Atmospheric Distributions of Polycyclic Aromatic Hydrocarbons (PAHs) in Coastal Northern Gulf of Mexico, USA, Associated with the *Deepwater Horizon* Oil Spill

by

Kimberly Scalise

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Director of Thesis: Siddhartha Mitra, Ph.D.

Major Department: Geological Sciences

The *Deepwater Horizon (DWH)* oil spill occurred April 20, 2010 to July 15, 2010, releasing a surface slick of crude oil extending to ~176,000 km^2 in the Gulf of Mexico (GOM). Crude oil is comprised of thousands of organic compounds, many of which are toxic or carcinogenic. There is concern that some petroleum-derived toxic and carcinogenic hydrocarbons from the *DWH* spill may have volatilized and transported landward to the Gulf Coast States. It is important to determine the fate of these oil-derived compounds since their landward transport and inhalation may compromise human health.

Polycyclic aromatic hydrocarbons (PAHs) are one suite of organic compounds that have been used to fingerprint oil to identify its source. In this study, the relative abundance of 34 PAHs derived from the *DWH* spill were compared to those found in oil from natural seeps in the northern GOM and from various sources in the Santa Barbara Channel, CA. The PAH distributions of the *DWH* oil were also compared to PAH distributions in air and water samples collected from several coastal sites in the Gulf Coast States sampled in July, 2010 and July, 2011. Additionally, the distributions of PAHs in air and water samples were compared before

and after passage of *Tropical Storm* (*TS*) *Bonnie* (2010) that traveled across the GOM in late July, 2010. Lastly, particulate organic carbon and black carbon (a combustion byproduct) were extracted from these air samples to provide more information on the sources of air masses in the region.

The results from this study suggest that the *DWH* riser oil contained ~3,600 $\mu g\ g^{-1}$ of total PAHs and an average ~500 $\mu g\ g^{-1}$ of PAHs in the surface slick. Ambient level of PAHs in air and water collected from coastal areas of the GOM were similar between 2010 and 2011, despite the presence of the oil slick from the *DWH* spill. However, our results indicate that the marine-to-land transport vector was facilitated by passage of *TS Bonnie* across the *DWH* oil slick in July, 2010. For example, the total atmospheric PAH loading to window film (a passive air sampler) increased by a factor-of-fifty after the passage of the storm, and the *TS Bonnie* rainwater contained dissolved organic carbon with a ^{14}C age of ~8,000 y BP. Together, these results suggest that marine-to-land atmospheric loading of organic carbon and contaminants may be important during tropical storms and hurricanes.

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Kimberly Scalise

APPROVED BY:

DIRECTOR OF THESIS:______________________________
(Siddhartha Mitra, Ph.D.)

COMMITTEE MEMBER: ______________________________
(Richard L. Miller, Ph.D.)

COMMITTEE MEMBER: ______________________________
(Terri L. Woods, Ph.D.)

COMMITTEE MEMBER: ______________________________
(Tom Rickenbach, Ph.D.)

CHAIR OF THE DEPARTMENT
OF GEOLOGICAL SCIENCES: ______________________________
(Stephen J. Culver, Ph.D.)

DEAN OF THE
GRADUATE SCHOOL: ______________________________
(Paul J. Gemperline, Ph.D.)

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OVERALL INTRODUCTION

Oil is a dominant energy fuel worldwide, with the greatest consumption in highly industrialized countries. In 2010, more than 19 million barrels of oil were consumed per day in the United States (Central Intelligence Agency World Factbook). In 2011, 9.02 million barrels of crude oil were produced per day in the U.S., less than half of the average daily consumption (Central Intelligence Agency World Factbook). The majority of the oil consumed within the U.S. is imported from all over the world, predominantly from the Atlantic Basin and the Persian Gulf (National Research Council, 2003). Oil is primarily transported by sea and usually handled at coastal petroleum facilities, providing a huge risk for operational and accidental discharge of oil from vessels and platforms into the marine and coastal environment. The occurrence of spills has diminished over the past several decades and may yet continue to decrease in frequency as technology improves and production is more strictly regulated (National Research Council, 2003). However, the expected growth in worldwide oil production and transport still poses a risk of accidental input of petroleum products to the oceans (National Research Council, 2003).

Recently, the *Deepwater Horizon* (*DWH*), an offshore drilling rig located in the northern Gulf of Mexico (nGOM), was the site of the largest offshore oil spill in United States history. On April 20, 2010, while drilling an exploratory well in the Mississippi Canyon lease block 252, a blowout occurred from the marine riser, causing a series of explosions. Over 4.9 million barrels (1 barrel = 42 gallons) of a light sweet crude oil leaked from the Macondo-1 wellhead over the course of 87 days until July 15 (Crone and Tolstoy, 2010; Operational Science Advisory Team, 2010). The scope of this disaster is on a scale greater than other marine oil releases around North America. For example, the Ixtoc I blowout of 1979 polluted the southern GOM with more than 3.2 million barrels of crude oil over a 10-month period (Oil Spill Intelligence Report, 1980).

At the time it was the largest unintentional oil spill in history (Oil Spill Intelligence Report, 1980). The amount of oil released during the Ixtoc I blowout was exceeded by the *DWH* spill in less than three months' time.

The crude oil leaking from the Macondo-1 wellhead was introduced at a water depth approximately 1.5 km below the sea surface (Crone and Tolstoy, 2010). The water depth of the initial release and the large volume of oil discharged, distinguish the *DWH* spill from other marine oil spills, which commonly occur at the ocean surface. Furthermore, natural weathering processes and the application of dispersants led to considerable quantities of the crude oil to be dissolved and dispersed in the nGOM subsurface environment (Operational Science Advisory Team, 2010). Of the total amount of oil released, the estimate for the total maximum oil-slick footprint in surface waters of the GOM was 176,000 km^2 (Cleveland et al., 2010).

The scientific approach to sampling and analysis of the 1989 *Exxon Valdez* oil spill in Prince William Sound, Alaska, set a precedent for handling the *DWH* spill, in that we have a better understanding of how petroleum products weather and infiltrate the marine environment. The *Exxon Valdez* spill released 10.8 million gallons (~257,000 barrels) of heavy crude oil to the sea surface over the course of eight weeks (Wolfe et al., 1994). Although the volume from the *Exxon Valdez* spill was lower than the *DWH* spill, studies conducted decades after the spill have found spill-related petroleum hydrocarbons in coastal sediments, and detectable (but not toxic) levels of hydrocarbons in marine animals (Short et al., 1999; Harwell et al., 2012). In another case, sixteen months after the *Amoco Cadiz* oil spill off the coast of France, weathered oil was detectable within the littoral zone of the shore (Atlas et al., 1981). Studies such as these that have examined the transport and fate of oil pollutants released during spills, indicate that pollutants released from the *DWH* spill may have a significant long-term impact due not only to the unprecedented amount of crude oil released, but also to the subsurface nature of the spill.

The continuous release of oil, both natural and anthropogenic, accounts for the majority of input of petroleum hydrocarbons to the marine environment (National Research Council, 2003). Crude oil is a fossil fuel naturally formed through geological or geochemical processes acting upon decaying animal, plant, or mineral remains most often in ancient marine sediment beds (National Research Council, 2003). Crude oil is comprised of approximately 84-87% carbon and 12-14% hydrogen, 1-5% sulfur, and less than 1% each of other elements including oxygen, nitrogen, and various metals and salts (Simanzhenkov and Idem, 2003). Hydrocarbons are the primary component of crude oil, structured as straight chains, branched chains, and fused rings (e.g. aromatic). Polycyclic aromatic hydrocarbons (PAHs) (Figure I.1) are arranged in two or more fused aromatic rings formed at elevated temperatures either by diagenesis of sedimentary organic matter or incomplete combustion of organic material (plant and animal substances) (Blumer and Youngblood, 1975).

Oil begins weathering immediately upon release into the environment by abiotic and biological processes that break down oil into its hydrocarbon components. Due to the natural occurrence of petroleum hydrocarbons in marine environments, a diverse set of microorganisms have evolved to utilize hydrocarbons as a source of carbon and energy (Atlas and Hazen, 2011). Light crude oil, such as that released from the *DWH* spill, contains a higher proportion of simple lower molecular weight hydrocarbons that are more biodegradable than heavier crude oil (Atlas and Hazen, 2011). The rate of biodegradation decreases with the number of alkyl groups (Prince, 2003). Biodegradation may therefore play a significant role in the weathering of a light crude oil as the non-alkylated PAHs are much more susceptible to breakdown by microorganisms (Atlas, 1995; Prince, 2003).

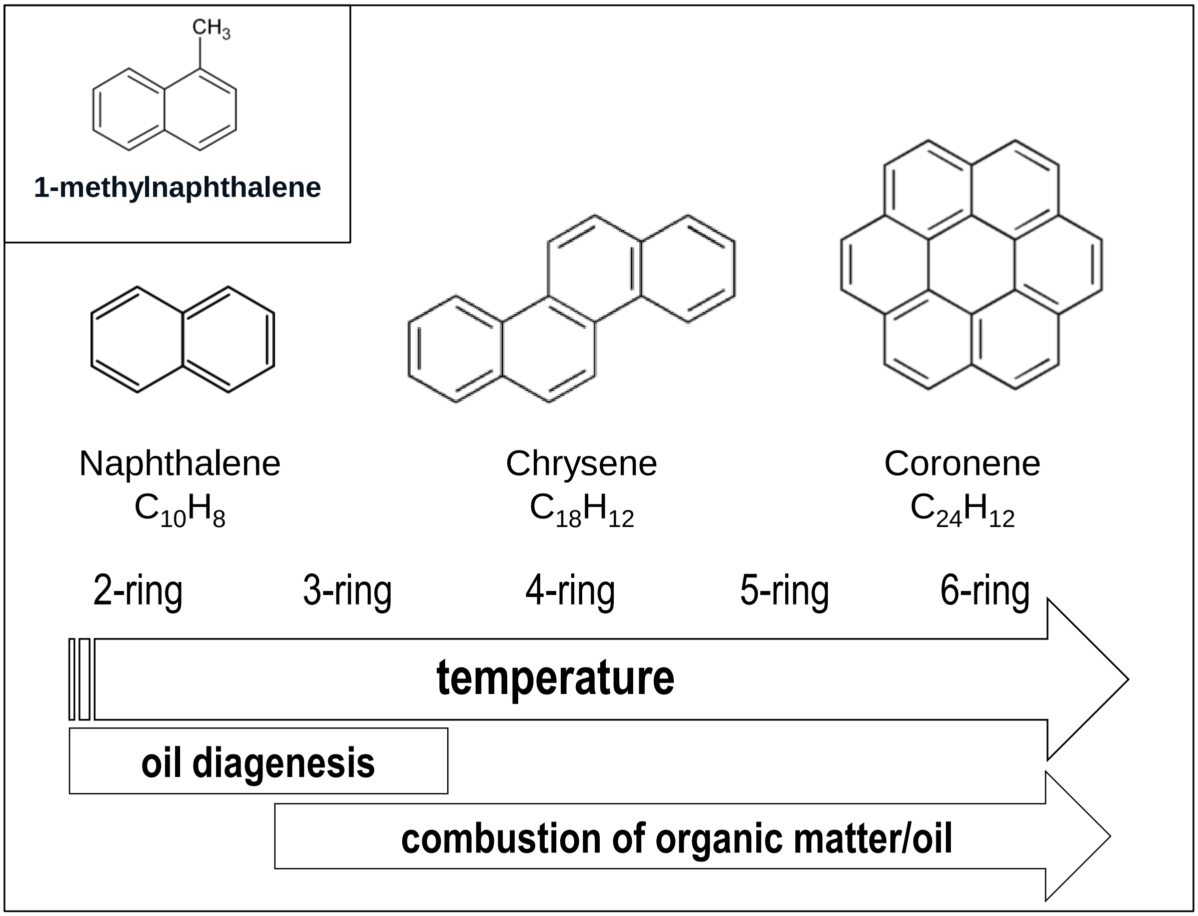

Figure I.1. During oil diagenesis PAHs generate up to three rings as temperature increases. An increase of temperature due to combustion of organic matter generates PAHs of three or more rings. In this study, a range of 2-ring (naphthalene) to 6-ring (coronene) PAHs are used along with various alkylated PAHs (inset). An alkylated PAH has at least one straight carbon side chain (e.g. 1-methylnaphthalene). Alkyl groups are more likely to be preserved at low temperatures and lost at higher temperatures.

In addition to biodegradation, PAHs may also be broken down by physical and chemical weathering processes such as evaporation. The main factors controlling evaporation of oil are: oil composition (i.e. the abundance and vapor pressure of various chemical constituents); the area and thickness of an oil slick; air and water temperature; and wind speed across the surface of the slick (Mackay et al. 1973; Stiver and Mackay 1984; Stiver et al. 1989). For PAHs, volatilization is a major removal mechanism from the water, and deposition of these compounds through precipitation can contaminate remote regions from the specific emission source (Mackay et al., 1986).

Upon release, petroleum-derived PAHs rapidly oxidize to photolysis products (e.g. hydrogen ions). Naphthalene, a two-ringed PAH, has a mean half-life in air of ~1 day compared to ~2 days for the three-ringed acenaphthene, fluorene, phenanthrene, and anthracene, and ~7 days for four- and five-ringed PAHs (Mackay et al., 1992). Monoaromatic and naphthalene compounds will degrade 90% three-to-four days after evaporation and 99% will be degraded in less than a week (Wolfe et al., 1994). The half-life of individual PAHs that degrade through photolysis depends on, in addition to the properties of the compound, the physio-chemical properties of the substrate to which the PAH may be sorbed (Behymer and Hites, 1985). Pyrene, for example, in a lab experiment by Behymer and Hites (1985), has a 21-hour half-life for photolysis on silica gel and a half-life greater than 1,000 hours when sorbed to black carbon. Black carbon has a larger surface area than silica gel, therefore PAHs on black carbon are slower to desorb and photodegrade than PAHs would from a smaller surface area (Behymer and Hites, 1985). Due to the high affinity of PAHs to the structure of soot (e.g. black carbon) PAH concentration in the atmosphere has a strong dependence on aerosol soot content (Dachs et al., 2002).

As mentioned previously, oil-derived compounds will remain in the marine environment for decades after an oil spill (Atlas et al., 1981; Short et al., 1999; Harwell et al., 2012). Despite the rapid-weathering process of PAHs, their persistence at significant levels suggests there may be a negative ecological impact long after oil spill containment. The presence of PAHs in the environment at elevated levels is a concern because many PAHs are carcinogenic and range in toxicity due to their complex nature. For example, methyl-substituted homologs (i.e. alkylated PAHs) of the parent PAHs exhibit carcinogenic and mutagenic properties (Grimmer et al., 1983). The United States Environmental Protection Agency (EPA) has designated several PAH compounds as priority pollutants, including: naphthalene, acenaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo [*a*] anthracene, chrysene, benzo [*b*] fluoranthene, benzo [*k*] fluoranthene, benzo [*a*] pyrene (United States Environmental Protection Agency, 2001).

Although PAHs do not comprise the majority of carbon-containing compounds in oil, as a class of compounds they have a broad range in physio-chemical properties such as molecular weight, solubility, and vapor pressure. As a result, PAHs have been used to successfully "fingerprint" oil released into the environment from numerous marine oil spills (Short et al., 1999; Reddy et al., 2002). A unique relative abundance and distribution pattern within a suite of PAHs is considered to be a fingerprint, which may identify and distinguish the source of those PAHs (e.g. oil) (Saber et al., 2005). The variability of the relative abundances of individual PAHs across different crude oils and their refined products allows for the chemical fingerprinting of the oil (Boehm et al., 1997). Subsequently, knowledge of the fate of these PAHs due to natural weathering processes (e.g. microbial and photochemical) helps in understanding how the chemical fingerprint may be altered during transport from the source oil (Boehm et al., 1997; Christensen et al., 2004; Saber et al., 2005).

With regards to the *DWH* oil spill, there are various transport pathways by which *DWH*-derived PAHs may travel in the nGOM, so a PAH fingerprint would be a useful tracer of the oil. Specifically, the weathering of surface slick oil would result in volatilization of PAHs to the atmosphere. The Gulf Coast region receives air currents that travel north across the GOM, consequently passing directly over the location of the *DWH* oil release, ~60 km southeast of Louisiana (Harrison, 1989). Cho et al. (1998) noted that there are essentially two seasons in the nGOM in which wind stress vectors are altered. The summer season of June, July, and August experiences wind stress toward the north, mainly onshore, while the wind stress is directed west/southwest during the non-summer months (Cho et al., 1998). The typical warm atmospheric and marine water temperatures and the seasonal winds varying in speed and direction facilitate oil weathering, pre-dominantly through biodegradation and evaporation. The subsequent transport of oil-derived PAHs may presumably be directed onshore in the U.S. Gulf Coast during the summer season.

The introduction of elevated levels of PAHs into the nGOM environment as a result of the *DWH* oil spill is of concern because of the potential impact of these toxic compounds to the important fisheries resources and heavily populated coastal areas. The GOM supports nurseries to drive the fishing and shrimping industries and hosts the some of the most productive fisheries in the world (Binninger and Allen, 2012); five U.S. Gulf states alone harvested 1.3 billion pounds of commercial fish and shellfish in 2010 (Binninger and Allen, 2012). Furthermore, a $20 billion tourist industry relies on the Gulf’s beaches for swimming, sun, and water sports (Binninger and Allen, 2012).

Recent studies on the *DWH* oil spill used PAHs to identify *DWH*-specific products distributed throughout the ecosystem of the GOM (Diercks et al., 2010; Rosenbauer et al., 2010; Reddy et al., 2011; Mitra et al., 2012). These observations, coupled with potential weathering of PAHs that may occur in warm waters of the GOM, suggest compounds derived from the *DWH* oil spill may be detected in atmospheric samples in the Gulf Coast states. Thus, I hypothesize the following:

1. *Overall Hypothesis*: A unique pattern of 34 PAHs originating from oil released from the Macondo-1 wellhead during the *DWH* oil spill can be detected in air and water samples taken at select sites in the Gulf Coast states (Florida, Alabama, Mississippi, and Louisiana) during the summer of 2010.
2. *Alternate Hypothesis*: The PAH signatures detected in air and water samples collected from the Gulf Coast states in the summer of 2010 are not representative of *DWH* spill oil.

Hypothesis Testing

In the next three chapters I describe my tests of these hypotheses through a series of objectives:

- Establish a PAH signature (or fingerprint) of oil from the *DWH* slick and subsurface riser.
- Determine if the PAH signature from the *DWH* oil slick is detectable in terrestrial air and water samples from the 2010 field sampling campaign.

