Chemical Composition of Macondo and Other Crude Oils and Compositional Alterations During Oil Spills

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A thick layer of weathered oil from the Deepwater Horizon oil spill blowout floats atop the Gulf of Mexico. *Photo credit: David L. Valentine, University of California, Santa Barbara*

> The distribution and average molecular weight of the compounds in crude oils determine the oil's viscosity, density, and emulsion-forming potential at any temperature, as well as the ease of evaporation and aqueous dissolution.

ABSTRACT. Crude oils are some of the most complex and diverse organic mixtures found in nature. They contain thousands of different compounds belonging to several compound classes, with the main ones being hydrocarbons and their heteroatom (N, S, and O)-containing analogs, called non-hydrocarbons. In general, all crude oils contain the same types of chemical structures, but these compounds can be in highly variable proportions in crude oils drawn from different reservoir conditions and locations. Both the types of compounds and their respective quantities change rapidly once the crude oil is spilled into the environment, making the circumstances associated with every spill unique. In general, smaller and lower molecular weight oil compounds are more susceptible to processes such as evaporation, dissolution, and biodegradation, while the heavier, more hydrophobic compounds tend to adhere to living organisms or particulates and persist. The presence of certain compounds, such as PAHs (polycyclic aromatic hydrocarbons), also determines the acute and chronic toxicity of the spilled oil. Natural processes can degrade virtually all compounds in crude oils, with aerobic oxidation proceeding much faster than anaerobic degradation, although not all crude oil components are degraded with the same speed. The environmental fate and effects of crude oil degraded by biodegradation and photooxidation are yet to be fully determined. Due to the submarine and offshore setting of the Macondo well blowout, components of the spilled oil were distributed throughout the marine environment—water column, sediments, surface waters, and the coast. The light and nonviscous nature of Macondo crude oil favored its removal through natural degradation, evaporation, dissolution, and dispersal processes. In spite of the unprecedented quantities of oil that spilled, the final fate and effects of the oil, the more recalcitrant fractions of Macondo oil, and the oil weathering products have not been totally elucidated. Responders with knowledge of the physical properties of the Macondo oil executed their preplanned response efforts and kept a majority of the oil from reaching the more sensitive coastal areas.

INTRODUCTION: WHAT ARE CRUDE OILS?

Generally, crude oils are very complex fluid mixtures made up of thousands of hydrocarbons, non-hydrocarbons, and small amounts of metals that are refined into a wide array of petroleum products to become important sources of global energy as well as feedstocks for the chemical manufacturing industry. The term "crude oil" has different connotations to different individuals. For example, geochemists think of crude oil as the material within petroleum reservoirs, while environmental scientists often associate crude oil with an oil spill or release. Both perspectives will be presented within the context of this paper; however, the main focus will be on the composition and respective chemical and physical properties relevant for crude oil released into the environment.

Crude oil released into the environment can have harmful impacts via several mechanisms. Aromatic compounds with molecular weights from 78 to ~300 dalton (Da) constitute only 5% to 10% of the weight of typical oils, but they are known to be toxic to a wide variety of organisms. Because crude oil is hydrophobic (water-repelling) in nature, it tends to coat or stick to surfaces such as sediments, feathers, and plant leaves, or other solid surfaces of living organisms. This effect frequently results in the death of those organisms. Crude oil in the environment can also result in oxygen depletion when microorganisms degrade the oil. Most oil-degrading microorganisms require oxygen as they breakdown crude oil and will utilize what oxygen is available until it is depleted. As a result, the

environment can go from having plenty of oxygen (oxic) to low oxygen concentrations (suboxic) or even no oxygen (anoxic), which causes death to organisms and plants that need the oxygen to survive. Although it is rare for seawater to become completely anoxic, it is a normal occurrence in sediments and in estuarine environments. Further, as natural microorganisms degrade the oil, their populations greatly expand, and this carbon enrichment may cause cascading food chain impacts. While these four factors (toxicity, coating and smothering, oxygen depletion, and carbon enrichment) are documented to cause harm to the environment during oil spills, it is also well documented that natural chemosynthetic ecosystems thrive in areas of active and relic oil seepage in marine sediments and near the bottom by using methane and crude oil components as their carbon sources (Kennicutt et al., 1985). In summary, oil spills can negatively impact the environment not only because the oils contain toxic compounds but also because of the physical properties of the spilled material, the spills' distributions in environmental compartments, and the ability of these reduced forms of carbon (i.e., hydrocarbons) to be oxidized by microorganisms, thus using up available oxygen and producing unusual amounts of biomass.

Most of the compounds in crude oil contain only the elements hydrogen (10% to 14% by weight) and carbon (~83% to 87%), hence the term hydrocarbon. However, crude oil also has compounds, termed non-hydrocarbons, that contain the heteroatoms nitrogen (0.1% to 2% of an oil), oxygen (0.1% to 1.5%), or sulfur (0.5% to 6%) in addition to their carbon and hydrogen contents. In extreme cases, sulfur content can reach over 10% in some very viscous crude oils (bitumens) from oil sands. Typically, in these dense crude oils, non-hydrocarbons are present in very high concentrations. The molecular weights of the organic components in crude oil can range from 16 Da for methane to well over 1,000 Da for the asphaltenes. It is important to point out that even though crude oils are composed mostly of hydrocarbons, not all hydrocarbons in the environment are from crude oils. All living things contain biogenic hydrocarbons known as lipids, so many organisms are sources of biogenic hydrocarbons (e.g., plant waxes).

All crude oils, regardless of their sources, are made up of similar types of molecular species whose quantitative compositions can vary greatly. These include: (1) saturated hydrocarbons, (2) aromatic hydrocarbons, (3) non-hydrocarbons that contain heteroatoms such as S, N, and O in the molecular structures, and (4) small quantities of certain trace metals. Traditional solubility and chromatography based compositional schemes refer to oils as being composed of saturates, aromatics, resins, and asphaltenes (SARA), with the latter two fractions being mostly composed of non-hydrocarbons. Figure 1 shows typical structures of organic compounds that form crude oils. It should be noted that the exact structures of asphaltenes and resins are the subjects of continuing debates (Snowdon et al., 2016).

The quantities of specific hydrocarbon molecules in crude oil from a given reservoir depend upon the reservoir's location, depth, temperature, and pressure, and on the initial organic materials present in the source rocks. However, the same types of compounds are found in all crude oils and various refined products. Refining the crude oil into useful fuels not only changes the oil's initial quantitative and qualitative composition of saturate aliphatic and aromatic hydrocarbons but also may add new species such as olefins (alkenes) to the fuel's composition.

It is important to recognize that hydrocarbons in crude oils originated from the conversion of atmospheric carbon dioxide (CO_2), via photosynthesis, into terrestrial and marine biomass. This reaction converts stable oxidized carbon, CO_2, into labile reduced carbon biomass that makes up all living organisms. Once buried, the biomass material undergoes chemical transformation (diagenesis), loses oxygen content, and ultimately, after exposure to temperatures above 100°C for extended (geological) time periods, is converted to the highly reduced hydrocarbon-rich mixtures that make up crude oils. Because they are reduced, crude oil hydrocarbons are effective electron donors, and are capable of being readily oxidized in the environment by electron acceptors such as oxygen (O_2) or sulfate ($SO_4^=$), which are common in seawater. Thus, while some of the components in crude oils are toxic and destructive in the natural environment, there are natural microbial processes in the presence (aerobic) and absence (anaerobic) of oxygen that are capable of converting hydrocarbons in spilled oil back to CO_2 and new biomass on various time scales.

