Chapter 3

Spilled Oil Composition and the Natural Carbon Cycle: The True Drivers of Environmental Fate and Effects of Oil Spills

Edward B. Overton, Dana L. Wetzel, Jeffrey K. Wickliffe, and Puspa L. Adhikari

Abstract Rachel Carson's 1962 landmark book, *Silent Spring*, describing the toxic effects of the persistent organic pesticide, DDT, was instrumental in bringing awareness to the notion of environmental pollution (Carson, Silent spring. Houghton Mifflin, Boston, 1962). This work was a catalyst that began the advancement of the global environmental pollution movement and the concern for persistent chemical pollutants (POP). By intentional design, POPs are chemically nonreactive and are resistant to degradation in aerobic environments. It is important to realize that oil pollution and toxicity derived from the polycyclic aromatic hydrocarbon (PAH) components in crude oil are fundamentally different from the chemistry of persistent organic pollutions and its bioaccumulation and magnification that were learned in the 1960s and 1970s. Petroleum hydrocarbons are not stable; they are, in fact, quite reactive in aerobic environments via microbial (Varjani, Bioresour Technol 223:277–286, 2017; Atlas and Hazen, Environ Sci Technol 45:6709–6715, 2011; Salminen et al., Biodegradation 15:29–39, 2004; Widdel and Rabus, Curr Opin Biotechnol 12:259–276, 2001) and photochemical (D'Auria et al., J Hazard Mater

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S. A. Murawski et al. (eds.), *Scenarios and Responses to Future Deep Oil Spills*,
https://doi.org/10.1007/978-3-030-12963-7_3

164:32–38, 2009; Plata et al., Environ Sci Technol 42:2432–2438, 2008; Garrett et al., Environ Sci Technol 32:3719–3723, 1998; Overton EB, Laseter JL, Mascarella SW, Raschke C, Nuiry I, Farrington JW (1980) Photochemical oxidation of IXTOC I oil, pp 341–383. In: Proceedings of symposium on preliminary results from the September 1979 Researcher/Pierce IXTOC I Cruise. Key Biscayne, Florida, June 9–10, 1980, NOAA Office of Marine Pollution Assessment, Boulder, CO) oxidations. To understand the implications of oil spills, we need to recognize that we are dealing with the reduced form of a pollutant that can readily react in most of the environments. The goal of this chapter is to present the dynamics of an oil spill from the molecular level with a description of the carbon cycle, the role of photosynthesis, diagenetic production of oil, its ultimate conversion back to carbon dioxide, and the fundamental carbon cycle processes in environmental chemistry. Only by understanding what happens chemically to spilled oil can we accurately predict and understand the biological consequences of these spills and the harm done by exposures to hydrocarbons from oil.

Keywords Carbon cycle · Diagenesis · Catagenesis · Live oil · Dead oil · Oxidation

3.1 Introduction

Rachel Carson's 1962 landmark book, *Silent Spring*, describing the toxic effects of the persistent organic pesticide, DDT, was instrumental in bringing awareness to the notion of environmental pollution (Carson 1962). This work was a catalyst that began the advancement of the global environmental pollution movement and the concern for persistent chemical pollutants. Listed by the International Stockholm Convention as chemicals targeted for elimination, persistent organic pollutants (POPs) were originally manufactured to be stable compounds (Stockholm Convention on Persistent Organic Pollutants 2005, http://www.pops.int/). By intentional design, POPs are chemically nonreactive (neither oxidizing nor reducing) and are resistant to degradation in an aerobic environment. It is important to realize that oil pollution and toxicity derived from the polycyclic aromatic hydrocarbon (PAH) components in crude oil are fundamentally different from the concepts of pollution that were learned in the 1960s and 1970s. Petroleum hydrocarbons are not stable; they are, in fact, quite reactive and readily react in an aerobic environment, e.g., microbial (Varjani 2017; Atlas and Hazen 2011; Salminen et al. 2004; Widdel and Rabus 2001) and photochemical (D'Auria et al. 2009; Plata et al. 2008; Garrett et al. 1998; Overton et al. 1980) degradation of petroleum hydrocarbons. To understand the implications of oil spills, we need to recognize that we are dealing with the reduced form of a pollutant that can readily react in most of the environments. The goal of this chapter is to present the dynamics of an oil spill from the molecular level with a description of the carbon cycle, the role of photosynthesis, diagenetic production of oil and its ultimate conversion back to carbon dioxide, and the fundamental carbon cycle processes in environmental chemistry. Only by understanding what happens chemically to spilled oil can we accurately predict and understand the biological consequences of these spills and the harm done by exposures to hydrocarbons from oil.

3.2 Carbon Cycle

In order to fully appreciate the consequences of oil spills, we should have a general understanding of the environmental chemistry of oil's major component, carbon. Of all the elements in the periodic table, carbon is the primary element in all animals and living systems as well as dead and decaying matter. Further, carbon, in the form of molecules made up of a backbone carbon and hydrogen structures, together with lesser amounts of other atoms like oxygen, nitrogen, and sulfur, forms the major composition of living organisms and their nonliving residues. Thus, understanding the carbon cycle and the fates and effects of carbon-containing compounds in our environment is a first step toward understanding the chemistry, implications, and mitigative actions associated with oil spills.

3.3 Biologically Stored Energy

Basically, all organic matter on earth was derived from the most chemically stable form of carbon, carbon dioxide (CO_2). Through the process of photosynthesis, energy from sunlight, with the help of chlorophyll catalysts, breaks the carbon-oxygen bonds of CO_2 and the hydrogen-oxygen bonds of water (H_2O) and forms new molecules containing carbon, hydrogen, and oxygen with a general molecular ratio of $\{CH_2O\}$ (as in glucose). This is the approximated molecular ratio of the many organic components of living organic matter. The organic matter on earth is produced through photosynthesis. Life, in turn, requires the use of the energy stored in the carbon-hydrogen bonds of biomass, as food for metabolism and energy for motion. Hydrocarbons are produced with energy from the sun and have some of the sun's energy stored because of hydrocarbons' ability to react with oxygen, thus going back to the stable form of carbon, CO_2, while releasing stored energy. This reaction of hydrocarbon-type compounds with molecular oxygen releases the stored energy, through either metabolism or combustion, and can produce additional biomass. This reaction also clearly demonstrates that hydrocarbon-type compounds are chemically very reactive.

3.4 Environmental Redox Reactions

Chemists refer to reactions that reduce the oxygen content of molecules containing carbon as a "reduction reactions," while reactions that increase the oxygen content of molecules containing carbon as "oxidation reactions." Reduction reactions