- Compare the PAH signature from terrestrial air and water samples from the same field stations a year later in the summer of 2011 to establish a typical background PAH signature of the coastal air quality.

In Chapter 1, I make a comparison of the distributions of PAHs of the *DWH* oil samples to those distributions of the PAHs in nGOM seep oil and various oils from the Santa Barbara Channel, CA. This comparison is meant to determine if there was a unique PAH fingerprint associated with the DWH oil. In Chapter 2, I quantify carbon and PAH abundances on aerosols in U.S. coastal areas of the nGOM from samples collected in the summer of 2010 and then again in 2011. There are very few existing studies of aerosol PAHs along the Gulf Coast states prior to the *DWH* incident. With the spill being remediated by the fall 2010, I consider the following year, 2011, to be representative of "background" levels. Given this assumption, comparison of the PAH distributions across the two summers, allowed me to determine how much typical aerosol carbon and PAH levels in the Gulf Coast states were influenced by the spill. Finally, in Chapter 3, I report on the results from passive air sampling of PAHs and measurements of natural abundances of radiocarbon in rainwater to indicate that the marine-to-land atmospheric transport vector was facilitated by passage of a tropical storm (*TS Bonnie*) traversing over the *DWH* oil slick. Additionally, I show passive air sampling by way of swabbing window films is an excellent method for analyzing aerosols as a representation of air quality.

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CHAPTER 1: A UNIQUE FINGERPRINT OF POLYCYCLIC AROMATIC HYDROCARBONS DERIVED FROM THE *DEEPWATER HORIZON* OIL SPILL

ABSTRACT

The *Deepwater Horizon* (*DWH*) oil spill, resulting from a blowout of the Macondo-1 wellhead on April 20, 2010, is the largest accidental oil spill in United States history. The three-month duration of the spill and the subsequent cleanup activities, caused widespread damage to coastal habitats, affected tourism and fishing and caused concern for human health. It is important to identify *DWH*-specific products distributed throughout the Gulf of Mexico (GOM) resulting from the spill for an accurate assessment of environmental impacts for the region.

The fate of oil in the marine environment depends on factors including composition, source, and weathering. One group of chemicals found in oil, polycyclic aromatic hydrocarbons (PAHs), has been used to fingerprint oil. The relative abundance of a suite of PAHs is a fingerprint of the source oil. A suite of 34 PAHs were used in this study to fingerprint various oil samples, including the *DWH* subsurface riser, the *DWH* surface slick, GOM natural seep oil, and various oils from the Santa Barbara Channel, CA. The total PAH concentration was 3,610 $\mu g\ g^{-1}$ oil for the subsurface riser, and ranged from 540 to 549 $\mu g\ g^{-1}$ oil for the surface slick. The fingerprinting methodology for this study involved chromatographic data processing and multivariate data analysis in order to identify the PAH signatures of the *DWH* oils. Using hierarchical cluster analysis, I show that the PAH distributions for the *DWH* oil differed from the other oil samples by clustering in a separate branch, suggesting a unique chemical fingerprint. The distributions of PAHs were extremely similar between the subsurface riser oil and oil slick, other than low molecular weight PAHs, suggesting a degree of weathering (e.g. volatilization or microbial respiration) influenced PAH distributions associated with the spill.

INTRODUCTION

The *Deepwater Horizon* (*DWH*) oil spill in the northern Gulf of Mexico (nGOM) began April 20, 2010 and is considered the largest oil spill in the history of the United States. Over 4.9 million barrels (1 barrel = 42 gallons) of crude oil spilled from the Macondo-1 wellhead in the Mississippi Canyon lease block 252, from April to July of 2010 (Crone and Tolstoy, 2010). Considering the volume of this spill, oil-derived contaminants affected a large portion of the nGOM.

Oil, formed predominantly from diagenesis of ancient algal material, is largely comprised of hydrocarbons. One particular group of oil-derived hydrocarbons commonly studied is polycyclic aromatic hydrocarbons (PAHs). Crude oil contains 0.2% to more than 7% total PAH (National Research Council, 2003). These hydrocarbons are arranged in two or more fused aromatic rings made up of carbon and hydrogen atoms. Oil-derived PAHs have been used in previous research to trace the fate of chemical compounds released from other oil spills globally (Short et al., 1999; Reddy et al., 2002).

The relative abundance and distribution of a suite of PAHs are considered to be a “fingerprint” of the source (e.g. oil). Fingerprinting PAHs has been useful in tracing oil spills through the surrounding ecosystem (Boehm et al., 1997, Christensen et al., 2004, Saber et al., 2005). For example, Short et al. (1999) studied PAH abundances in benthic sediments of Prince William Sound, Alaska, nearly a decade after the *Exxon-Valdez* oil spill of 1989. The researchers determined the presence of a distribution of PAHs, derived not only from terrestrial coal in the region, but also from the Katalla oil field nearby in the Gulf of Alaska, using the PAH fingerprints as markers to trace the sources (Short et al., 1999). Additionally, in West Falmouth, MA, Reddy et al. (2002) determined that hydrocarbons in marsh sediments retained the characteristic signature of a fuel oil years after a spill. The results from that study suggested that, while some compounds derived from oil spills were almost completely degraded after 30 years, others (e.g. some PAHs) were still present in the sedimentary record, demonstrating that characteristic spill-derived hydrocarbons persist in the environment for decades after release from the original spill (Reddy et al., 2002).

The two most prominent offshore regions in North America with a significant marine input of hydrocarbons due to natural seeps are southern California and the GOM (National Research Council, 2003). Combined, the oil seep rate to the ocean from these two regions is 160,000 tons yr^{-1} (~42 million US gal yr^{-1}) (National Research Council, 2003). This amount is much greater than any anthropogenic input of oil-derived hydrocarbons into the marine environment (National Research Council, 2003). In regards to the *DWH* oil spill, several studies have assessed the fate and transport of low molecular weight oil-derived compounds (C_6-C_{11}) and the impact of this disaster on the nGOM coastal system through subsurface oil plumes and atmospheric hydrocarbon plumes (Camilli et al. 2010; Crone and Tolstoy 2010; Diercks et al. 2010; Reddy et al. 2011; Ryerson et al. 2011a; Ryerson et al., 2011b). However, an in-depth study of the transport and fate of PAHs associated with the *DWH* spill is still lacking. Furthermore, there has not yet been a comparison of the PAHs released from the DWH spill with PAHs isolated from other crude oils, such as natural seeps in the GOM or other regions. Specifically, the oil released during the *DWH* spill was a light, sweet crude oil – a high quality petroleum containing less than 0.5% sulfur (Oil and Gas IQ, 2012). The objective of this chapter is to determine if there is a PAH “fingerprint” of the DWH oil which can be distinguished from seep oil in the GOM.

I hypothesize that a characteristic fingerprint PAH distribution of *DWH* oil exists. Specifically by fingerprint I mean that the relative abundance of each PAH to the sum of PAHs extracted from *DWH* oil will be distributed in a unique manner relative to PAHs in other oils. To test my hypothesis, the distributions of PAHs from the *DWH* oil samples were compared to PAH distributions of oil from cores of an oil seep in the nGOM. I also extracted PAHs from various oils isolated from the Santa Barbara Channel to look for a difference in PAH distribution in samples from a location geographically separated from the *DWH* spill site.

METHODS

Study Sites and Sample Collection

Samples of the *DWH* subsurface riser oil were collected at the Macondo-1 wellhead (Figure 1.1A) from the riser insertion tube aboard the *Discoverer Enterprise* (May 21, 2010). Surface slick samples were obtained manually with I-Chem jars on May 8, 2010 (all provided by B & B Laboratory of TDI-Brooks International, College Station, Texas). The samples were free of defoamer and dispersant. All samples were collected, processed, and shipped under standard chain-of- custody protocols according to methods listed in the USGS National Field Manual for the Collection of Water-Quality Data as well as other USGS standard operation procedures (Wilde et al., 2010). Four natural seep samples from the nGOM were collected in 2002 from two cores at the Mississippi Canyon Block 853 and preserved at -20 °C at the USGS Menlo Park (Figure 1.1A). The Santa Barbara Channel samples (provided by USGS, Figure 1.1B) consisted of sludge, seep, and produced oil, collected in 2001, 2005, and 2008. These samples were stored frozen (-20°C) at the USGS Menlo Park and sent on dry ice to East Carolina University in 2010 for extraction and analysis of PAHs.

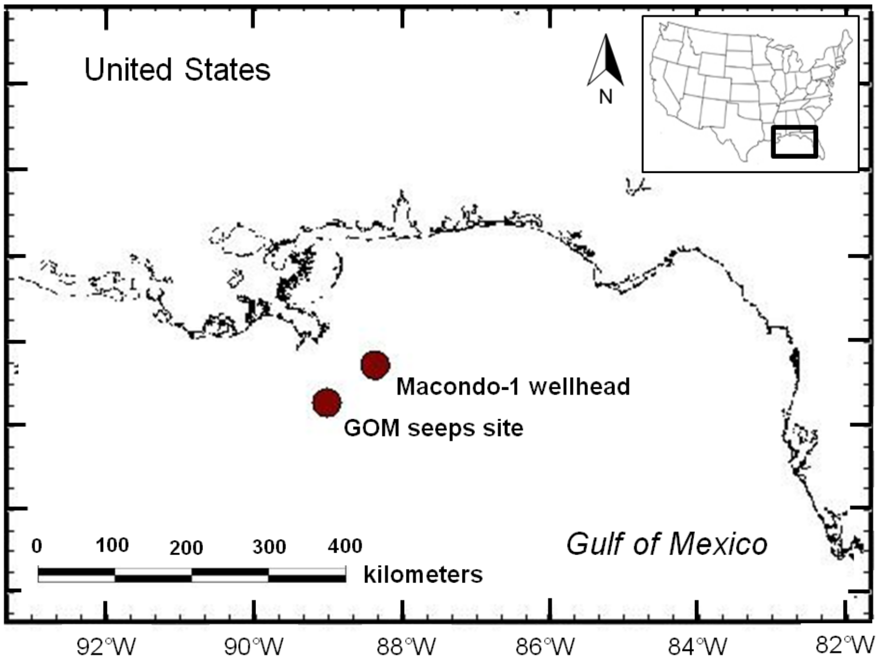

Figure 1.1A. Sample location map of the nGOM and northern Gulf Coast, U.S., with sampling sites for the *DWH* oil at the Macondo-1 wellhead and GOM seep oil.

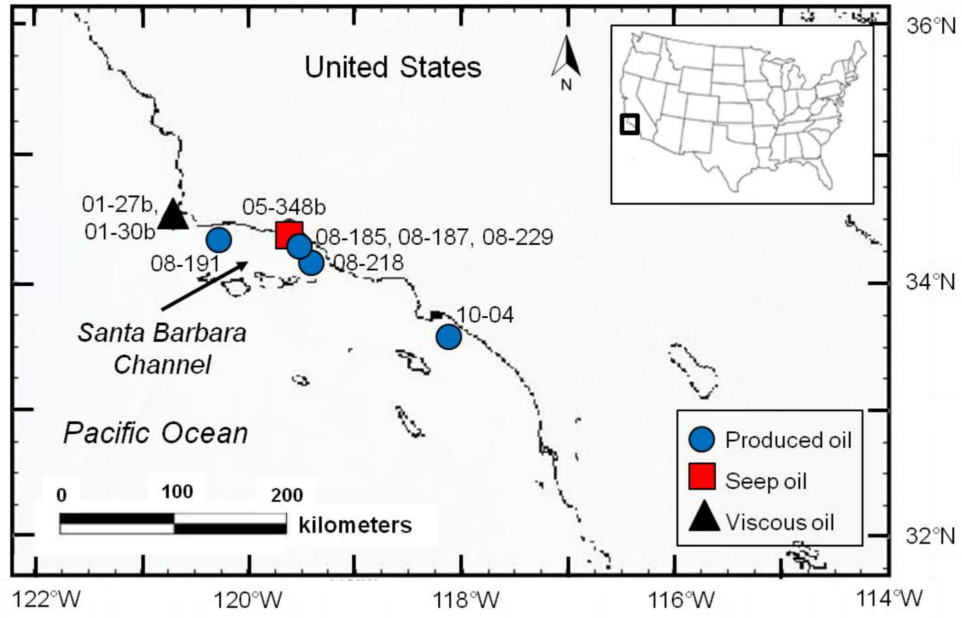

Figure 1.1B. Sample location map of the Santa Barbara Channel on the coast of California, U.S., with sampling locations of assorted oils (Appendix A). The circles are produced oil, the square is seep oil and the triangle is a free-floating viscous oil.

Sample Preparation and Analyses

All samples were extracted for PAHs in the Organic Geochemistry Laboratory, Geological Sciences Department at East Carolina University. There were 34 targeted PAH compounds used in this study to chemically fingerprint oil. Those 34 PAHs were quantified by gas chromatography/mass spectrometry (GC/MS). The mass spectra information can be used to detect patterns characteristic of oil-derived hydrocarbons, thus revealing the fingerprint of the substance. The target PAH compounds in this study included: naphthalenes, phenanthrenes/anthracenes, chrysenes, fluorenes, pyrenes and a selection of alkylated homologs (Table 1.1).

All samples were kept frozen (-20°C) until ready for extraction, at which point they were allowed to thaw to room temperature. All glassware used for sample extraction was pre-cleaned in a bath of Alconox® detergent, rinsed with deionized water, and ashed (450°C, 4h). Less than one gram of each oil sample was weighed on aluminum foil tins and transferred to 30 mL scintillation vials and mixed with 10-20 mL of a 1:1 solution of acetone/hexane. Two mLs of PAH surrogate standard (1 mL each of deuterated naphthalene, anthracene, benz [*a*] anthracene, benz [*a*] pyrene, benz [*g,h,i*] perylene, in 100 mL acetone) were added to each sample. Sample extracts were concentrated to ~1 mL of solution by rotary evaporation and a stream of compressed nitrogen gas. Purification using silica open-column fractionation (Dickhut and Gustafson, 1995) was necessary to isolate the aromatic hydrocarbons from the aliphatic (open hydrocarbon chain) alkane, alkene, cyclo-alkane, and alkyne compounds that are also common to crude oil. These non-aromatic compounds interfere with interpretation of PAH chromatograms. Long (~30 cm) glass columns were filled with 10 grams of pre-cleaned, ashed (450°C, 4h) silica (100-200 mesh) and saturated with hexane. The oil samples were eluted from the columns with

25 mL of hexane and then 75 mL of an 80:20 hexane:dichloromethane (DCM) solution, separating the aliphatic and aromatic fractions, respectively (Dickhut and Gustafson, 1995). The hexane:DCM solution containing the aromatic PAH fraction was collected in a flask and reduced to ~0.25 mL using rotary evaporation and then a stream of pure, compressed nitrogen gas. Samples were spiked with 2 mL of PAH internal standard (1 mL each of deuterated acenaphthylene, phenanthrene, chrysene, perylene, and indeno [1,2,3-*c*,d] pyrene in 100 mL hexane) before the final concentration to 0.25 mL. The samples were transferred with hexane to 2 mL crimp vials and analyzed using a Shimadzu QP2010s-GC/MS (gas chromatograph/mass spectrometer) operating under split-less mode and SIM (selected ion monitoring).

Target PAH compounds were identified by their mass spectrum and retention time (Appendix A). Each batch of samples was run with a lab blank, field blank if available, as well as a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1941b (Marine Sediments), for quality assurance. Results from analysis of a batch of samples were considered not quantifiable if the PAH abundance in a sample was less than twice the abundance of the lab blank, if the recovery of the deuterated surrogate standard compared to the deuterated internal standard, was less than 60%, or if the PAH abundance extracted from the SRM1941b reference sample was not within 10% of the abundances listed on the SRM certificate for 1941b.

Data Analyses

The absolute concentrations of PAHs varied widely across samples, so in many cases the results are represented as a ratio of each individual PAH to the sum total PAHs within each sample (PAH_i/PAH_t). Relationships between the PAH distributions across oil samples were characterized using hierarchical cluster analysis - a two-stage multivariate analysis. Hierarchical cluster analysis of PAHs has been used to quantitatively fingerprint PAH distributions to understand the distribution pattern of individual PAH compounds (Golobočanin et al., 2004). In this study, the cluster analysis was applied in order to characterize the similarity of the PAH distribution patterns of each oil sample to one another. Samples grouped on the same branch are a cluster, therefore most similar, and the height difference of the branches represents the degree of similarity between clusters. Concentrations of PAHs isolated from the water column of the nGOM after the spill (Diercks et al., 2010, Reddy et al., 2011), were also included in the cluster analysis. These data are the results of measurements of the *DWH* oil from an integrated subsurface of 15 to 1500 m depth (Reddy et al., 2011) and PAH measured from immediately below the surface of the water column near the spill site (Diercks et al., 2010).

Data analyses were conducted using the R statistical software version 2.14.0 (©R Foundation for Statistical Computing, 2011). The agglomerative, hierarchical cluster analysis of a matrix of distances was performed using the dist.prop function in the R library ade4 (Dray and Dufour, 2007) to calculate distances between rows based on the suite of PAH compounds. The cluster analysis was conducted using the hclust function using Ward's linkage. Graphical presentations of the results were conducted using SigmaPlot (Systat Software, Inc., San Jose, CA).

RESULTS

All extracted PAH concentrations for the oil samples were several orders of magnitude higher than the PAH concentrations extracted from lab blanks (Appendix F). The concentrations of PAHs from the *DWH* oil (Table 1.1) are presented in Figure 1.2 as histograms.

Table 1.1. PAH concentrations in oil from the *DWH* oil spill, the GOM seep, and the Santa Barbara Channel, CA (µg g^{-1} oil)*.