The terms crude oil and petroleum are often used intermittently to describe the same material, and this can lead to some confusion as to their respective compositions. The following definitions may be useful in understanding the different types of petroleum that are frequently encountered.

Petroleum is a comprehensive term for a series of subsurface fluids, composed significantly, but not entirely, of hydrocarbons that occur concentrated in reservoirs and can be commercially produced by drilling and excavation as crude oil or natural gas, or both, and sometimes as liquid condensates and bitumens (Larter and Head, 2014).

Natural gases are petroleum fluids found in the gas phase in the subsurface. They are composed of hydrocarbon mixtures dominated by methane, with contributions from ethane, propane, butanes, and the pentanes and traces of inorganic gases, principally CO_2 and nitrogen. Gases by definition contain no components with more than six carbon atoms.

Gas condensates are petroleum fluids found in the gas phase in subsurface reservoirs, but they contain significant

amounts of hydrocarbons with six or more carbon atoms that condense out as a liquid (the liquid condensate) when pressure and temperature are reduced either during production or when they come to the sea surface during releases. These components include hydrocarbons and non-hydrocarbons, with ratios (by mass) of gas (C_1–C_5) to C_{6+} components in gas condensates ranging from about 3:1 to very large values.

Crude oil, as defined by geochemists, is petroleum that is in the liquid phase in the subsurface and that can contain up to 50 weight percent of natural gas in solution at reservoir pressures (England et al., 1987). According to the relative amount of "solution gas," the crude oil can be termed "live" (with gas) or "dead" (no gas) and termed "volatile oil" or "black oil," depending on the gas content. Thus, crude oil is a liquid mixture

of hydrocarbons and non-hydrocarbons. It contains many thousands of individual components with from 1 to 100 or more carbon atoms per molecule. The average size of the molecules in a "light" crude oil would be in the range of 10–20 carbon atoms per molecule. In most petroleum, methane is the most abundant individual molecule on a molar basis. When oil is produced, spilled, or seeped, the gas comes out of solution, leaving molecules

Representative Molecular Structures Found in All Crude Oils

- **GC-MS: up to MW ~400 to 500 Dalton**
- **FTICR-MS: 150 to >2,000 Dalton**
- **SARA Analysis: bulk analysis of main compound classes fractionated into saturates, aromatics, resins and asphaltenes**
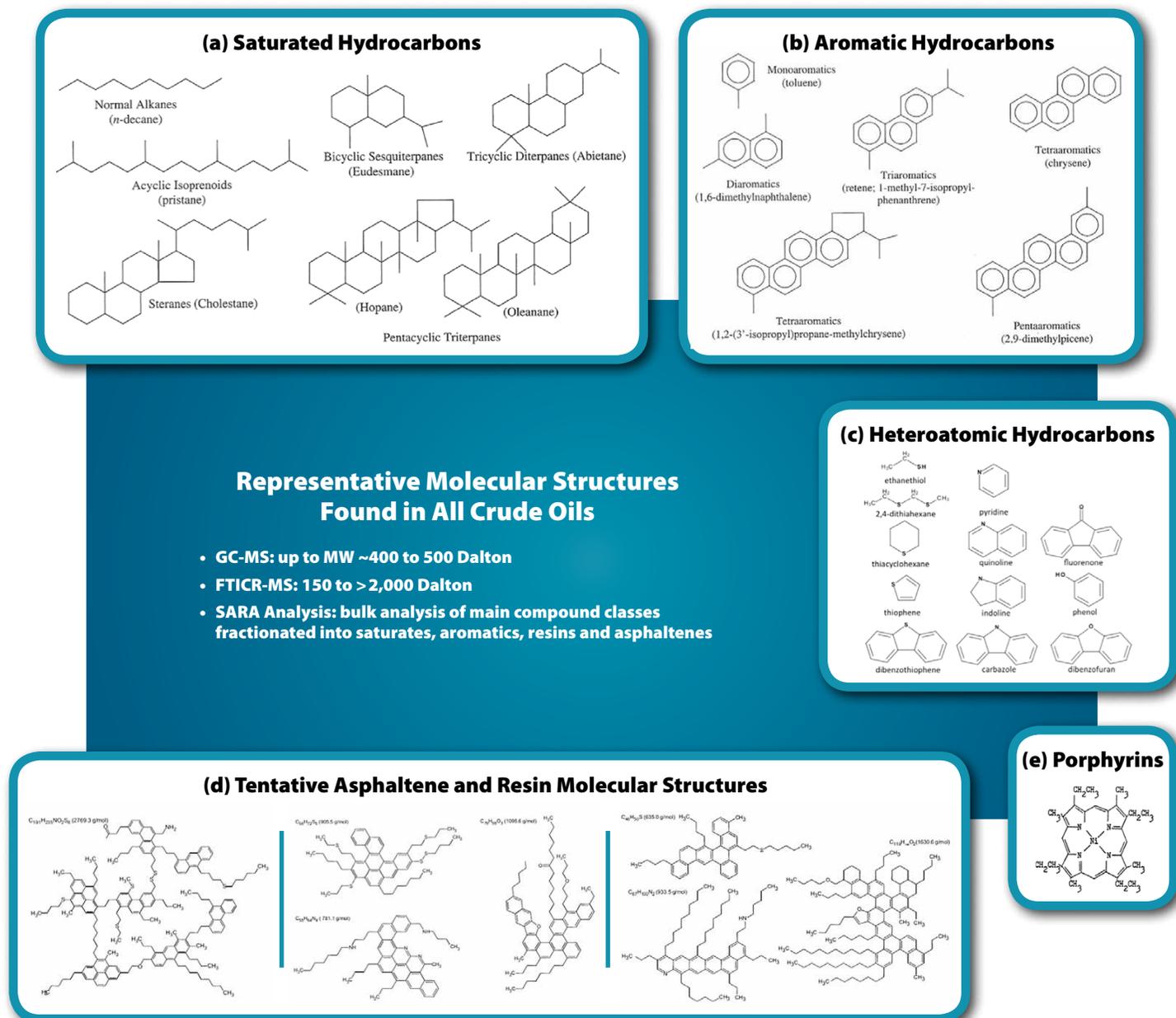
FIGURE 1. Representative types of chemical structures typically found in crude oils, including various types of (a) saturate hydrocarbons, (b) aromatic hydrocarbons, (c) heteroatomic hydrocarbons (e.g., NSOs), (d) asphaltenes and resins, and (e) porphyrins. Conventional gas chromatography-mass spectrometric analytical methods are used to detect structures with molecular weights up to approximately 500 Da while new high-resolution mass spectrometry methods are used to elucidate molecular formulas up to and above 2,000 Da. Chromatographic and precipitation methods are used to separate oil components into four classes: bulk saturates, aromatics, resins, and asphaltenes (SARA).

with six or more carbon atoms in the liquid crude oil, and this liquid also contains non-hydrocarbon compounds. The largest-sized molecules abundantly present in solution in crude oil are the asphaltenes, which probably have up to an average of 70 or more carbon atoms, attendant hydrogen atoms, and several oxygen, nitrogen, or sulfur species per molecule (Snowdon et al., 2016). Some asphaltenes may have even larger numbers of carbon and other associated atoms in their molecules. The diverse array of chemical and physical alteration processes that affect crude oil in reservoirs means that the physical property range of nonrefined degassed crude oils (stock tank oils or dead oils) spilled or leaked into the environment can be very large, with densities as low as 750 kg m^{-3} to densities much greater than that of water, and with viscosities at ambient conditions near that of water (1 centipoise, cP) up to thousands of cP, or even greater. The Macondo oil spilled in the Deepwater Horizon incident and collected at the surface, for example, had a density of 860 kg m^{-3} and an initial viscosity of 3.9 cP at 32°C (Daling et al., 2014).