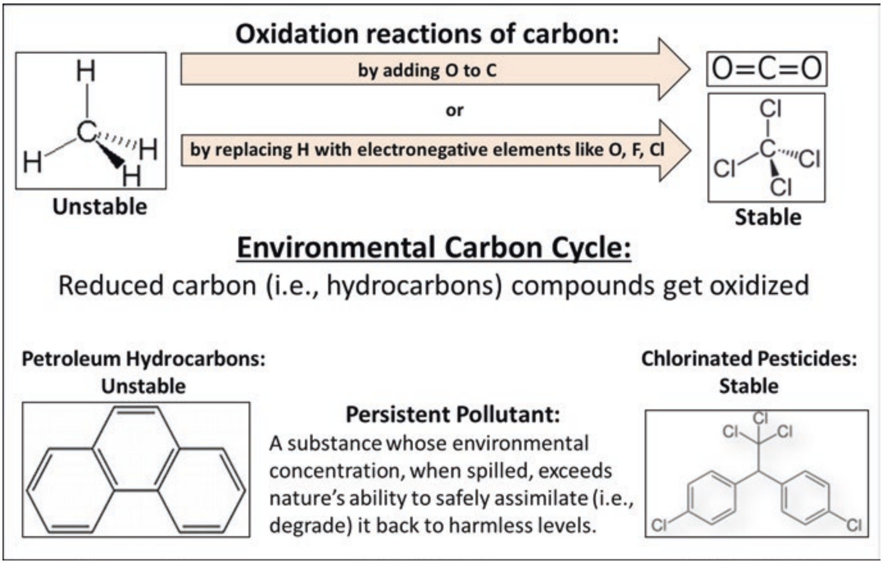


Fig. 3.1 Carbon cycle – oxidation of hydrocarbons to more stable compounds involves replacing hydrogen with more electronegative elements

require energy to cause the reaction to occur, while oxidation reactions release energy. Thus, photosynthesis is a reduction reaction, while metabolism and combustions are oxidation reactions (Fig. 3.1). Photosynthesis requires energy from the sun (or possibly some other source such as geothermal), while oxidations give off energy useful for life and movement. The bottom line is that reduced forms of carbon contain stored energy and are reactive, while the oxidized forms of carbon, like CO_2, are stable to further reactions. It is also important to realize that unstable forms of carbon (like hydrocarbons), while these compounds have the ability to react with oxygen, first require either the input of "activation energy" to start the reaction (such as a spark) or a catalyst to lower this activation energy, thus allowing the oxidation to proceed and evolve energy. Further, there must be an opportunity for oxidation reaction to occur, where the reactive hydrocarbons and oxygen are mixed. For example, if methane and air are mixed, but the methane levels are either below the LEL (lower explosion limit), or above the UEL (upper explosion limit), even with a spark, no oxidation will occur. Similar requirements exist for metabolism or combustion. Burning occurs in the air, and compounds with very low vapor pressures do not produce enough vapors to support combustion without being heated. Metabolism will not occur unless the hydrocarbons are soluble enough to be ingested by some mechanism, thus allowing enzymatically catalyzed oxidations. This is why asphalt roads do not degrade and why asphalt lakes exist around deep-sea oil seeps. Even though these lakes are made of a reduced form of carbon, they are so insoluble that they cannot be readily degraded by natural organisms.

Carbon- and hydrogen-containing compounds can go through a sequence of steps that lessens the stored energy content of these molecules. For example, each addition of an oxygen atom to carbon-containing molecules lowers the stored energy content in that molecule, until all of the carbon has been converted to its most stable form, CO_2. Thus, as hydrogen atoms in hydrocarbon-type molecules are replaced with oxygen, the resulting molecule will give off less energy when either metabolized or combusted (ethanol gasoline produces less miles per gallon than normal gasoline). Chemists have formulated various descriptions to describe oxidation reaction that releases energy. The most common definition is that when an atom like carbon loses an electron, the carbon atom is oxidized. Another way of looking at this is that when a hydrogen atom in a hydrocarbon is replaced by an element like oxygen, which is more electronegative than hydrogen, this reaction is an oxidation. Thus, reducing the number of hydrogen atoms attached to a carbon atom in hydrocarbons or increasing the number of oxygen atoms in hydrocarbon molecules results in an oxidation reaction, and this reaction will release energy. This is the carbon cycle where CO_2 is converted into hydrocarbon-type molecules which have stored energy (Fig. 3.1). As these hydrocarbon-type molecules react with oxygen during metabolism or combustion, the stored energy is released in the conversion of carbon back to its most stable form, CO_2.

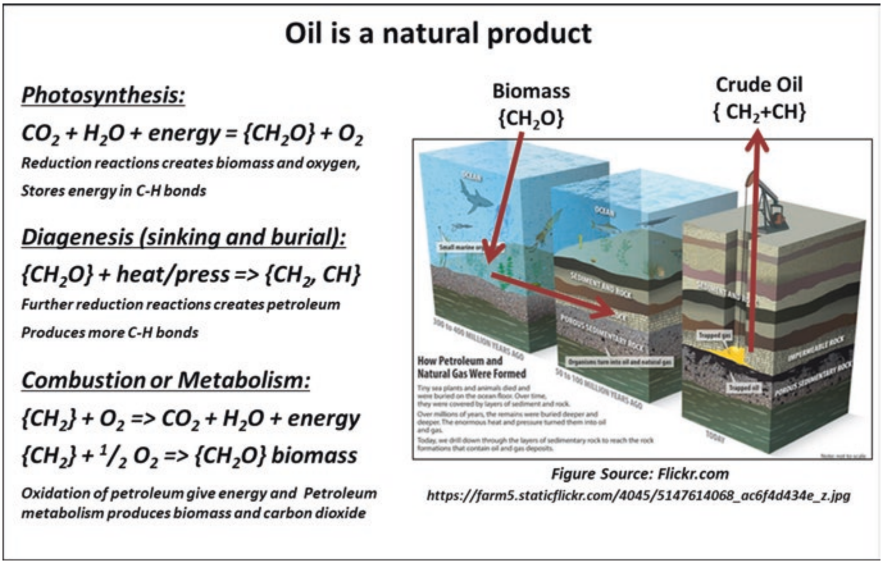
3.5 Understanding the Differences Between Persistent and Reactive Pollutants

To understand what happens when oil is spilled into our environment, we need to recognize the implications of the carbon cycle. All hydrocarbon-type molecules, which make up the complex mixture we call crude oil, are reactive and can be oxidized back to CO_2. The advent of the environmental movement in the 1960s and 1970s with the recognition of human activity putting hazardous chemicals into our environment was the impetus for the formation of the Environmental Protection Agency (EPA) and the passage of environmental laws like the Clean Air Act and the Clean Water Act, the Toxic Substance Control Act, and other important environmental legislations. This movement and these laws recognized that certain manufactured chemicals, such as the environmentally stable chlorinated chemicals (chlorinated pesticides, chlorofluorocarbons (CFCs), PCBs, etc.), were accumulating in our environment, implying that they were not being removed by the natural carbon cycle (Fig. 3.1). The resulting accumulation of these chemically stable compounds caused unanticipated harmful consequences on natural resources and human life. Why was this accumulation happening? In essence, during their manufacturing process, when the hydrogen atoms in the carbon-hydrogen bonds of these new man-made chemicals were replaced with atoms that are more electronegative than hydrogen (like chlorine or fluorine), an oxidation reaction occurred creating compounds that were much more environmentally stable than the hydrocarbons they replaced. For example, when methane (CH_4) is converted to a CFC like Freon (CCl_2F_2), an oxidized form of carbon is produced that is stable to further oxidation, meaning that the CFCs will not naturally react in our tropospheric environment. For many applications, this inertness was a key characteristic. These CFC compounds were not toxic and would not explode and were very useful industrial chemicals in many important applications, from air conditioning to spray-can propellants. However, because these compounds were now an oxidized form of carbon, this means that they would not react, and they would also not degrade in our troposphere. The stability of these molecules, so important for use in a number of industrial applications, led to a buildup of CFC compounds in the tropospheric atmosphere. This buildup in the lower atmosphere ultimately caused severe environmental damage as these CFCs, stable in the troposphere, moved into the upper atmosphere (i.e., the stratosphere) encountering the extremely high solar energy UV radiation. This UV radiation caused CFCs to break apart, and then a chlorine atom reacted with upper-level ozone, removing ozone from the stratosphere. Removal of upper-level stratospheric ozone then allowed this extremely high solar energy UV radiation to penetrate into the zone of our atmosphere where all life occurs and where this high-energy radiation causes unwanted and very damaging reactions in living plants and animals (Solomon 1999). The same scenario, characterized by environmental persistence, initially thought useful in agricultural application, was encountered with chlorinated pesticides, such as the legacy pesticide DDT. Tragically, it was soon found that the buildup of DDT had significant, unanticipated, and harmful environmental effects associated with any number of hormonal reactions in fish and fowl, followed by insidious accumulation in the food chain consumed by humans (Pimentel 2005; Longnecker et al. 1997).