PAH	Molecular Weight (g mol^{-1})	*DWH*-2 surface slick	*DWH*-3 surface slick	*DWH* subsurface riser	GOM Seep 1	GOM Seep 2	GOM Seep 3	GOM Seep 4	08-185	08-187	08-191	08-218	08-229	01-27b	01-30b	05-348b	10-04
naphthalene	128.10	0.04	0.48	1527	0.25	2.19	1.03	0.34	11.4	7.37	7.31	2.44	5.79	6.95	3.06	2.90	2.50
1-methyl naphthalene	142.05	0.05	0.72	432	0.16	2.41	1.09	0.37	13.5	15.1	6.89	3.82	7.17	12.1	4.95	4.69	3.88
2-methyl naphthalene	142.05	0.06	0.71	0.00	0.25	1.77	0.80	0.26	8.54	10.1	4.73	2.89	4.52	8.05	3.01	2.85	2.61
acenaphthene	152.05	0.34	0.87	35.1	0.05	0.08	0.03	0.01	0.52	0.73	0.32	0.22	0.24	0.59	0.12	0.11	0.50
acenaphthylene	154.10	0.22	0.00	0.00	0.80	0.00	0.01	0.00	0.52	1.15	0.43	0.46	0.38	0.45	0.47	0.45	0.95
fluorene	166.10	15.4	18.6	276	0.00	0.30	0.08	0.03	1.40	1.48	1.33	0.36	0.94	2.14	0.68	0.64	0.30
phenanthrene	178.15	98.0	91.9	446	1.93	1.49	0.31	0.14	3.10	3.19	2.59	0.65	1.98	4.16	1.42	1.35	1.10
anthracene	178.05	4.54	3.34	24.5	0.32	0.05	0.01	0.01	0.30	0.24	0.16	0.08	0.17	0.16	0.05	0.05	0.12
2-methylanthracene	191.45	57.9	56.2	136	7.30	2.06	0.37	0.16	1.54	1.70	1.19	0.29	0.95	3.92	0.97	0.92	0.73
1-methylanthracene	192.25	50.1	47.6	120	3.84	1.11	0.20	0.08	1.52	1.73	1.03	0.29	0.94	3.09	0.77	0.73	0.88
1-methylphenanthrene	191.25	31.8	29.5	76.5	3.74	1.11	0.20	0.08	1.57	1.75	0.80	0.33	1.02	2.63	0.62	0.59	0.62
9-methylanthracene	192.55	2.07	1.67	6.04	0.22	0.03	0.01	0.00	0.11	0.07	0.06	0.10	0.04	0.20	0.09	0.09	0.26
fluoranthene	202.25	6.82	10.1	20.8	0.47	0.04	0.02	0.01	0.06	0.07	0.06	0.03	0.06	0.21	0.00	0.00	0.13
2,3-dimethylanthracene	206.05	17.7	17.0	30.8	3.44	0.24	0.04	0.01	0.19	0.25	0.11	0.04	0.13	0.33	0.10	0.09	0.12
pyrene	202.20	12.3	12.1	26.1	0.59	0.21	0.05	0.02	0.27	0.21	0.25	0.12	0.13	0.28	0.08	0.07	0.19
9,10-dimethylanthracene	206.30	49.5	56.3	79.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-methylfluoranthene	216.20	17.8	3.08	44.0	1.04	0.31	0.04	0.01	0.57	0.61	0.15	0.23	0.37	0.43	0.14	0.13	0.43
9-phenylanthracene	254.10	0.07	0.14	0.57	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
benz [*a*] anthracene	228.10	2.72	2.75	11.8	0.10	0.02	0.00	0.00	0.08	0.08	0.06	0.00	0.07	0.23	0.05	0.04	0.04
chrysene	228.15	30.0	39.1	70.8	0.63	0.24	0.03	0.01	0.33	0.33	0.08	0.00	0.21	0.36	0.08	0.07	0.20
6-methylchrysene	242.15	93.8	107	152	0.63	0.34	0.02	0.01	0.17	0.30	0.03	0.08	0.05	0.32	0.05	0.05	0.08
4-methylchrysene	242.15	6.51	6.22	11.7	0.29	0.08	0.01	0.00	0.09	0.10	0.01	0.01	0.02	0.11	0.02	0.02	0.01
6,8-dimethyl benz [*a*] anthracene	256.20	12.1	12.8	7.68	0.16	0.03	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.09	0.00	0.00	0.02
3,9-dimethyl benz [*a*] anthracene	256.15	7.92	8.40	26.1	0.16	0.05	0.01	0.00	0.00	0.02	0.00	0.01	0.00	0.05	0.02	0.01	0.01
benz [*b*] fluoranthene	252.10	3.46	4.13	6.52	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
benz [*k*] fluoranthene	252.10	2.62	1.91	6.86	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7,12-dimethyl benz [*a*] anthracene	256.15	4.61	5.44	10.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
benz [*e*] pyrene	252.15	6.62	7.11	12.3	0.14	0.03	0.01	0.00	0.30	0.23	0.14	0.18	0.15	0.13	0.04	0.03	0.33

benz [*a*] pyrene	252.15	1.13	1.34	3.18	0.04	0.00	0.09	0.03	0.31	0.16	0.19	1.65	0.26	0.00	0.00	0.00	0.30
perylene	252.20	0.03	0.24	0.41	0.35	0.09	0.00	0.00	0.28	0.20	0.13	0.58	0.11	0.00	0.00	0.00	0.41
indeno [1,2,3-*c*,*d*] pyrene	276.00	0.17	0.00	1.32	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
dibenz [*a*,*h*] anthracene	278.00	1.40	0.24	4.41	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
benz [*g*,*h*,*i*] perylene	276.15	2.66	2.55	4.31	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
coronene	300.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Σ PAH (calc) ->		540	549	3610	27.0	14.32	4.48	1.60	46.7	47.2	28.1	14.9	25.7	47.0	16.8	15.9	16.7

*See Figure 1.1B for sample locations.

When comparing the PAH distributions, the subsurface *DWH* riser oil contains a greater relative abundance of lower molecular weight PAHs relative to higher molecular weight PAHs, and is enriched in naphthalenes, anthracenes and chrysenes (Figure 1.2A). These lower molecular weight PAHs have the highest vapor pressures of the PAHs analyzed in this study. In contrast, the PAH distribution of the *DWH* surface slick oil (Figure 1.2B) is not very abundant in many of the lowest molecular weight PAHs, naphthalene through acenaphthalene. However, the relative abundances of the remaining PAHs are notably similar to the subsurface riser oil (Figure 1.2A).

The histogram of Figure 1.2C shows the PAH distribution pattern for the GOM seep oil. The seep oil is similar to the subsurface riser oil in that the low molecular weight compounds, ranging from naphthalene to acenaphthalene, are abundant within the samples. Also in the seep samples, compounds of higher molecular weight are less abundant compared to the rest of the PAHs. One GOM seep oil sample (GOM Seep 1) differs from the other three GOM seep oil samples in that it contains a greater total of extracted PAHs (27.0 $\mu g\ g^{-1}$, Table 1.1) as well as a greater abundance of most of the individual PAHs larger than phenanthrene. In comparison with the Santa Barbara Channel oil samples, the GOM seep samples have lower total PAH concentrations (except for GOM Seep 1), however they are alike due to the abundance of low molecular weight PAHs and relative lack of higher molecular weight PAHs (Table. 1.1).

In Figure 1.3, cluster analysis divides the oil samples into two distinct groups: one containing all three *DWH* oil samples and one GOM natural seep oil sample (GOM Seep 1), and the second group comprising of the rest of the GOM seep oil as well as all the Santa Barbara Channel oil samples. The PAH measurements from the subsurface riser oil from Reddy et al. (2011) and the water column from Diercks et al. (2010) cluster closely with the PAHs from the subsurface riser, as they are all measurements taken below the sea surface and close to the wellhead. The water column PAH distribution from Diercks et al. (2010), in particular, is the most similar to the subsurface riser PAH distribution (Figure 1.3). For example the ratio of naphthalene to total PAHs for the riser oil is 0.42, while the average ratio of naphthalene in the water column in Diercks et al. (2010) is 0.34. The *DWH* surface slick samples also cluster to the same branch and are most similar to the GOM Seep 1 sample.

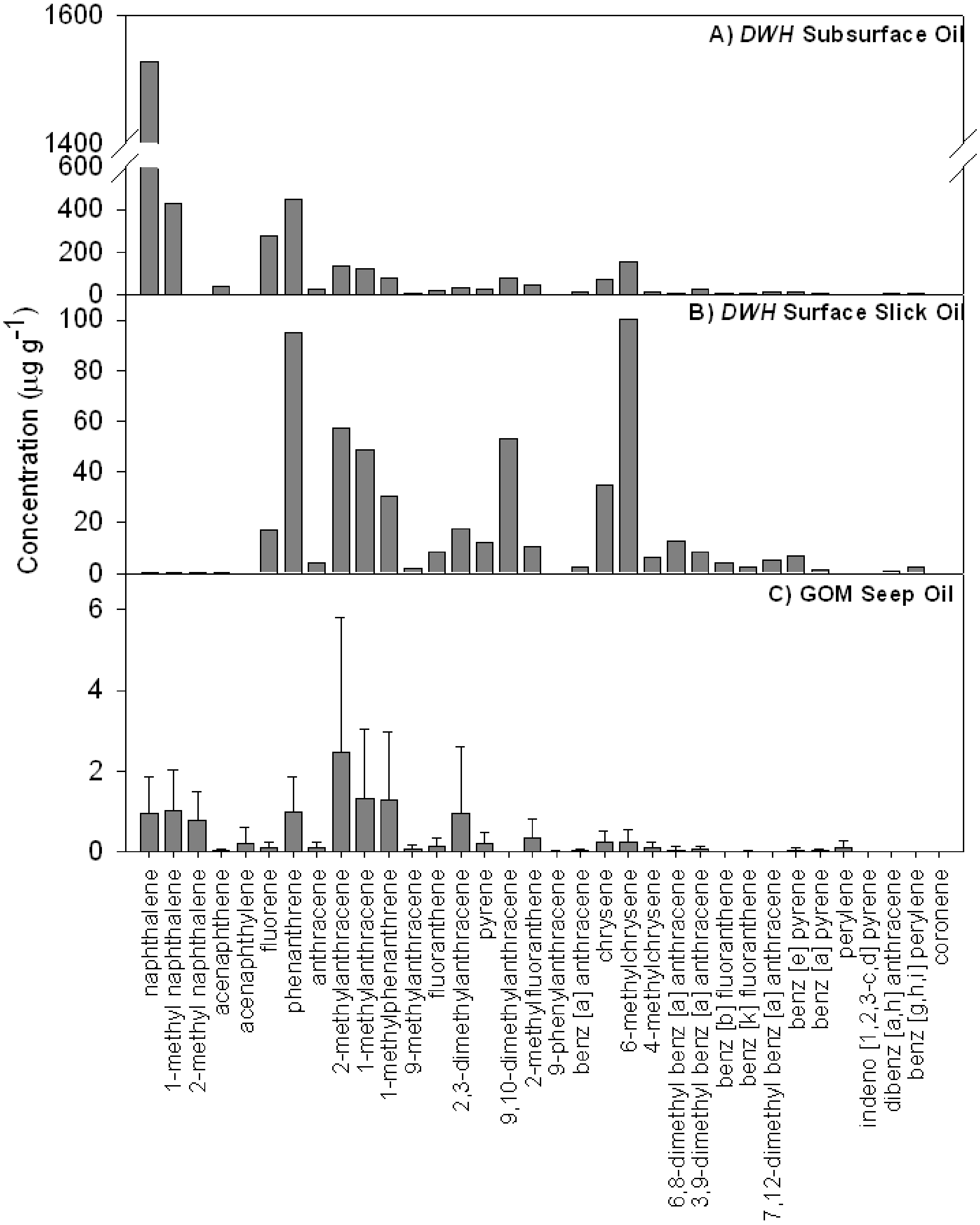

Figure 1.2. A-C. The PAH distribution profile for *DWH* oil sampled from the subsurface riser (A), the surface slick (B) and the oil from the GOM seep (C), all reported in µg PAH g^{-1} oil. The scales are different for each panel. The error bars represent standard deviations (n=4). Compound molecular weight increases proceeding from left to right.

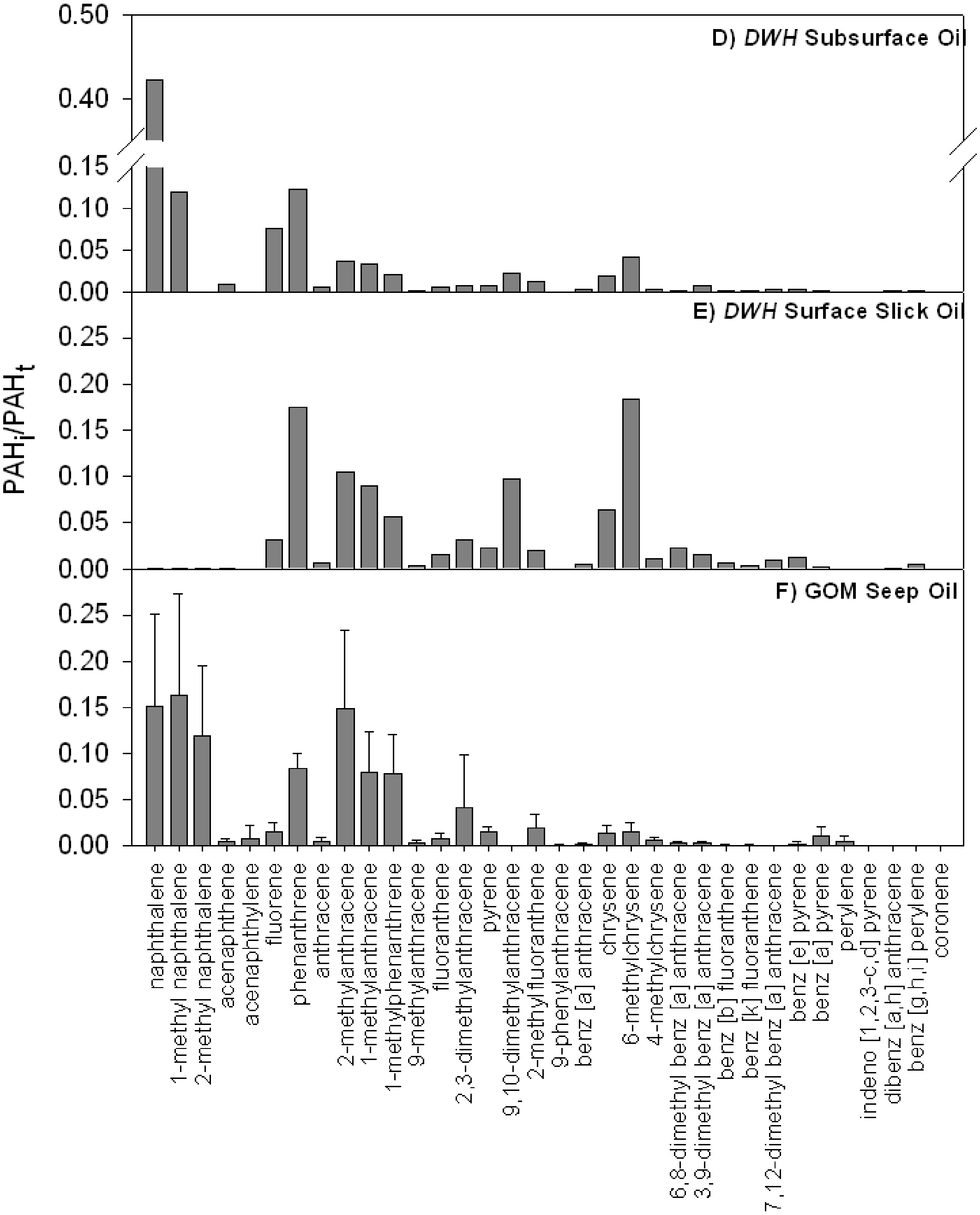

Figure 1.2. D-F. The relative abundance ratios (PAH_i/PAH_t) for the PAH distributions of the *DWH* oil sampled from the subsurface riser (D), the surface slick (E) and the oil sampled from the GOM seep (F). The PAH concentrations are normalized, showing the relative abundance of each compound to the sum of all 34 PAH compounds measured within the sample. The error bars represent standard deviations for each compound (n=4). Compound molecular weight increases proceeding from left to right.

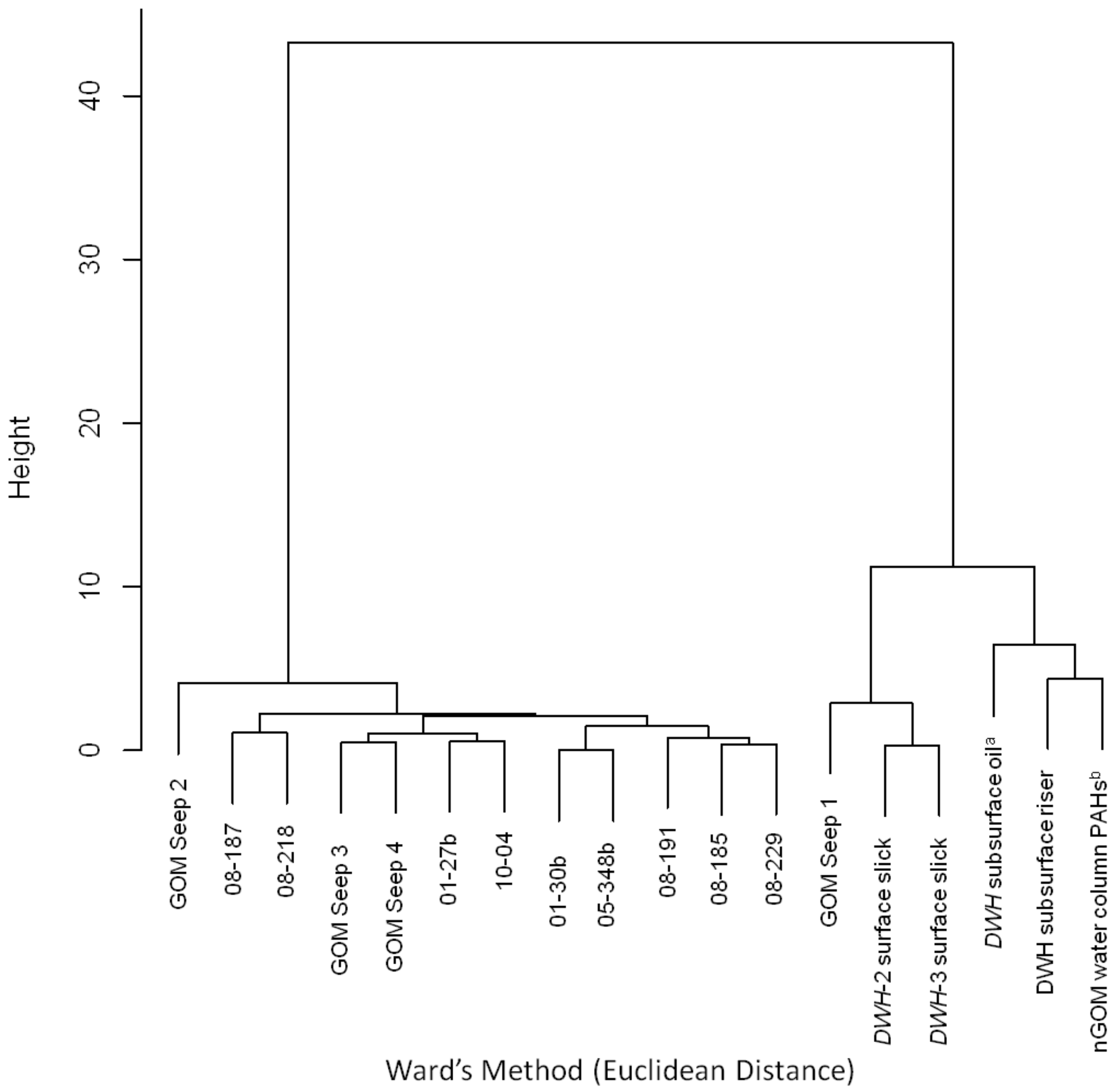

Figure 1.3. The cluster dendogram for the hierarchical cluster analysis groups the *DWH* oil samples together in one branch, along with one sample of the GOM seep oil, and all the remaining oil samples from the GOM seeps and Santa Barbara Channel (the numbered samples) in separate branches. The data from Reddy et al. (2011) are PAHs extracted from the subsurface oil plume and integrated from 15 m to 1500 m below the sea surface. The data from Diercks et al. (2010) are an average of *DWH*-derived PAHs measured from three water column sample sites at or just below sea surface.