Heavy oils and tars are petroleum fluids whose compositions have been altered by a variety of in-reservoir processes that usually reduce the commercial value of the oil, complicate its extraction, and impact its environmental behavior when spilled. Several processes are involved in petroleum alteration in the reservoir, with in-reservoir anaerobic biodegradation probably being the most important. This process generates the volumetrically dominant heavy oils and bitumens (oils denser than water, with viscosities greater than 10,000 cP at ambient conditions), the so-called "Group V oils", and the heavy bitumen components of dilbit and synbit oils (processed oils from oil sands production). These heavy oils have drastically different characteristics than the more familiar light oils. They have very high viscosity, which prevents them from flowing, and their non-hydrocarbon

content can be as high as 25% to 60% of the oil in, for example, Canadian oil sands (Larter and Head, 2014). Further, subsurface anaerobic methanotrophic microbial biodegradation affects many oils, and to a lesser extent, natural gases, in shallower petroleum accumulations where the reservoir temperature is less than about 80°C. This subsurface microbial degradation, involving both bacteria and archaea, results in the destruction of lighter hydrocarbons in the reservoir and the consequent production of a denser, more viscous crude oil (Head et al., 2003). These viscous, heavy, non-hydrocarbon rich crude oils, sometimes called **unconventional oils**, will be transported and spilled in much greater volumes in the twenty-first century.

CHEMICAL COMPOSITIONS OF CRUDE OILS

Traditionally, crude oil is defined as a naturally occurring liquid mixture consisting mainly of **hydrocarbons** (>80%) and other organic compounds containing sulfur, nitrogen, oxygen, metals, and other elements (i.e., **non-hydrocarbons**; Speight, 2006). The following types of compound classes are found in crude oils.

Saturated hydrocarbons are also called alkanes. In these molecules, carbon atoms are connected by single bonds to four other carbon or hydrogen atoms. The simplest saturated hydrocarbon is methane (CH_4). Carbon-carbon chains in larger saturated hydrocarbons can be either linear or branched (acyclic alkanes), and their general formula is C_nH_{2n+2}. Ring structures are also present in hydrocarbons, and these types of compounds are called cycloalkanes. Cycloalkanes, also termed naphthenes or alicyclic hydrocarbons, have the general formula C_nH_{2n}, with only one ring present (they are saturated and cyclic hydrocarbons, but they do not contain carbon-carbon double bonds). Cycloalkanes can have several saturated rings in their molecular structures.

Aromatic hydrocarbons are characterized by molecular structures that contain at least one, and generally several, fully conjugated aromatic rings. Linear, branched, or cyclic alkyl substituents can be bonded to the aromatic ring structures. The simplest aromatic molecule is benzene (C_6H_6). Depending on the number of condensed aromatic rings in the molecule, aromatic hydrocarbons can be monoaromatic or polyaromatic (i.e., polycyclic aromatic hydrocarbons, PAHs). Variations in aromatic ring number and alkylation degree will modify the behavior and fate of these species in the environment, for example, changing aqueous solubility, photosensitivity, and biodegradability. Many of these aromatic components in crude oils are known to be toxic to living organisms.

Figure 2 shows some of the more abundant PAHs and their respective alkylated relatives (homologs) commonly found in the Macondo oil spilled during the Deepwater Horizon incident. These are representative of the typical aromatic hydrocarbon content in oils and include those PAH compounds that are known to have toxic properties. In crude oils, the unsubstituted or parent PAH compounds are always found together with aromatic compounds that have the same ring structure but also have a number of alkyl groups, from one to four or more, attached at various locations on the aromatic rings (Overton et al., 1980b). These alkyl homologs of the parent PAHs can have several structural isomers because of the placement of the alkyl groups at different positions around the PAH rings. Figure 3 shows example compositions of the homologous structural isomers in the Macondo oil for the petrogenic PAH compounds dibenzothiophene, phenanthrene, and their respective alkylated homologs.