A vital step in assessing potential impacts of any chemicals introduced into our environment, including those from oil spills, is to recognize the difference in molecular reactivity between hydrocarbon (oil) pollution, the reduced form of carbon, and the oxidized form of carbon found in chlorocarbon pollutants. Hydrocarbons are extremely reactive compounds, and with the appropriate catalysts in place (microorganisms and/or tropospheric sunlight) and the opportunity to react, they can react quickly when entering the environment (Ward et al. 2018; Aeppli et al. 2014; Atlas and Hazen 2011; Garrett et al. 1998; Overton et al. 1980). This ability to react is the basis of concern for causing harm during an oil spill, as opposed to the inertness (persistence) of oxidized pollutant impacts found with environmental contaminants like the chlorocarbons. Oxidized environmental contaminants will build up in the environment and can be biomagnified to harmful levels, whereas reduced environmental contaminants readily react, and it is this reaction that can causes environmental harm. Thus, understanding the impacts and consequences of oil spills requires an understanding of the composition of crude oil.

3.6 Origin of Crude Oil

Crude oil is the common name for a very complex chemical mixture of many thousands of hydrocarbon-type compounds (and some small amounts of chelated heavy metals) that is extracted from deep below the earth's surface. This mixture has been



Oil is a natural product

Photosynthesis:

$CO_2 + H_2O + energy = \{CH_2O\} + O_2$

Reduction reactions creates biomass and oxygen,

Stores energy in C-H bonds

Diagenesis (sinking and burial):

$\{CH_2O\} + heat/press \Rightarrow \{CH_2, CH\}$

Further reduction reactions creates petroleum

Produces more C-H bonds

Combustion or Metabolism:

$\{CH_2\} + O_2 \Rightarrow CO_2 + H_2O + energy$

$\{CH_2\} + {}^1/_2\, O_2 \Rightarrow \{CH_2O\}$ biomass

Oxidation of petroleum give energy and Petroleum metabolism produces biomass and carbon dioxide

Figure Source: Flickr.com

https://farm5.staticflickr.com/4045/5147614068_ac6f4d434e_z.jpg

Fig. 3.2 The process of formation of oil in natural environments. (Image from: https://socratic.org/questions/how-does-the-formation-of-coal-differ-from-that-of-natural-gas-and-oil, http://creativecommons.org/licenses/by-nc-sa/4.0/)

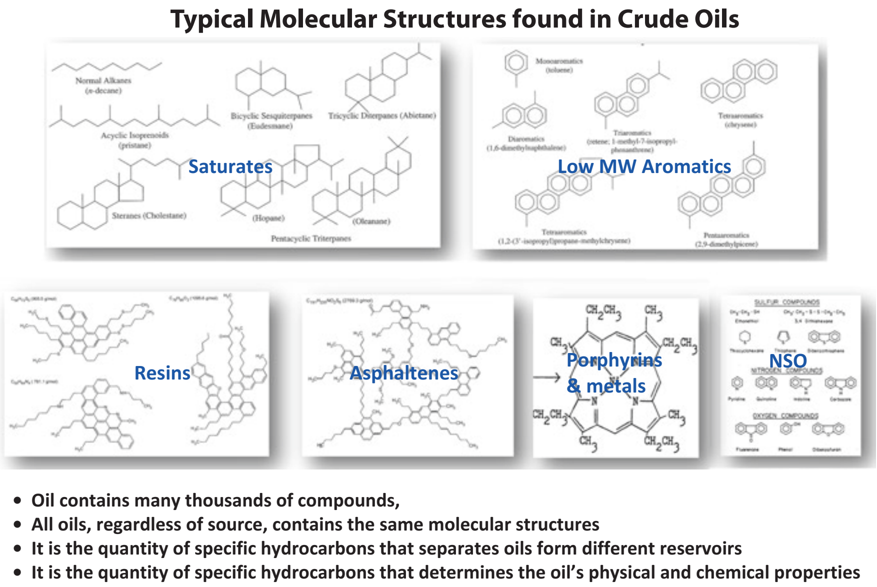
produced from the long-ago deposition and degradation of mostly plant biological material. When organic biomass from plant residues were deposited deep within the earth's crust, the organic material was subjected to high temperatures and pressures (diagenesis), which over time transformed the plant residues into natural petroleum carbon resources (catagenesis) that can be extracted from the earth as crude oil and natural gas. So, oil and natural gas are derived from biological materials whose composition has been modified by diagenesis and catagenesis over many millions of years to produce the complex mixture of hydrocarbon and heteroatom hydrocarbon compounds that make up petroleum and the various fossil fuels (Overton et al. 2016). Typically, all crude oils, regardless of their source, are made up of the same types of molecular hydrocarbons. However, the quantities of specific hydrocarbon molecules in crude oil from a given reservoir will depend upon the reservoir's location, depth, and age. So, the same types of molecular structures are found in all oils, but their respective quantities will vary depending upon the source reservoir.

Figure 3.2 highlights the process leading to the formation of crude oil reservoirs deep beneath the earth's surface. Photosynthesis produces a reduced form of carbon with the general molecular formula $\{CH_2O\}$, which is the approximate carbon/hydrogen/oxygen ratios in all living matter and its residues. A portion of the plant residues from living matter were carried to the ocean floors and deposited deep within the earth's crust. Over the millennia, some of this organic material was further stripped of its remaining oxygen content, a reduction reaction, producing further reduced forms of organic compounds. The very complex chemical mixture, produced through a variety of subsurface processes, results from the conversion of

{CH_2O} biomass material into compounds containing mostly {CH_2} carbon-hydrogen ratios, with lesser amounts of {CH} carbon-hydrogen ratio compounds (i.e., aromatic compounds). Most of these newly reduced carbon compounds do not resemble their initial starting material found in the deposited biomass. However, there are some molecular structures in this complex mixture that are closely associated with their initial molecular compositions, with fused saturated rings similar to those structures found in steroid- and pigment-type biomass compounds. Also, some of the reduced material has incorporated sulfur and nitrogen atoms in their molecular structures. In general, diagenesis/catagenesis processes, acting on buried biomass, produce the complex mixture of carbon-containing molecules in deep earth reservoirs with from one to over a hundred carbon atoms in their molecular structures. The longer these organic-rich reservoirs are subjected to elevated temperatures and pressures, the more this buried material is converted to low molecular weight compounds such as methane and ethane (i.e., natural gas).