[a] Data from Reddy et al., 2011.

[b] Data from Diercks et al., 2010

DISCUSSION

Crude oils of varying geographic origin will have characteristic differences in chemical makeup, even if only a select number of compounds are compared (Grimmer et al., 1983). For example, a compilation of a select subset of PAH concentrations in light and heavy crude oils (Table 1.2) suggests that oil collected at the *DWH* spill site is characterized by PAH abundances greater than oil collected from around the Arabian Peninsula. Since many PAHs are toxic and carcinogenic, higher concentrations of individual PAHs within the *DWH* oil compared to these other samples globally, suggests that the *DWH* oil may have exerted considerably higher toxicity to the ecosystem of the nGOM than in these other study areas. Furthermore, because PAH fate is a function of their fugacity (escaping tendency) and their diffusive and advective fluxes (Harrison et al., 1975; Mackay et al., 1986), the release of PAHs during the *DWH* incident may have had far-reaching ecological implications.

From this study, the data show that the abundance of the low molecular weight compounds, primarily naphthalene through acenaphthalene, is lower in the oil samples from the surface slick than the subsurface oil sample (Figure 1.2). For example, the abundance of naphthalene present in the subsurface oil was found to be several orders of magnitude higher (526.62 $\mu g\ g^{-1}$) than in the surface slick samples (0.04 $\mu g\ g^{-1}$ and 0.48 $\mu g\ g^{-1}$). This observation is expected because of the weathering of hydrocarbons; naphthalenes and other low molecular weight/high vapor pressure PAHs evaporate quickly once exposed to the atmosphere (Mackay et al., 1986). The low molecular weight PAH compounds are preferentially weathered through evaporation, dissolution and biodegradation, therefore readily leaving the oil slick within 2-3 hours of reaching the sea surface (Stiver and Mackay, 1984; Fingas, 1994; Atlas, 1995). The alkylated homologs of PAHs tend to be more stable with respect to evaporation and dissolution, but the

Table 1.2. Select PAH concentrations in crude oil of different origins in comparison to *DWH* spill oil (μg g^{-1} oil).

Location	Sample	pyrene	benz [*a*] anthracene	chrysene	benz [*e*] pyrene	benz [*a*] pyrene	perylene	Reference
Nigeria	Nigerian light	3.1	3.6	-	1.2	0.6	-	Grimmer et al., 1983
Saudi Arabia	Arabian medium	3.7	1.0	-	3.3	0.2	-	Grimmer et al., 1983
Qatar	Qatar	10.7	6.7	-	28.9	3.6	-	Grimmer et al., 1983
nGOM	*DWH* subsurface riser	20	20	80	-	-	-	Ryerson et al., 2011
nGOM	*DWH* subsurface riser	26.1	11.8	70.8	12.3	3.18	0.41	This Study
nGOM	*DWH* surface slick	12.3	2.72	30.0	6.62	1.13	0.03	This Study
nGOM	*DWH* surface slick	12.1	2.75	39.1	7.11	1.34	0.24	This Study

rate of photooxidation will increase with alkylation of PAHs (Prince et al., 2003).

The *DWH* oil has an enriched relative abundance of anthracenes and chrysenes (mid-molecular weight compounds) compared with other PAHs. It is not common to find perylene in oil; this is evident as well in the *DWH* oil samples, in which perylene is scarce (<1.00 µg g^{-1}). Perylene is considered to result from terrestrial sources, such as the breakdown of abietic acid from trees, and subsequently carried into the marine environment (Aizenshtat, 1973). Other higher molecular weight PAHs are also not as abundant as low and mid-molecular weight PAHs in the *DWH* riser oil.

Aside from the depletion of the naphthalenes in the surface slick oil samples, the PAH distribution for the *DWH* oil matches between the surface slick and subsurface oil samples. The subsurface riser oil contained a greater average abundance of all the analyzed PAHs relative to the PAHs from the surface slick, presumably because PAHs in the surface slick are expected to undergo more weathering as a result of photodegradation and volatilization in addition to dissolution and biodegradation in the subsurface. As a result, the relative abundance of PAHs ranging from anthracene to chrysene constitutes the fingerprint of the *DWH* surface slick and subsurface riser samples based on their relative abundance ratios (Figure 1.2D-E).

The concentrations of PAHs from the oil samples from the Santa Barbara Channel have a different PAH distribution than that observed in the *DWH* riser and surface oils. The Santa Barbara oil samples are enriched in the low molecular weight compounds – naphthalenes and anthracenes, but have relatively small abundances of the high molecular weight compounds, including chrysenes and pyrenes. This absence of high molecular weight PAHs is similar across all the Santa Barbara Channel samples, irrespective of sampling dates and the differing oil types (refer to Appendix A), suggesting that these PAHs are not as common to oil as the lighter PAHs.

The GOM seep samples also have a different PAH distribution pattern from that of the *DWH* oil (Figure 1.2D-F). The seep oil is enriched in the low molecular weight PAH compounds (i.e. naphthalenes), similar to the *DWH* subsurface oil sample. But, the PAH distribution of the GOM oil seep samples is more uniform across the suite of compounds, dissimilar from the *DWH* oil distribution pattern. Nonetheless, the oil from the natural seeps, like the subsurface riser oil, is not exposed to the degree of weathering via volatilization or photodegradation that occurs at the sea surface, so a general similarity in the relative abundance patterns of the various PAHs as a function of molecular weight is not surprising for each type of sample.

This comparison is encouraging for developing the fingerprint for the *DWH* oil because all *DWH* samples group together in the cluster analysis (Figure 1.3), regardless of collection location in the water column (and therefore assumed degree of weathering). According to Christensen el al. (2004), a different chemical signature can be obtained from spill samples exposed to different degrees of weathering. So, separation between the *DWH* surface slick and riser oil in the dendogram is not surprising because the surface slick oil was exposed to greater weathering than the subsurface riser oil. As such, the *DWH* surface slick samples and *DWH* subsurface samples are clustered to separate branches within the larger *DWH* cluster, showing that although the PAH distributions are similar between the *DWH* samples, there is enough dissimilarity between the surface slick and subsurface samples to cause them to cluster separately from one another.

The distribution pattern of these PAHs is likely to evolve over time as a result of biodegradation, dissolution, evaporation and photodegradation at the sea surface. For example, low molecular weight, non-alkylated PAHs have a simpler structure than higher molecular weight PAHs, therefore they are more easily dissolved into the water column and more susceptible to breakdown by microorganisms (Atlas, 1995; Prince 2003). These PAHs are also the first to evaporate upon reaching the sea surface due to their high vapor pressure (Mackay et al., 1986). Hence, the *DWH* surface slick oil is relatively enriched in higher molecular PAHs due to weathering of the low molecular weight PAHs during travel through the water column and at the surface. However, it is beyond the scope of this study to speculate further on how the PAH distributions change with time.

SUMMARY

The ultimate fate of oil in the marine environment depends on the oil's composition, source, and degree of weathering. Natural seeps, spills to the sea surface and deepwater subsurface releases behave differently (National Research Council, 2003). Evaporation and dissolution are the primary weathering processes affecting the chemical composition and fingerprint of spilled oil in the time post-release (National Research Council, 2003).

The fingerprinting method of the *DWH* oil spill described in this chapter includes sample preparation and GC/MS analysis of PAHs, chromatographic data processing, and multivariate data analysis to discern the identifying signature for the source oil. In this study, the results of the PAH extraction for chemical fingerprinting reveal the abundance of the low-molecular weight compounds, primarily the naphthalenes, within the *DWH* oil, is much lower in samples from the surface slick in the GOM compared with the subsurface oil sample obtained from the riser. The degree of weathering was observed in both the distribution patterns of the PAH compounds within the oil samples, as well as in the clustering of oil samples from the same provenance. Ultimately, the *DWH* oil differed from the oil samples of the GOM seeps and Santa Barbara Channel by clustering to a separate branch in hierarchical cluster analysis on account of dissimilar PAH distribution patterns, thus suggesting a unique chemical fingerprint for the *DWH* oil.

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CHAPTER 2: MEASUREMENTS OF AEROSOL CARBON AND POLYCYCLIC AROMATIC HYDROCARBONS IN COASTAL NORTHERN GULF OF MEXICO, UNITED STATES

ABSTRACT

Active and passive air samples were collected using a high volume air sampler and window organic films, respectively, from coastal states of the Gulf of Mexico (GOM) in July, 2010 and 2011. Organic carbon (OC), black carbon (BC), and polycyclic aromatic hydrocarbons (PAHs) were extracted from aerosols collected using the high volume air sampler at each of the five sampling locations: Gulf Breeze, FL, Dauphin Island, AL, Turtle Cove, LA, Cross Lake, LA, and Lake Okatibbee, MS. The concentrations of total suspended particulates (TSP) ranged 71.89 to 451.42 μg m^{-3}, the highest of which was measured at the EPA station at Gulf Breeze, FL. The average aerosol carbon concentrations ranged from 1.62 ± 0.76 to 10.74 ± 0.98 μg OC m^{-3} and 2.31 ± 0.34 to 14.06 ± 0.83 μg BC m^{-3}. In general, aerosols were more enriched in OC and BC in 2010 than in 2011. The average $\delta^{13}C_{TOC}$ ranged from -21.36 ± 5.21 ‰ at Dauphin Island in 2011 to -10.08 ± 2.61 ‰ at Turtle Cove in 2010.

In 2010 and 2011, aerosol samples were enriched in low molecular weight, high vapor pressure PAHs at sampling locations. In contrast, the PAHs extracted from window films showed a slightly different PAH distribution from the aerosols. Higher molecular weight PAHs were less abundant on window films, likely due to the weathering of PAHs through rapid photooxidation in the gas phase and probable photochemical reactivity within the film. The ∑PAHs on window films ranged from 3.36 ng m^{-2} at Lake Okatibbee in 2010, to 250 ng m^{-2} at the Gulf Breeze station, also in 2010. Similar aerosol and window film PAH distributions at all stations at sampling periods in both two summers suggests a uniform source for background levels of PAHs across the U.S. Gulf Coast.

INTRODUCTION

Few studies have quantified the transfer of organic matter from marine systems onto land via atmospheric processes. The oceans are an important source of organic matter to the atmosphere (National Research Council, 2003), and surface waters in many coastal areas are extensively polluted with high vapor pressure organic contaminants (Pérez et al., 2003). Because coastal areas receive persistent landward winds derived from marine environments, marine-to-land atmospheric fluxes of aerosols and vapors and associated organic contaminants via wet and/or dry deposition may be significant.

Marine-to-land atmospheric transport of organic carbon (OC) has been shown to occur in a few studies. For example, it has been shown that bulk organic matter derived from a mixture of fossil fuels and fresh marine organics are introduced onto land by marine-to-land atmospheric processes, which are enhanced by Atlantic hurricanes (Raymond et al., 2005). In models of OC cycling, it has been shown that the net transfer of continental OC in rainfall to the ocean is nearly zero because of the significantly higher marine-to-land flux (Raymond et al., 2005). Furthermore, transfer of trace organic pollutants in sea breezes is a mechanism that has been shown to drive organic pollutant exchange between terrestrial and marine environments as a function of wind regime (Pérez et al., 2003). An increase in temperature and wind speed over a coastal water body facilitates volatilization of organic matter (especially low molecular weight compounds) thus acting as a source of marine organic matter to the atmosphere. Subsequent landward breezes would then introduce any volatilized chemicals onshore.

Polycyclic aromatic hydrocarbons (PAHs) may be introduced to the atmosphere from marine environments through the air-water exchange process (Figure 2.1), in which volatilization is the major removal mechanism from the sea surface (Mackay et al., 1986). The magnitude and direction of air-water exchange is determined by the various physiochemical properties of the compound (e.g. molecular weight, vapor pressure, solubility), temperature (through latitude, climate, and season), and wind speed (Mackay et al., 1986, Pérez et al., 2003). Generally, PAHs like benzo (*g*,*h*,*i*) perylene, which have high Henry's law constants (> 10 Pa m^3 mol^{-1}), are more susceptible to cycling between air and water (Mackay et al., 1986). Additional parameters affecting volatilization of organic chemicals include boundary layer air thickness, depositional velocity of particles and degradation rates in air and water (Zhang et al., 2005).

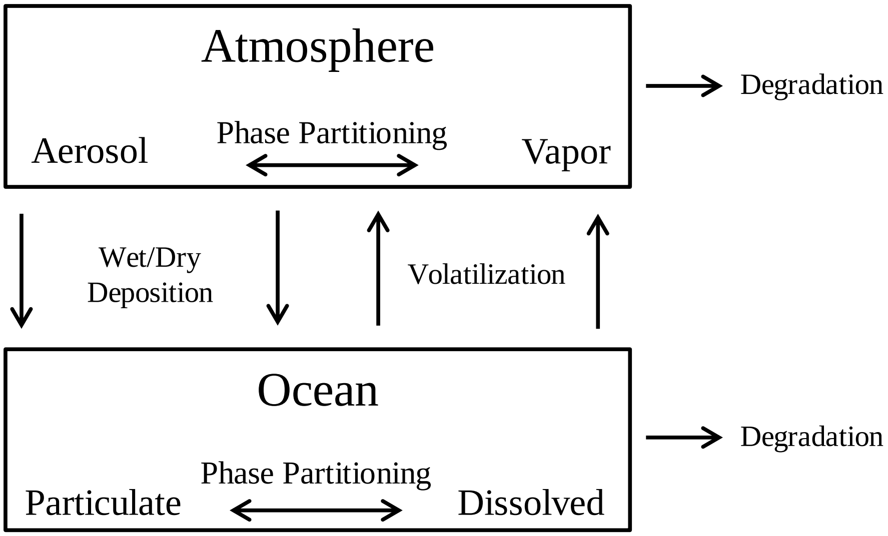

Figure 2.1. Schematic of processes of air-water exchange of PAHs in which wet and dry deposition occurs for both aerosol- and vapor-phase PAHs, as well as volatilization from the water surface of both particulate- and dissolved-phase PAHs. Degradation (e.g. biodegradation and photodegradation) of these compounds results in their removal from the atmospheric or oceanic reservoir.

The residence time of PAHs in the atmosphere varies according to their physio-chemical properties and ambient atmospheric conditions. After volatilization from the sea surface, PAHs can remain in the atmosphere for a time of just a few hours to 4,000 days (Pérez et al., 2003). When PAHs are associated with the particulate phase of elemental carbon, their atmospheric residence time is longer because they are almost entirely bound in accumulation mode particles (diameter 0.1-2 μm, formed by coagulation of smaller particles), allowing for long-range transport (Müller, 1984). Phenanthrene (a 3-ring PAH) and pyrene (a 4-ring PAH) have respective atmospheric residence times of 9 and 677 days (Pérez et al., 2003). The residence time of an aerosol, independent of meteorological parameters, depends mainly on size (Müller, 1984). Generally, high molecular weight/low vapor pressure PAHs will have a longer atmospheric residence time than low molecular weight/high vapor pressure PAHs.

The Gulf of Mexico (GOM) is a marine system that has several sources of PAHs, including natural seepage, accidental discharge from oil production and transport activities, coastal and riverine runoff, and atmospheric exchange (Kennicutt et al., 1988). The most hydrocarbon-polluted areas of the GOM are the coasts of Texas, Louisiana, and Alabama (Kennicutt et al., 1988). Dissolved hydrocarbon concentrations in the northern GOM (nGOM) have ranged from 1 $\mu g\ L^{-1}$ to 75 $\mu g\ L^{-1}$ (Iliffe and Calder, 1974). Mitra and Bianchi (2003) reported dissolved PAH levels ranging from 0.07 $ng\ L^{-1}$ to 65 $ng\ L^{-1}$. The concentrations reported by Mitra and Bianchi (2003) are generally lower than dissolved PAH concentrations measured within the nGOM water column related to the *Deepwater Horizon* (*DWH*) oil spill: 0.7 $ng\ L^{-1}$ to 160 $ng\ L^{-1}$ (Wade et al., 2011). Considering the elevated levels of PAHs in the water column as a result of the *DWH* spill, the nGOM was most likely a significant contributor of PAHs to the atmosphere via volatilization, as has been noted in other polluted coastal waters (Pérez et al., 2003).

As summarized by Fingas (1994), several oil-evaporation models have been developed since the 1970’s. However, very little research has been conducted modeling the subsequent atmospheric transport of the volatilized oil-derived compounds. The *DWH* oil spill released a total of 21 million kg PAHs to the water column (Reddy et al., 2011). A light crude oil, such as that released in the spill, may evaporate up to 75% of the initial oil mass sitting on the sea surface just a few days post-release (Fingas, 1994). According to Ryerson et al. (2011a), airborne *in situ* measurements of *DWH* surface slick emissions in June 2010 showed an evaporation rate of ~258,000 kg d^{-1} of *DWH*-derived hydrocarbons (C_2-C_{11}) into the atmosphere. Since 16% of the total hydrocarbon mass from the spill oil is composed of PAHs (Reddy et al., 2011), then theoretically ~41,280 kg d^{-1} (258,000 kg d^{-1} x 0.16) of PAHs were evaporating from the *DWH* oil slick into the atmosphere above the nGOM.