Biomarkers are a small fraction of commonly recalcitrant crude oil molecules whose structures are closely related to biochemical precursors (Head et al., 2003; Peters et al., 2005). They are
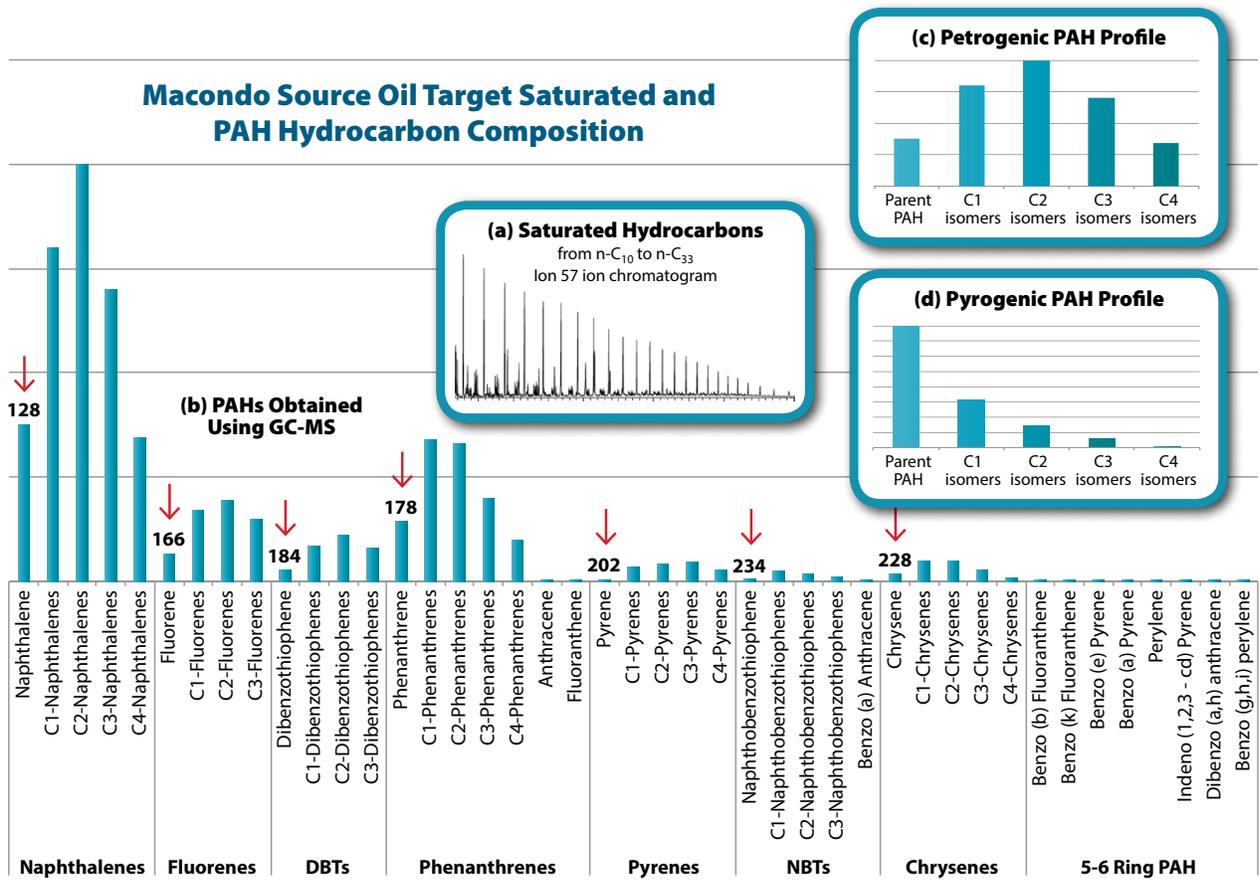
FIGURE 2. Analytical data on the relative quantitative composition of Macondo oil showing (a) saturated and (b) polycyclic aromatic hydrocarbons (PAHs) that are typically obtained using conventional gas chromatography-mass spectrometric analytical methods. The red arrows indicate the composition of unsubstituted or parent PAHs, with the chemical names given for the various families of parent and alkyl homolog PAH compounds typically found in crude oils. The insets show typical compositions for PAHs from (c) petrogenic and (d) pyrogenic sources. The saturated hydrocarbon data are displayed as the high-resolution selected ion chromatogram showing normal (i.e., straight chain) saturated hydrocarbons eluting with carbon numbers from 10 to 33, as well as other branched and cyclic saturated hydrocarbons.
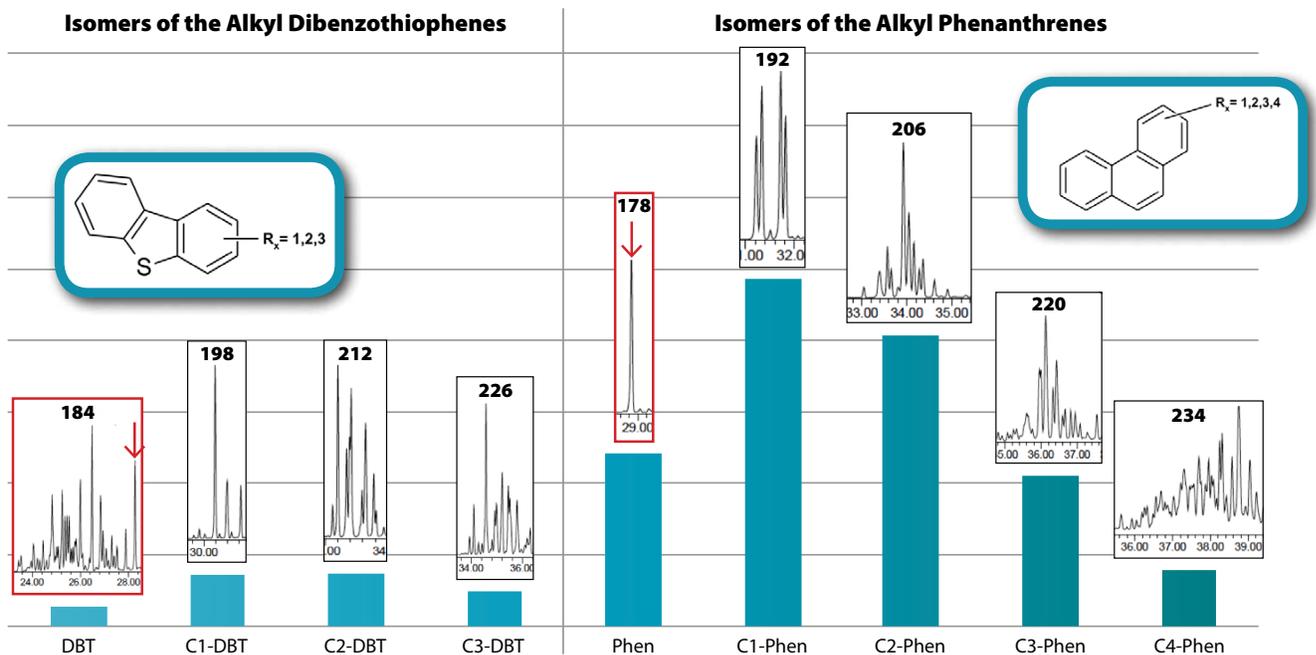
FIGURE 3. The relative quantitative composition (blue bars) of the dibenzothiophene (DBT) and phenanthrene (Phen) families of PAH compounds in the Macondo oil, along with the chemical structures of these two chemicals. The red-bordered insets show selected ion chromatograms for DBT (ion 184) and Phen (ion 178), and the other insets show the alkyl homolog isomer patterns of the C1 (ion 198), C2 (ion 212), and C3 (ion 226) DBTs, and the C1 (ion 192), C2 (ion 206), C3 (ion 220), and C4 (ion 234) Phens.

(a) Hopanes

SIM Ion 191

(b) Steranes

SIM Ion 217

SIM Ion 218

(c) Triaromatic Steroids

SIM Ion 231
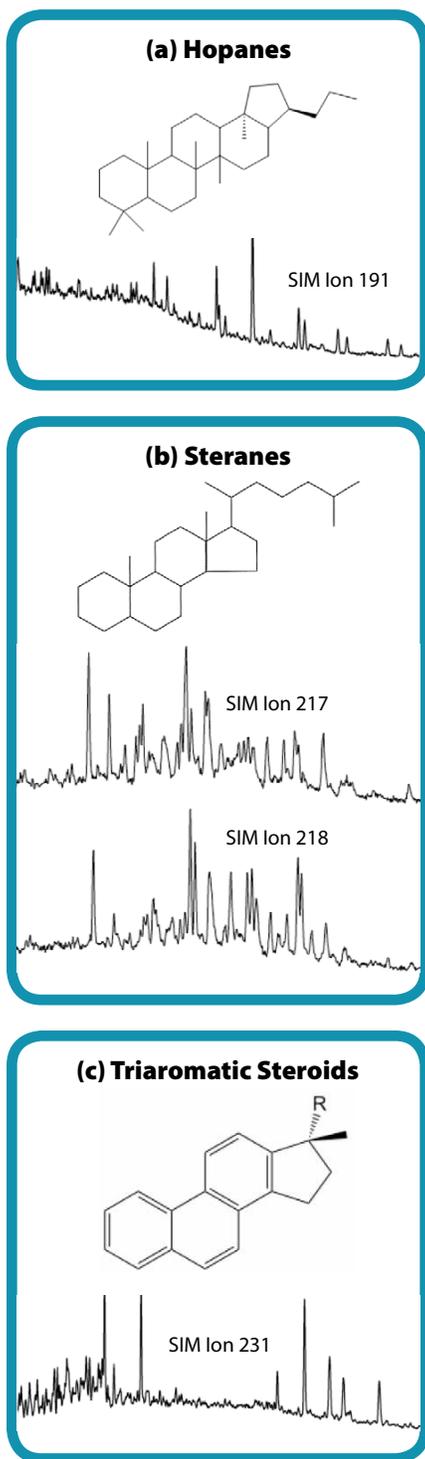
FIGURE 4. The representative chemical structures of forensic biomarker compounds and their respective selected ion chromatograms for the (a) hopanes (ion 191), (b) steranes (ions 217 and 218), and (c) triaromatic steroids (ion 231) found in the Macondo crude oil. These compounds are resistant to natural degradation processes and are frequently used to link spilled crude oils to their sources.

typically composed of alkylated, saturated, or partially aromatized cyclic hydrocarbons that are created during oil formation from the initial organic matter in the source rock, making their occurrences and distributions specific for crude oils from different source rocks and thermal histories. The compound 17β-hopane (Figure 4a) is routinely used as a "conserved internal marker," assuming its concentration in a weathered oil residue is unaltered during normal weathering biodegradation (in timeframes of several months to years), in an effort to quantify how much degradation has occurred in a spill (Prince et al., 1994). However, several studies (Wang et al., 2001; Aeppli et al., 2014; Atlas et al., 2015) show that even these biomarker compounds are susceptible to biodegradation under prolonged exposure, but they are generally the slowest to biodegrade and are late in the alteration succession of petroleum compounds. Figure 4 shows representative distributions of these cyclic biomarker molecules from analysis of the Macondo oil via their characteristic gas chromatography-mass spectrometry (GC-MS)-derived selected ion chromatograms. Because biomarkers are particularly resistant to environmental weathering processes (e.g., biodegradation), they can be used in environmental forensic studies as proxies to track the sources and fates of specific oil spills (Peters et al., 2005).

