Long-term weathering and continued oxidation of oil residues from the *Deepwater Horizon* spill

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4 **ABSTRACT**
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7 To investigate the long-term weathering of oil from the *Deepwater Horizon* (DWH)
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9 incident, oil-soaked sand patties were collected from Gulf of Mexico beaches from
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11 Florida to Alabama over a three-year period from 2012 to 2014. Analysis of oil residues
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13 by gas chromatography with flame ionization detection (GC-FID), thin-layer
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15 chromatography with flame ionization detection (TLC-FID), and Fourier transform
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17 infrared spectroscopy (FT-IR) indicated uniformity in their chemical composition. Some
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19 variability within and between samples was observed, arising from differences in
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21 exposure to light and water, which increase the amount of weathering. Oxygenated
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23 hydrocarbons (OxHC) produced by weathering processes dominate the majority of oil
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25 residues. These OxHC have continued recalcitrance in the environment, and increase in
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27 relative abundance over time. Analyses of the bulk characteristics of oil residues via
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29 TLC-FID and FT-IR should be continued as these techniques provide important insight
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31 into the weathering state of oil residues.
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41 **KEYWORDS**
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43 Petroleum; infrared spectroscopy; biodegradation; oxygenated; hydrocarbon
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INTRODUCTION

Following the 2010 *Deepwater Horizon* (DWH) disaster, oil was observed along more than two thousand kilometers of shoreline in the northern Gulf of Mexico (GoM) (Nixon et al., 2016). Years after the spill, oil-soaked sand patties, also known as surface residue balls (SRBs), continue to wash ashore and can be found on beaches as well as oiled splotches on rocks (e.g. Aeppli et al., 2012). Visual characteristics and chemical fingerprinting of hopane and diasterane biomarkers indicate that the oil residues extracted from the sand patties originate from the DWH spill (e.g. Mulabagal et al., 2013; White et al., 2014). Several studies have documented the chemical composition of the oil residues present in sand patties and rock scrapings and how this changes over time as the oil is weathered from exposure to water, light and microbial activity (Hall et al., 2013; Aeppli et al., 2014; Elango et al., 2014; Gros et al., 2014; Radović et al., 2014; Yin et al., 2015). Chemical analyses of the oil residues indicate a decrease in the abundance of *n*-alkanes and polycyclic aromatic hydrocarbons (PAH), and an increase in oxygen content due to the formation of oxygenated hydrocarbons (OxHC; Aeppli et al., 2012), also supported by Lewan et al. (2014). The OxHC formed are thought to be derived from both aromatic and saturated components of oil (Hall et al., 2013), and analysis via Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has provided unambiguous support that the OxHC are indeed produced and not preferentially enriched (Ruddy et al., 2014). The OxHC are of significant interest as they have been hypothesized to degraded more slowly than oil residues found in sediments and on marsh plants (Pendergraft et al., 2014), and have the potential to persist in the environment for years to come.