In 2010, after the wellhead blowout of the *Deepwater Horizon* drilling rig, several researchers began work to determine the transport and fate of low molecular weight oil-derived compounds (C_6-C_{11}) and assess the impact of the *DWH* oil spill on the coastal system of nGOM (Camilli et al. 2010; Diercks et al. 2010; de Gouw et al., 2011; Reddy et al. 2011; Ryerson et al. 2011a; Ryerson et al., 2011b). These studies focused on atmospheric hydrocarbon plumes above the oil slick, and subsurface oil plumes detectable as far as 13 km from the spill (Diercks et al., 2010). Ryerson et al. (2011a) identified narrow plumes of C_6-C_{11} hydrocarbons downwind of the *DWH* spill site with levels substantially greater than the atmospheric background levels of those same compounds measured upwind of the spill site. However, the spatial and temporal extent of impact from PAHs associated with the *DWH* spill has yet to be investigated. As noted in Chapter 1, concentrations of PAHs in the surface slick oil were approximately 540 $\mu g\ g^{-1}$. Furthermore, some of this surface slick was combusted as a means of remediation (National Commission, 2010), and combustion of oil is known to produce elevated levels of pyrogenic PAHs and carbonaceous aerosols such as black carbon (Lima et al., 2005). Diercks et al. (2010) confirmed

DWH-derived PAH levels in the subsurface water column reached 1.89 x 10^5 μg L. When considering PAH Henry's Law constants and warm nGOM water temperatures, these PAHs would volatilize into the atmosphere.

Since summer wind patterns in the GOM are northward (Cho et al., 1998), I hypothesize that elevated levels of PAHs and carbonaceous aerosols from the *DWH* oil slick either directly volatilized to the atmosphere above the nGOM or volatilized after combustion. Specifically, I hypothesize that the concentration of PAHs and aerosol carbon in the atmosphere of the coastal states of the nGOM were higher in summer of 2010 during the presence of the *DWH* oil slick than in 2011 after the spill was largely remediated and naturally weathered. I tested my hypotheses by measuring aerosol carbon and PAH abundance and composition at five sites on the nGOM coast at one time period each in the summers of 2010 and 2011.

METHODS

Two field campaigns were undertaken July 19-26, 2010 and July 18-22, 2011 in which air, rain, and lake water samples were collected from several land-based sites along the nGOM coast (Figure 2.2). Table 2.1 lists the sampling locations, dates, weather conditions and sample volumes of air and water collected. The weather conditions we recorded during both field campaigns were similar with mostly clear skies and light wind (speeds < 3.58 m s^{-1}). Ambient air temperature at the onset of air sampling (Table 2.1) ranged from 28.6 °C to 36.3 °C. Air samples were collected using an active and a passive method by high volume air sampling and organic window film sampling, respectively. In August 2011, air samples spatially integrated across the nGOM were collected by deploying a high volume air sampler from the bow area of the R/V *Cape Hatteras* along a transect in the nGOM (Figure 2.2). The samples obtained from the field campaigns were extracted for total suspended particles (TSP), aerosol OC, aerosol black carbon

(BC), and a suite of 34 PAHs ranging in molecular weight and solubility, as described previously in Chapter 1. There were two precipitation events during the week of sampling in 2010 (Table 2.1). These did not interfere with air sampling, but rather aided in information gathering from window film sampling, to be discussed in detail in Chapter 3.

While in the field, all samples were kept frozen (-20°C) on dry ice and stored in darkness until return to the lab. All samples were extracted within nine months of collection. Glassware used for sample extraction was pre-cleaned in a bath of Alconox® detergent, rinsed with deionized water, and ashed (450°C, 4h).

Particle back-trajectory analysis of the coastal air masses at the time of sampling was done using the NOAA HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (Draxler and Rolph, 2003). This model allows one to trace historical pathways of aerosols as a function of time (back trajectory results reported in Appendix G).

Table 2.1. Sampling sites in Coastal Northern Gulf of Mexico, United States, including locations, dates, air and water surface temperatures and sample volume collected.

Sampling Site	Latitude, Longitude	Sampling Date	Ambient Air Temperature[a] (°C)	Average Lake Surface Water Temperature[b] (°C)	Active Air Sample Volume[d] (m^3)	Passive Air Sample Area (m^2)	Rainwater Sample Volume (L)	Lake Water Sample Volume (L)
EPA at Gulf Breeze, FL	30.3160, -87.1625	19-Jul-10	31.5	-	313 (rep 1), 270 (rep 2)	1.80	-	-
		18-Jul-11	30.7	-	350 (rep 1), 135 (rep 2)[c]	1.80	-	-
Dauphin Island, AL	30.2474, -88.0774	20-Jul-10	33.4	-	298	2.21	-	-
		19-Jul-11	33.1	-	335	2.21	-	-
Turtle Cove (Lake Maurepas), LA	30.2768, -90.3974	21-Jul-10	34.4	32.6	243	0.398	-	11.2
		24-Jul-10	30.0	-	-	0.398	0.06	-
		20-Jul-11	31.0	31.9	371	-	-	16.2
Cross Lake (Shreveport), LA	32.5153, -93.8556	22-Jul-10	28.6	32.1	427	1.21	4.90	9.96
		21-Jul-11	36.3	33.2	821	1.21	-	11.5
Lake Okatibbee, MS	32.4767, -88.8077	26-Jul-10	32.0	29.4	504	20.2	-	9.42
GOM transect	start: 28.7029, -90.7779 end: 29.4665, -92.2340	05-Aug-11 to 06-Aug-11	32.9	-	1380	-	-	-

[a] Ambient air temperatures were recorded at 9 a.m. at the start of sampling with the high volume air sampler. Start of air sampling at the Cross Lake site in 2011 was 3 p.m.

[b] Lake sampling took place from 10 a.m. to 12 p.m. at Turtle Cove, and 6 p.m. to 8 p.m. at Cross Lake and Lake Okatibbee.

[c] The replicate data from the EPA station in 2011 are reported in Appendices D and E but not included in the results because the motor for the air sampler overheated and broke down after less than three hours, potentially contaminating the filters.

[d] A sample air flow calculation example is presented in Appendix B.

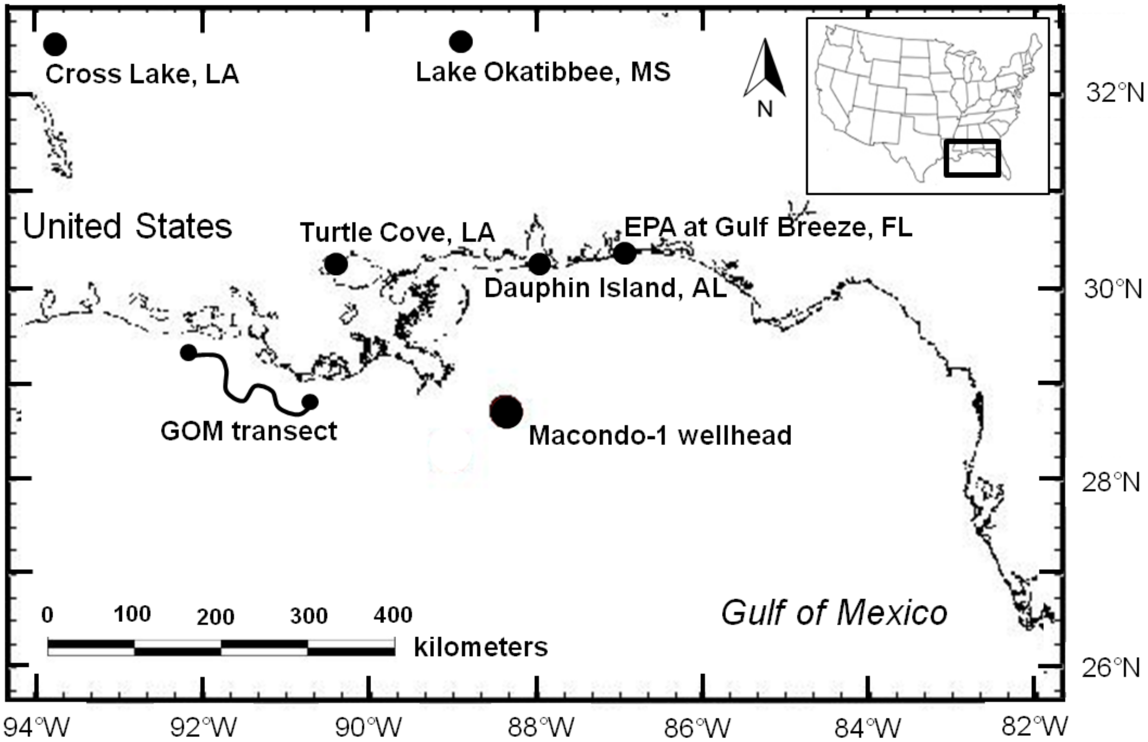

Figure 2.2. Sample location map of the five field sites at which air and water samples were collected in July 2010 and July 2011. Included is the GOM transect of the R/V *Cape Hatteras* from August 2011 as well as the location of the Macondo-1 wellhead, site of the *DWH* oil spill.

Passive air sampling (window films)

Window films have been shown to be effective passive samplers of vapor phase and particulate phase atmospheric chemicals (Diamond et al., 2000, Lam et al., 2005). These atmospherically-derived window films act like atmospheric particulate matter in that they attract and accumulate atmospheric gas-phase compounds (Lam et al., 2005). Organic film on impervious surfaces may grow at a rate of 2.1 nm d^{-1} and are capable of reaching an air-film equilibrium within hours (Wu et al., 2008), eliminating concern of interference from any recent precipitation events. Window film samples were taken for this study by wiping south-facing windows using pre-extracted (refluxing in hexane for 24h) laboratory Kimwipes™ (Diamond et al., 2000). The samples were stored frozen (-20°C) in muffled (450 ^{o}C for 4 hours) Mason Jars lined with clean, ashed (450 ^{o}C for 4 hours) aluminum foil. The same set of windows was sampled at each location for both field campaigns. Windows had not been wiped nor cleaned in the weeks before sampling events. Window area was recorded to obtain PAH loading per unit area (ng m^{-2}).

Active air sampling (high volume air samples)

Air samples were collected at each field site using a Thermo Andersen Model GS2310 Total Suspended Particulates High Volume Air Sampler (Smyrna, GA) to extract particle- and gas-phase organic compounds within the air mass. I used two ashed 20.3×25.4 cm (8×10") Gelman Type A/E glass fiber filters (GFF) to isolate the particulate (aerosol) fraction (>0.7 μm). Two in-line 8 cm diameter× 7.6 cm long polyurethane foam (PUF) plugs were connected downstream of the GFFs for vapor phase isolation. Prior to sampling the PUF plugs were refluxed in GC-grade organic solvents – acetone, dichloromethane (DCM) and hexane (Dickhut and Gustafson, 1995). The GFFs and PUF plugs were arranged in series in the air sampler in order to minimize breakthrough of vapor-phase compounds. The air sampler was set up at the same location at both times of sampling at each site.

Lake and rainwater sampling

At three field sites (Turtle Cove, Cross Lake, and Lake Okatibbee), I collected lake water from a nearby lake surface for analysis of dissolved and particulate carbon and PAH concentrations at the top of the water column. Water was collected at each sampling station using a 1 L glass Mason jar that was used repeatedly to fill a 20 L pressure vessel for an integrated collection of the surface water. Surface water temperatures at time of lake water sampling (Table 2.1) ranged from 31.4 °C to 34.2 °C.

Rainwater was collected at the Turtle Cove and Cross Lake sampling sites during the 2010 field campaign using two clean 30 L pressure vessels, fitted with a large diameter (25 cm) funnel on top with an aluminum mesh screen placed in the narrower portion. The total assembly was securely placed on the ground.

Immediately after lake/rainwater collection, a Gast Vacuum Pump (Sterlitech Corporation, Kent, WA) was used to pressure filter (10 psi) the water through pre-muffled GFFs (0.7 μm) to isolate dissolved organic carbon (DOC), OC, BC and PAHs. A 42 mm diameter GFF was placed in a 47 mm diameter glass Buchner funnel and the filtrate was used for DOC analysis. Particulate OC and BC were trapped on 25 mm diameter GFFs (two GFFs each) placed in 30 mm diameter glass Buchner funnels through which 200 mL of water was filtered per GFF. Two 142 mm diameter GFFs were placed in series with XAD-2 resin (a polymeric substance with high sorption affinity for trace organic contaminants) to collect the particulate- and dissolved-phase PAHs, respectively. The filtrate (collected in pre-cleaned 100 mL glass vials with caps lined with clean, ashed aluminum foil) and GFFs and XAD were frozen (-20°C) until extraction.

Carbon extraction

Bulk carbon concentrations were measured from aerosols isolated on GFFs using the high volume air sampler, and particulate and dissolved OC in lake and rainwater. Four round subsamples, totaling 11.3 cm^2, were punched out using a cork borer from the high volume air sampler GFFs and placed in a desiccator for 7-10 days along with ~50 mL concentrated (12N) HCl. Two replicate punch-outs were stored in crimped tin capsules (5x9 mm) and used for total organic carbon (TOC) analysis. The other two replicates were further treated with a chemothermal oxidation (CTO-375) method to isolate soot-like BC. These GFF punch-outs were heated up to 375 ^{o}C over six hours in a Lindberg/Blue M box furnace (Ashville, NC) and held at that temperature for eighteen hours to oxidize organic matter (Elmquist et al., 2006). The residual carbon on the GFFs after the CTO-375 method is refractory BC (resistant to heat). The difference between TOC and BC is operationally defined as labile (chemically unstable) organic carbon (OC) (refer to Appendix C for the calculated OC concentrations). The BC punch-outs were also crimped in tin capsules (5x9 mm). All samples were sent to the Earth System Center for Stable Isotopic Studies at Yale University, New Haven, CT or the University of California at Davis Stable Isotope Facility, Davis, CA for quantification of TOC and BC abundance and stable isotopic composition.

Dissolved organic carbon was analyzed in the sample of rainwater collected at Cross Lake, LA in 2010. A 30 mL aliquot of filtrate was treated with 2N HCl and immediately analyzed for TOC and total dissolved nitrogen (TDN) using a Shimadzu TOC-VCPN/TNM-1 with the combustion catalytic oxidation method and chemiluminescence detector. Field blanks for DOC (20 mL each) consisted of distilled deionized water filtered through the same apparatus.

PAH extraction

Polycyclic aromatic hydrocarbons were extracted from the Kimwipe^{TM} and GFF samples using a Dionex Accelerated Solvent Extractor 350 (ASE-350). Samples were placed in 66 or 100 mL sample cells and spiked with1 mL of deuterated PAH surrogate standard (as described in Chapter 1). Heated solvent [acetone:hexane cocktail (2:1 v:v)] at 100 ^{o}C was purged through the sample cell over three static cycles of three minutes each and 40% by volume rinse between each static cycle. Polyurethane foam plugs from the high volume air sampler were extracted using a

Soxhlet apparatus by refluxing with acetone, DCM, and hexane at 50 ^{o}C for 24h each (Dickhut and Gustafson, 1995).

All organic solvent extracts were purified using silica open-column fractionation (Dickhut and Gustafson, 1995) and then quantified by gas chromatography-mass spectrometry (GC/MS) after adding 1 mL of deuterated PAH internal standard (as described in Chapter 1). The samples for PAH extraction were injected on a Shimadzu QP-2010-S operated in selected ion monitoring (SIM) mode.

Quality control

All samples were extracted in batches of six to twelve. Each batch included a lab blank and a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1941b (Organic Marine Sediment) following the PAH extraction procedures as described above. Data were considered not quantifiable (NQ) if the PAH abundance in a sample was less than the abundance from the lab blanks (averaged over 18 months), if the recovery of the deuterated surrogate standard compared to the deuterated internal standard was less than 50%, or PAH concentrations deviated by more than 10% from certified values in the SRM.

RESULTS

Proceeding from east to west from the EPA station at Gulf Breeze, FL to Cross Lake, LA, aerosol mass concentrations varied from 451 μg m^{-3} air to 194 μg m^{-3} air in 2010, and 160 μg m^{-3} air to 72 μg m^{-3} air in 2011 (Figure 2.3). The highest level of aerosol TSP was measured at the EPA station in 2010 at 451 μg m^{-3} air, which is a located directly on the coast. The lowest TSP concentration, also in 2010, was measured at 55.6 μg m^{-3} air at Lake Okatibbee, which is a site 260 km inland from the nGOM coastline. In 2010, the TSP concentrations were higher than in

2011 at the EPA and Cross Lake stations (a coastal site and inland site, respectively). The TSP concentrations were lower in 2010 than 2011 at the DISL and Turtle Cove stations, both of which are coastal sites.

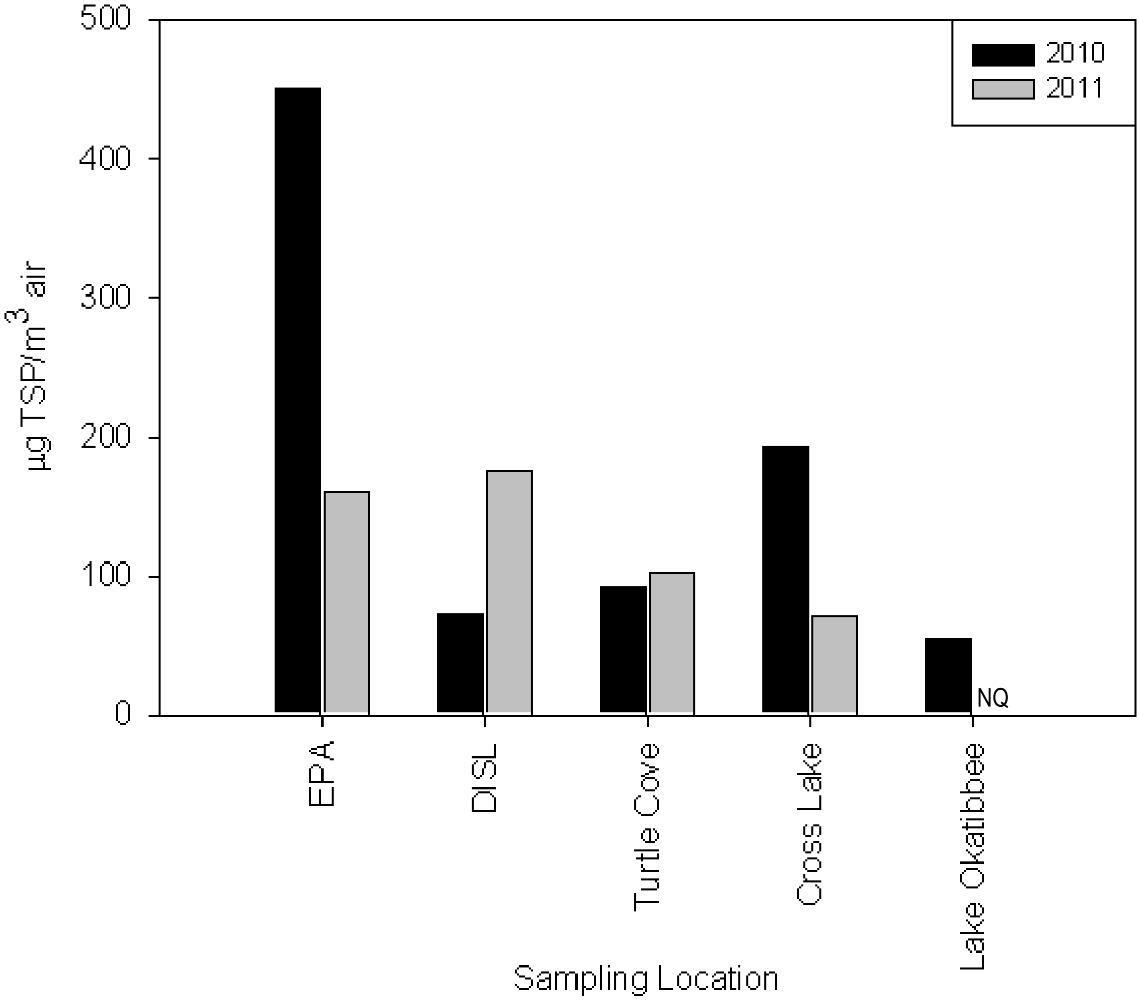

Figure 2.3. The total suspended particles (μgTSP m^{-3}) measured on glass fiber filters collected using the high volume air sampler. The black bars are the measurements from sampling in 2010 and the grey bars are from sampling in 2011. No sample taken at Lake Okatibbee in 2011 (NQ = not quantified).