Non-hydrocarbon aromatic oil fractions (sometimes termed NSO compounds) are complex and heterogeneous mixtures of compounds that, in addition to containing carbon and hydrogen, have one or more heteroatoms such as N, S, and O. They are mostly alkylated heteroatom-containing aromatic compounds with similar molecular weights to the PAHs in crude oils, and they can be detected by GC-based analytical methods. They comprise mostly alkylated benzothiophenes and dibenzothiophenes (contain S) or alkylated carbazoles (contain N). However, other non-hydrocarbons

have high enough molecular weights and polarities to be less amenable to routine coupled GC-MS methods for hydrocarbon analysis, but they can be analyzed by more advanced (and expensive) mass spectrometric methods such as high-resolution Fourier transform mass spectrometry (FTICR-MS). Typically, these high molecular weight and polar non-hydrocarbon compounds can be further classified into the following two solubility and liquid chromatography defined groups (Yen and Chilingarian, 2000).

Resins are high molecular weight NSO compounds that are soluble in light alkanes (e.g., *n*-pentane, *n*-hexane, *n*-heptane) as well as in more polar solvents such as toluene and methanol. These high molecular weight non-hydrocarbons can contain several aromatic rings in their molecular structures. Other resin NSO compounds, such as oxygen-containing naphthenic acids, are non-aromatic, very polar, and somewhat water soluble non-hydrocarbons that are particularly abundant in heavy, nonconventional crude oils, for example, bitumens.

Asphaltenes are a solubility-defined, high molecular weight fraction of crude oils, insoluble in light alkanes (e.g., *n*-pentane, *n*-hexane, *n*-heptane) but soluble in more polar solvents such as toluene or dichloromethane. They constitute overall the most water insoluble fraction in crude oil, but the solubility behavior of individual highly functionalized asphaltene components is not yet well understood. It is speculated that some of these NSO high molecular weight hydrocarbon components can end up in marine dissolved organic matter (DOM; Liu and Kujawinski, 2015). Although the exact structures are still debated, it is accepted that this fraction mainly contains functionalized and alkylated aromatic and heterocyclic (aromatic and naphthenic) compounds, which, depending on crude oil history, may represent dissolved species or aggregated groups of large molecules suspended in the crude oil. These

are highly alkyl-substituted species that have molecular weights up to and over 1,000 Da. Besides N, S, and O heteroatom systems, this fraction also contains molecules with incorporated metals, predominantly nickel (Ni) and vanadium (V), in porphyrin and other structures.

CHEMICAL AND PHYSICAL PROPERTIES AS DETERMINED BY CRUDE OIL COMPOSITION

The overall quantitative distribution of hydrocarbon and non-hydrocarbon compounds in crude oils and their molecular sizes, structures, and polarities determine the oil's viscosity at any temperature and pressure (under both subsurface and degassed surface conditions). The molecular size, structure, and polarity of individual compounds and the overall bulk oil composition determine the oil/water partition behavior of individual compounds based on their respective water solubilities and volatilities, and also determine rates of degradation by natural microorganisms under aerobic and anaerobic conditions. These properties also determine the routes of exposure to toxic compounds in crude oils. Crude oils that are largely composed of small, low molecular weight compounds (i.e., light oils) have low viscosities, abundant compounds such as alkylbenzene with relatively high water solubility, and high vapor pressures, and they are more readily biodegradable. The aromatic compounds in these light oils are also toxic and can have environmental routes of exposure through both vaporization and dissolution. Thus, fresh, light crude oils not only impact the water's surface but also contain components that can readily dissolve in the water column and evaporate into the air above the oil slick. Obviously, environmental parameters such as temperature, pressure, and wind speed can dramatically affect crude oil properties and behavior.

Crude oils that are composed of a larger proportion of higher molecular weight compounds (i.e., heavy crudes) are more viscous, less volatile, and overall less water soluble, but can have high concentrations of relatively soluble non-hydrocarbons, such as naphthenic acids (organic acids with alicyclic saturated structures), which are produced during in-reservoir biodegradation. These more viscous crude oils generally can form oil-in-water emulsions, and thus can persist much longer in the environment. Most are quite sticky and readily adhere to and cover surfaces or sediment that they contact. Because most of the toxic aromatic compounds in heavy crudes are larger in molecular size than those in lighter oils, with very high octanol/water partition coefficients, they are not as readily water soluble as the toxic compounds in light crudes. Thus, even though these high molecular weight PAH compounds are generally more toxic, their limited routes of exposure can also limit environmental impacts.

In summary, the distribution and average molecular weight of the compounds in crude oils determine the oil's viscosity, density, and emulsion-forming potential at any temperature, as well as the ease of evaporation and aqueous dissolution.

oils and the heavier weathered residues of all spilled oils are more persistent and are more likely to be incorporated long term into sediment compartments.

NATURAL AND ANTHROPOGENIC SOURCES OF CRUDE OILS TO MARINE WATERS

Input of petroleum to marine waters takes place via four major routes: natural seepage, spillage related to extraction (oil and gas recovery and processing), transportation, and consumption-related leakage. The fluxes to the environment are estimated and periodically updated by a committee of experts organized by the National Academy of Sciences. The latest estimates are published under the title *Oil in the Sea III: Inputs, Fates, and Effects* (NAS, 2003). These estimates are for average releases and are based on data from 1990 to 1999 for various global regions, including North American marine waters. These estimates have large uncertainties and are reported as minimum, maximum, and best estimates. The esti-

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These latter two physical properties provide a potential route for environmental exposure to the toxic compounds in crude oil. While lighter oils are considered more immediately dangerous because of the routes of exposure to their respective toxic compounds via evaporative and aqueous dissolution mechanisms, heavy

mated total input of petroleum, per year, for North America is 256 kilotons (Kt). Of this estimated total, typically 62% comes from natural seepage, 33% from consumption, 4% from transportation, and 1% from extraction related activities. The report's annual estimated input from spills is 17.6 Kt, which represents 6.9%

of the estimated total input, with recreational vessels and tank vessels accounting for 62% of this total.

- The estimated annual input of PAHs to North America is 4.9 Kt with 0.19 Kt (3.8%) coming from spills. The major inputs for PAH in marine waters are from natural seepage (51%) and consumption (45%). Regulations have resulted in reduced inputs due to consumption, extraction, and transportation (NAS, 2003) compared to the 1980s.

- By comparison, the estimated inputs of petroleum from the Ixtoc I (0.42 Kt) and BP Deepwater Horizon (0.59 Kt, according to the National Oceanic and Atmospheric Administration, or 0.46 Kt, according to the court settlement) oil spill incidents are 3.4% or less of the estimated annual inputs for spills and less than 0.2% of total estimated annual inputs to the marine environments in North America.

- Major spills take on both global and local perspectives. They are harmful events and correctly receive a lot of public attention. It has been estimated that on a global scale, the Deepwater Horizon spill petroleum input was 10% of the average annual seepage (GESAMP, 2007). On an average annual basis, spills in general represent a small percentage of total petroleum entering the marine environment. However, spills are a major concern in the near field, such as when the spilled oil occurs as a concentrated discharge in a restricted area of typically low annual discharge and, for example, reaches estuaries and beaches.

