

THE OFFICIAL MAGAZINE OF THE OCEANOGRAPHY SOCIETY

Oceanography

CITATION

Tarr, M.A., P. Zito, E.B. Overton, G.M. Olson, P.L. Adhikari, and C.M. Reddy. 2016. Weathering of oil spilled in the marine environment. *Oceanography* 29(3):126–135, <http://dx.doi.org/10.5670/oceanog.2016.77>.

DOI

<http://dx.doi.org/10.5670/oceanog.2016.77>

COPYRIGHT

This article has been published in *Oceanography*, Volume 29, Number 3, a quarterly journal of The Oceanography Society. Copyright 2016 by The Oceanography Society. All rights reserved.

USAGE

Permission is granted to copy this article for use in teaching and research. Republication, systematic reproduction, or collective redistribution of any portion of this article by photocopy machine, reposting, or other means is permitted only with the approval of The Oceanography Society. Send all correspondence to: info@tos.org or The Oceanography Society, PO Box 1931, Rockville, MD 20849-1931, USA.

Weathering of Oil Spilled in the Marine Environment

By Matthew A. Tarr, Phoebe Zito, Edward B. Overton,
Gregory M. Olson, Puspa L. Adhikari, and Christopher M. Reddy

ABSTRACT. Crude oil is a complex mixture of many thousands of mostly hydrocarbon and nitrogen-, sulfur-, and oxygen-containing compounds with molecular weights ranging from below 70 Da to well over 2,000 Da. When this complex mixture enters the environment from spills, ruptures, blowouts, or seeps, it undergoes a continuous series of compositional changes that result from a process known as weathering. Spills of petroleum involving human activity generally result in more rapid input of crude oil or refined products (diesel, gasoline, heavy fuel oil, and diluted bitumens) to the marine system than do natural processes and urban runoffs. The primary physicochemical processes involved in weathering include evaporation, dissolution, emulsification, dispersion, sedimentation/flocculation, microbial degradation, and photooxidation.

INTRODUCTION

Weathering changes oil's physical properties, chemical reactivities, and toxic chemical content across a wide range of time scales. For example, evaporation can remove significant amounts of light, low boiling hydrocarbon compounds in hours, while biodegradation can lag and follows a degradation succession driven mostly by compound class. These natural weathering progressions can be augmented by anthropogenic responses such as burning, addition of dispersants, shoreline washing, and shoreline fertilization. This article focuses mainly on natural chemical transformations (enzymatic and photo induced) of crude oil through abiotic and biotic processes, with an emphasis on the 2010 Deepwater Horizon (DWH) spill, which released oil from the Macondo well into the Gulf of Mexico.

WEATHERING

When fresh crude oil enters the environment from spills, it contains a large proportion of low boiling compounds that are more readily water-soluble than other components; it floats, has its lowest viscosity when fresh, and easily spreads out from the source. These characteristics mean that fresh oil spills generally pose the largest environmental risk. As oil weathers, it initially loses the lower molecular weight, volatile, water soluble components, causing the remaining oil residue to become more viscous and more likely to aggregate in wind rows rather than spreading out in a thin film. Over time, the weathering processes can continue to change the composition of the oil residue, potentially reducing it to small quantities of solid residue such as tar balls. Because their physical and chemical properties are different, the weathered products of crude oil should be called oil residues, not oil.

Oil residues often mix with water and emulsify, forming a viscous mixture that is fairly resistant to further weathering. Emulsification greatly slows the weathering processes and inhibits

remediation by skimming, dispersing, or burning. Fortunately, emulsified oil generally poses less environmental risk because it becomes mostly a sticky material that causes problems through covering or smothering as opposed to toxic interactions. However, if emulsified oil is ingested (e.g., through preening of feathers), it can have significant toxicity. Heavily emulsified oil residues are slower to degrade so they remain in the environment longer than non-emulsified liquid oil.

Figure 1 outlines the various weathering processes acting on the initially released oil (#1) as well as the various types of oil residues (#2 through #6) that occur in the environment during weathering. Chemical-, microbial-, and photo-induced degradations, primarily oxidations, occur on both the oil residues and the individual hydrocarbon and non-hydrocarbon compounds that have been released into the environment.

When crude oil (#1) enters the environment, either at the surface or in deep water, it rapidly loses components to evaporation (surface releases) and/or dissolution (surface and deepwater releases). As these physical weathering processes act on the released crude oil, its composition changes significantly by loss of low molecular weight hydrocarbon molecules, which are good solvents and low-viscosity liquids. The original crude oil is transformed into a more viscous oil residue (#2) that generally takes the form of small drops or patches of floating material. For deepwater releases, the larger oil droplets make their way to the surface, while the very tiny oil droplets, and much of the entrained natural gas, are advected from the release point by deep ocean currents. Individual chemicals released by dissolution from the initial spilled crude oil are also transported by advection and are subjected to microbial- and/or photo-induced oxidations. While in the water column, oil droplets are subject to a process known as continuous liquid-liquid extractions with seawater. The resulting

oil residues (#2) are more depleted of their water-soluble alkanes and one and two ring aromatic compounds than are the larger droplets of the released crude oil. This extraction of light hydrocarbon components from the released oil droplets increases the density of these small droplets, slowing their rise time to the surface and allowing for the formation of near neutrally buoyant emulsion flocs. The compositions and physical properties of surface residues (#2) from deepwater releases can vary depending upon the droplet size by which the released oil was transported to the surface.

The composition of the oil residues continues to be altered by weathering processes, allowing formation of emulsions and changes from a moderately viscous liquid to a very viscous material (#3) or even a semisolid (#4). As the oil residues and the specific chemicals leached from the residues weather, their respective compositions continually change through microbial and photo degradations.

Particularly when the viscous residues (#3) interact with shorelines, some of the floating oil residue mixes with sediment and nearshore detritus, becoming denser than water, and it can then be buried as tar mat or surface residual balls. Some of the stranded shoreline residues can also be entrapped in various types of below-surface burrows. When these buried residues (#4 and #5) are deposited in anoxic zones, oxidative weathering becomes very slow, and the composition will change little over extended periods of time on the scale of years (Slater et al., 2005).

Most crude oils are less dense than water, and even after weathering, the oil residues (#2, #3, and #4) remain buoyant. In order for these types of oil residues to sink, they must interact with dense materials like sand, sediment, shells, or dense marine snow. Some other crude oils, particularly some unconventionally produced crude oils that contain high bitumen content and low wax content, are very viscous and have densities near or

slightly above that of freshwater. Once spilled, even moderate weathering loss by evaporation or dissolution can result in oil residues (#6) that will sink, even in seawater. Sunken and buried oil residues are very slow to degrade and generally exist as clumps of solid residue, or as oil residue-mineral aggregates.

Recent research established that weathering can add new chemical structures to the content of oil residues. These new components include products of photo-induced oxidations of the hydrocarbons and non-hydrocarbons in the residues. High-resolution mass spectral evidence shows them to be high

molecular weight, nitrogen-, sulfur-, and oxygen-containing compounds not initially in the released crude oil. New evidence also supports the formation of high molecular weight, water-soluble marine dissolved organic matter (DOM), sometimes called photooxidized dissolved organic matter (PODOM).