3.7 Composition of Crude Oils

Figure 3.3 outlines the various types of molecular structures found in crude oils. It is important to realize that, in addition to the many chemical structures that are in crude oil as reduced carbon, the molecular size or weight of these hydrocarbon compounds establishes the physical properties of the crude oil. Compounds with one to four carbons are gaseous at normal environmental temperatures and are called the natural gas components of the extracted reservoir fluids. Hydrocarbon-type compounds with ≈5–20 carbon atoms are nonviscous, are less dense than water, and exist as liquids at environmental conditions (volatiles and semi-volatiles). Further, hydrocarbon-type compounds with >20 carbons are viscous liquids to waxes and even solids, and these compound's densities are approaching and can exceed the density of water (non-volatiles). Therefore, the physical properties of this complex mixture of hydrocarbon-type compounds which comprise crude oil are dependent upon its relative composition of liquid compounds, viscous liquid compounds, and solid compounds. Light crude oils contain relatively large quantities of low molecular weight compounds that are volatile, nonviscous, less dense than water, and liquid and will solubilize readily when spilled in water. Heavier crude oils contain relatively larger proportions of the viscous liquid/solid hydrocarbon materials and are almost as dense as water (sometimes more dense) (Overton et al. 2016; Martínez-Palou et al. 2011). These heavy crudes tend to stick together or "glob" when spilled, strongly coat plants and animals, don't readily dissolve or evaporate, and are difficult to clean up. Thus, petroleum is made up of hydrocarbon-type compounds with molecular weights from 16 to 2000 or 3000 atomic mass units, and are generally classified as either saturates, aromatics, resins, or asphaltenes (SARA), and can be grouped into the following three hydrocarbon categories: Alaphatic Hydrocarbons, Aromatic Hydrocarbons, and Non-Hydrocarbons (Overton et al. 2016).



Typical Molecular Structures found in Crude Oils

- **Oil contains many thousands of compounds,**
- **All oils, regardless of source, contains the same molecular structures**
- **It is the quantity of specific hydrocarbons that separates oils form different reservoirs**
- **It is the quantity of specific hydrocarbons that determines the oil's physical and chemical properties**

Fig. 3.3 Typical molecular composition and structure of crude oils. (Molecular structures from Overton et al. (2016, Fig. 1))

3.7.1 Aliphatic Hydrocarbons

An aliphatic is a hydrocarbon compound containing carbon and hydrogen joined together in straight chains, branched chains, or nonaromatic rings. While aliphatic hydrocarbons may be saturated (e.g., hexane and other alkanes) or unsaturated (e.g., hexene and other alkenes, as well as alkynes), only saturated aliphatics are produced during crude oil formations. Thus, crude oil contains mostly reduced aliphatic hydrocarbons and lesser amounts of aromatic compounds and (the so-called) non-hydrocarbon compounds (mostly aromatic compounds containing other atoms such as sulfur, nitrogen, or oxygen in addition to carbon and hydrogen) (Overton et al. 2016; Reddy et al. 2012). The saturated compounds can be as small as a one carbon compound (i.e., methane) to much larger molecules that contain many dozens of carbons atoms linked together. However, petroleum is mostly comprised of straight chain saturated hydrocarbon molecules, ranging from the simple one carbon methane compound up to molecules containing 40 or more carbons along with their associated branched and cyclic structures in this molecular size range (16 to almost 600). A small fraction of the saturated cyclic hydrocarbon structures in crude oils are ruminates of their initial molecular structures in the deposited biomass. These compounds are particularly resistant to natural biodegradation, and are known as petroleum biomarkers, useful for oil fingerprinting (Wang et al. 2006; Prince et al. 1994).

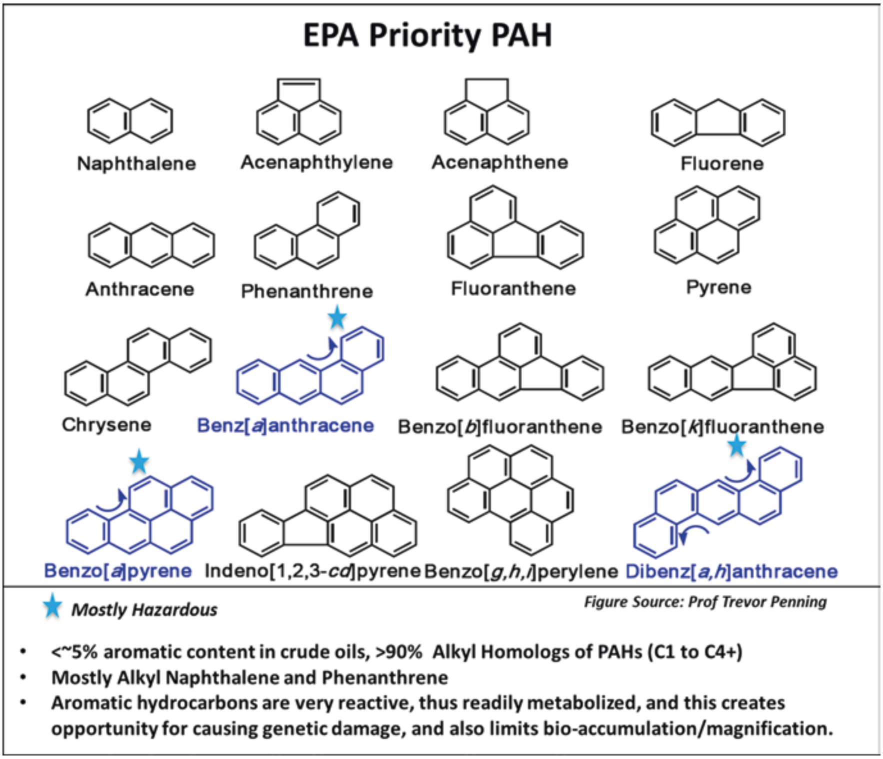


Figure Source: Prof Trevor Penning

- <~5% aromatic content in crude oils, >90% Alkyl Homologs of PAHs (C1 to C4+)
- Mostly Alkyl Naphthalene and Phenanthrene
- Aromatic hydrocarbons are very reactive, thus readily metabolized, and this creates opportunity for causing genetic damage, and also limits bio-accumulation/magnification.

Fig. 3.4 Molecular structures of 16 PAHs listed as priority pollutants by the US EPA

3.7.2 Aromatic Hydrocarbons

One class of reduced hydrocarbon compounds produced from plant biomass by diagenesis/catagenesis processes is called the aromatics. Aromatic compounds are a slightly oxidized form of carbon, relative to the completely reduced saturate alkanes (the loss of some hydrogen atoms in these hydrocarbons is a partial oxidation, not complete oxidation to CO_2) (Fig. 3.4). Most of the aromatic hydrocarbons in oils have multiple rings in their molecular structures and are called polycyclic aromatic hydrocarbons (PAHs) (Overton et al. 2016; Neff 1979). This ring structure provides these aromatic compounds with unique shapes and reactivities when compared to saturated hydrocarbons (Fig. 3.4). First and foremost, these aromatic compounds can be readily metabolized by liver enzymes, and this enzymatic oxidation is the process designed to facilitate elimination of pollutants from the body (excretion). For example, this is why these oxidized metabolites are readily found in bile salts in fish as they are on their way out of the body. However, the enzymatic reactions can also produce unstable oxidized by-products that can react with cellular genetic material causing cell death, mutation, or permanent genetic change, potentially leading to future tolerance or lack thereof to these petroleum compounds (Yan et al.