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4 In addition to being degraded more slowly than other forms of oil from the DWH
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6 spill, oil-soaked sand patties are predominantly small (< 5 cm in diameter currently), and
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8 are able to be transported in the nearshore environment (Hayworth et al., 2015; OSAT-3,
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10 2014). A numerical model of sand patty mobility for Alabama and Florida coasts showed
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12 that they are also likely to be repeatedly buried and exhumed, with movement along the
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14 shore being largely restricted to storm conditions, which are seasonal (Dalyander et al.,
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16 2014). The size, mobility and location of oil-soaked sand patties influences their exposure
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18 to different types of weathering, and the degree of weathering has been found to depend
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20 on the location on the beach. For example, more weathering occurs in samples from the
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22 supratidal zone than in submerged oil mat samples from the intertidal (Elango et al.,
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24 2014). Similarly, rock scrapings have been found to be more susceptible to weathering
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26 processes than sand patties due to their higher surface area-to-volume ratio, leading to
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28 increased exposure to light and water (Aeppli et al., 2012; Radović et al., 2014).
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36 The potential for biodegradation of weathered oil residues is extensive, but not yet
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38 fully constrained. The nutrient and microbial content of oil-soaked sand patties has been
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40 described, including the presence of bacteria (Tao et al., 2011; Urbano et al., 2013) and
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42 fungi (Simister et al., 2015). The microbial communities that are present in beach sands
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44 impacted by the DWH spill have also been described (Kostka et al., 2011 and Rodrigues-
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46 R. et al., 2015). Analysis by comprehensive two-dimensional gas chromatography
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48 (GC×GC) has provided insight into the biodegradation of often-overlooked oil-derived
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50 compounds present in weathered oil samples (Nelson et al., 2016 and references therein)
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52 such as oil-derived saturates in the *n*-C₂₂ to *n*-C₂₉ elution range (Gros et al., 2014), and
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54 hopane and sterane biomarkers (Aeppli et al., 2014). In addition to the documentation of
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4 the loss of specific oil in the aforementioned weathering studies (and summarized in Tarr
5 et al., 2016), it is also necessary to probe oil-derived compounds that are formed from the
6 weathering process. As previously described, FT-ICR-MS has been particularly useful in
7 providing more specific, molecular-level information about the oxidation products of oil
8 that has been weathered (McKenna et al., 2013; Ruddy et al., 2014).
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Molecular-level analysis of oil residues in the environment provides critical insight into changes in chemical composition of oil and the weathering processes responsible for these changes. While PAHs can be measured via widely available gas chromatography mass spectrometry (GC-MS) instrumentation and techniques (John et al., 2014; Yin et al., 2015), these compounds comprise a relatively small amount of the native oil (16%) and complete loss of two-ring PAHs and >65% loss of three-ring PAHs is observed in weathered oil (Gros et al., 2014). Analysis of a broader range of compounds via GC×GC and FT-ICR-MS, however, is not widely available, can take months to complete, and the resulting data requires significant experience to interpret (White et al., 2016). Depending on the question at hand, the level of selectivity and sensitivity that GC×GC and FT-ICR-MS provide may not be necessary. Considering the need for more scientists and government agencies to integrate OxHC as a target analyte in routine analyses following an oil spill, other more routine methods may be preferable.

In this study, we utilized widely available methods to characterize oil residues that persist following the DWH spill with a particular emphasis on the bulk properties of OxHC, the oil-derived compounds that are being produced as a result of weathering processes. To this end, gas chromatography-flame ionization detection (GC-FID) was used to determine the composition of the oil residues present, but because much of the

GC amenable compounds have been lost (Gros et al., 2014), fractions of saturated (F_{Sat}), aromatic (F_{Aro}), and oxygenated (F_{Oxy1} and F_{Oxy2} ; together described as OxHC) oil were detected and quantified on a bulk level using thin layer chromatography–flame ionization detection (TLC–FID). Oxygenated moieties were examined via Fourier transform infrared spectroscopy (FT-IR; as in Aske et al., 2001; Boukir et al., 1998; Castro et al., 2006). By examining weathered oil over the course of three years, we sought to determine the utility of these three approaches for following long-term weathering in easily accessible coastal oil residues. In particular, these approaches focus on the production and fate of the OxHC, and extend the record of Aeppli et al. (2012 and 2014) that ended in 2012.

MATERIALS AND METHODS

Sampling Information. Over a period of three years from June 2012 to June 2014, 134 samples were collected from Gulf of Mexico coastal beaches (see Figure S1 in the Supporting Information (SI)) including oil-soaked sand patties (115 samples) and rock scrapings were (19 samples). Specific dates and sampling locations of the samples are shown in Table S1. All samples were collected and placed in pre-combusted (450°C, 8 hours) glass jars, shipped to Haverford College, Haverford, PA, and frozen at -20°C prior to analysis.

Oil Residue Extraction. Samples were air-dried for 24 hours at 50°C to determine water content. The samples were then solvent extracted as in Aeppli et al. (2012) using 3x10 mL of dichloromethane:methanol (DCM:MeOH, 8:2). The combined extracts were dried

over sodium sulfate prior to being weighed to provide the mass of total extractable hydrocarbons.