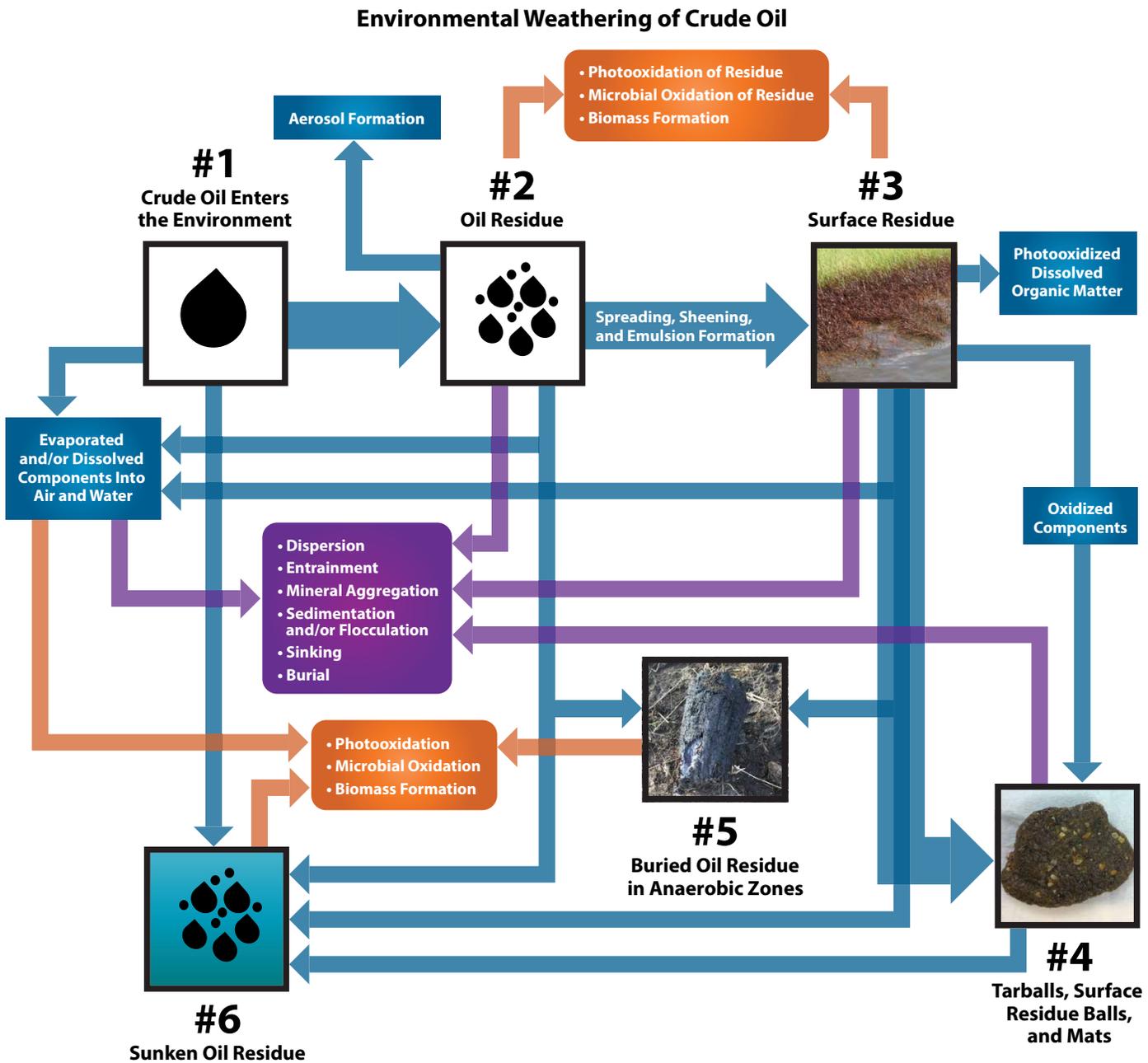


FIGURE 1. Diagram of the various stages of environmental weathering of crude oil. The initial oil that enters the environment is depicted as #1. After loss of some components by dissolution and evaporation, it becomes an oil residue (#2). Upon further weathering and movement, the residue becomes more viscous and may mix with water to form an emulsion (#3). Further weathering through biodegradation and photooxidation produces a semisolid residue (#4). Some of the surface residue (#3) may be buried in anaerobic zones, becoming residue #5, and its further weathering is very slow. Some heavy crude oils can sink after evaporative/dissolution losses, and other oil residues can sink associated with sedimentation, flocculation, and mineral aggregate formation. Components lost from the oil and oil residues undergo microbial and photooxidations with differing time scales. Microbial and photooxidations also cause changes in the oil residues themselves, including the formation of high molecular weight compounds. Some of the oxidized high and low molecular material can be assimilated into the water column and become dissolved organic matter.

Evaporation

Numerous reports have appeared since the 1970s on the role of evaporation after an oil spill (Mackay and Shiu, 1976; Fingas, 1995; Gros et al., 2014a). In modeling crude oil evaporation rates and mechanisms, Fingas (1995) found that up to 75% of light crude oil volume evaporates after the first few days following an oil spill. A mass transfer model developed by Gros et al. (2014a) to describe the first day of an oil spill showed evaporation to be the dominant fractionation process. Aerosol formation by wind and wave action can also transfer oil components into the atmosphere (Arey et al., 2007; Aeppli et al., 2013).

Dissolution

Dissolution occurs at the interface between oil and seawater and is highly dependent on the oil's surface area. Most crude oil components have low solubility in water. However, small monoaromatic hydrocarbon compounds, such as benzene and the alkyl benzenes, as well as alkanes with one to five carbon atoms, have significant seawater solubility. This solubility can also extend to larger aromatic compounds, such as naphthalene and its alkyl homologs, and even to three-ring aromatic compounds such as the phenanthrenes and the dibenzothiophenes. Nevertheless, most of the components of crude oil are not very soluble in seawater, but they are highly soluble in the crude oil mixture itself. Hydrocarbon solubility in seawater generally decreases with increasing molecular weight. Crude oil is an excellent solvent for crude oil components and can readily maintain higher molecular weight components in the crude oil phase residues.

Dissolution of components from oil droplets and slicks is controlled by solubility (Nicodem et al., 1998), the surface area of the oil-water interface, and diffusion and other transport processes (Arey et al., 2007; Gros et al., 2016). In cases where small oil droplets pass through the water column over extended periods of time, a process called liquid-liquid

extraction occurs continuously and can transfer significant amounts of low molecular weight saturated and aromatic hydrocarbons into the water column. In the case of the Macondo wellhead discharge, the rapid, turbulent injection of gas and oil deep in the column produced a dynamic, multiphase environment where crude oil and crude oil components were partitioned and dispersed by currents into the deep ocean.

Biodegradation

Biodegradation is the process by which microorganisms degrade crude oil compounds using various enzymatic reactions, turning them eventually into carbon dioxide, biomass, and water-soluble compounds (Atlas and Hazen, 2011). Many species of bacteria, archaea, mold, yeast, and fungi capable of using crude oil compounds as a food source (Atlas et al., 2015) are widely distributed throughout the environment. However, biodegradation effects on the composition of oil in the environment are highly dependent on the amount of oil spilled and on the weathered oil's physicochemical properties, as well as other site-specific environmental factors such as redox conditions, nutrient availability, temperature, salinity, and wave/mixing energy.

Under ideal aerobic conditions, most crude oil compounds are readily biodegradable and generally follow a clear degradation pattern, with most rapid degradation occurring in a sequential manner: *n*-alkanes → branched alkanes → low molecular weight aromatics → high molecular weight aromatics and cyclic alkanes (Wang and Fingas 2003).