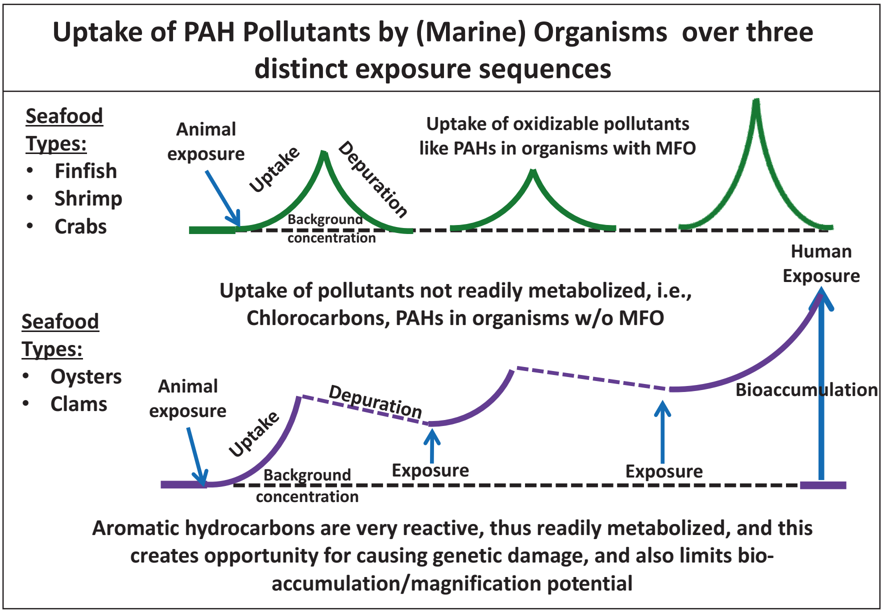


Fig. 3.5 Uptake of PAH pollutants by (marine) organisms over three distinct exposure sequences

2004; Albers 2003; Samanta et al. 2002). Further, these aromatics tend to be more water soluble than their equivalently sized completely saturated hydrocarbon counterparts and thus have readily available routes of exposure out of the oil phase into the water phase. This movement into the aqueous phase provides routes of exposure via ingestion, sorption, and/or inhalation for a number of organisms including humans (Tao et al. 2009; Albers 2003; Sverdrup et al. 2002). Of all of the components found in crude oil, it is because of their reactivity and solubility that aromatics have the greatest potential to cause harm. However, as outlined in Fig. 3.5, this reactivity and solubility also generally means that these aromatic compounds are not persistent pollutants, and they do not tend to bioaccumulate or magnify in living organisms that possess enzymes for xenobiotic metabolism. Thus, any bioaccumulation is followed by rapid depuration. PAH exposure in organisms without MFO metabolism results in slow depuration with corresponding accumulation in the organism's tissues.

The most common PAH compounds in crude oils typically have from two to five or six aromatic rings (Fig. 3.4). In general, PAHs can also have from one to four saturated carbon atoms attached to their basic ring structures (i.e., -CH_3 groups). These are called alkyl groups, and the various isomers resulting from the attachment of these alkyl groups are known as alkyl homologs of the parent PAHs. Some PAH homologs can have enhanced toxic properties when compared to their parent PAH compounds (Turcotte et al. 2011; Wang et al. 2007). In addition to their enzyme-mediated reactivity, one- to three-ringed PAHs and their alkyl homologs are fairly water soluble, especially when compared to the saturated hydrocarbons in crude oil with a similar molecular size (Albers 2003; Neff 2002). It is this solubility that provides a route of exposure for animals and plants that live in or near the water column and the reason that most of the toxic consequences from crude oil exposure are associated with the one- to three-ringed PAH compounds. Larger, higher-numbered ring PAHs are much more potent carcinogens, but these compounds are also very insoluble in water, and this greatly limits their routes of exposure and potential for causing harm in most marine environments (Albers 2003; May et al. 1978; Mackay and Shiu 1977).

PAHs in the marine environment come from primary two sources, leaked and spilled petroleum (petrogenic) and incomplete combustion of the fossil carbon in various fuels and from the burning of terrestrial plants as in forest fires (pyrogenic). Additionally, very small number of PAH compounds can be produced anaerobically. These two primary petrogenic and pyrogenic sources of environmental PAH compounds can be readily identified by observing the composition of alkyl homolog isomers attached to the various PAH parent compounds (Fig. 3.6). Elevated concentrations in the parent PAH compounds compared to the concentrations of their respective alkyl homologs are a sure indication that these PAHs were produced from incomplete combustion (Fig. 3.6) and are called pyrogenic PAHs (Yunker et al. 2002). If the alkyl homolog compositions are higher than the corresponding parent PAH compounds, then they are petrogenic PAHs from sources such as crude oils (Bence et al. 2007; Yunker et al. 2002).

It is important to point out that PAH compounds are ubiquitous in the environment, and essentially all sediment and water samples collected from anywhere in the world contain very low yet detectable levels of PAH compounds. This is because, even though PAHs are a reduced form of carbon, and thus reactive, they can be sequestered and protected from oxidation by adsorption onto particles such as carbon black/soot or in total organic carbon (TOC) content of soils and sediments (Flores-Cervantes et al. 2009; Lima et al. 2005; Lohmann et al. 2005). This sorption/sequestration process possibility limits the reactive carbon's access to oxygen and/or the catalyst that facilitates oxidation (OH), thus preventing reaction and preserving the original PAH molecular structures at very low concentrations in environmental samples.

3.7.3 Non-hydrocarbons

Crude oils also contain compounds, called non-hydrocarbons, with mostly aromatic molecular structures that have atoms such as sulfur and nitrogen (and some oxygen) in addition to their aromatic hydrocarbon structures. Most of these non-hydrocarbon aromatic structures are also comprised of one to four or more alkyl groups attached to the parent ring structure. Crude oils also generally have small quantities of very large molecular structures, with some chelated heavy metals such as iron, nickel, copper, and vanadium. These very large crude oil components, known as resins and asphaltenes, are not very useful as a common source of fuels except for some cargo