- The major sources of PAHs discharged into the environment are from seeps and petroleum-based activities, and from combustion of fossil fuels (e.g., coal), including those from natural combustion events such as forest and marsh fires. The composition of the PAH mixtures from these different sources, however, are quite different. Petroleum-based PAHs are composed of a greater abundance of the C_1-C_4 alkylated isomers of the parent PAHs, even in heavily weathered residues of petroleum. PAHs are ubiquitous in the environment, and those from combustion sources, called pyrogenic PAHs, have a greater abundance of the non-alkylated parent compound, and a relatively greater abundance of the four to six ring parent PAH compounds. These latter PAHs and their alkyl homologs are the compounds associated with increased toxicity and health effects compared to the lower molecular weight PAHs. The toxicity and impacts of the analogous hetero-aromatic species, abundant in heavy oils, are as yet poorly described.

Pre-spill background concentrations of TPH (total petroleum hydrocarbons) and PAHs in water samples from the Gulf of Mexico, though limited, were compared with samples collected in response to the Deepwater Horizon incident (Wade et al., 2016). Samples were collected by multiple response agencies, trustees, and BP, and are publicly available (http://gulfsciencedata.bp.com/go/doc/6145/1942326). The strategies for sample collection were varied, and many were collected based on differing requirements (e.g., for federal agency Natural Resource Damage Assessment, response activities, state beach baseline studies, response to fishing closures and fish kills, documenting biotic effects and oil seeps, studies of dispersants in the surface and subsurface and other scientific inquiries). The sampling was biased in areas suspected or known to have higher hydrocarbon concentrations. The samples were collected from a few meters to over 800 km in all directions from the wellhead. The highest concentrations were clustered within 25 km of the wellhead and from the surface to 1 m deep, or in the deep subsurface layers (900 m to 1,200 m depth). The highest TPH and PAH concentrations were in samples collected proximal to the wellhead or from surface slicks and near dispersant use. Of the 13,172 water sample TPH concentrations reported, 84% were below 1 μg L^{-1} (background). Of the 16,557 water sample PAH concentrations reported, 79% were below 0.056 μg L^{-1} (the median field blank, background). The percentage of samples below background increased rapidly after the well was capped (Wade et al., 2016). The Gulf Science Data reports (Beyer et al., in press; Boehm et al., 2016) are a valuable resource that provides documentation of the spatial and temporal range and distribution of hydrocarbon concentrations in the northern Gulf of Mexico during and after a major oil spill event.

WEATHERING OF OILS IN THE ENVIRONMENT: COMPOSITIONAL AND PHYSICAL CHANGES

Weathering involves a continuous series of processes that change the composition of crude oils that seep, spill, or leak into the environment. Weathering is caused by evaporation, dissolution, emulsification, sedimentation, and microbial and photo-oxidation of oil's components. Figure 5 shows the chemical compositions of saturated hydrocarbons (chromatographic data) and PAHs (quantities obtained via GC-MS analysis) in oily residues from the Macondo spill extracted from three sediment samples that represent different degrees of environmental weathering. This weathering changed the composition of the original spilled oil, as shown in similar data presented in Figure 1. The weathering also changed the residue's physical and toxicological properties. Fresh, light oil is more volatile, contains more water-soluble components, commonly floats on water, is typically not very viscous, and easily spreads out from the source. As oil weathers, it initially loses volatile components, which are also the most water-soluble components, and the oil becomes more viscous and is more likely to aggregate, as opposed to spreading out in a thin film. Over time, weathering continues to change the composition of the oil until it has been degraded in the environment, leaving behind only small

quantities of a refractory residue known as "tarballs." Typically, during the weathering process, much of the oil (especially heavier oil) will mix with water and emulsify, forming a viscous mixture that is fairly resistant to rapid weathering. Consequently, emulsification greatly slows down the weathering process. Furthermore, emulsified oil is also more difficult to remediate by skimming, dispersion, or burning. If organisms ingest oil or emulsified oil through, for example, preening of feathers, it can have significant toxic effects on internal organs. Heavily emulsified oil is slower to biodegrade and will stay in the environment longer than non-emulsified liquid oil.

Evaporation is the most important process in terms of disappearance for petroleum spills that are on, or reach, the ocean's surface (NAS, 2003). A spill of light crude oil can lose up to 75%, and medium crude oil up to 40%, of their light low molecular weight components (NAS, 2003) in a period of hours to days. Further, breaking bubbles and waves can rapidly transport small quantities of surface oils into the air as *aerosols* (Bahreini et al., 2012). As opposed to evaporated oil components, aerosols contain a broader range of both low and high molecular weight crude oil components.

Dissolution of crude oil components in water comprises a very complex series of interactions between low molecular weight molecules in crude oils and the surrounding water column. Dissolution
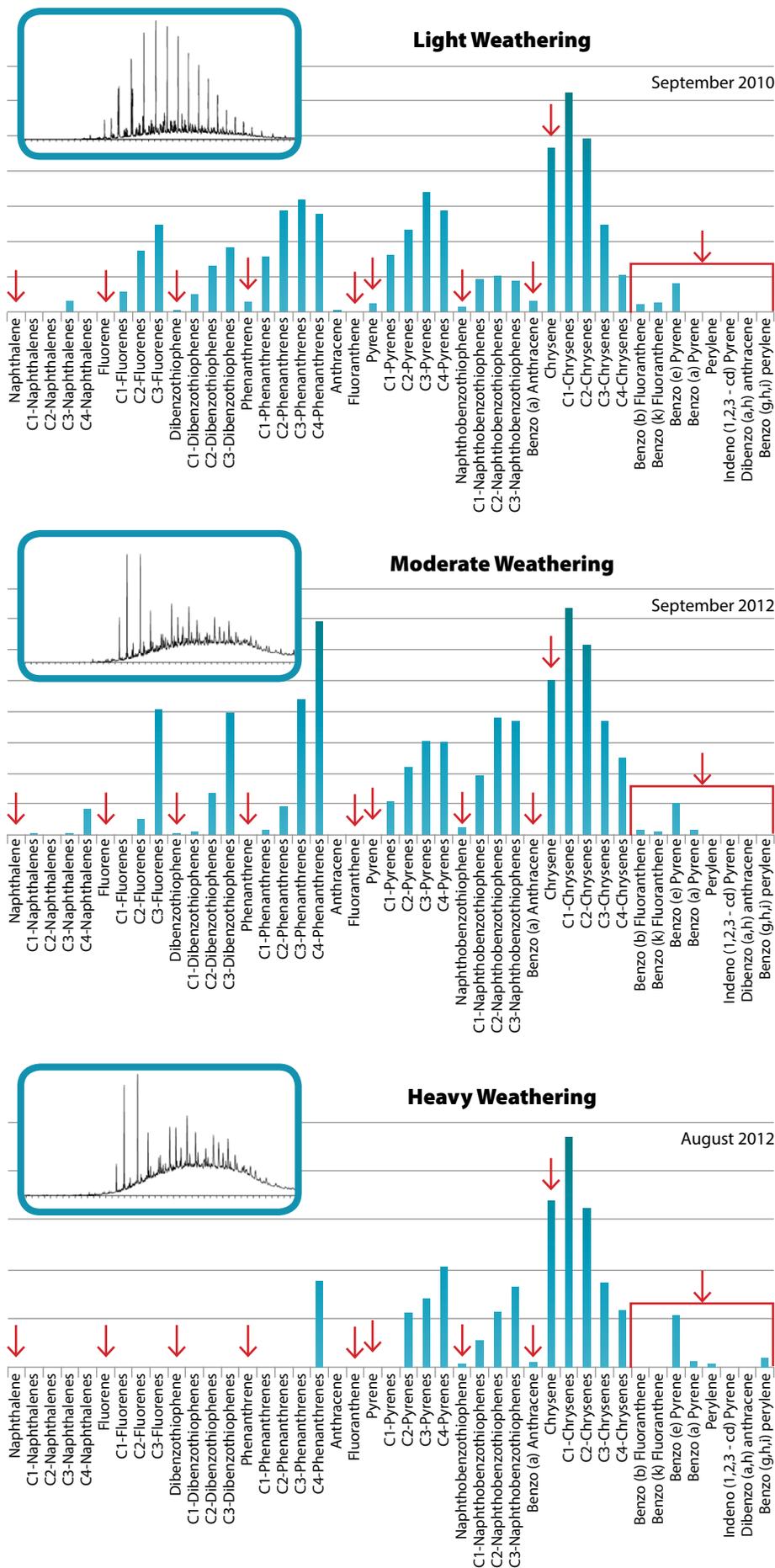
FIGURE 5. Alkane chromatograms (inset boxes) and petrogenic PAH quantities (graphs) found in three coastal marsh soil samples impacted by the Deepwater Horizon oil spill. The red arrows indicate quantities of parent PAHs for each family of parent and alkyl homolog isomers. The oil residues in these three samples had been subjected to various intensities of environmental weathering, showing loss of the lower molecular weight PAH compounds with increased weathering as well as the increased size of the unresolved complex mixture (hump) evident in the baseline of the alkane chromatograms.