Anaerobic degradation is a dominant process in petroleum reservoir systems and in reduced oxygen environments in water and shallow-water sediment environments. Degradation can be accomplished by consortia of a diverse range of bacteria and some methanogenic archaea (Atlas et al., 2015). In comparison to aerobic biodegradation, anaerobic biodegradation is a much slower process (Atlas et al., 2015). As a result,

crude oil compounds can remain relatively unaltered in reduced sediments and environments for longer periods of time and may even appear as relatively fresh oil compared to the same oil exposed at the surface to aerobic conditions (Gros et al., 2014b).

Photodegradation

Photodegradation of petroleum can induce physical and chemical changes (Nicodem et al., 1998). Payne and Phillips (1985) published one of the first extensive reviews on the photochemistry of petroleum in water. Early studies were performed with water (Hansen, 1975) and without water (Larson et al., 1977), with natural sunlight versus mercury lamps (Hansen 1975), and with different petroleum blends (Payne and Phillips, 1985). This work identified a variety of oxidation products, such as alcohols, ethers, and sulfoxides (Payne and Phillips, 1985; Plata et al., 2008).

Photochemistry must initially involve a molecule that absorbs radiation in the solar spectrum (a chromophore). Polycyclic aromatic hydrocarbons (PAHs) are chromophores that likely dominate oil photochemistry. Larger PAHs typically absorb at longer wavelengths, so PAHs with three or more rings have a greater overlap with sunlight and are more likely to be involved in photochemistry. Several pathways for PAH photochemistry have been investigated (Fasnacht and Blough, 2003a,b). Two main categories include direct photolysis (the chromophore degrades) and indirect or sensitized photolysis (the chromophore transfers energy to another species, which then reacts further). Upon photon absorption, PAHs can form excited states, including singlets, triplets, and radical cations (photoionization). Excited singlets and triplets readily transfer energy to ground state oxygen ($^3\text{O}_2$) to form singlet oxygen ($^1\text{O}_2$), a form that reacts readily with aromatic molecules. Photoionization or electron transfer from other excited states can result in reduction of oxygen to form superoxide (O_2^-), which leads to formation

of hydroxyl radical (Ray and Tarr, 2014a), a very strong oxidant that can react with saturated, unsaturated, and aromatic molecules. In the presence of water and oxygen, exposure of oil to sunlight results in extensive oxygenation across a wide range of oil molecule types (Ray et al., 2014) through the formation of excited triplets, singlet oxygen, and hydroxyl radical (Ray and Tarr, 2014a,b,c).

Griffiths et al. (2014) exposed neat oil (a light-sour crude) to ultraviolet radiation (254 nm) or to light from a SoLux bulb (surrogate for sunlight) in open watch glasses for up to 938 hours. After exposure to the SoLux lamp, the oil had lost much of its liquid character, and high-resolution mass spectrometry revealed oxygenation of the oil. King et al. (2014) showed that PAHs in thin oil films on water quickly photodegraded. Larger PAHs were observed to photodegrade much more rapidly than smaller PAHs, most likely due to better overlap

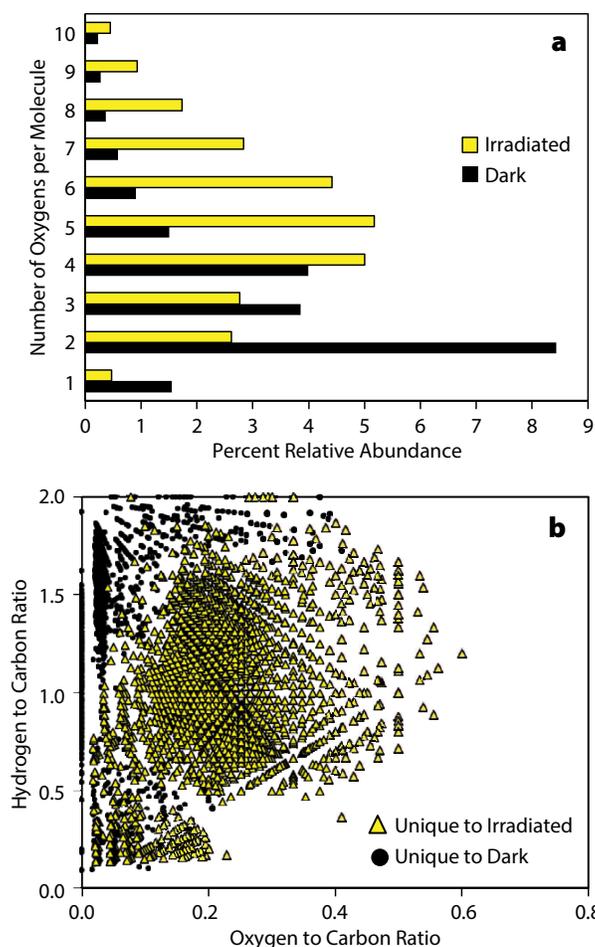
with the solar spectrum. In contrast, loss of alkanes due to photodegradation was much slower. An increase in toxicity of water in contact with oil during solar exposure was observed through screening with *Aliivibrio fischeri* (formerly *Vibrio fischeri*), a planktonic facultative anaerobic Gram-negative bacterium. The toxicity was attributed to water-soluble photoproducts. Ray et al. (2014) used high-resolution mass spectrometry to determine molecular formulas of oil photoproducts, showing that oil compounds are broadly susceptible to oxygenation when exposed to sunlight. The observed oxygenation of alkanes suggests that the hydroxyl radical is an important intermediate, because singlet oxygen cannot readily oxidize alkanes. The majority of photoproducts were found in acidic fractions, indicating that formation of carboxylic acids is likely. Figure 2a shows the number of oxygen atoms per molecule of water-soluble compounds for dark and

simulated sunlight irradiated Macondo oil. As many as 10 oxygen atoms per molecule were observed from irradiated oil. A clear shift to higher oxygen content is apparent for the aqueous photoproducts, and oxidation was observed across saturated, monoaromatic, and condensed aromatic compounds (Figure 2b). These photoproducts exhibited increased water solubility. Enhanced toxicity, biodegradation, and transport are possible as a result of the oxygenation and solubilization.

Incubation of seawater with oil (light-sweet crude) in sunlight resulted in changes in microbial community structure and reduced bacterial diversity (Bacosa et al., 2015). Sunlight-selected phylotypes from laboratory studies were consistent with microbial communities found in mousse from the Deepwater Horizon spill, suggesting that sunlight influences pollutant fate through impacts on microbial communities.

Sedimentation/Settling

Oil and oil residues can interact with settling particles in the water column, providing a natural removal process. As the oil/residue attached to the sediment eventually sinks, it can be buried in the seafloor sediment (Bandara et al., 2011). Oil-sediment interactions in marine systems include formation of oil-suspended particulate matter aggregates (OSAs), partitioning of oil droplets onto suspended particulate matter, and association of oil components with marine snow and with fecal pellets. OSAs can remove up to 65% of the oil released into the marine systems (Bandara et al., 2011). Dissolved oil components with low water solubility readily partition onto settling particles, preferentially those composed of organic carbon, soot, or black carbon, and sink with these particles (Adhikari et al., 2015). Such partitioning plays a role in determining long-term fate and transport of oil and its components. Marine snow incorporates smaller organic and inorganic particles (bacteria, plankton, detritus, and minerals) in a mucous web formed by bacterial oil-degraders in the floating oil



layer, which can sink after losing its buoyancy and transport a significant amount of oil components to the seafloor (Passow et al., 2012). Marine snow formation during the DWH oil spill was estimated to remove up to 15% of the spilled oil from the northern Gulf of Mexico water column to the seafloor sediment (Joye, 2015). Rapidly sinking fecal pellets form when oil droplets pass undigested through marine organisms, removing a significant amount of aliphatic and aromatic components of spilled oil (Bouloubassi et al., 2006). The vertical transport flux has been documented to be an important pathway of oil removal from the marine water column, and seafloor sediments can be a long-term repository of the oil (Lipiatou et al., 1997).