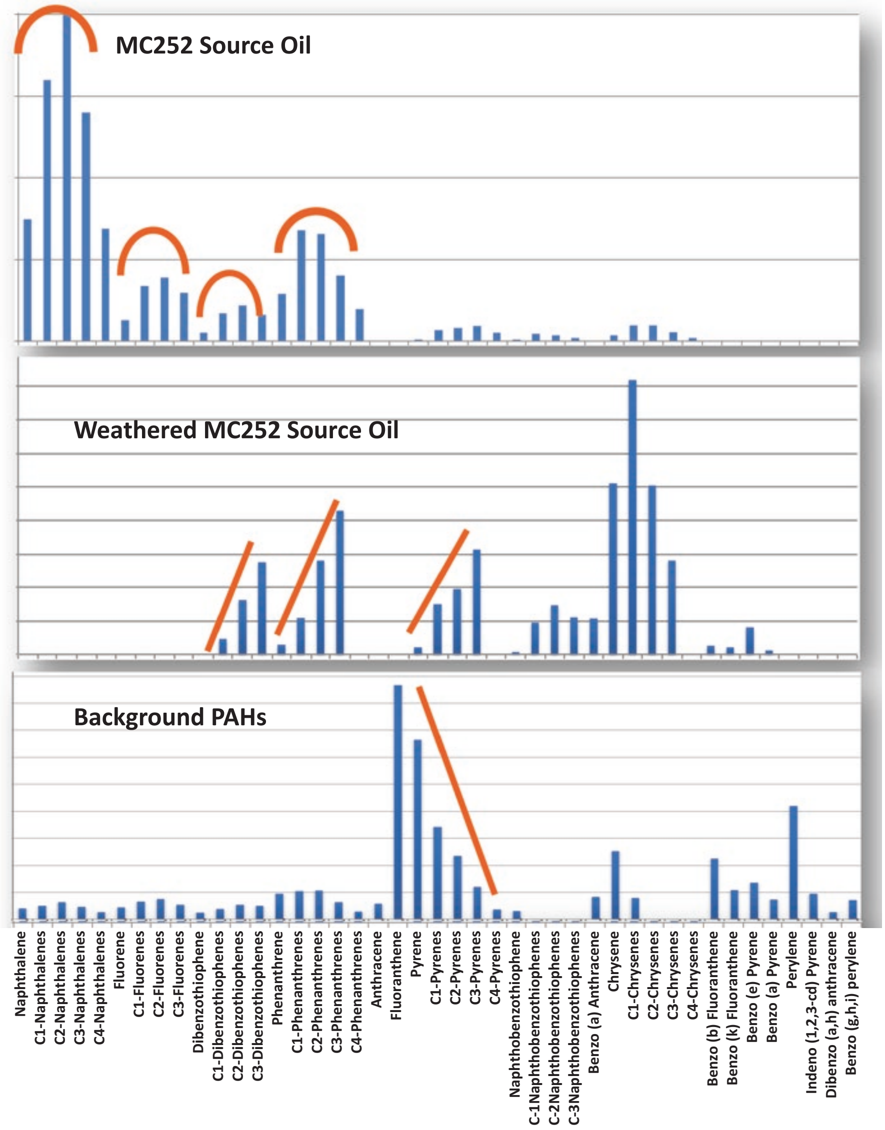


Fig. 3.6 Distribution of PAH compounds in MC252 source oil, weathered MC252 oil residues, and a coastal sediments with no oil residue contamination (no hopane biomarkers) – differentiation between petrogenic and pyrogenic sources of PAHs by alkyl homologs abundance. The red lines represent a typical distribution of parent and their alkylated homologs in petroleum vs pyrogenic sources

ships and fixed location power plant fuels and are practically resistant to microbial degradation. Refinery residues containing these types of very large insoluble compounds are commonly used as roofing tar and road asphalt. Crude oils produced from tar sands do contain mostly these large molecular weight asphaltene and resin-type compounds and can be encountered in spills of dilbit (diluted bitumen)- and synbit (synthetic bitumen)-type fossil fuels and the so-called Group 5-type fuels. Refinery residues containing these types of very large insoluble compounds are commonly used as roofing tar and road asphalt. While asphaltenes and resins are not easily reactive and bioavailable, and practically resistant to microbial degradation (Aeppli et al. 2014), their by-products of long-term photochemical leaching from roofing and paving structures can potentially have environmental effects.

3.7.4 Live Oil Versus Dead Oil

Crude oils that come out of deep reservoirs are generally a mixture of oil and natural gas (and can contain some produced water in depleted reservoirs) and are called "live oil" due to dissolved gas in solution with the oil. When this oil is processed at a surface facility (floating platform or ship) for transport to refineries, the gaseous components are separated from the liquid crude, and the crude is transported as a liquid product that typically has a vapor pressure of less than 10 psi. Once the gas is liberated, this liquid product is now called "dead oil." This vapor pressure is much reduced from the vapor pressure of the source oil. Consequently, oil spills from tanker accidents or pipeline ruptures (dead oil) are much less volatile than oils entering the environment from well blowouts such as the *Deepwater Horizon* (DWH) incident. Most of the experience gained from past oil spills has been from tanker accidents or pipeline ruptures.

High gas content crude oils behave differently when entering the marine environment. As the pressure of gassy oil is rapidly reduced upon entering the aquatic environment, the gas effervesces from the oil causing much of the liquid oil to be broken down into tiny droplets. These droplets have a variety of sizes, some very small, and this affects how the oil moves away from the source. Larger-sized droplets tend to rise to the surface fairly rapidly, while smaller droplets take longer. Extremely small droplets experience significant flow resistance from the water column and, in effect, become neutrally buoyant. These naturally dispersed extremely tiny droplets are carried away from the source, diluted with seawater, and biodegraded with natural microorganisms without ever rising to the surface. Much of the more water-soluble aliphatic and aromatic hydrocarbons in these tiny droplets can be dissolved into the water column and are carried away from the source by deep ocean currents. Again, these are reduced forms of carbon; they are highly reactive and have high water solubility that provides routes of exposure to marine organisms in deep-sea environments (Fig. 3.5). Their reactivity is both a removal mechanism and an opportunity for causing harm from both their toxicity and oxygen depletion potential.

Small droplets that have buoyancy rise to the surface but are continually being extracted as the droplets pass through the water column. This continuous liquid-liquid extraction process removes many of the small aliphatic hydrocarbons in the oil droplets, as well as the more soluble aromatic compounds with one and two aromatic rings. As the composition of the droplets change, so do the droplet's physical properties, including density and ability to form emulsions by mixing with seawater. The net effect is that oil released from blowouts can be significantly modified by its rapid decompression as well as the interactions with and in the water column. Surface oil slicks, produced from oil released in deep water, have undergone significant change from the original composition in their reservoir, and this change impacts the oil's surface behavior and reactivity. Generally, surface oil from deep releases is a mixture of oil and water called emulsions, which are generally thick and fairly viscous compared to the released oil. Many of the low molecular weight, solvent-type molecules in the released oil will have been extracted by water column contact, thus changing the floating oil's viscosity, stickiness, and ability to be removed by mechanical skimming, burning, or dispersing.

3.8 Oil Weathering

It is important to emphasize that spilled oil can cause environmental damage through several primary mechanisms. These include (a) the toxic and irritative effect caused when aromatic and possibly aliphatic components are ingested, inhaled, or adsorbed, (b) the smothering or coating effect from oil, (c) the oxygen-depleting effect as oil components are degraded by natural bacteria, and (d) carbon enrichment into the normal marine food web from bacterial degradation of spilled oil. The weathering process changes all of the fundamental implications associated with these mechanisms for causing environmental damage (toxicity, routes of exposure, bioavailability, carbon enrichment) and, in general, lessens the acute opportunity for environmental damage from oil hydrocarbons retained in the floating or stranded oil residues.

Weathering includes physical processes such as evaporation, dissolution, emulsification, sedimentation, as well as chemical oxidations caused by microbe metabolism and absorption of energy from the sun (photooxidation) (Meyer et al. 2018; Overton et al. 2016; Tarr et al. 2016; Aeppli et al. 2014; Atlas and Hazen 2011). Weathering, by changing the composition of the original spilled oil, changes the oil's physical and toxic properties. Fresh oil is more volatile, contains more water-soluble components, floats, is not very viscous, and easily spreads out from the source. All of these characteristics mean that fresh oil is the most environmentally dangerous type of spilled oil. Fresh oil hydrocarbons are readily available for ingestion, adsorption, and inhalation as well as for coating and oxidizing. As oil weathers, it first loses volatile components, which are the most water soluble; the oil then becomes more viscous and more likely to glob together in stringers as opposed to spreading out in a thin film (Tarr et al. 2016; Aeppli et al. 2014). Over time, these weathering changes continue to alter the composition of the oil until it has been severely degraded in the environment, leaving behind only small quantities of insoluble, solid-like residues known as tarballs or surface residue mats. Even though weathered oil residues contain higher concentrations of the larger more toxic four to six ringed PAHs (Fig. 3.6), the routes of exposure for these more hazardous compounds is severely limited, and thus their capability for causing harm is limited (Tarr et al. 2016). Typically, during the weathering process, much of the oil (especially heavier oil) mixes with water and emulsifies, forming a viscous mixture that is fairly resistant to rapid weathering changes. Consequently, emulsification greatly slows down the weathering processes (Tarr et al. 2016; Belore et al. 2011; Garo et al. 2004). Further, emulsified oil is also somewhat more difficult to remove by skimming, dispersing, or burning. Fortunately, emulsified oil is generally less environmentally dangerous, becoming a mostly nuisance material that causes damage through covering or smothering as opposed to damage through toxic interactions. However, if emulsified oil is ingested through, for example, the preening of feathers, it can have significant toxic effects on internal organs. Heavily emulsified oil is slower to degrade and will stay in the environment longer than non-emulsified oil (Tarr et al. 2016; Belore et al. 2011).