Bulk carbon concentrations (TOC, OC and BC μg m^{-3} air) were measured for aerosols at each of the five sampling locations. Total organic carbon comprised up to 26% of the TSP at all sampling locations. The trends in aerosol OC and BC are similar to that of aerosol TOC (Figure 2.4). The TOC in aerosols was greater in 2010 for all samples than 2011 (Figure 2.4A). Similarly, average OC (Figure 2.4B) and BC (Figure 2.4C) values at all sites were greater in 2010 and ranged from 8.47 to 26.64 μg OC and 11.84 to 16.20 μg BC compared to 2011 (5.97 to 8.99 μg OC and 5.47 to 14.21 μg BC). Air masses at DISL and Turtle Cove had higher concentrations of TOC, OC, and BC than at the EPA, Cross Lake, and Lake Okatibbee sampling sites for both years.

The stable isotopic composition of TOC, OC, and BC for aerosols was measured and used to differentiate between marine and terrestrial sources (see table in Appendix C). The average value of δ^{13}C of TOC of aerosols was more depleted in 2011 (-16.3 ‰) than in 2010 (-13.4 ‰). Stable isotopic signatures of aerosol TOC at DISL showed the greatest inter-annual change, decreasing from -10.2 to -21.4 ‰ between 2010 and 2011. Likewise, $\delta^{13}C_{OC}$ of the 2011 samples were, again, generally more depleted in $\delta^{13}C_{OC}$ (averaging -20.2 ‰) than in 2010 (averaging -16.5 ‰) (Figure 2.5B). Conversely, the $\delta^{13}C_{BC}$ in 2010 was more enriched than in 2011 at the EPA and DISL sites, but depleted at Turtle Cove, and Cross Lake (Figure 2.5C). The average annual trend for $\delta^{13}C_{BC}$ of aerosols at all samples was similar to the TOC and OC trends in that the 2011 aerosol BC was more depleted (averaging -11.6 ‰) than it was in 2010 (averaging -10.1 ‰).

Concentrations of PAHs on aerosols at all sampling stations were similar in both 2010 and 2011. In all aerosol samples, the concentrations of naphthalene, phenanthrene, fluoranthene, pyrene, and chrysene and benzo [*b*] fluoranthene, indeno [1,2,3,*c*,*d*] pyrene, and benzo [*g*,*h*,*i*] perylene are elevated with respect to all other measured PAHs (Figure 2.6).

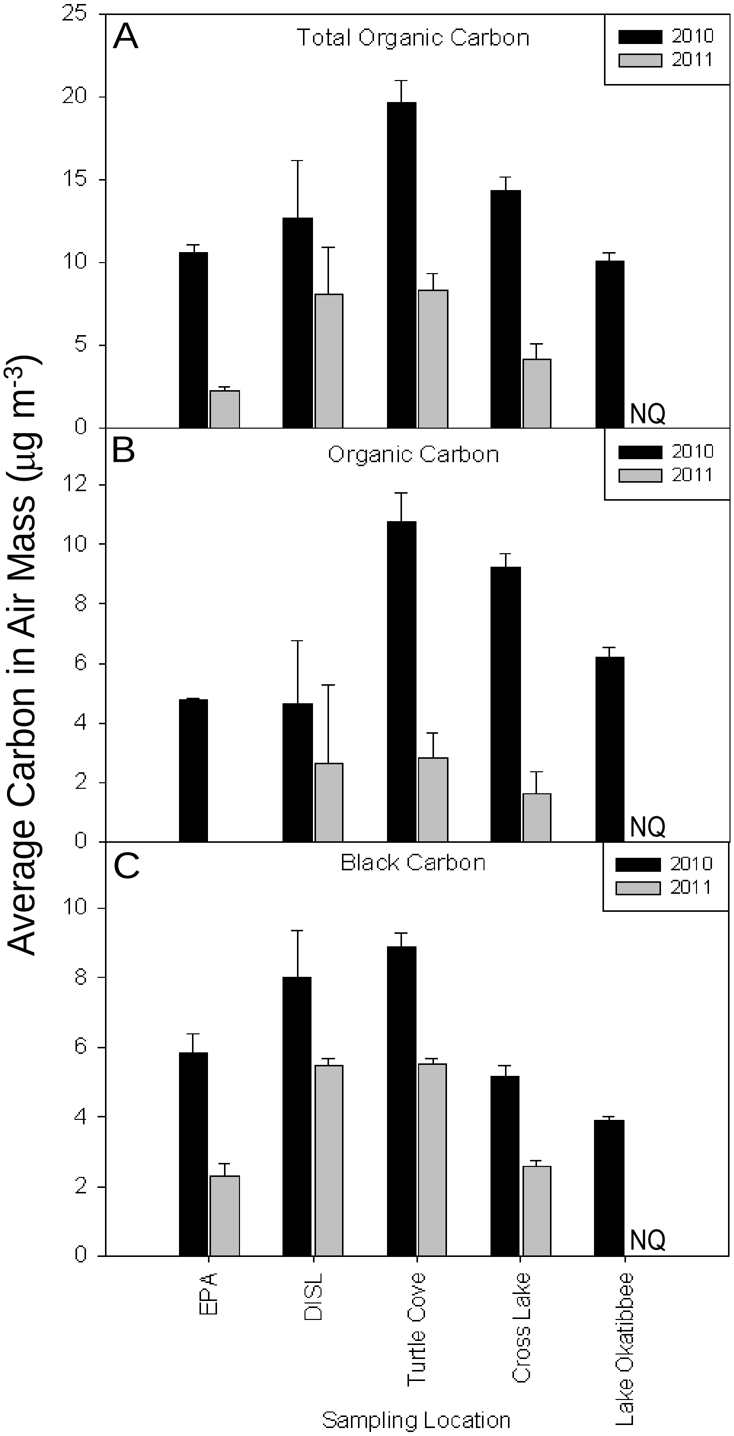

Figure 2.4. Average concentrations (µg m^{-3}) of two samples each of A) total organic carbon (TOC), B) organic carbon (OC) and C) black carbon (BC) on aerosols collected at each site. The error bars are standard deviations. The black bars are the measurements from sampling in 2010 and the grey bars are from sampling in 2011. No sample was collected at Lake Okatibbee in 2011 (NQ = not quantified).

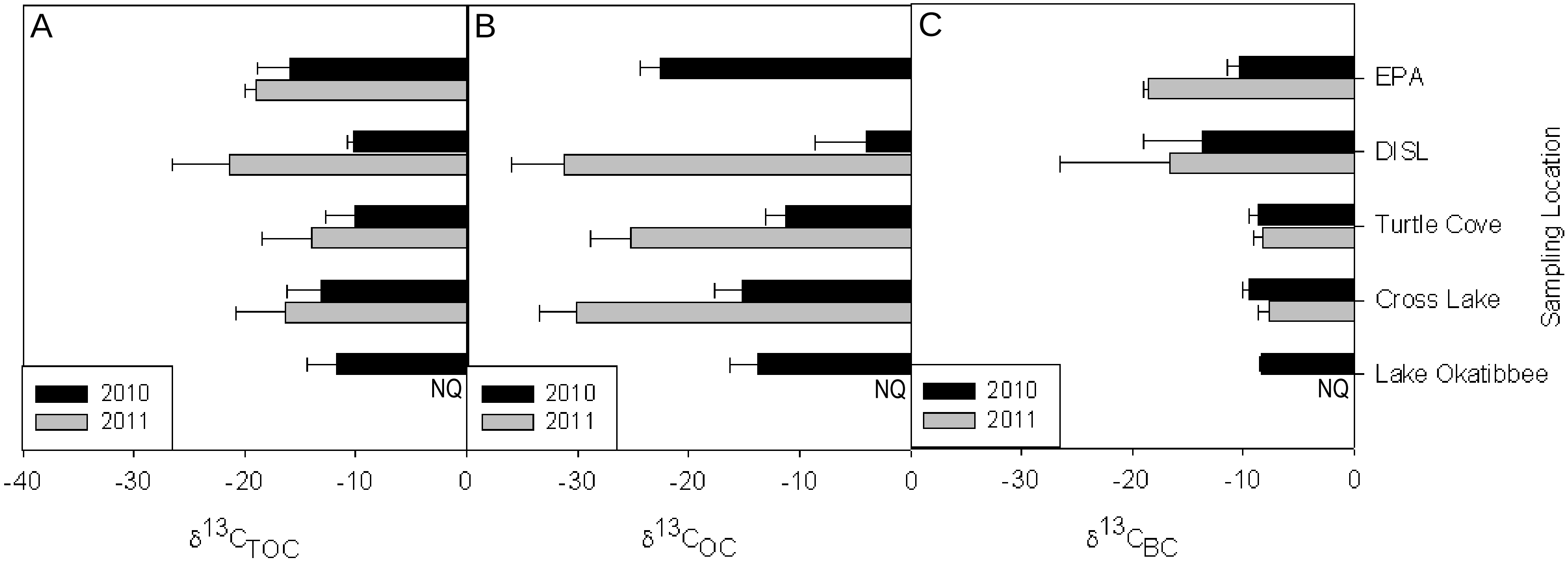

Figure 2.5. Average carbon isotope signature (‰) of two samples of A) total organic carbon (TOC), B) organic carbon (OC), and C) black carbon (BC). Error bars are standard deviation. The black bars are the measurements from sampling in 2010 and the grey bars are from sampling in 2011. No sample was collected at Lake Okatibbee in 2011 (NQ = not quantified).

As noted in Chapter 1, the relative abundance ratios of PAHs can be used as a tracer for PAH source. In both years, aerosols across all sampling sites were enriched in low molecular weight PAHs relative to high molecular weight PAHs (Figure 2.6). Aerosol PAH levels at the Turtle Cove (Figure 2.6C) and EPA (Figure 2.6A) stations were similar in 2010 and 2011. For PAHs on aerosols at DISL (Figure 2.6B) concentrations were greater in 2011, while Cross Lake (Figure 2.6D) had higher PAH concentrations in 2010.

The PAH distribution patterns for the window film samples are shown in Figure 2.7. Window film PAHs at the EPA station, were more concentrated in 2010 than in 2011, but the distribution pattern of the PAH relative abundance are similar over both years (Figure 2.7A, 2.7D). The DISL site has a similar pattern (Figure 2.7B, 2.7E) to that at the EPA station except there are a few compounds that have a greater concentration in 2011 at DISL, such as phenanthrene. At the Cross Lake inland site (Figure 2.7C, 2.7F), the window film had accumulated more PAHs in 2011 than 2010, except for a couple alkylated compounds that had a greater abundance in 2010, while overall the Cross Lake site had lower concentrations of PAHs compared to the other sampling sites. The PAH distribution pattern on window film shows similar relative abundance of PAHs from one sampling site to the next, despite the distance from one another and proximity to the coast (Figure 2.7D-F).

The majority of PAHs on PUF plugs and GFF from water samples were not quantifiable, due to poor recovery during the PAH extraction process, or the detected concentrations were below those on the lab blanks. Additionally, the data from EPA rep 2, 2011 are reported in Appendix D but excluded from the figures because the second air sampler ceased functioning less than three hours into sampling. All quantifiable data are listed in Appendix D.

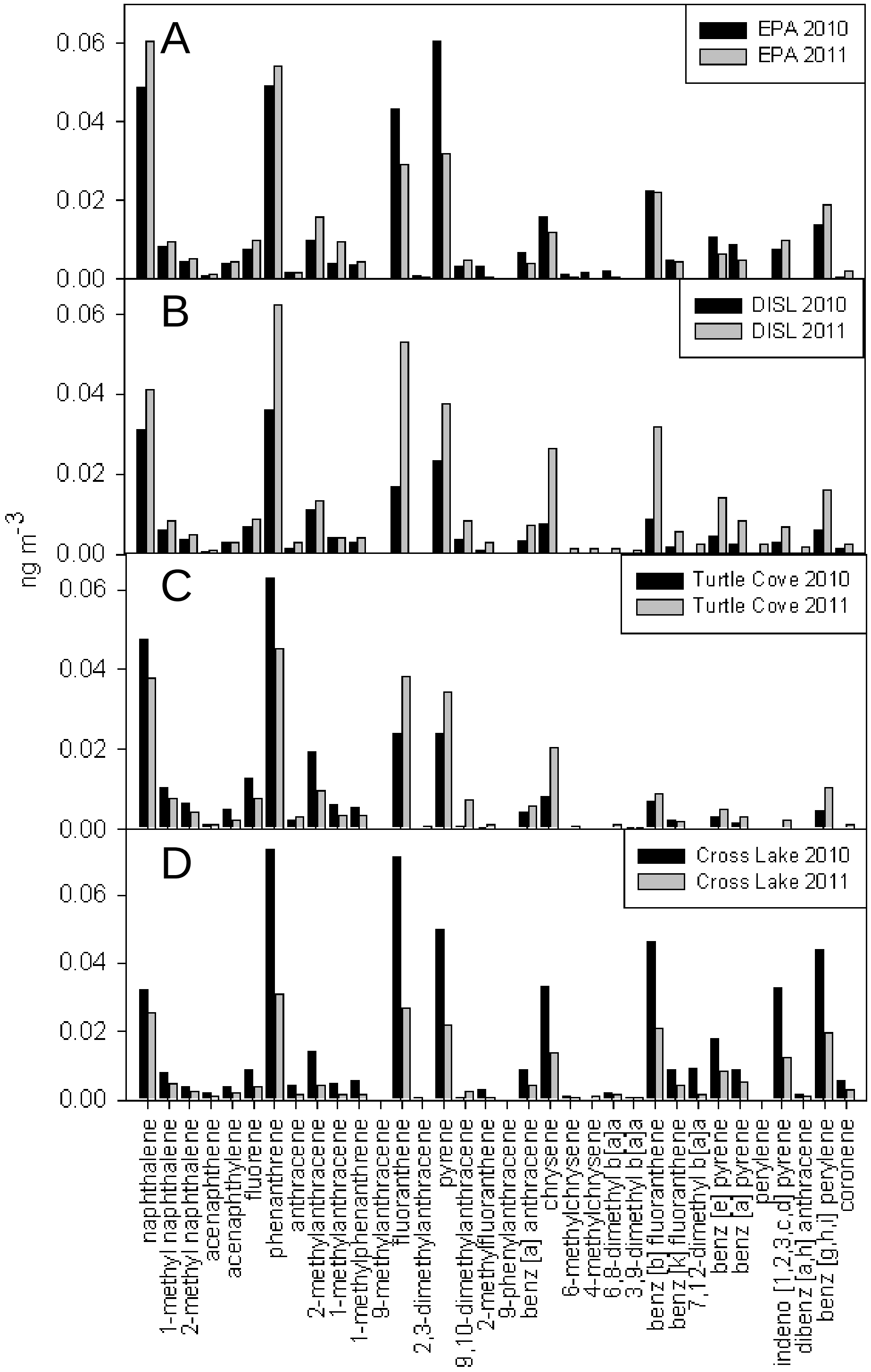

Figure 2.6A-D. Concentrations of PAHs measured on aerosols (ng m^{-3}) at the A) EPA, B) DISL, C) Turtle Cove and D) Cross Lake sampling stations in July 2010 and July 2011. Compound molecular weight increases proceeding from left to right. The black bars are the measurements from sampling in 2010 and the grey bars are from sampling in 2011.