INNOVATIVE ANALYTICAL TECHNIQUES FOR STUDYING OIL WEATHERING

GC×GC for Oil Source Identification

Numerous studies have employed comprehensive two-dimensional gas chromatography (GC×GC) to characterize the Macondo well oil and fingerprint and track weathering processes in samples collected following the Deepwater Horizon disaster. The GC×GC analytical technique can separate and resolve at least an order of magnitude more compounds than single-dimension GC methods, has a much larger signal-to-noise ratio, and provides ordered and cleaner chromatograms for identifying unknown compounds in complex mixtures of

petroleum hydrocarbons (Frysjer et al., 2003). GC×GC retention data can be used to deconvolve quantitatively the effects of phase transfer processes such as water washing (liquid-liquid extractions) and evaporation (Gros et al., 2014; Nelson et al., 2016).

Developing Highly Refined Indices for Saturated Hydrocarbon Biodegradation

As Figure 3 shows, GC×GC analyses revealed that within one year, weathering yielded residues containing molecules with 20+ carbon atoms enriched in saturates, likely by reaching terminal removal through evaporation and near-complete water-washing. Biodegradation would be the only remaining weathering process

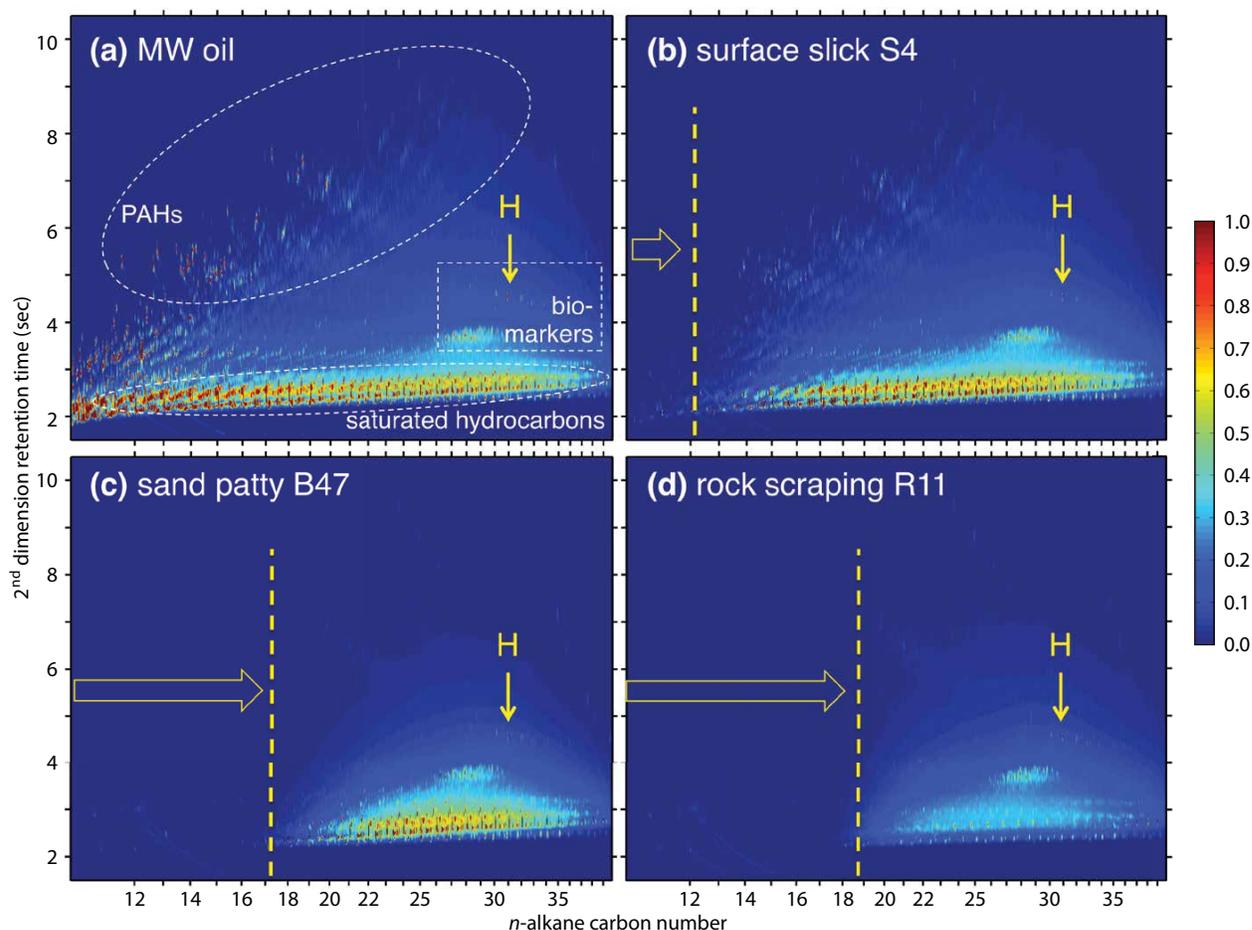


FIGURE 3. Weathering of Macondo well oil as observed by two-dimensional gas chromatography (GC×GC). All chromatograms are normalized to the peak height of 17 α (H),21 α (H)-hopane (“H”). With increasing weathering, loss of early eluting compounds (evaporation, indicated by horizontal arrows) and selective removal of classes of compounds such as polycyclic aromatic hydrocarbons (PAHs) and *n*-alkanes (dissolution, photooxidation, and biodegradation) can be seen. *Reproduced with permission from IOSC Proceedings, Aeppli et al. (2014a)*

that could be easily monitored by gas chromatographic methods in these samples. While countless studies have examined microbial biodegradation of crude oil, little work has been done on saturates beyond normal alkanes due to the lack of resolving power of one-dimensional GC, which can only provide an unresolved complex mixture (Frysiner et al., 2003). Gros et al. (2014b) harnessed the power of GC×GC by analyzing seven oiled sand patties whose one-dimensional gas chromatograms appeared to be similar. By performing algebraic operations to compare the samples with one another and with the Macondo well oil, normal alkanes were found to be preferentially degraded, followed by methylalkanes (independent of the position of the methyl group) and cycloalkanes. Cyclic and acyclic isoprenoids were the least degraded families of saturated hydrocarbons. This effort resulted in a highly refined index for biodegradation for at least the DWH oil spill.

The Future of Oil Spill Analysis: Combining GC×GC with High-Resolution FT-ICR-MS

McKenna et al. (2013) argued that gas chromatography cannot adequately characterize heavier crudes, fuel oils, and weathered products, for example, non-volatile or thermally unstable compounds. Fourier transform ion-cyclotron resonance mass spectrometry (FT-ICR-MS) can analyze compounds with lower volatilities and lower thermal stabilities, especially when coupled with electrospray ionization. In addition, its ultrahigh resolving power and mass accuracy allow unambiguous identification of molecular formulas. FT-ICR-MS was combined with GC×GC to investigate weathered products of Macondo well oil found on sand samples from Pensacola Beach, Florida (Ruddy et al., 2014). Numerous oxidized species were detected by FT-ICR-MS (Figure 4), and ketones were observed in the complex GC×GC chromatograms.