Light Weathering

September 2010

Moderate Weathering

September 2012

Heavy Weathering

August 2012

occurs at the interface between the oil and the seawater, and is highly dependent on the spilled oil's surface area and thickness. Most crude oil components have fairly low solubility in water and thus have large partition coefficients between oil and water. As a general rule, small mono aromatic hydrocarbons, such as benzene and the alkyl benzenes, as well as one to five carbon hydrocarbons found in natural gas, have significant seawater solubility. This significant water solubility also extends to larger aromatic compounds, such as naphthalene and its alkyl homologs, and also even to three-ring aromatic compounds such as the phenanthrenes and the dibenzothiophenes with prolonged oil/water mixing. However, most crude oil components are not very soluble in seawater but are highly soluble in the crude oil mixture itself. Further, seawater solubility decreases with molecular weight for similar hydrocarbon-type compounds. For example, the solubilities of benzene (molecular weight, MW, 78), naphthalene (MW 128), and phenanthrene (MW 178), all aromatic hydrocarbons, in seawater at 25°C, are 1700, 30, and 1 mg L^{-1}, respectively. All of these compounds are highly soluble in crude oil. Figure 6 shows the saturated and aromatic hydrocarbon levels in seawater that have been equilibrated with fresh South Louisiana crude oil, producing what is commonly named a "water-accommodated fraction" or WAF. WAFs are primarily but not exclusively made up of dissolved oil components. As Figure 6 shows, the lower molecular weight aromatic hydrocarbons, like the alkyl naphthalenes, are much more soluble than the higher MW aromatic species, and the aromatic species are more soluble in water than equivalent carbon number saturated hydrocarbons in WAF samples. Crude oil, however, is an excellent solvent for crude oil hydrocarbon-type components, and the crude oil can readily
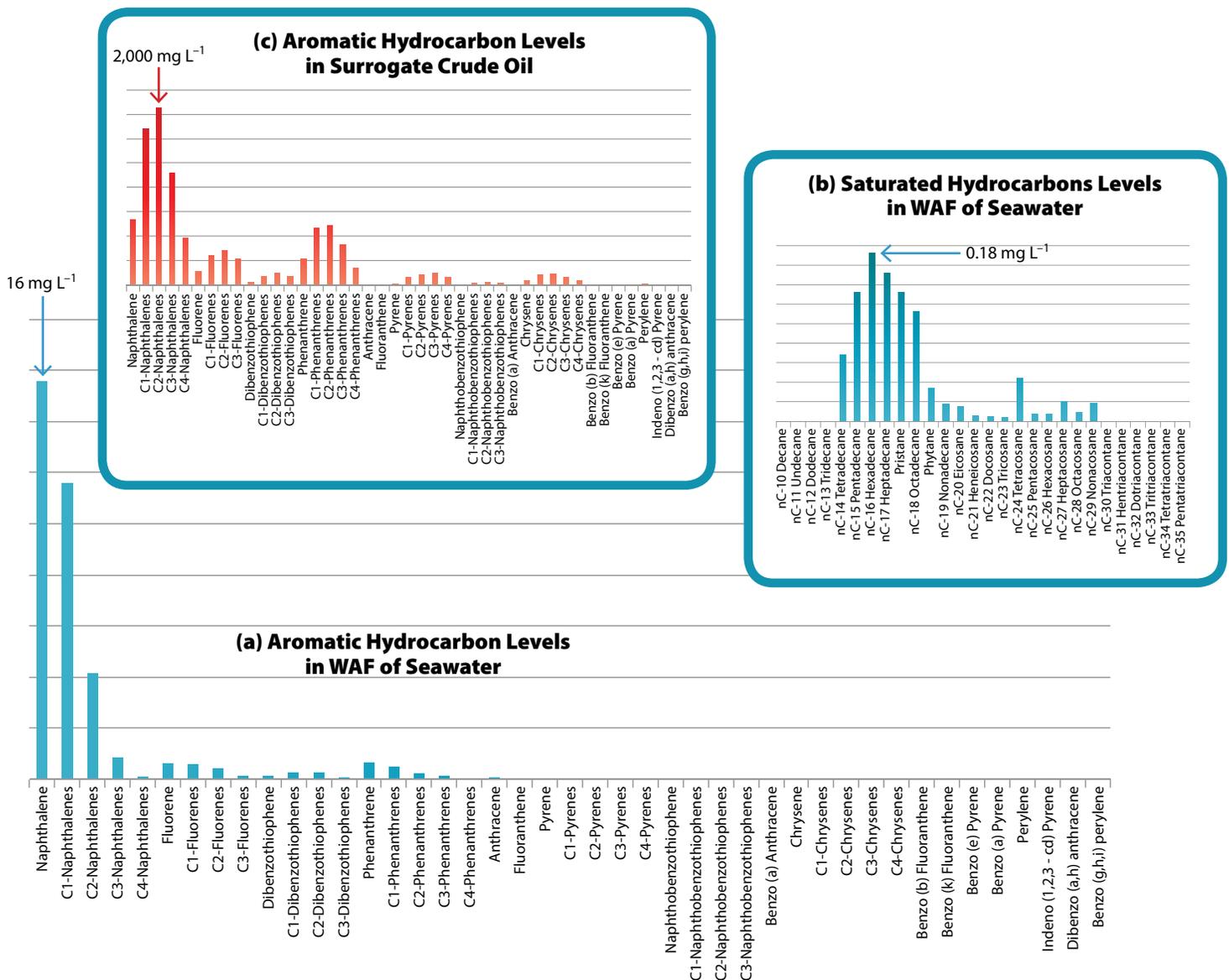
FIGURE 6. (a) Parent and alkyl homolog PAHs and (b) saturated hydrocarbons quantities in the water accommodated fraction (WAF) of the Merlin surrogate crude oil. For comparisons purposes, the (c) insert in red shows the same PAH distribution found in the unweathered Merlin oil.

retain higher molecular weight components. The net effect is that the partition behavior of oil components between seawater and oil is highly favored toward the oil. However, some high molecular weight polar non-hydrocarbons, such as oxygen-containing naphthenic acids, are known to be quite water soluble. Further research on the solubility and toxicology of the highly functionalized, but poorly described hetero-aromatic NSO species found in heavy oils and bitumens, is still needed.

