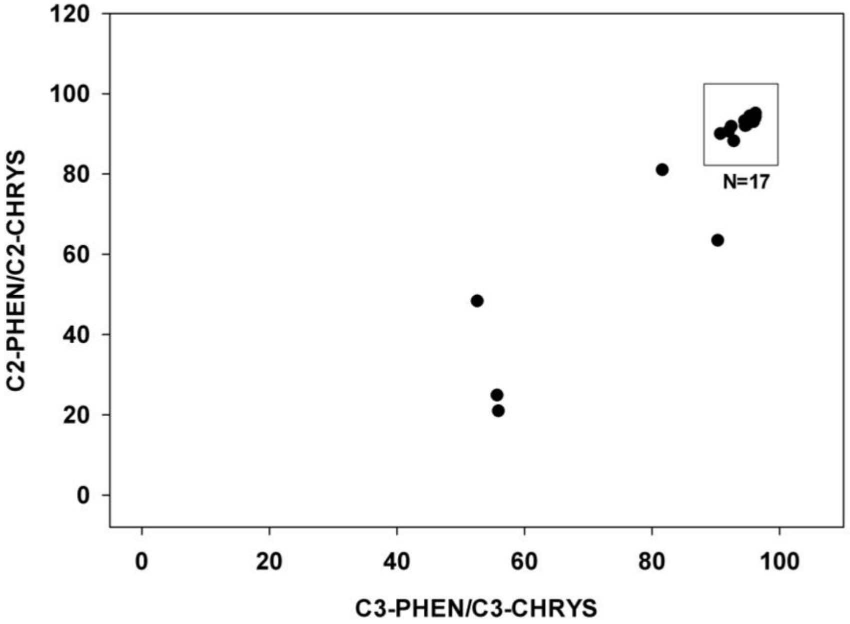


Figure 3. C2 and C3 phenanthrene to chrysene indices for subsurface (top) and surface (bottom) samples. Reference line for the alkylated phenanthrene to chrysene weathering index for surface oil near wellhead (~100 miles away) (Diercks et al., 2010) included for comparison. Subsurface locations classified as having greater than (triangles) or less than (circles) 1% MC252 oil in the sample. Numbered samples in subsurface (N=16) and surface (N=17) graphs represent unweathered samples.

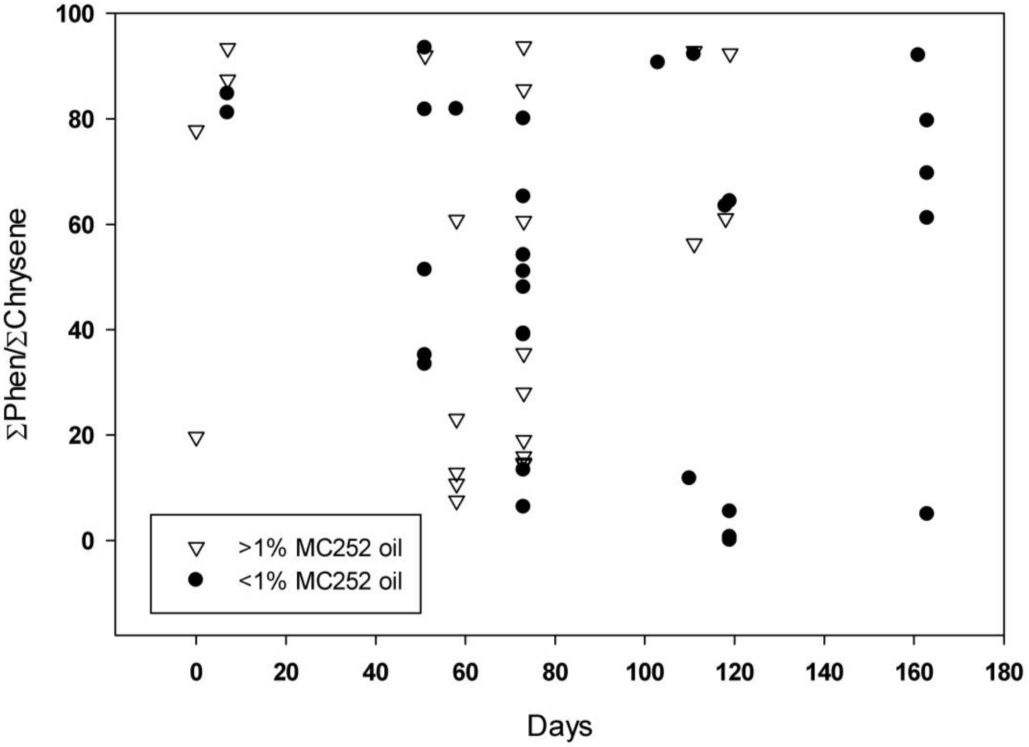


Figure 4. Alkylated phenanthrene to chrysene index for subsurface samples on Fourchon Beach over time. Subsurface locations classified as having greater than (triangles) or less than (circles) 1% MC252 oil in the sample.