OIL RESIDUES ALONG COASTAL AREAS Weathering in Coastal Wetlands

Several oil spills have impacted coastal wetlands, with the most recent major event being the Deepwater Horizon well blowout in 2010. After the weathered oil residues (#3 in Figure 1) from this spill reached beaches and marshes along the northern Gulf of Mexico, they were distributed in a very nonhomogenous manner, and their weathering rates varied dramatically with time. Figure 5 compares the distribution of alkane and PAH compounds in fresh unweathered oil (#1 in Figure 1) to that found along the Louisiana coastline in typical samples. The oil residue that came ashore along most Louisiana marsh coastlines had been both evaporatively and microbially weathered, losing the alkanes smaller than about $n\text{-C}_{14}$ as well as most of the lower molecular weight aromatics such as the naphthalenes and fluorenes, with the parent and C_1 homologs being lost in preference to the C_2 to C_4 homologs. The sulfur-containing PAHs degraded at a faster rate than the similar sized hydrocarbon PAH compounds.

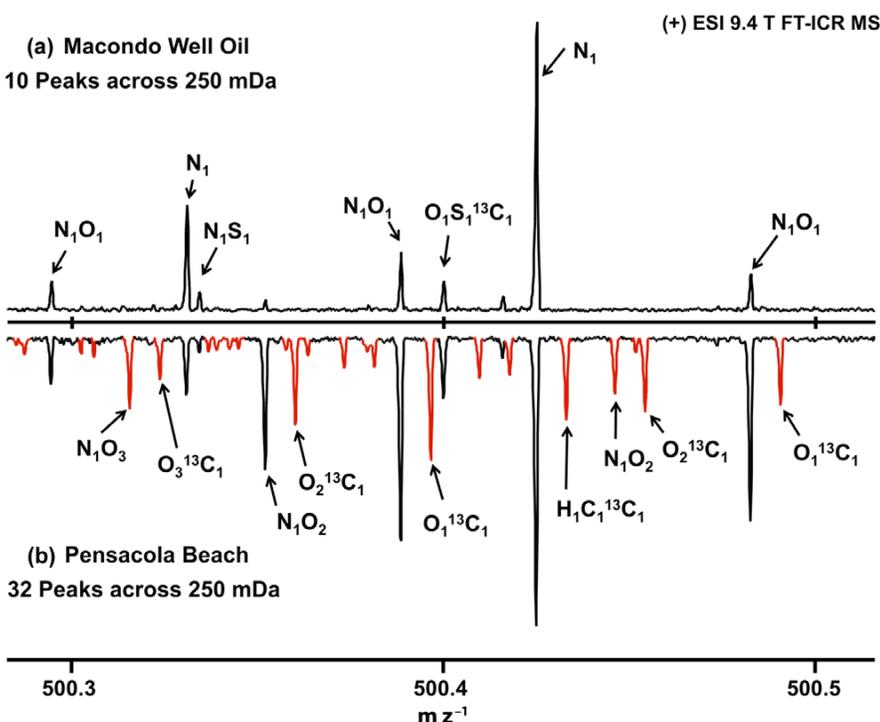


FIGURE 4. Comparison of (a) Macondo well oil released during the Deepwater Horizon spill, and (b) extract from an oiled sand collected in Pensacola, Florida, in June 2010 and compared with Macondo well oil with positive electrospray FT-ICR-MS. A mass scale-expanded segment reveals at a nominal m/z 500 numerous oxidized species that were produced from weathering in support of Aeppli et al. (2012). Reprinted with permission from Ruddy et al. (2014), ©2014, American Chemical Society

Figure 5 displays analytical data showing several indicators of microbial weathering. One is a decrease in the ratio of heptadecane ($n\text{-C}_{17}$) to pristane (a branched unsaturated alkane, or isoprenoid) or octadecane ($n\text{-C}_{18}$) to phytane. Another indicator is the appearance of a hump or unresolved complex mixture (UCM) in the chromatographic baseline. As the normal alkanes rapidly weather by evaporation/dissolution and microbial attack, leaving behind the slower degrading branched and cyclic alkanes, aromatics, and resins, the relative amount of the chromatographically unresolved compounds increases. Another indication of microbial weathering is the loss of the parent and C_1 alkyl homologs of PAH compounds relative to their respective C_2 to C_4 alkyl homolog isomers.

In addition to alkane and PAH degradation during the DWH oil spill, the patterns of petroleum biomarker compounds

in most oil residues found in marsh sediments showed some alterations. The hopane, sterane, and triaromatic steroid compounds are generally considered to be recalcitrant and not affected by weathering processes (Wang and Fingas, 2003). However, degradative weathering altered the biomarker compositions in typical samples from Louisiana coastal

marshes. Most marsh samples showed a progression with time from the biomarker patterns in Macondo oil through slightly degraded biomarker compositions to severely degraded biomarker patterns. Figure 6 shows analytical data for the Macondo source oil and two heavily weathered marsh sediment samples. These samples exhibit compositional

patterns similar to those found in many of the samples collected from impacted areas in Bay Jimmy and Bay Baptiste from 2010 to 2015. Generally, samples collected earlier in the spill showed biomarker patterns like those in row 2 of the selected ion chromatograms with mass/charge 191 (hopanes), 217 and 218 (steranes), and 231 (triaromatic steroids),