It is important to point out that oil spills, particularly spills of live oil from deep-sea releases such as the DWH incident, introduce extremely large quantities of highly reactive saturate and aromatic hydrocarbons into the oceans in both an oil phase and a dissolved phase (Reddy et al. 2012; Diercks et al. 2010). In the dissolved aqueous phase, hydrocarbon molecules are readily available for uptake and metabolism, can cause irritations, and can be photooxidized in the upper water column. Dissolved hydrocarbons are readily available for reaction which, coupled with the exposure to a biocatalyst and a source of oxygen, provides an opportunity for causing harm not only through a variety of toxic and irritation reactions in animals but by removal of dissolved oxygen from the water column. Hydrocarbons in the oil phase, on the other hand, are less immediately available for reaction, but the oil phase can cause harm through coating and smothering, in addition to being ingested and adsorbed by cleaning processes such as preening.

3.8.1 Floating or Subsurface Oil

Fresh oil has a density that is less than water, so fresh oil floats or has a tendency to rise to the surface. As oil weathers, its density increases and can approach the density of water, making it less buoyant. In rare occasions, some heavy oils (like dilbit, synbits, Group 5 oils), when weathered, become more dense than water and sink. Some emulsified weathered oil, with near-neutral buoyancy, can pick up sediments and near-shore detritus and sink to the bottom in intertidal areas. Sunken oil poses potential exposure risk to intertidal organisms and bivalves such as oysters and clams. Some sunken oil residues can be buried in intertidal areas off sandy beaches. These tar-mats degrade very, very slowly, and normal coastal erosion processes can dislodge these buried tar-mats during storm and weather fronts. Typically, this dislodged tar-mat material breaks apart and will wash up on beaches following storm events. This process of dislodging buried oil can last for several years following an oil spill and cause episodic recontamination of recreational beaches with tarballs.

Offshore floating oil can be dispersed by the action of winds and waves, as well as the application of chemical dispersants. Dispersion is the process of breaking oil residues into very tiny droplets and allowing these tiny droplets to move away from the oil slick (i.e., get dispersed) by currents and possibly by wind actions. These tiny droplets, because of their small size, act as though they were neutrally buoyant when mixed into the upper water column. Currents then move the droplets away from their source, and this movement causes a spreading out of the droplets in three dimensions of the upper water column. This is dispersion, and it results in diluting the quantity of oil residue floating in the oil slick down into the water column, allowing it to be further diluted by distributing it within the water column. However, the low molecular weight hydrocarbon compounds in the dispersed oil droplets can now be more readily dissolved into the water column, and this represents an enhanced route of exposure for animals residing in these regions of the upper water column near dispersed oil. This same analogy can be found with regard to subsurface injection of dispersants directly into a damaged and leaking seafloor oil well. Dispersion causes dilution of the oil phase but also enhances dissolution from the oil phase into the water column. Hydrocarbons in the tiny droplet oil phase, as well as in the dissolved aqueous phase, are available for biodegradation (metabolic oxidation) and any number of harmful and irritating interactions with living marine resources. The rationale for using oil dispersion is that diluted oil is less potentially damaging than concentrated oil, so dispersion should always be carried out in marine environments that allow ample dilution (i.e., in deep water and with strong currents).

3.8.2 Oil Impacts in Coastal Marshes

Oil floating on the surface can cause damage to organisms that live near or on the surface. Offshore, this damage is confined to near-surface environments unless the oil is dispersed into the water column with chemicals. As surface oil interacts with shoreline marshy coastal environments, it can cause damage through smothering and coating, or by the dissolving of toxic oil components in shallow water environments, and in and around the root structures of coastal plants (Meyer et al. 2018; Overton et al. 2016). Smothering can cause significant damage to coastal grasses and habitat dwellers, as does the dissolution of the toxic components into shallow water environments. Weathered oil has a significantly less soluble toxic component composition, and thus the potential damage comes mainly from its smothering/coating effect and ability to use up available dissolved oxygen. Some of the oxidized components from the microbial and photo-induced weathering of oil in these shallow coastal environments that are not well mixed can also cause harm.

3.8.3 Subsurface Oil at Released Depth

The oil from the DWH well blowout entered the environment 1500 meters below the Gulf's surface (Reddy et al. 2012; Diercks et al. 2010). As such, it contained very high quantities of natural gas which caused natural dispersion of much of the oil in the deep Gulf. The oil exiting the wellhead was also mixed for a while with chemical dispersant causing further dispersion at depth. The net effect of both natural and chemical dispersion is that much of the oil was broken into very tiny droplets with diameters less than 100 microns. Droplets of this size or smaller face significant flow resistance from the water column in their effort to rise to the surface, and essentially are trapped in the deep Gulf environment until degraded by natural bacteria. As this dispersed at-depth oil moves away from the wellhead, it becomes diluted with Gulf water; some components readily dissolve into the water column and were available for fairly rapid biodegradation (Baelum et al. 2012). The residual is dispersed and degraded by natural bacteria in the depths of the Gulf. Some heavily weathered oil residues were retained in deep-water sediments and deposited biomass from oil biodegradation. Because the concentration of the dispersed oil is well below the concentration of oxygen in the deep Gulf, no significant oxygen depletion has been observed from the degradation of the oil in the deep Gulf waters.

3.8.4 Subsurface Oil's Slow Transit to the Surface

Oil droplets larger than 100 microns in diameter will have a tendency to rise to the surface. Larger drop will rise faster than smaller drops. In this progression to the surface, small drops are extracted of their more water-soluble components by movement through the water column, and this caused some of the oil reaching the surface to be already weathered by dissolution and microbial degradation. Remember that water solubility is closely associated with volatility, particularly with the aromatic components in oil, so continuous water extraction on the 1500 m journey to the surface significantly alter the composition of oil in these small droplets. The net effect of this process of rising to the surface meant that surface oil was a mixture of weathered and fresh oil that took on a variety of appearances. Further, since this spill continued for 87 days, in essence a new spill occurred each of these days, oil at the surface was always a complex mixture of relatively fresh oil, oil weathered by movement to the surface, and oil weathered by processes at the surface (mostly evaporation and photooxidation). Further, since the spill occurred far offshore 50–100 miles from coastal impacts, and without strong Gulf currents or wind conditions moving it ashore, significant weathering of the oil occurred before coastal landfall. Most coastal oiling was from weathered oil, which posed primarily a smothering/coating hazard and, to a lesser extent, an oxygen-depriving hazard in near-coastal environments and a toxic hazard from dissolution and oxidation of its aromatic components. Oil residues in coastal marshes are subjected to continuous washing by wave action with muddy water, and the mineral organic-rich suspended sediments in these Mississippi River-laden waters can and do interact with coastal oil residues to form oil mineral aggregates (OMA) (Daly et al. 2016; Passow 2016). Organic carbon particles in soil and sediments (TOC or POC) including combustion-derived soot/BC-type particles in these riverine muds as well as atmospheric particles preferentially sorb to hydrophobic hydrocarbons in oil residues (Adhikari et al. 2015; Flores-Cervantes et al. 2009). This interaction with suspended minerals represents an important mechanism for the gradual removal from, as well as for redistribution of, oil residues and soluble hydrocarbons in coastal marsh environments not initially impacted by the spill. It also provides a re-partitioning and low-level route of exposure to soluble hydrocarbons and insoluble oil residues for filter feeding coastal organisms such as oysters and clams.