Gas Chromatography. Extracts were analyzed on an Agilent 7890 series gas chromatograph (GC) interfaced to a flame ionization detector (FID). Compounds were separated on a J&W DB-XLB capillary column (30 m, 0.25 mm internal diameter (I.D.), 0.25- μ m film) with helium carrier gas at a constant flow of 1 mL min⁻¹. The GC oven had an initial temperature of 40 °C (1 min hold) and was ramped at 5 °C min⁻¹ until 320 °C (15 min hold). Total GC-amenable petroleum hydrocarbons were quantified by integrating the (blank-corrected) total area of the FID signal and response factors determined from weathered Macondo well (MW) oil standards. These standards were prepared at Haverford College by extracting oil residues from oil-soaked sand patties collected in January 2014 from a single location on the beach at Fort Morgan, AL. The extraction procedure for this standard sample was performed according to the procedure outlined in this paper. The *n*-alkane equivalent GC-elution range and quantities of resolvable hydrocarbons including *n*-alkanes (C₁₀-C₄₀), and pristane and phytane were determined using response factors from standard compounds. Subtracting the sum of the resolvable compounds (res) from the total area of the FID signal provided the quantity of unresolvable hydrocarbons referred to as the unresolved complex mixture (UCM). Laboratory blanks (1-2 g of combusted sand) were run with every 10 samples and were free of petroleum hydrocarbons. Extracts were also analyzed on the aforementioned GC coupled to an Agilent 5975 mass selective detector (MSD), which was operated in the selected-ion monitoring (SIM) mode for analysis of hopane (ion *m/z* 191) and

sterane/diasterane (ions m/z 217 and 218) biomarkers. Specific biomarker ratios were calculated according to their relative abundance are shown in Table S2 of the SI.

Thin Layer Chromatography-Flame Ionization Detection. To determine the relative amount of saturated (F_{Sat}), aromatic (F_{Aro}), and oxygenated fractions (F_{Oxy1} and F_{Oxy2} ; together described as OxHC of oil residues), which are all operationally defined, extracts were quantified using a TLC-FID analyzer (Iatroscan MK-5, Iatron Laboratories, Tokyo, Japan) using methods described in Aeppli et al., 2012. All samples were run in duplicate (average difference between samples $\pm 2\%$), and analyses of blank rods were devoid of any detectable signal. Statistical analyses of these fractions of oil residue extracts collected in different years were performed with JMP software (JMP version). A Levene's test was applied to each parameter to determine equality of group variances (samples were grouped by oil residue fraction and by year i.e. 2012, 2013, 2014). For parameters that presented equal group variances, one-way analyses of variance (ANOVA) were employed with a Tukey's Honestly Significant Difference (HSD) test at $p < 0.05$ to test for differences between groups.

Fourier transform-infrared spectroscopy. Aliquots of oil residue extracts were dried and solvent exchanged into tetrachloroethylene (C_2Cl_4 ; Group 2A carcinogen) for analysis via Fourier transform infrared spectroscopy (FT-IR). Extracts were injected into a Harrick demountable liquid cell (DCL-M25) fitted with 250-micron spacers and calcium fluoride plates. Spectra were collected on a Thermo Scientific Nicolet 6700 FT-IR with 32 scans at a 2 cm^{-1} resolution measuring from 400 to 4000 cm^{-1} . A background solvent spectrum of C_2Cl_4 was subtracted from all sample spectra collected. Peaks were integrated using Omnic Software, 8.0 and were normalized to the area of the C-H peak

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4 between 2750 and 3100 cm^{-1} . Specific attention was paid to the O-H stretching band at
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6 3390 cm^{-1} , the C=O stretching band at 1712 cm^{-1} , and the C-OH stretch in alcohols at
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8 1024 cm^{-1} . In addition, oil-derived aromatic hydrocarbons were examined using the C=C
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10 stretch at 1608 cm^{-1} . Data for other major absorbances that appeared in the spectra were
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12 also collected, including the CH_2 and CH_3 bending at 1460 cm^{-1} and CH_3 bending at 1376
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14 cm^{-1} . The areas of these specific FT-IR absorbances were normalized to the C-H
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16 absorbance area at 2910 cm^{-1} and are displayed in Table S3.
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23 RESULTS AND DISCUSSION