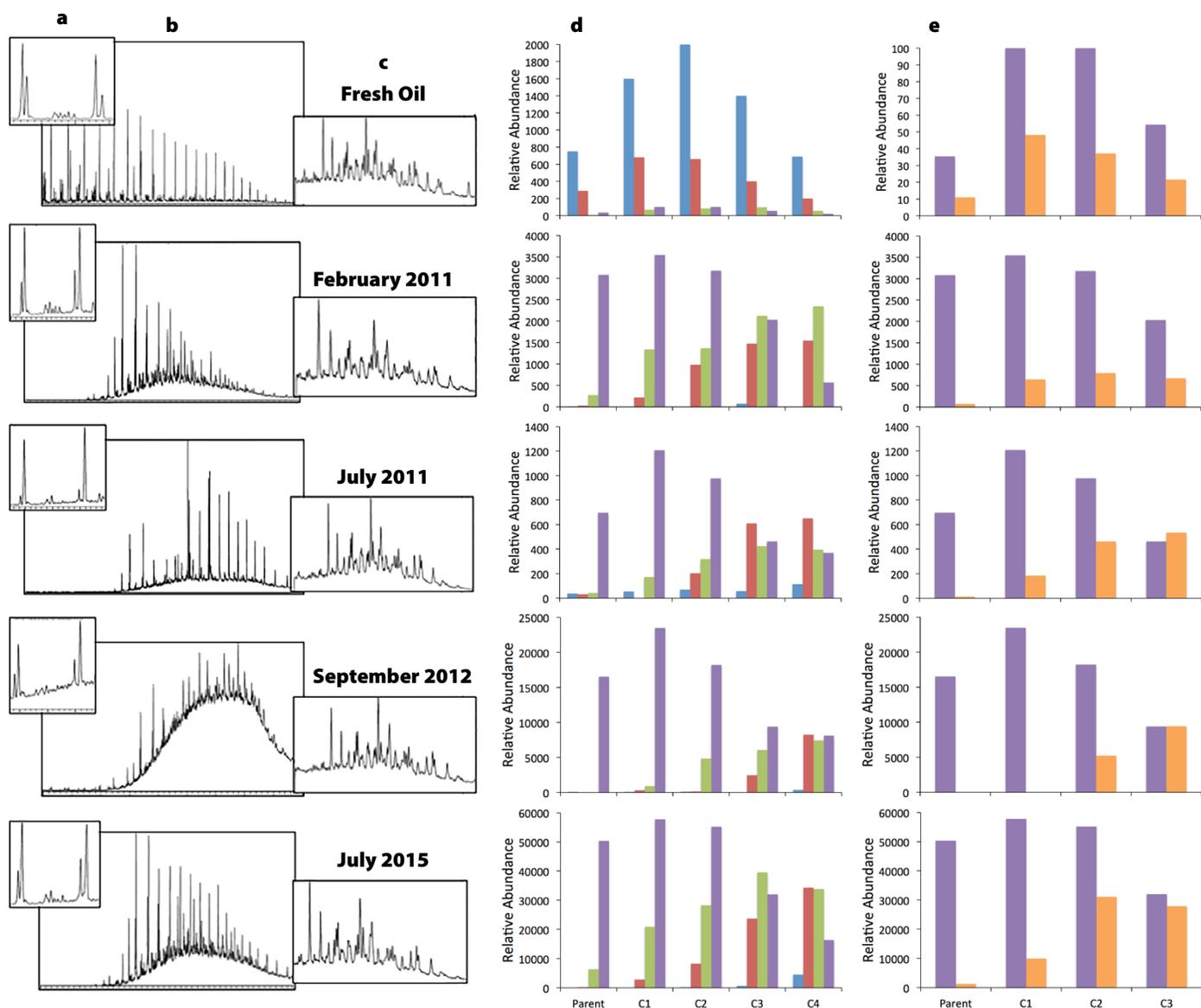


FIGURE 5. Selective analytical data from fresh, unweathered Macondo oil and four marsh sediment extracts collected from impacted areas in Barataria Bay, Louisiana, in February and July 2011, September 2012, and July 2015. (a) Chromatograms of n -C₁₇/pristane and n -C₁₈/phytane. (b) Chromatograms of saturate hydrocarbons from n -C₁₀ to n -C₃₃. (c) 217 m/z selected ion chromatograms of the sterane biomarkers. (d) Concentrations of the parent 2, 3, and 4 ring PAH compounds and their respective C₁ to C₄ alkyl homologs, showing weathering changes associated with ring size and molecular weight. (e) Concentrations of the parent and alkyl homologs of chrysenes and the sulfur-containing naphthylbenzothiophene showing more rapid weathering of heteroatom PAHs, a characteristic of microbial-induced degradations. Note that the February 2011 and July 2015 residues appear very similar, even though the latter sample was collected after three additional years of environmental weathering. The sterane biomarkers were relatively unchanged by weathering during the time frame in these samples, even though the normal alkane to isoprenoid ratios and the unresolved complex mixtures data indicate these oil residues were heavily weathered.

while samples collected mostly in later years generally showed a biomarker pattern similar to the data in row 3. In general, the 191 ion chromatograms were relatively unchanged by weathering, but the 217 and 218 sterane and 231 triaromatic steroid ion chromatograms showed significant degradation from the initial Macondo oil pattern.

Understanding biomarker weathering is important because oil spill damage assessments are mandated by the Natural Resources Damage Assessment (NRDA) sections of the Oil Pollution Act of 1990. The NRDA identifies oil sources using these forensic petroleum biomarker compounds and diagnostic ratios of select hopanes, steranes, and triaromatic steroids. After reviewing many biomarker patterns in hundreds of samples from impacted areas along the northern Gulf coastline and in Louisiana coastal marshes, it is clear that weathering exposure often degraded biomarker

compounds. Further, these degradations followed a pattern of compositional alterations from the initial source oil as shown in Figure 6, row 1 to the gradual alterations seen in row 2, and on to the final pattern shown in row 3. Degradation of the sterane biomarker compounds contrasts with the reported biomarker degradation of oil residues in samples collected along the sandy beaches of the northern Gulf (Aeppli et al., 2014b).

LONG-TERM FATE OF OIL FROM THE DWH SPILL

Oil that has been chemically transformed to other compounds has been permanently removed from the environment and replaced by new materials, which may further degrade or accumulate in the environment. Oil residues sequestered into compartments where there is minimal contact with oxygen or light may remain in place for extended periods. These oil residues can reenter other parts

of the environment if a major disruption of the sequestered system occurs, such as physical excavation or extensive erosion. While study of the DWH spill has improved our understanding of the fate and transport of spilled oil, there are still many unanswered questions regarding its ultimate fate as well as how the properties of the oil and the ecosystem control that fate. Further study is needed to better understand the detailed chemical and physical processes that affect spilled oil. 

REFERENCES

- Adhikari, L., K. Maiti, and E.B. Overton. 2015. Vertical fluxes of polycyclic aromatic hydrocarbons in the northern Gulf of Mexico. *Marine Chemistry* 168:60–68, <http://dx.doi.org/10.1016/j.marchem.2014.11.001>.
- Aeppli, C., C.A. Carmichael, R.K. Nelson, K.L. Lemkau, W.M. Graham, M.C. Redmond, D.L. Valentine, and C.M. Reddy. 2012. Oil weathering after the *Deepwater Horizon* disaster led to the formation of oxygenated residues. *Environmental Science & Technology* 46(16):8,799–8,807, <http://dx.doi.org/10.1021/es3015138>
- Aeppli, C., R.K. Nelson, C.A. Carmichael, D.L. Valentine, and C.M. Reddy. 2014a. Biotic and abiotic oil degradation after the *Deepwater Horizon* disaster leads to formation of recalcitrant oxygenated hydrocarbons: New insights