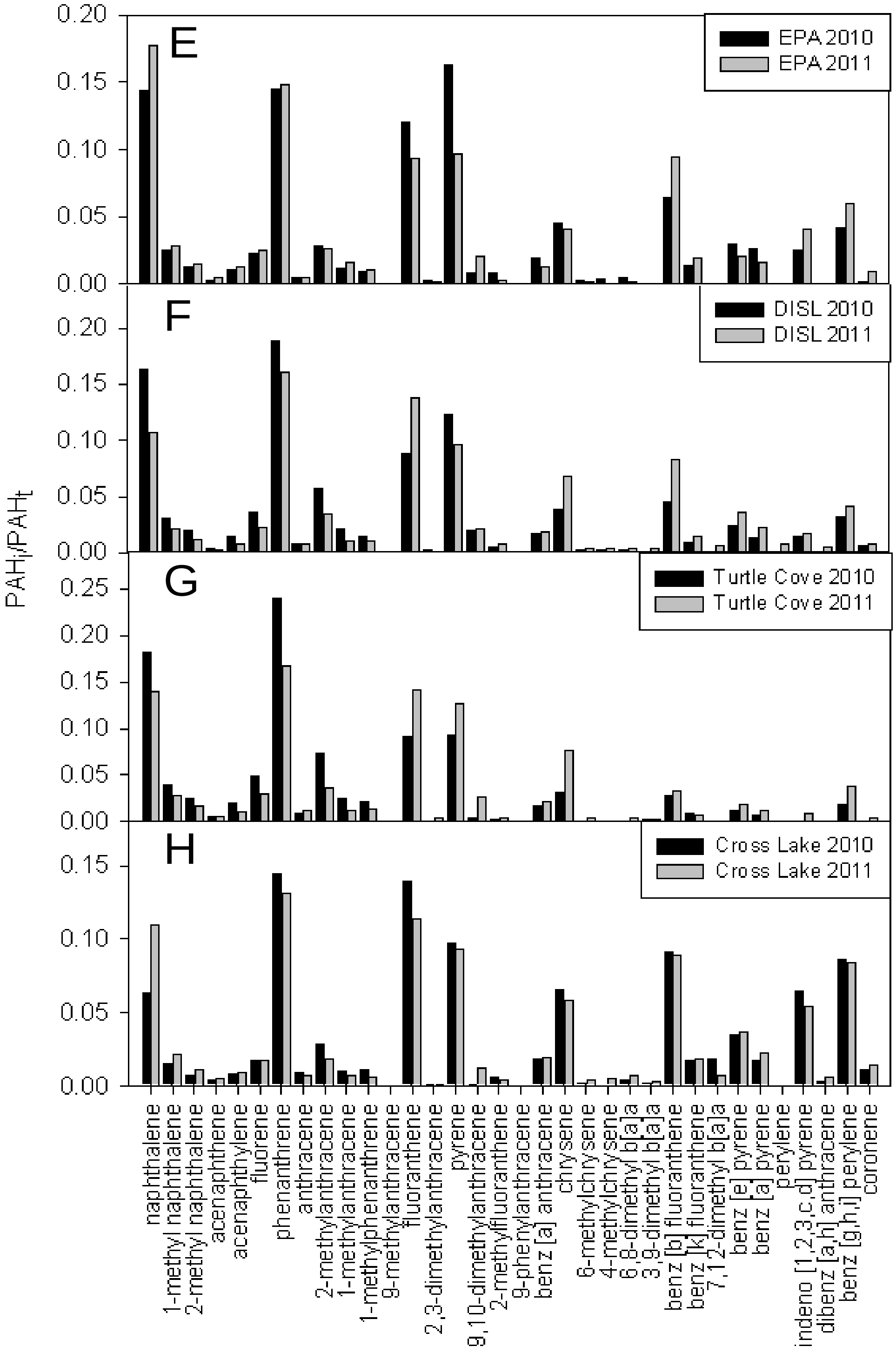

Figure 2.6E-H. Relative abundance ratios of the individual PAH to the sum per sample (PAH$_i$/PAH$_t$) measured on aerosols from E) EPA, F) DISL, G) Turtle Cove and H) Cross Lake. Compound molecular weight increases proceeding from left to right. The black bars are the measurements from sampling in 2010 and the grey bars are from sampling in 2011.

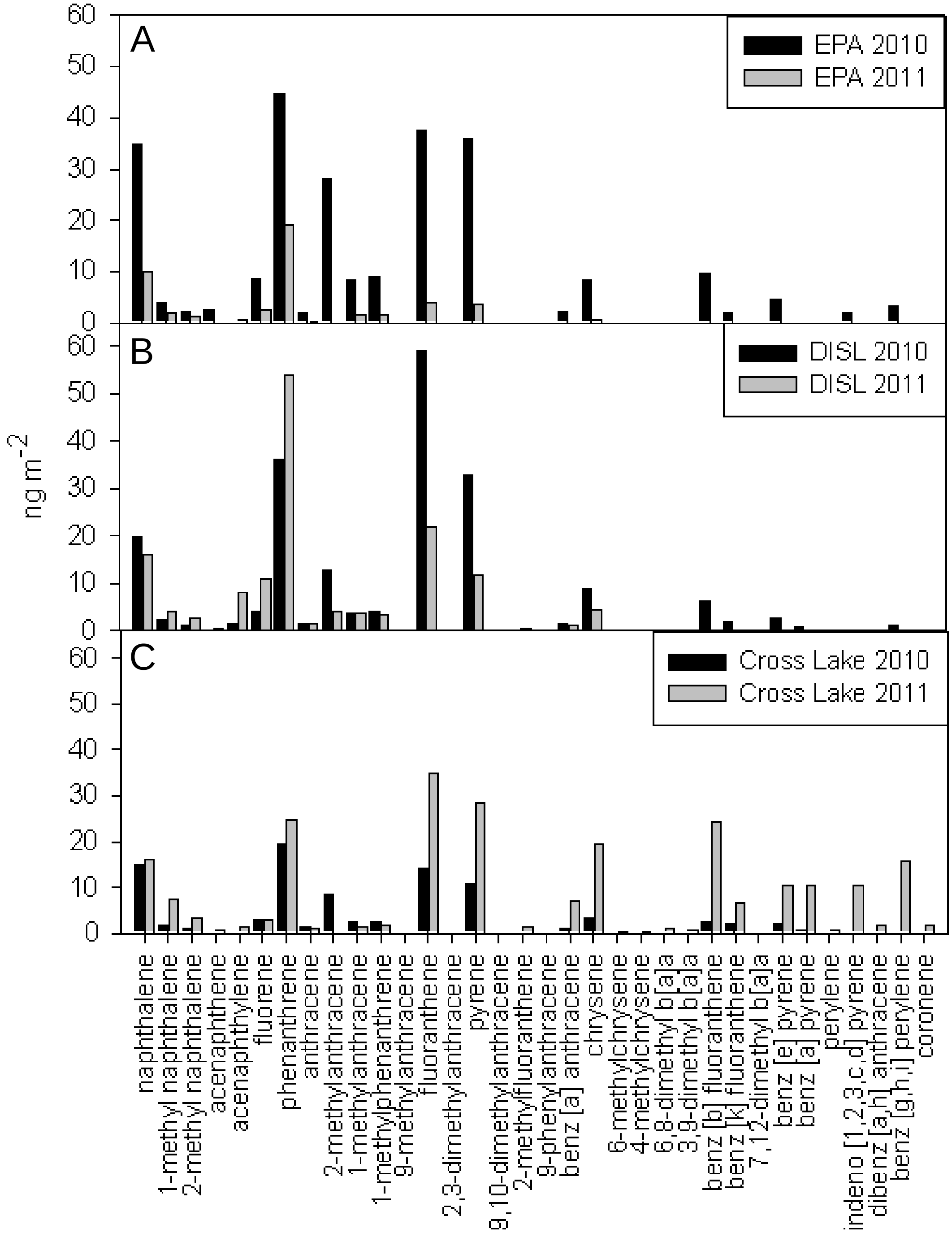

Figure 2.7A-D. Concentrations of PAHs measured on window films (ng m^{-2}) at the A) EPA, B) DISL and C) Cross Lake sampling sites in July 2010 and July 2011. Compound molecular weight increases proceeding from left to right. The black bars are the measurements from sampling in 2010 and the grey bars are from sampling in 2011.

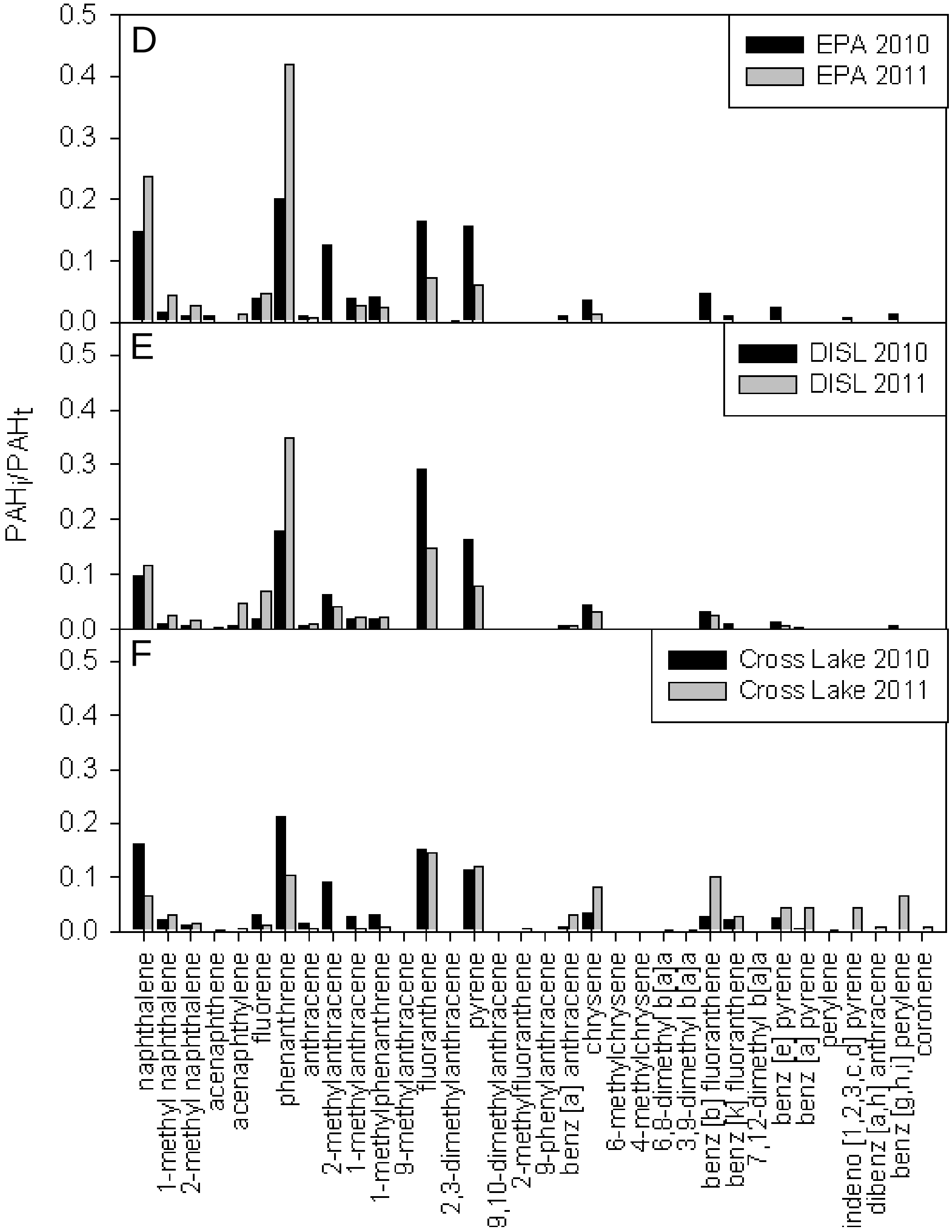

Figure 2.7D-F. Relative abundance ratios of the individual PAH to the sum per sample (PAH_i/PAH_t) measured on window film at D) EPA, E) DISL and F) Cross Lake. Compound molecular weight increases proceeding from left to right. The black bars are the measurements from sampling in 2010 and the grey bars are from sampling in 2011.

DISCUSSION

The coastline of the nGOM a region contains urban and rural areas, providing an ideal opportunity to compare air quality across different areas because of the proximity of oil production offshore and a variety of both primary carbon sources (e.g. diesel combustion, wood burning, etc.) and secondary carbon sources (e.g. atmospheric oxidation of volatile organic carbon) (Ding et al., 2008). Air quality in this region has been extensively studied over the past few decades, largely through data from the Southeastern Aerosol Research and Characterization Network (SEARCH). Carbon is the largest component of fine particulate matter, annually, within urban areas of the southeastern United States and average carbon concentration fluctuates seasonally (Hansen et al., 2003, Ding et al., 2008). Secondary organic carbon (SOC) in the nGOM states, for example, is at its lowest average concentration in the winter months, and highest in the late spring-summer (Ding et al., 2008). Average summertime carbon concentrations in this region are greater than anywhere else in the U.S., and it is even thought that these values are regularly underestimated (Bhave et al., 2007, Yu et al., 2004).

It is important to study the distribution of carbon in this highly industrialized region of the nGOM where high aerosol carbon concentrations are mainly attributed to regional diesel exhaust from urbanized areas of the southeast U.S., like the coastal cities of Pensacola, FL and Gulfport, MS (Zheng et al., 2002). Moreover, the inner shelf area of the nGOM hosts numerous oil platforms, so the water column in this area is a likely contributor to carbon emissions to the coastal atmosphere. Lastly, an oil spill on the scale of that of the *DWH* is also likely to contribute to atmospheric loading of bulk and trace carbon in the GOM.

Air Mass Transport

To conclude how PAHs from the *DWH* oil slick may have been introduced into the atmosphere and land at the coast, it is important to determine air mass transport pathways. Due to dominant wind patterns in the region, there is potential for *DWH* oil-derived compounds to travel to the U.S. nGOM Coast via onshore winds. There are two main vectors by which seasonal air masses travel over the GOM (Cho et al. 1998). In the summer season (June, July, and August) winds travel to the north, landward, while during the non-summer months winds travel to the west/southwest (Cho et al., 1998). This is an important distinction and holds implications for PAH deposition at the coast because the *DWH* oil slick occurred in the nGOM at the time of the characteristic southerly summer wind patterns. During the week of sampling in July 2010, the back-trajectory analyses suggested that the pathways of air particulates collected at each sampling site in this study originated primarily from the atmosphere above the water column in the nGOM, than from land (refer to Appendix G for all back-trajectory analyses). Thus, on each sampling date aerosols collected as part of this sampling effort originated from or travelled over the nGOM before arrival at the sampling site. Hence, there was potential for the *DWH* oil slick to be an important contributor of PAHs to the Gulf Coast states during its presence in the nGOM.

Aerosol Carbon Content

The results of the air sampling conducted for this study show a change in regional aerosol carbon content from previous atmospheric monitoring of the northern Gulf Coast. The TSP content has increased over the past few decades, whereas the OC concentration remains about the same. Wolff et al. (1983) conducted a study of airborne particles in the United States that included a sampling site at Abbeville, LA within the nGOM coastal region. After summertime sampling of both continental and marine air masses that passed over the site, they measured a mean TSP value of 53.3 μg m^{-3} (ranging 29.7 μg m^{-3} to 74.9 μg m^{-3}) (Wolff et al., 1983). The highest TSP values from Wolff et al. (1983) are comparable to the lowest TSP measured in this study of 55.59 μg m^{-3} and 72.59 μg m^{-3} at Lake Okatibbee and DISL, respectively, in 2010. For example, the lowest concentrations for TSP in 2011 were 83.87 μg m^{-3} and 71.89 μg m^{-3} at EPA and Cross Lake, respectively. Other than these four measurements, the aerosol TSP in this study was an order of magnitude higher (up to 451 μgTSP m^{-3} at the EPA station in 2010) than any reported by Wolff et al. (1983).

Despite the increase in aerosol TSP over time, these data indicate that the aerosol OC content has generally decreased in the past decade. Wolff et al. (1983) measured a mean OC (defined as TOC in this study) value for aerosol samples of 10.8 μg m^{-3} (ranging from 8.2 μg m^{-3} to 14.9 μg m^{-3}). These values are similar to the TOC measured in this study from 2010 and 2011; which ranged from 4.18 μg m^{-3} to 19.6 μg m^{-3} (mean = 10.1 μg m^{-3}). These carbon values are greater than what has been observed more recently as part of the SEARCH initiative in the southeastern U.S. In the summer of 1999, average TC (total carbon, inclusive of elemental and organic carbon) ranged from 2.64 μg m^{-3} to 7.33 μg m^{-3} (Bhave et al., 2007). A compilation of aerosol OC and BC (as well as some corresponding PAH data) from multiple studies are listed in Table 2.2. This comparison suggests that OC concentrations are relatively consistent over time and across the region. A slight increase in aerosol OC in 2010 and 2011 is shown by the data provided by this study.

Black carbon values show a greater change than the OC measurements over time and a definite increase in BC concentration on aerosols in 2010 and 2011. This increase in aerosol BC suggests a greater influence of combustion-derived aerosols to the atmosphere in 2011 compared to 2010. Such an increase could be the result of growing urban centers and increased population density, and/or industrialization related to the offshore oil rigs of the GOM (National Research Council, 2003). Additionally, Ding et al. (2008) discovered a high correlation of fossil and modern SOC between their sampling sites in the U.S. Gulf Coast, suggesting a regional character for aerosol formation even though primary-source carbon formation (i.e. wood-burning and diesel combustion) is variable between urban and rural settings.

Carbon Isotope Data

Marine OC is enriched in $\delta^{13}C$ with respect to terrestrial carbon and can be used as a tracer of carbon flow in a marine system (Fry and Sherr, 1984). The $\delta^{13}C$ signatures of the GOM TOC on aerosols generally showed a trend of enriched $\delta^{13}C$ in 2010, relative to the $\delta^{13}C$ of 2011, indicating the aerosol carbon across the sampling sites is influenced by the mixing of $\delta^{13}C$-enriched marine OC (Fry and Sherr, 1984). Wet depositions is enriched in bulk and trace OC molecules via vapor scavenging and aerosol washout (Bidleman, 1988). Organic carbon scavenged from the atmosphere by rainwater in coastal areas originates from several different sources, a significant portion of which is fossil fuels and marine OC (Raymond, 2005). The values in our study for rainwater $\delta^{13}C$ (-25.7 ‰ and -23.5 ‰, Appendix C) are within typical values associated with marine versus terrestrial organic material. This suggests a more heterogeneous source for the aerosol-associated carbon than strictly fossil fuels (e.g. methane, crude oil, coal) (-75 ‰ to -27 ‰) or terrestrial plant material (-30 ‰ for C_3 trees and -15 ‰ for C_4 grasses) (Gaines et al., 2009).

Table 2.2. Carbon and select PAH concentrations measured in aerosols in the southeastern United States.