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25 **Composition of oil residues.** The 134 samples of oil-soaked sand patties and rock
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27 scrapings examined were collected from sampling locations described in previous studies
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29 (e.g. Aeppli et al., 2012). Sand patty samples (n=113) contained median values of 8.6%
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31 solvent extractable oil residues (mean = 9.2%, SD = 5.0) and 0.5% water (mean = 2.3%,
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33 SD = 3.2) by weight (Table S1 of the SI). Rock scrapings (n=21) contained median
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35 values of 15.1 % solvent extractable oil residues (mean = 16.1%, SD = 8.1) and 1.2%
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37 water (mean = 1.4%, SD = 1.6) by weight (Table S1 of the SI). Based on the color, size,
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39 and shape of the samples (representative images in Figure S2-S4 of the SI), and the
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41 hopane and sterane biomarker ratios of the extracted oil residues (Table S2 of the SI), all
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43 134 samples originated from oil from the MW that was released during the DWH oil
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45 spill. In contrast to rapid changes observed in the chemical composition of oil residues
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47 collected in the 100 days following the spill (Aeppli et al., 2012), the oil residues
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49 extracted from the majority of samples in this study had similar compositions, as
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51 determined by GC-FID, TLC-FID and FT-IR (Table S3 of the SI).
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GC-FID chromatograms of oil residues showed signs of weathering for all samples, including the loss of compounds, at least, eluting earlier than n -C₁₃ and the dominance in the chromatogram of an UCM ranging between C₁₃-C₄₀ (Figure 1A and 2A and Table S3 of the SI). When present, the amounts of GC-resolvable (res) compounds were substantially less than the UCM with a median ratio of res/UCM of 0.002 (mean = 0.017, SD = 0.069; Table S3 of the SI). The absence of pristane and phytane in the majority of samples indicates that they have undergone extensive biodegradation. In addition, for the 36 samples that contained these compounds, the pristane to phytane ratios were lower (median value of 0.52, mean = 0.51, SD = 0.24; Table S3 of the SI) than that of the MW oil (1.63-1.99; Valentine et al., 2014), indicative of severe weathering. Moderately weathered surface slicks have higher pristane to phytane ratios than this (1.16; Aeppli et al., 2012) whereas more weathered slicks and floating debris have lower values (0.11 and 0.29 respectively; Aeppli et al., 2013 and Carmichael et al., 2012).

Oxygen-containing functional groups were observed in the FT-IR spectra of all oil residues as evidenced by a O-H stretching band at 3390 cm⁻¹, a C=O stretching band at 1712 cm⁻¹, and a C-OH stretch at 1024 cm⁻¹ (Figures 1 and 2 and Table S3). A moderate positive correlation between the magnitude of the O-H and C=C absorbances was observed by FT-IR analysis (Figure 3a) indicating that during oil oxygenation, the relative proportion of both hydroxy-groups as well as aromatic moieties increases. This is also observed in the relationship between C=O and C=C, which has a weaker positive correlation (Figure 3b). Overall, F_{Aro} decreases as oil is weathered, and thus the increase in the relative proportion of aromatic compounds is likely due to the persistence of

compounds that are relatively resistant to weathering such as alkylated chrysenes (John et al., 2014), leading to a preferential enrichment of these persistent PAHs, along with oxygenation of other oil compounds.

Examination of all oil residues via TLC-FID indicated a range of values for the F_{Sat} , F_{Aro} , F_{Oxy1} and F_{Oxy2} from 8-66%, 1-20%, 8-42% and 11-78% respectively (Table S3 of the SI). In general, F_{Oxy2} was the most abundant in the oil residues with a median value of 49% (mean = 49%, SD = 2; Table S3 of the SI). The F_{Sat} and F_{Oxy1} were present in similar abundances with median values of 23% (mean = 23%, SD = 9) and 22% (mean = 23%, SD = 6) respectively. F_{Aro} comprised the smallest fraction of the oil residues with a median value of 5% (mean = 5%, SD = 3; Table S3 of the SI), highlighting the decreasing quantitative importance of PAHs as oil is weathered. All except four samples cluster around similar values of F_{Sat} of ~10-40% and $F_{\text{Oxy1+2}}$ of ~50-90% and (Figure S5). The four outliers are EI24, EI34, DI44 and SI61, which have $F_{\text{Sat}} > 40\%$ and $F_{\text{Oxy1+2}} < 50\%$ (Table S3). These outliers represent oil residues that are dominated by saturated hydrocarbons with F_{Sat} values of 44, 45, 53, and 66% respectively, and are less weathered as evidenced by the presence of *n*-C₁₇, pristane, *n*-C₁₈, and phytane in their oil extracts (Table S3 of the SI).