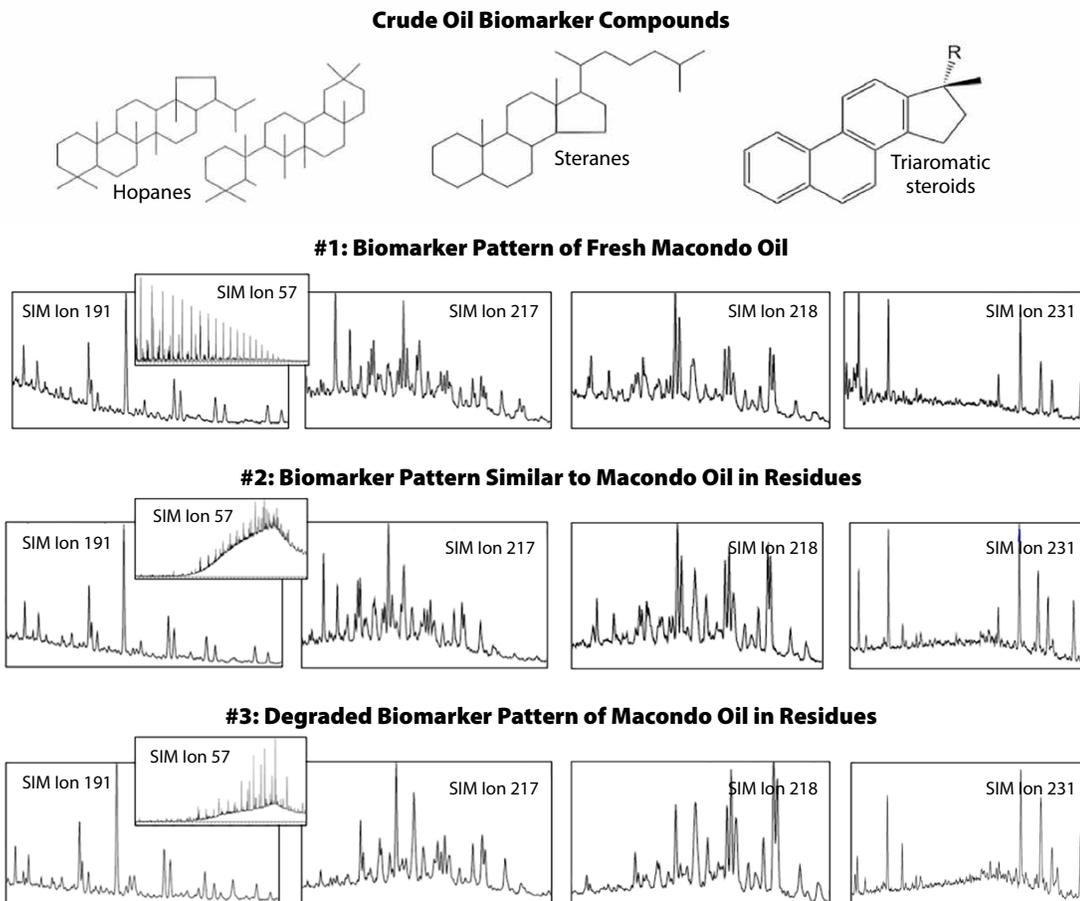


FIGURE 6. Representative structures of the forensic petroleum biomarker compounds found in crude oil with their respective selected ion monitoring (SIM) mass chromatograms for ion mass/charge 57 for saturates hydrocarbons and 191 showing the pattern for the hopane distribution in Macondo oil, mass/charge 217 and 218 for the sterane distributions, and mass/charge 231 for the triaromatic steroid distributions. SIM chromatographic data in line #1 shows the biomarker pattern in fresh Macondo oil, line #2 shows the patterns in heavily weathered Macondo oil extract from a marsh sediment sample collected in 2014 with slight biomarker weathering, and line #3 shows a different pattern with extensive biomarker weathering of Macondo oil extracted from coastal marsh sediment samples collected in 2015.