3.9 What About the Next Big Spill?

3.9.1 Critical Review of DWH Incident

First and foremost, in preparation for the next big oil spill, scientists should now re-examine the basic assumptions associated with our understanding of not only the DWH incident but all we have learned regarding spill oil. These assumptions should be evaluated and then re-evaluated by looking back at what actually happens during the spill, not by what was thought to be happening during the spill. Massive amounts of data and results were generated by both government and BP and Natural Resource Damage Assessment (NRDA) efforts, as well as through the research funded by GoMRI and others. These results should be evaluated in terms of their scientifically verified, and not litigated, environmental impacts. For example, did the assumption that no petrogenic PAHs from this spill bioaccumulated into the marine web hold true? It is one thing for carbon from the spill to be incorporated into the food web, but quite another to say that specific and toxic PAH compounds were bioaccumulated at levels dangerous for human and environmental consumption. What do the data show? Another important investigation might be evaluating whether laboratory-observed toxic impacts were detected, and if so, did they persist in the GOM environment? Were species alterations and subsequent changes in distributions observed as a result of the spill? Is there evidence of modification of environmental genetics as the result of the spill? Did dispersing of the oil help or hurt recovery? We assumed that natural bacteria were available to degrade spilled oil, but did this recovery system get modified and permanently changed by the massive amount of this spill?

We certainly learned a lot about how natural microbial communities responded to oiling, is there anything we can do next time to enhance these useful processes and not do those that may have inhibited mother nature's natural processes (such as dispersing)? What did we learn about deep-water releases of oil and natural gas? It's interesting to find new marine species in the deep, but what did we learn about oil getting degraded in dark and cold environments and its mechanism for deposition and causing harm? Were there documented incidences of human health damages from oil exposures? The bottom line is that it's important and essential during a massive spill to look for and detect damages, but it's also equally important to observe and substantiate recovery and to understand what worked and what didn't. The litigative NRDA process is designed as a preventative measure, to make sure that the financial pain of an oil spill is sufficient incentive to do everything reasonable for prevention. Human response efforts should work in harmony with the environment's natural adaptive and recovery processes. Science should be used for pre-spill monitoring, to support future spill contingency and planning efforts and to observe, verify, and where possible improve natural processes of recovery. The next big spill will occur, and it's now time to fully understand what happened during and after the DWH event.

3.9.2 Importance of Multidisciplinary Studies and Their Implications

A number of the following broad scientific disciplines are needed to not only help understand the environmental and human health consequences of an oil spill but to contribute to the human interventions used for mitigating or minimizing these consequences. These disciplines include nearly all subdisciplines of chemistry (analytical, physical, organic, inorganic, biochemistry); physics; multiple subdisciplines of biology and microbiology; oceanography; toxicology, human health, epidemiology, and geology (land loss issues in marshes); marine fisheries; environmental and circulation modeling; sociology and psychology; and economics. The implications of applying all of these broad disciplines toward understanding oil spill impacts and its consequences are profound. We quickly get into an issue of understanding of the big picture versus getting absorbed by understanding intricate disciplinary scientific details. Further, most disciplinary science has its own terminology, and frequently words have different means in different disciplines. A tiny oil droplet can be a particle to modelers, but there are important differences between droplets and particles in oceanography. Commonly used disciplinary terminology can cause misunderstanding in interpretation of results and confusion concerning impacts. The bottom line is multidisciplinary investigations are important, but we must keep in focus the challenges associated with integrating other science disciplines that are outside of our respective areas of competence.

3.9.3 Multidisciplinary Scientific Publications

Oil spill science must be multidisciplinary but must also be subjected to the same rigors of peer review as is found with conventional scientific discovery. This implies discipline in publications with results presented to support hard scientifically established understandings of the spill. Oil spill science should allow and encourage thinking and study outside of the box, but we should never forget the foundations of understanding that were used to build the box. For example, many papers describing scientific studies or findings from the DWH spill have upward of 10 or more authors representing many different scientific disciplines. The normal peer review process, the foundation of our method of ensuring the integrity and validity of scientific results in the archival literature, usually involves three anonymous, discipline-specific scientific reviews of the submitted paper. With several broad scientific disciplines present in many multi-author published papers, one has to question the veracity of these three peer review processes. While it is incredibly important toward understanding oil spills for scientists to pull together the big picture results, perhaps these multidisciplinary publications need a different type of peer review process. We should try and present our results to disciplinary-focused journals. This means that not all aspects may have been peered reviewed in a given published article. The peer review process is way too sacred to not be fully used during review of oil spill science publications and its presentation to the wider scientific community. Perhaps broad multidisciplinary scientific papers should get reviewed by multidisciplinary panels prior to publication.

3.9.4 Explaining What Happened to Broad Audiences

Oil spills are events that generate intense interest not just from the scientific disciplines dealing with and studying marine pollution but communities that live in or make their living from and around coastal environments. Understanding and disseminating the implications associated with oil spills are not just a scientific imperative, it is our responsibility to be able to explain these findings to communities that are most affected by these devastating events. Clearly, hyped hyperbole associated with the anger over massive oil spills can cause a great deal of anxiety with communities affected by oil spills. Comments given publically must be made responsibly and must take into consideration the impacted audience. These are real people and this is their world. There is a very big difference between postulating a possible outcome and a probable outcome, and these differences should always be elucidated in both public presentations and scientific publication. Exaggerated improbable outcomes cause unnecessary and unneeded public apprehension and can cause further complications for the communities dealing with such traumatic events. Scientists studying oil spills and their impacts are regarded for their knowledge and wisdom and should stick to credible and proven/known facts when discussing their findings with society.

3.10 Conclusions

Our natural world is a wonderful and very complex system involving living and nonliving resources. Into this serene environment, humans have added many potentially useful (to them) activities, but they have also introduced chemicals that add stress to the natural environment. Oil spills are one of these stresses, and this stress affects both our natural environment and humans living in this environment. Society has recognized the buildup of persistent man-made chemicals in our environment as harmful additions, and oil spills are commonly thought of as contributing additional burdens of persistent pollutants. However, as much as we decry the tragedy of an oil spill, the dangerous compounds in oils do react quickly, are readily oxidized and degrade, and do not persist. Thus, understanding the potential effects of oil spills on our natural environment and its inhabitants begins with a need for a fundamental understanding of the implications associated with molecular formational and reactive processes of carbon in our environment.

This understanding requires detailed knowledge from many scientific disciplines being applied to these infrequent but high-profile events with impacts ranging from deep ocean to the dinner table. With these diverse multidisciplinary types of research investigation comes incredible opportunity to factually document the comprehensive impacts of oil spill. At the same time, the broad aspects of these studies present challenges of working outside of our individual areas of expertise. Good science is only as good as its weakest link in the chain of discovery. It is important for all oil spill-related scientific research to be conducted within the objective framework, recognizing the constraints imposed by studies covering diverse scientific areas of expertise. Imagine and investigate possible outcomes, but be sure to understand and explain what's probable.

Acknowledgments This research was made possible by a grant from the Gulf of Mexico Research Initiative through its consortia C-IMAGE and CWC.

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