Recalcitrance of oxygenated hydrocarbons. The time scale of OxHC formation and potential degradation is still largely unknown. An analysis of variance (ANOVA) was therefore conducted to determine if F_{Sat} and the OxHC fraction $F_{\text{Oxy1+2}}$, of the oil residues changed over the three years: 2012 ($n=82$), 2013 ($n=18$) and 2014 ($n=30$). The aforementioned samples EI24, EI34, DI44 and SI61 were treated as outliers (Figure 4; outside of range of error bars), and F_{Aro} was excluded from this analysis due to its low

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4 abundance in the total oil residues for all samples (<12%). Significant differences
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6 between year groups were observed for F_{Sat} ($p=0.009$) and $F_{\text{Oxy1+2}}$ ($p=0.0047$; Figure 4a
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8 and b). Tukey post-hoc analysis revealed that in 2014, oil residues were significantly
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10 lower in the proportion of F_{Sat} ($p=0.0011$) and significantly higher in $F_{\text{Oxy1+2}}$ ($p=0.0031$),
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12 compared to the oil residues collected in 2012. Significant differences between samples
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14 from 2013 compared to 2012 and 2014 were not observed. This data reveals a temporal
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16 decrease in median F_{Sat} and a corresponding increase in median $F_{\text{Oxy1+2}}$, suggesting
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18 continued oxidation and an increase in OxHC beyond the first 100 days of weathering,
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20 when compositional changes are most rapid (Aeppli et al., 2012).
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26 The outliers EI24, EI34, DI44 and SI61 (Figure 4) have likely been exposed to
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28 less intense weathering processes than the other samples collected and display a greater
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30 F_{Sat} (Figure 4a) and lower $F_{\text{Oxy1+2}}$ (Figure 4b). Upon collection, the outlier samples were
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32 also noted to differ in appearance from the characteristic color and consistency of
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34 weathered oil typically found following the DWH spill. DI44, SI61, EI24 and EI34 had a
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36 softer, looser consistency than most of the weathered sand patties collected, and DI44
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38 was black in color rather than the distinctive orange-brown associated with MW oil.
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40 Despite the difference in appearance the consistent biomarker ratios of the oil extracted
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42 from the sand patties (Table S2 of the SI), suggest that they are derived from the DWH
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44 spill. Similar samples noted as “gooey” and “less weathered” that also originate from the
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46 DWH spill, have been documented elsewhere (OSAT-3, 2014).
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53 **Uniformity of oil residue composition.** Differences between oil residues collected from
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55 different sample locations are not observed and the lack of visible clustering by location
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57 (Figure 3) suggests a uniformity of source material and weathering processes independent
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of location, collection date and sample type (i.e. sand patty compared to rock scraping). The correlations in FT-IR absorbances are shown in Figure 3, however, no correlations were observed between this data and TLC-FID data. This is likely due to the fact that all of the samples have a similar OxHC content and a similar amount of oxygen-containing functional groups. FT-IR analysis remains a useful tool, however, as a selective and sensitive approach to provide information regarding overall trends in the composition of weathered oil (Figure 3).

To highlight the uniformity of source material and weathering processes for oil residues collected in this study, four examples are shown in Figure 1 compared to the MW oil from the spill (Figure 1). Samples GS22 and DI19 (Figure 1b and c) were collected on the same day from different locations (~25 miles apart, shown in Figure S2 of the SI), and have no discerning differences in their oil residue compositions. Rock scraping GP02 and sand patty GP04 (Figure 1d and e), collected on the same day from the same location, also have similar compositions with minor differences only observable by a more prominent C-OH stretch in the FT-IR spectra for GP02. This slightly higher abundance of C-OH in GP02 indicates that this sample contains relatively more OxHC due to increased weathering. Increased weathering has previously been described for other rock scrapings compared to sand patties (Aeppli et al., 2012; Aeppli et al., 2014; Radovic et al., 2014) because they are exposed to more light and water due to their higher surface area-to-volume ratio.