Dissolution of components from oil droplets and slicks is controlled by the oil/water partition behavior of various components and the surface area of the oil-water interface, as well as diffusion and other transport processes that carry oil components from the interior to the exterior of oil slicks and droplets, thus allowing partitioning into the water column. In cases where small oil droplets pass through the water column over extended periods of time, as in deepwater releases, a continuous liquid-liquid extraction process occurs that can remove significant amounts of low molecular weight saturated and aromatic hydrocarbons and other compounds from the spilled oil, which then can disperse into the water column. In the case of the Macondo wellhead discharge, the rapid, turbulent injection of gas-charged oil into a deep, high-pressure water column produced a dynamic, multiphase environment where crude oil and crude oil components were partitioned and dispersed into the deep water (Reddy et al., 2011).

Biodegradation is the process by which microorganisms break down crude oil compounds using various enzymatic reactions, turning them eventually into carbon dioxide, water-soluble compounds, and biomass (Atlas, 1981; Peters et al., 2005; Atlas and Hazen, 2011). Many widely distributed species of bacteria, archaea, and fungi are fully capable of using the reduced carbon crude oil compounds as a food source in the presence of appropriate electron acceptors or even

in methanogenic environments (Prince and Walters, 2007; Atlas et al., 2015). However, the mechanisms by which biodegradation affects the composition of oil in the environment is highly dependent on the weathered oil's physicochemical properties and the amount spilled, as well as other environmental factors such as redox conditions, nutrient availability, temperature, salinity, and wave/mixing energy. All of these factors greatly influence the microbial ecology and the degradation dynamics, rendering biodegradation rates very site-specific (Atlas et al., 2015).

Under ideal aerobic conditions, most crude oil compounds are readily biodegradable (Prince and Walters, 2007) and are generally thought to follow a clear degradation pattern, with most rapid degradation occurring in an apparently sequential manner: n-alkanes $\rightarrow$ branched alkanes $\rightarrow$ low molecular weight aromatics $\rightarrow$ high molecular weight aromatics and cyclic alkanes (Wang and Fingas, 2003). In reality, all compounds degrade synchronously but at quite different rates. The most readily biodegradable compounds are normal, iso-, and isoprenoid alkane hydrocarbons and one- and two-ring PAHs. For larger PAHs and their associated alkyl homologs, the parent compound is typically the first to enzymatically degrade while the alkyl homologs are slower to degrade (i.e., increasing alkylation slows biodegradation; Wang and Fingas, 2003).

Anaerobic degradation of petroleum is one of the dominant processes in petroleum reservoir systems, where it occurs over geological time scales (Head et al., 2003), and in reduced oxygen environments in estuarine water and shallow sediment environments. Degradation can be driven by methanogenesis or via active electron acceptors such as sulfate, nitrate, or transition metal ions, and it is accomplished by consortia of a diverse range of bacteria and some methanogenic archaea (Atlas et al., 2015). As compared to aerobic biodegradation, anaerobic

biodegradation is a much slower process (Atlas, 1981). As a result, crude oil compounds can remain relatively unaltered in reduced sediments and similar environments for long periods of time, and the composition of this buried oil may even appear as relatively "fresh" oil, compared to the same oil exposed to aerobic conditions at the surface.

Photooxidation and biodegradation are the only weathering processes that chemically transform the components of spilled oil to oxidized products. Sunlight can affect spilled oil in several ways; the most obvious takes place on the surface of the oil slick, but it can also cause reactions of dissolved oil components in the water column down to the base of the photic zone, typically 100–200 m. Finally, sunlight also affects the oil and oil residues that are washed and/or deposited on the coastline (e.g., rock jetties, plants). In all these cases, solar radiation will help transform oil components by a variety of different reaction mechanisms.

In ***direct photooxidation***, light-absorbing oil molecules will be excited by solar energy, resulting in a chemical reaction and the formation of new products (Albaigés et al., 2016). Molecules that readily absorb visible light, such as aromatic compounds (e.g., PAHs), are called ***chromophores*** and are usually electron-rich. Direct photooxidation of oil chromophores in the ocean typically proceeds via radical reactions involving oxygen. Resulting molecules can be stable but can also undergo further secondary reactions among themselves or with other molecules.

Indirect photooxidation, on the other hand, is a process that affects oil components that do not absorb light directly but instead absorb it through a pathway that involves other molecules called ***photosensitizers***, which are present in the seawater (e.g., DOM) or in the oil itself. Photosensitizers are chromophores that can be easily excited by sunlight to produce highly reactive oxygenated species (Albaigés et al., 2016).

These reactive species will then initiate a series of radical reactions to indirectly oxidize oil components normally unaffected by direct photolysis, such as the saturated hydrocarbons.

The main change in the general oil residue composition caused by photooxidative weathering is production of new compounds that analytically reside in a separated resin or asphaltene fraction due to the formation of oxygen-containing polar species via radical oxidation. Concomitantly, this causes a decrease of the aromatic hydrocarbon fraction and, in part, the saturated compounds. Such trends were seen in laboratory and field-exposed samples of Macondo well oil, and oils from other spills, such as the Prestige and Ixtoc I spills (Patel et al., 1979; Overton et al., 1980b; Radović et al., 2014).

Photooxidation of aromatic compounds commonly proceeds via direct mechanisms, while the saturated hydrocarbon fraction can be photodegraded through indirect pathway(s) involving sensitizer molecules. Detailed chemical analyses reveal photosensitivity in aromatic systems increases with the number of condensed aromatic rings (e.g., chrysene will be more affected than phenanthrene), and with increasing alkylation. This degradation sequence is quite different from biodegradation, where the more alkylated and/or larger ring aromatic hydrocarbons are more refractory to biodegradation than less alkylated and smaller ring species. Furthermore, the presence of heteroatoms in aromatic molecules affects the degree of photooxidation. For example, inclusion of a sulfur atom in alkylated dibenzothiophenes will reduce the level of photolysis compared to non-NSO PAH compounds, while the presence of nitrogen (e.g., in alkylated carbazoles) will enhance it (Radović et al., 2014). The presence of chromophoric aromatic rings will also cause photosensitivity in molecules that are typically considered to be recalcitrant, and that are therefore commonly used as resistant biomarkers in

oil spill fingerprinting, such as triaromatic steroid hydrocarbons (Figure 4c; Radović et al., 2014). Photosensitive higher-molecular-weight compounds can also cross-link upon photooxidation, increasing in molecular weight and decreasing in solubility (Thominette and Verdu, 1984) and thus likely becoming more resistant to biodegradation.

The environmental fate and effects of the oxygenated products of photooxidation and incomplete biodegradation are still being evaluated. Depending on molecular weight and structure, the addition of oxygen can modify the partition behavior (i.e., octanol/water partition coefficient) of the products (Liu and Kujawinski, 2015). Given the wide carbon number distributions in crude oil, oxygenation could affect the mobility of certain species, affecting their solubility or interactions with other marine organic species (e.g., DOM) and potentially changing their bioavailability and toxicity as compared to the initial crude oil components. Because highly aromatic and already oxygenated oils, such as heavy oils and oil sands bitumen, may pose a challenge in this regard, much further investigation of their environmental behavior is warranted. ⓒ

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