- using GC×GC. *International Oil Spill Conference Proceedings* 2014(1):1,087–1,098, <http://dx.doi.org/10.7901/2169-3358-2014.1.1087>.
- Aeppli, C., R.K. Nelson, J.R. Radović, C.A. Carmichael, D.L. Valentine, and C.M. Reddy. 2014b. Recalcitrance and degradation of petroleum biomarkers upon abiotic and biotic natural weathering of Deepwater Horizon oil. *Environmental Science & Technology* 48:6,726–6,734, <http://dx.doi.org/10.1021/es500825q>.
- Aeppli, C., C.M. Reddy, R.K. Nelson, M.Y. Kellermann, and D.L. Valentine. 2013. Recurrent oil sheens at the Deepwater Horizon disaster site fingerprinted with synthetic hydrocarbon drilling fluids. *Environmental Science & Technology* 47:8,211–8,219, <http://dx.doi.org/10.1021/es4024139>.
- Arey, J.S., R.K. Nelson, D.L. Plata, and C.M. Reddy. 2007. Disentangling oil weathering using GC×GC: Part 2. Mass transfer calculations. *Environmental Science & Technology* 41:5,747–5,755, <http://dx.doi.org/10.1021/es070006p>.
- Atlas, R.M., D.M. Stoeckel, S.A. Faith, A. Minard-Smith, J.R. Thorn, and M.J. Benotti. 2015. Oil biodegradation and oil-degrading microbial populations in marsh sediments impacted by oil from the Deepwater Horizon well blowout. *Environmental Science & Technology* 49:8,356–8,366, <http://dx.doi.org/10.1021/acs.est.5b00413>.
- Atlas, R.M., and T.C. Hazen. 2011. Oil biodegradation and bioremediation: A tale of the two worst spills in US history. *Environmental Science & Technology* 45:6,709–6,715, <http://dx.doi.org/10.1021/es2013227>.
- Bacosa, H.P., Z. Liu, and D.L. Erdner. 2015. Natural sunlight shapes crude oil-degrading bacterial communities in northern Gulf of Mexico surface waters. *Frontiers in Microbiology* 6:1325, <http://dx.doi.org/10.3389/fmicb.2015.01325>.
- Bandara, U.C., P.D. Yapa, and H. Xie. 2011. Fate and transport of oil in sediment laden marine waters. *Journal of Hydro-Environment Research* 5:145–156, <http://dx.doi.org/10.1016/j.jher.2011.03.002>.
- Bouloubassi, I., L. Méjanelle, R. Pete, J. Fillaux, A. Lorre, and V. Point. 2006. PAH transport by sinking particles in the open Mediterranean Sea: A 1 year sediment trap study. *Marine Pollution Bulletin* 52:560–571, <http://dx.doi.org/10.1016/j.marpolbul.2005.10.003>.
- Fasnacht, M.P., and N.V. Blough. 2003a. Kinetic analysis of the photodegradation of polycyclic aromatic hydrocarbons in aqueous solution. *Aquatic Science* 65:352–358, <http://dx.doi.org/10.1007/s00027-003-0680-7>.
- Fasnacht, M.P., and N.V. Blough. 2003b. Mechanisms of the aqueous photodegradation of polycyclic aromatic hydrocarbons. *Environmental Science Technology* 37:5,767–5,772, <http://dx.doi.org/10.1021/es034389c>.
- Fingas, M.F. 1995. A literature review of the physics and predictive modeling of oil spill evaporation. *Journal of Hazardous Materials* 42:157–175, [http://dx.doi.org/10.1016/0304-3894\(95\)00013-K](http://dx.doi.org/10.1016/0304-3894(95)00013-K).
- Frynsinger, G.S., R.B. Gaines, L. Xu, and C.M. Reddy. 2003. Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental Science & Technology* 37:1,653–1,662, <http://dx.doi.org/10.1021/es020742n>.
- Griffiths, M.T., R. Da Campo, P.B. O'Connor, and M.P. Barrow. 2014. Throwing light on petroleum: Simulated exposure of crude oil to sunlight and characterization using atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectrometry. *Analytical Chemistry* 86:527–534, <http://dx.doi.org/10.1021/ac4025335>.
- Gros, J., D. Nabi, B. Würz, L.Y. Wick, C.P.D. Brussaard, J. Huisman, J.R. van der Meer, C.M. Reddy, and J.S. Arey. 2014a. First day of an oil spill on the open sea: Early mass transfers of hydrocarbons to air and water. *Environmental Science & Technology* 48:9,400–9,411, <http://dx.doi.org/10.1021/es502437e>.
- Gros, J., C.M. Reddy, C. Aeppli, R.K. Nelson, C.A. Carmichael, and J.S. Arey. 2014b. Resolving biodegradation patterns of persistent saturated hydrocarbons in weathered oil samples from the Deepwater Horizon disaster. *Environmental Science & Technology* 48:1,628–1,637, <http://dx.doi.org/10.1021/es4042836>.
- Gros, J., C.M. Reddy, R.K. Nelson, S. Socolofsky, and J.S. Arey. 2016. Simulating gas–liquid–water partitioning and fluid properties of petroleum under pressure: Implications for deep-sea blowouts. *Environmental Science & Technology*, <http://dx.doi.org/10.1021/acs.est.5b04617>.
- Hansen, H.P. 1975. Photochemical degradation of petroleum hydrocarbon surface films on seawater. *Marine Chemistry* 3:183–195, [http://dx.doi.org/10.1016/0304-4203\(75\)90001-8](http://dx.doi.org/10.1016/0304-4203(75)90001-8).
- Joye, S.B. 2015. Deepwater Horizon, 5 years on. *Marine Science* 349:592–593, <http://dx.doi.org/10.1126/science.aab4133>.
- King, S., P. Leaf, A. Olson, P.Z. Ray, and M.A. Tarr. 2014. Photolytic and photocatalytic degradation of surface oil from the Deepwater Horizon spill. *Chemosphere* 95:415–422, <http://dx.doi.org/10.1016/j.chemosphere.2013.09.060>.
- Larson, R.A., L.L. Hunt, and D.W. Blankenship. 1977. Formation of toxic products from a #2 fuel oil by photooxidation. *Environmental Science & Technology* 11:492–496, <http://dx.doi.org/10.1021/es06128a002>.
- Lipiatou, E., I. Tolosa, R. Simó, I. Bouloubassi, J. Dachs, S. Marti, M.-A. Sicre, J.M. Bayona, J.O. Grimalt, A. Saliott, and J. Albaiges. 1997. Mass budget and dynamics of polycyclic aromatic hydrocarbons in the Mediterranean Sea. *Deep Sea Research Part II* 44:881–905, [http://dx.doi.org/10.1016/S0967-0645\(96\)00093-8](http://dx.doi.org/10.1016/S0967-0645(96)00093-8).
- Mackay, D., and W.Y. Shiu. 1976. Aqueous solubilities of weathered northern crude oils. *Bulletin of Environmental Contamination and Toxicology* 15:101–109, <http://dx.doi.org/10.1007/BF01686201>.
- McKenna, A.M., R.K. Nelson, C.M. Reddy, J.J. Savory, N.K. Kaiser, J.E. Fitzsimmons, A.G. Marshall, and R.P. Rodgers. 2013. Expansion of the analytical window for oil spill characterization by ultrahigh resolution mass spectrometry: Beyond gas chromatography. *Environmental Science & Technology* 47:7,530–7,539, <http://dx.doi.org/10.1021/es305284t>.
- Nelson, R.K., C. Aeppli, J.S. Arey, H. Chen, A. de Oliveira, C. Eiserbeck, G.S. Frynsinger, R.B. Gaines, K. Grice, J. Gros, and others. 2016. Applications of comprehensive two-dimensional gas chromatography (GC×GC) in studying the source, transport, and fate of petroleum hydrocarbons in the environment. Pp. 339–448 in *Standard Handbook of Oil Spill Environmental Forensics*. S.A. Stout and Z. Wang, eds, Elsevier.
- Nicodem, D.E., C.L.B. Guedes, and R.J. Correa. 1998. Photochemistry of petroleum: Part I. Systematic study of a Brazilian intermediate crude oil. *Marine Chemistry* 63:93–104, [http://dx.doi.org/10.1016/S0304-4203\(98\)00053-X](http://dx.doi.org/10.1016/S0304-4203(98)00053-X).
- Passow, U., K. Ziervogel, V. Asper, and A. Diercks. 2012. Marine snow formation in the aftermath of the Deepwater Horizon oil spill in the Gulf of Mexico. *Environmental Research Letters* 7:035301, <http://dx.doi.org/10.1088/1748-9326/7/3/035301>.
- Payne, J.R., J.R. Clayton, and B.E. Kirstein. 2003. Oil/suspended particulate material interactions and sedimentation. *Spill Science and Technology Bulletin* 8:201–221, [http://dx.doi.org/10.1016/S1353-2561\(03\)00048-3](http://dx.doi.org/10.1016/S1353-2561(03)00048-3).
- Payne, J.R., and C.R. Phillips. 1985. Photochemistry of petroleum in water. *Environmental Science & Technology* 19:569–579, <http://dx.doi.org/10.1021/es00137a602>.
- Plata, D.L., C.M. Sharpless, and C.M. Reddy. 2008. Photochemical degradation of polycyclic aromatic hydrocarbons in oil films. *Environmental Science & Technology* 42:2,432–2,438, <http://dx.doi.org/10.1021/es702384f>.
- Ray, P.Z., H. Chen, D.C. Podgorski, A.M. McKenna, and M.A. Tarr. 2014. Sunlight creates oxygenated species in water-soluble fractions of Deepwater Horizon oil. *Journal of Hazardous Materials* 280:636–643, <http://dx.doi.org/10.1016/j.jhazmat.2014.08.059>.
- Ray, P.Z., and M.A. Tarr. 2014a. Petroleum films exposed to sunlight produce hydroxyl radical. *Chemosphere* 103:220–227, <http://dx.doi.org/10.1016/j.chemosphere.2013.12.005>.
- Ray, P.Z., and M.A. Tarr. 2014b. Solar production of singlet oxygen from crude oil films on water. *Journal of Photochemistry and Photobiology A: Chemistry* 286:22–28, <http://dx.doi.org/10.1016/j.jphotochem.2014.04.016>.
- Ray, P.Z., and M.A. Tarr. 2014c. Formation of organic triplets from solar irradiation of petroleum. *Marine Chemistry* 168:135–139, <http://dx.doi.org/10.1016/j.marchem.2014.09.018>.
- Ruddy, B.M., M. Huettel, J.E. Kostka, V.V. Lobodin, B.J. Bythell, A.M. McKenna, C. Aeppli, C.M. Reddy, R.K. Nelson, A.G. Marshall, and R.P. Rodgers. 2014. Targeted petroleomics: Analytical investigation of Macondo well oil oxidation products from Pensacola Beach. *Energy and Fuels* 28:4,043–4,050, <http://dx.doi.org/10.1021/ef500427n>.
- Slater, G.F., H.K. White, T.I. Eglinton, and C.M. Reddy. 2005. Determination of microbial carbon sources in petroleum contaminated sediments using molecular ¹⁴C analysis. *Environmental Science & Technology* 39:2,552–2,558, <http://dx.doi.org/10.1021/es048669j>.
- Wang, Z., and M.F. Fingas. 2003. Development of oil hydrocarbon fingerprinting and identification techniques. *Marine Pollution Bulletin* 47:423–452, [http://dx.doi.org/10.1016/S0025-326X\(03\)00215-7](http://dx.doi.org/10.1016/S0025-326X(03)00215-7).

ACKNOWLEDGMENTS

The authors of this article received funding from the Gulf of Mexico Research Initiative (data are publicly available through the Gulf of Mexico Research Initiative Information & Data Cooperative [GRIIDC] at <https://data.gulfresearchinitiative.org>) and the National Science Foundation (CHE-1507295 and OSE-1333148).

AUTHORS

Matthew A. Tarr (mtarr@uno.edu) is Professor, Department of Chemistry, University of New Orleans, New Orleans, LA, USA. **Phoebe Zito** is Postdoctoral Fellow, Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, USA. **Edward B. Overton** is Emeritus Professor, Department of Environmental Sciences, Louisiana State University, Baton Rouge, LA, USA. **Gregory M. Olson** is Research Associate, Department of Environmental Sciences, Louisiana State University, Baton Rouge, LA, USA. **Puspa L. Adhikari** is Research Associate, Department of Environmental Sciences, Louisiana State University, Baton Rouge, LA, USA. **Christopher M. Reddy** is Senior Scientist, Department of Marine Chemistry & Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA.

ARTICLE CITATION

Tarr, M.A., P. Zito, E.B. Overton, G.M. Olson, P.L. Adhikari, and C.M. Reddy. 2016. Weathering of oil spilled in the marine environment. *Oceanography* 29(3):126–135, <http://dx.doi.org/10.5670/oceanog.2016.77>.