Differences in weathering state of oil residues. A difference in weathering state can also be observed for rock scrapings of oil residues of different thicknesses, and for the interior and exterior of sand patty samples (Figure 2). For example rock scraping WL06,

a thicker (4mm) scraping appears less weathered than WL13, a thinner (2mm) scraping collected from the same site on the same day (Figure 2b and c with images shown in Figure S3 of the SI). This is to be expected, given the smaller fraction of the oil residues in the thicker sand patty being exposed to weathering processes. Differences in the extent of weathering can be seen in the prominent *n*-alkane peaks of the GC-FID chromatograms of WL06, which are absent in WL13. Interestingly, differences in the oil residue composition are not observable between these two samples via FT-IR, but analysis via TLC-FID indicates that WL06 and WL13 have different F_{Oxy2} contents of 49 and 55% respectively. To explore further the differences in the chemical compositions of oil residues exposed to light and water, the inside (EI14) and outside (EI15) of an individual sand patty were examined. EI14 displays prominent *n*-alkane peaks (determined via GC-FID) compared to EI15 (Figure 2 d and e). TLC-FID indicates that EI14 has a larger saturated fraction (39%) than EI15 (16%), which also has more prominent C=O, C=C and C-OH stretches in its FT-IR spectra (Figure 2e). The contrast between these data provides evidence that the outside of the sand patty is more susceptible to weathering via processes such as evaporation, biodegradation, and photooxidation. To provide additional context for the samples shown in Figures 1 and 2, four sand patty samples containing oil with minor variations and also some similarities in weathering are shown in Figure S6 of the SI.

CONCLUSIONS

Overall, the chemical composition of weathered oil residues that persist on Gulf of Mexico beaches is relatively uniform (Figure 1), although variations are observed

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4 between some samples (Figure 2 and Figure S6) and also over time (Figure 4). With the
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6 analysis of oil-soaked sand patties presented in this study it is evident that the weathering
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8 trend observed by Aeppli et al. (2012) continues four years after the DWH spill. As
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10 weathering progresses, the GC-resolvable component of oil diminishes substantially and
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12 changes in chemical composition are difficult to discern by this method. Four years after
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14 the DWH spill, the majority of oil residues collected have reached terminal weathering as
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16 seen by GC-FID analysis (Table S3), but TLC-FID and FT-IR still allow observing
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18 ongoing changes in chemical composition of the weathered oil. FT-IR is useful in
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20 indicating changes in the presence of specific chemical bonds. TLC-FID provides a
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22 method to quantify the OxHC, which are produced by weathering, and proved to be the
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24 most useful method for analyzing relative changes in the chemical composition of
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26 weathered oil. Correlations between data obtained by TLC-FID and FT-IR were not
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28 observed likely due to the fact that the samples examined were all at a similar state of
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30 weathering.
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38 The increase in OxHC compounds between 2012 and 2014 indicates that the bulk
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40 chemical composition of the oil residues is changing even beyond the period of most
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42 rapid weathering described between 2010 and 2011 by Aeppli et al., 2012 (Figure 4).
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44 This change is subtle, but significant, and should be further explored. Optimization of the
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46 TLC-FID method is possible, for example, by normalizing the data to hopane content (as
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48 in Aeppli et al., 2012). Improved quantification of the OxHC would enable mass balance
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50 calculations similar to those described in Gros et al. (2014) to be performed. Inter-
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52 laboratory comparisons for TLC-FID analysis should also be performed. It is also worth
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54 noting that the TLC-FID-based quantification of OxHC formation worked well for the
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4 MW oil as source oil because it is a light sweet crude oil with a trace amount of
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6 asphaltenes and resins that are detected in the OxHC fraction (e.g. Figure 1(a)). This
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8 approach may be more challenging for an oil spill with a heavier fuel oil, containing a
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10 higher concentration of OxHC (Boduszynski, 1987), which might mask any weathering-
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12 induced increase in OxHC.
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16 A potential limitation of the employed method to quantify ongoing oil
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18 oxygenation is that continuing changes to the weathered oil from the DWH spill may not
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20 be observable via TLC-FID, if they occur within F_{Oxy2} . This is because the current
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22 method defines F_{Oxy2} as the fraction of the oil residue that does migrate on the silica rods
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24 during the solvent development, and in theory, more oxidized compounds would also not
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26 migrate on the rods. Adjustments to the development part of the TLC-FID methods (i.e.,
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28 using different solvent systems) to obtain a higher resolution analysis of F_{Oxy2} could
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30 address this.
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36 It is important to note that while bulk level characterization is useful, there is no
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38 replacement for molecular level characterization of oil residues, which is still not done
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40 comprehensively. Methods such as GC×GC (Nelson et al., 2016 and references therein)
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42 and FT-ICR-MS are necessary to examine complex and mixed OxHC present in
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44 weathered petroleum and provide the molecular-level information to determine how oil
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46 residues change in the environment over time (e.g. Ruddy et al., 2014). Bulk-level
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48 analysis of oil residues, however, has the potential to be a powerful screening tool to
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50 assess the general weathering state of oil residues, and can provide a good first pass look
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52 at samples that should be examined more closely by these advanced molecular-level
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54 techniques.
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SUPPORTING INFORMATION

Supporting Tables S1-S3 and Figures S1-S6. This data is also accessible through the Gulf of Mexico Research Initiative Information & Data Cooperative (GRIIDC) at <https://data.gulfresearchinitiative.org> (doi: [10.7266/N7FX77GK](https://doi.org/10.7266/N7FX77GK)).

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Figure 1. (A) GC-FID, (B) TLC-FID, and (C) FT-IR traces of (a) Macondo well (MW) oil (from Aeppli et al., 2012), and oil extracted from Gulf Shores, AL (GS), Dauphin Island, AL (DI), and Gulfport, MS (GP), specifically (b) GS22, (c) DI19, (d) GP02, (e) GP04 samples. GS22, DI19 and GP04 are sand patties, GP02 is a rock scraping.

Figure 2. (A) GC-FID, (B) TLC-FID, and (C) FT-IR traces of (a) Macondo well (MW) oil (from Aeppli et al., 2012), and oil extracted from Waveland, MS (WL), and Elmer's Island, LA (EI), specifically (b) WL06 and (c) WL13 rock scrapings and (d) EI14 and (e) EI15, which represent the inside and outside of a large sand patty respectively.

Figure 3. Absorbance areas from FT-IR analysis of oil from sand patties collected from 2012-2014 for (a) O-H at 3390 cm^{-1} and C=C at 1608 cm^{-1} (slope = 2.6, $R^2=0.55$), and (b) C=O at 1712 cm^{-1} and C=C at 1608 cm^{-1} (slope = 0.5, $R^2=0.22$). All absorbance areas shown are normalized to the C-H (2910 cm^{-1}) absorbance area. Symbols correspond to collection sites as noted in the key. Collection site abbreviations used are Pensacola, FL (PS), Fort Pickens, FL (FP), Perdido Beach, FL (PB), Gulf Shores, AL (GS), Fort Morgan, AL (FM), Dauphin Island, AL (DI), Ship Island, MS (SI), Gulfport, MS (GP), Waveland Jetty, MS (WL), State Park, Grand Isle, LA (GI), Elmer's Island, LA (EI) and Port Fourchon, LA.

Figure 4. Box plot of (a) saturated fraction (F_{Sat}) and (b) oxygenated fraction ($F_{\text{Oxy1+2}}$) of oil in sand patties collected from 2012-14 measured by TLC-FID. For each year, dark horizontal lines represent the median, with the box representing the 25th and 75th percentiles and the whiskers the 1.5 interquartile ranges of all sand patty extracts. Outliers are labeled.

Figure 1.

Figure 2.

Figure 3.

Figure 4.