Study Area	Date of Collection	Organic Carbon $\mu g\ m^{-3}$	Black Carbon $\mu g\ m^{-3}$	Carbon References	Pyrene ng m^{-3}	Benzo [*a*] pyrene ng m^{-3}	PAH Reference
Pensacola, FL	April 1999 - January 2000	4.61 ± 0.40	0.86 ± 0.48	Zheng et al., 2002[a]	0.04	0.05	Yu et al., 2004
Gulfport, MS	April 1999 - January 2000	4.06 ± 0.44	0.75 ± 0.49	Zheng et al., 2002[a]	0.02	0.04	Yu et al., 2004
Centreville, AL	April 1999 - January 2000	4.23 ± 0.63	0.50 ± 0.20	Zheng et al., 2002[a]	0.04	0.04	Yu et al., 2004
Atlanta, GA	April 1999 - January 2000	4.38 ± 0.44	1.75 ± 0.70	Zheng et al., 2002[a]	0.12	0.18	Yu et al., 2004
Pensacola, FL	May 2004 - April 2005	3.49	0.23	Ding et al., 2008[b]	-	-	-
Centreville, AL	May 2004 - April 2006	3.85	0.16	Ding et al., 2008[b]	-	-	-
Atlanta, GA	May 2004 - April 2007	6.28	0.65	Ding et al., 2008[b]	-	-	-
EPA, FL	July 2010	4.76 ± 0.04	5.81 ± 0.58	This Study[c]	0.09	0.01	This Study[c]
EPA, FL	July 2011	8.07 ± 2.15	14.06 ± 0.83	This Study[c]	0.03	0.01	This Study[c]
DISL, AL	July 2010	4.64 ± 2.14	8.03 ± 1.35	This Study[c]	0.02	0	This Study[c]
DISL, AL	July 2011	2.64 ± 2.65	5.48 ± 0.19	This Study[c]	0.04	0.01	This Study[c]
Turtle Cove, LA	July 2010	10.74 ± 0.98	8.90 ± 0.38	This Study[c]	0.02	0	This Study[c]
Turtle Cove	July 2011	2.83 ± 0.83	5.51 ± 0.18	This Study[c]	0.03	0	This Study[c]
GOM, oil burning plume	June 2010	-	150	Perring et al., 2011	-	-	-

[a] Organic and elemental carbon were distinguished using the thermal-optical reflectance (TOR) method

[b] Organic and elemental carbon were distinguished using the thermo-optical transmittance (TOT) method, reported values are a mean concentration

[c] Organic carbon values were calculated from a carbon mixing model and measurements of BC using CTO-375

PAH Distributions

In addition to the carbon data, the PAH data suggest a well-mixed air mass over the coast. Spatially, the PAH distributions are consistent from one sampling location to the next. Similar aerosol PAH distributions and concentrations between 2010 and 2011 suggest a uniform source for background levels of PAHs. The total PAH concentrations measured on aerosols varied from 0.19 ng m^{-3} at DISL in 2010, up to 0.51 ng m^{-3} at Cross Lake, also in 2010. These values are several orders of magnitude lower than what has been measured at urban sampling sites, like Chicago, IL, in which total PAH concentrations (of ~40 PAHs) on GFF were as high as 460 ng m^{-3} (Simcik et al., 1997). The rural sites of that same study contained total PAHs at levels similar to this study, ranging from 0.1 to 1.4 ng m^{-3} (Simcik et al., 1997). This is not surprising because none of our samples were taken directly within an urban center, but rather at sites that could be considered more rural.

Relative abundances of an individual PAH scaled to the total PAH content in a sample can provide a characteristic PAH distribution pattern, which can serve as a fingerprint. The coastal GOM aerosols were dominated by a combination of petroleum PAHs and combustion byproducts, mainly, non-alkylated and alkylated homologs of naphthalene and phenanthrene (2- to 3-ring PAHs). The sources for the PAHs of the air samples can vary from any biomass burn or fuel exhaust, an abundance of which is found in the southeast U.S. due to the presence of the oil industry. Generally, the PAH fingerprints for the coastal sampling sites of this study contain a slightly greater relative abundance of non-combustion aromatics (≤3-ring PAHs), perhaps because of the coastal location and proximity to offshore oil rigs and, even, the *DWH* oil slick.

Window Film Analysis

As previously mentioned, window films have been shown to be passive samplers of atmospheric contaminants, acting to attract and accumulate atmospheric gas-phase compounds (Diamond et al., 2000, Lam et al., 2005). The pure film thickness in an urban setting is measured at a magnitude of nanometers, and the PAH pattern is considered typical of “aged air” (Diamond et al., 2000). For example, organic window films collected in Toronto, ON, Canada that were extracted for a suite of 44 PAHs totaled 2,600 ng m^{-2} on those urban windows (Hodge et al., 2003). That is at least an order of magnitude greater than the sum of PAHs measured at the more rural sampling sites of this study. The total PAH concentrations on window films ranged from 3.36 ng m^{-2} at Lake Okatibbee in 2010, to 250 ng m^{-2} at EPA, also in 2010. The coastal GOM window film data had PAH distributions of the lower molecular weight compounds similar to those extracted from the aerosols at the same sampling locations (Figure 2.7). The greater relative abundance of low molecular weight compounds with respect to high molecular weight compounds extracted from window film samples suggests that these PAHs were depleted because of rapid photooxidation in the gas phase and probable reactivity within the film (Diamond et al., 2000, Simcik et al., 1997).

Naphthalene, phenanthrene, fluoranthene and pyrene were consistently the most abundant PAHs in window films at all sampling locations. In comparison to the aerosol PAH results, these four PAHs were far more abundant than high molecular weight PAHs (chrysene to coronene). Phenanthrene, for example, ranged in relative abundance from 0.1 to 0.4 in window film, but had a lower relative abundance and smaller range of 0.13 to 0.24 on aerosols. This could be due, in part, to breakdown of phenanthrene into smaller compounds by photooxidation, a dominant loss process for PAHs to the atmosphere during atmospheric transport before deposition to window film (Simcik et al., 1997). In Chapter 3 it will be shown that despite PAH loss between aerosol phase and window film phase, the ambient aerosol PAH distributions correlate with PAH distributions on window films isolated at all the locations sampled during calm meteorological conditions. It is therefore reasonable to assume that PAH distributions in window film samples are representative of the aerosols and background air quality of the region.

Coastal Air Quality with Respect to the DWH Oil Spill

The compositional analyses thus far suggest that the transport of aerosol carbonaceous material, including PAHs, from the GOM marine system to the sampling sites in this study, did occur to some extent. The particle back-trajectory analysis (Appendix G) shows aerosols collected at each of the sampling sites may have traveled by way of air masses originating over the GOM. This is complemented by carbon isotope analyses of the aerosol samples showing enrichment of $\delta^{13}C$, characteristic of marine carbon (Fry and Sherr, 1984). Reddy et al. (2011) reported $\delta^{13}C$ values from Macondo-1 well oil in June 2010 at -26.5 ‰ for aromatic hydrocarbons and -27.9 ‰ for saturated hydrocarbons. Hydrocarbon gases were even more depleted in $\delta^{13}C$, up to -57.5 ‰ for methane (Reddy et al., 2011). Thus, the widely ranging $\delta^{13}C$ of the coastal aerosols, as measured in this study (-32 ‰ to -4 ‰, Appendix C) must have been influenced by non-fossil fuel-derived sources, like marine phytoplankton. Otherwise, we would expect the coastal aerosols to be at least as depleted as -27 ‰ (Gaines et al., 2009).

A comparison of the PAH distribution patterns between the *DWH* oil extracts from Chapter 1 and the collected coastal aerosol samples show abundant amounts of low molecular weight PAHs, up to pyrene, rather than the presence of higher molecular weight PAHs. These lower molecular weight compounds have atmospheric residence times of many hours to days

(Pérez et al., 2003) and longer when associated with airborne particulates (Müller, 1984), therefore allowing long-distance travel. But, because the PAH fingerprints for the coastal sampling sites of this study contain a combustion-based suite of aromatics, the PAH fingerprint could be inclusive of diesel exhaust and fires from cities along the coast, and even combustion from *in situ* burning of the *DWH* oil slick as part of spill remediation (National Commission, 2010). The transport of PAHs volatilized from the *DWH* oil slick could be overshadowed by a mixing with other PAH sources in the region into a heterogeneous air mass.

SUMMARY

This study provides carbon data in coastal nGOM and contributes information regarding high molecular weight PAHs not extensively studied in the region. I hypothesized that the concentration of PAHs in the atmosphere in coastal nGOM, U.S. was higher in 2010 versus 2011, due to volatilization of these compounds at the sea surface from the *DWH* oil spill in 2010, and subsequent transport by way of southerly air masses. This hypothesis was not fully supported by the results of the field sampling. It is evident that TSP in the summer in coastal nGOM has increased over the past several decades. However, this may be due to increased oil production in the GOM and the heavy industrialization and population increase in the coastal community. The change in TSP and carbon and PAH loading to air samples between 2010 and 2011 was not significantly different so the amount of input from the *DWH* oil slick is difficult to separate. However, organic matter in air masses marine influence the coastal air quality based on δ^{13}C-enriched aerosol carbon, particle back-trajectory analyses that traced over the nGOM, and the abundance of petroleum-derived PAHs in aerosols and on window films. Taken together, these imply our sampled aerosols were transported from the nGOM and deposited along the U.S. Gulf Coast.

CHAPTER 2 REFERENCES

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CHAPTER 3: MARINE-TO-LAND TRANSPORT OF ATMOSPHERIC POLYCYCLIC AROMATIC HYDROCARBONS FROM THE *DEEPWATER HORIZON* OIL SPILL ENHANCED VIA *TROPICAL STORM BONNIE* (2010)

ABSTRACT

In this chapter I report on the marine-to-land atmospheric transport of polycyclic aromatic hydrocarbons (PAHs) from the *Deepwater Horizon* (*DWH)* oil slick to coastal states of the Gulf of Mexico (GOM) before and after passage of *Tropical Storm Bonnie* (*TS Bonnie*) in July 2010. Using the results from sampling of GOM-facing windows (passive samplers), active sampling (high volume air samplers), and measurements of natural abundances of radiocarbon in rainwater, these results indicate that the marine-to-land transport vector was facilitated by passage of *TS Bonnie* across the *DWH* oil slick. In particular, the total atmospheric PAH loading to window film increased by a factor-of-fifty after the passage of *TS Bonnie*. These tropical storm-enhanced levels of PAHs analyzed on a window film sample were comparable to typical PAH levels detected on windows sampled in inner-city Baltimore, MD suggesting that marine-to-land atmospheric transport may be an important vector for carbon and contaminant loading in coastal locations. These results suggest that as offshore oil exploration continues to expand globally, potential impacts to air quality in coastal locations should be taken into account.

INTRODUCTION

An abundance of research on the global carbon cycle addresses the flux of terrestrial organic material to the oceans, largely due to fluvial processes (Schlunz and Schneider, 2000). However, there have been few studies quantifying the transfer of material from marine systems onto land via atmospheric processes. Such marine-to-land atmospheric processes may be significant in contributing carbon to the terrestrial environment. For example, the net flux of water (continental to ocean water transfer minus ocean to continental transfers) is negative (Raymond, 2005) suggesting that carbon associated with precipitation may be recycled in the atmosphere. In polluted coastal waters, diurnal sea-breezes have been demonstrated to enhance the atmospheric transport of organic contaminants from marine systems to land (Pérez, et al., 2003). Thus, inclusion of the marine-to-land atmospheric transport vector in biogeochemical cycles may help more accurately constrain elemental and nutrient cycles in coastal systems. In that context, hurricanes, with their extensive turbulence may be important channel of marine-to-land atmospheric transport.

The 2010 *Deepwater Horizon* (*DWH*) oil spill resulted from a blowout of the Macondo-1 wellhead that released ~ 5 million barrels of sweet crude oil into the northern Gulf of Mexico (nGOM). By the time the well was capped, the total amount of oil released had spread to an area of 176,000 km^2 (Cleveland et al, 2010). The *DWH* oil spill introduced considerable amounts of relic petroleum hydrocarbons to the water column of the nGOM, an environment that experiences extreme weather events, such as hurricanes (Connor et al., 1989). The GOM is an effective conduit through which atmospheric low-pressure cells pick up warm water and frequently become severe hurricanes that impact the United States Gulf Coast. Observations of enhanced concentrations of organic aerosol- and vapor-phase compounds above the GOM as a result of the *DWH* spill suggest the atmosphere above the GOM was indeed affected by spill-derived hydrocarbons (de Gouw et al., 2011; Middlebrook et al., 2011; Ryerson et al., 2011). For example, a plume of low molecular weight (C1-C6) hydrocarbons was observed downwind of the *DWH* oil spill, with a larger, secondary plume of organic aerosol emitted from the area around the spill (de Gouw et al., 2011). Nonetheless, the atmospheric fate of polycyclic aromatic hydrocarbons (PAHs) associated with the oil spill have yet to be quantified. Concentrations of PAHs in the water column of the GOM after the spill were in the part per billion range (Diercks et al., 2010). The total loading of these fossil hydrocarbons to the water column of the northern GOM, coupled with the potentially high evaporative flux associated with seasonally-warm water temperatures (Harrison et al., 1975, Drivas, 1982, Sebastiao and Soares, 1995, Fingas, 1997, Avens et al., 2011,), and the possibility of hurricane-enhanced transport, led to the question of how much of the atmospheric PAH loading from the spill may have affected air quality in the coastal states of the GOM.

On July 23, 2010, *TS Bonnie* traversed the nGOM, weakening to a tropical depression by the time it made landfall in Louisiana, but bringing up to 12 cm of rain to southern Louisiana (Stewart, 2010). Coupled with the existing surface oil slick, this allowed testing of the hypothesis that marine-to-land transport of *DWH*-derived PAHs may have been intensified as a function of the passage of the storm. A suite of 34 PAHs and measurements of fossil carbon in rainwater were used to determine the net change in PAH loading as a result of their marine-to-land atmospheric transport due to storm activity. Specifically, the concentrations of PAHs were compared in passively- (window film) and actively- collected (high volume air sampler) air samples before and after the passage of *TS Bonnie*. Windows have been shown to be excellent passive samplers for air quality in both rural and urban areas, as gas-phase organics form readily on impervious surfaces, leading to increased deposition of particulate matter (Gingrich et al., 2001; Lam et al., 2005). Moreover, atmospherically-derived window films act like atmospheric particulate matter in that they scavenge atmospheric gas-phase compounds (Lam et al., 2005). Our results suggest that ambient atmospheric PAH concentrations along the Gulf Coast were strongly influenced by *TS Bonnie*.

METHODS

To gain insight into the atmospheric transport of carbon transported landward from the *DWH* oil release, two land-based field campaigns were undertaken in July 2010 and July 2011 in which air samples were collected from several sites along the U.S. Gulf Coast (Figure 3.1). Samples related to *TS Bonnie* were collected at the Turtle Cove Boat Shed and Classroom Facility of Southeastern Louisiana University, hereafter referred to as “Turtle Cove”. Spatially integrated air samples were also collected by deploying a high volume air sampler from the bow area of the R/V *Cape Hatteras* during a 2011 research cruise across the nGOM (Figure 3.1). Samples of *DWH*-derived oil from the slick and the subsurface riser were obtained and analyzed for PAHs (this study, Ch.1). The samples obtained from the field campaigns were extracted for the measurement of 34 PAHs ranging in molecular weight and solubility (discussed in Ch.2). The storm trajectory for *TS Bonnie* was confirmed using the National Oceanic and Atmospheric Association’s HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model, an internet-based trajectory model (Draxler and Rolph, 2003), which traced the 48-hr back-trajectory of atmospheric particulates carried by east-southeasterly storm winds to the windows at the Turtle Cove sampling station (Figure 3.2).

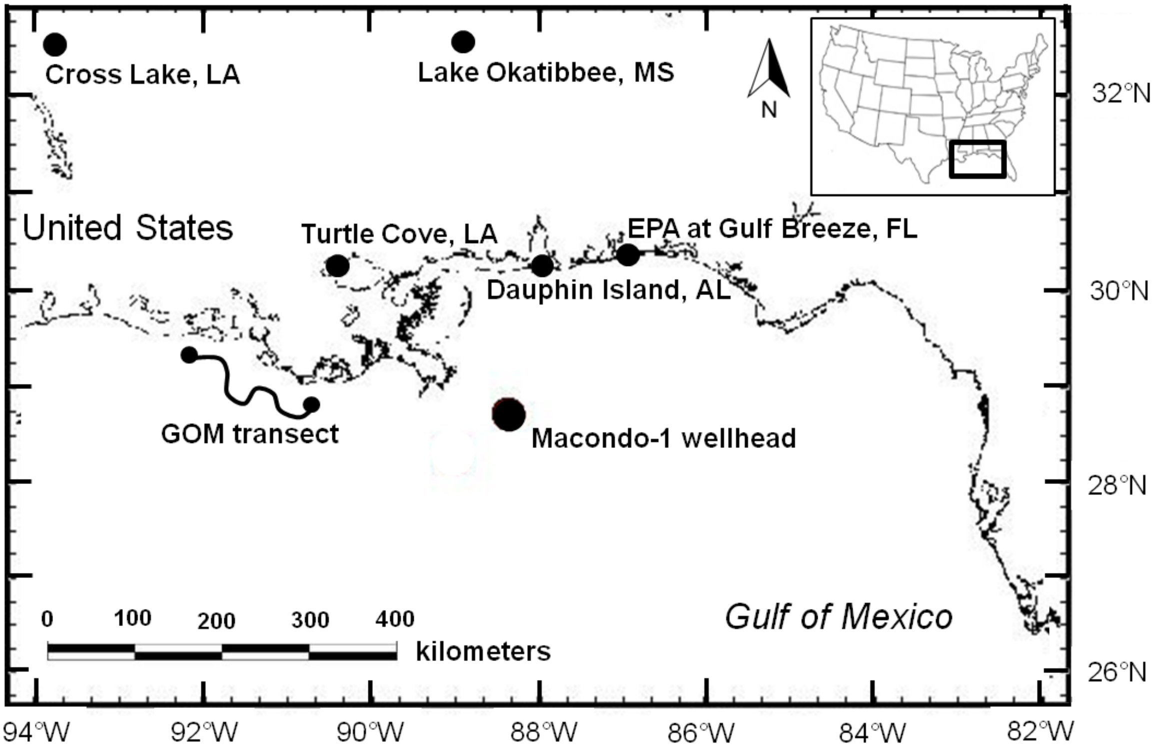

Figure 3.1. Sample location map of the five field sites at which air samples were collected in July 2010 and July 2011. Additional window film was collected at the Turtle Cove site post-*TS Bonnie.* Included is the GOM transect of the R/V *Cape Hatteras* from August 2011 as well as the location of the Macondo-1 wellhead, site of the *DWH* oil spill.

Briefly, window film samples were passively collected by wiping south-facing windows using pre-extracted (refluxed in methylene chloride (DCM) for 24h) laboratory-grade Kimwipes^{TM} (Diamond et al., 2000). These were stored frozen (-20°C) in muffled (450 ^{o}C for 4 hours) Mason Jars lined with muffled aluminum foil. Air samples were actively collected at each field site using a ThermoAndersen Model GS2310 TSP sampler (Smyrna, GA) high volume air sampler. Particulate (aerosol) samples were isolated using two muffled 20.3×25.4 cm (8×10") Gelman Type A/E glass fiber filters; vapor samples were collected on two 8 cm diameter× 7.6 cm long polyurethane foam (PUF) plugs refluxed in GC-grade organic solvents (Dickhut and Gustafson, 1995). The GFFs and PUF plugs were arranged in series in the air sampler in order to minimize compound breakthrough.

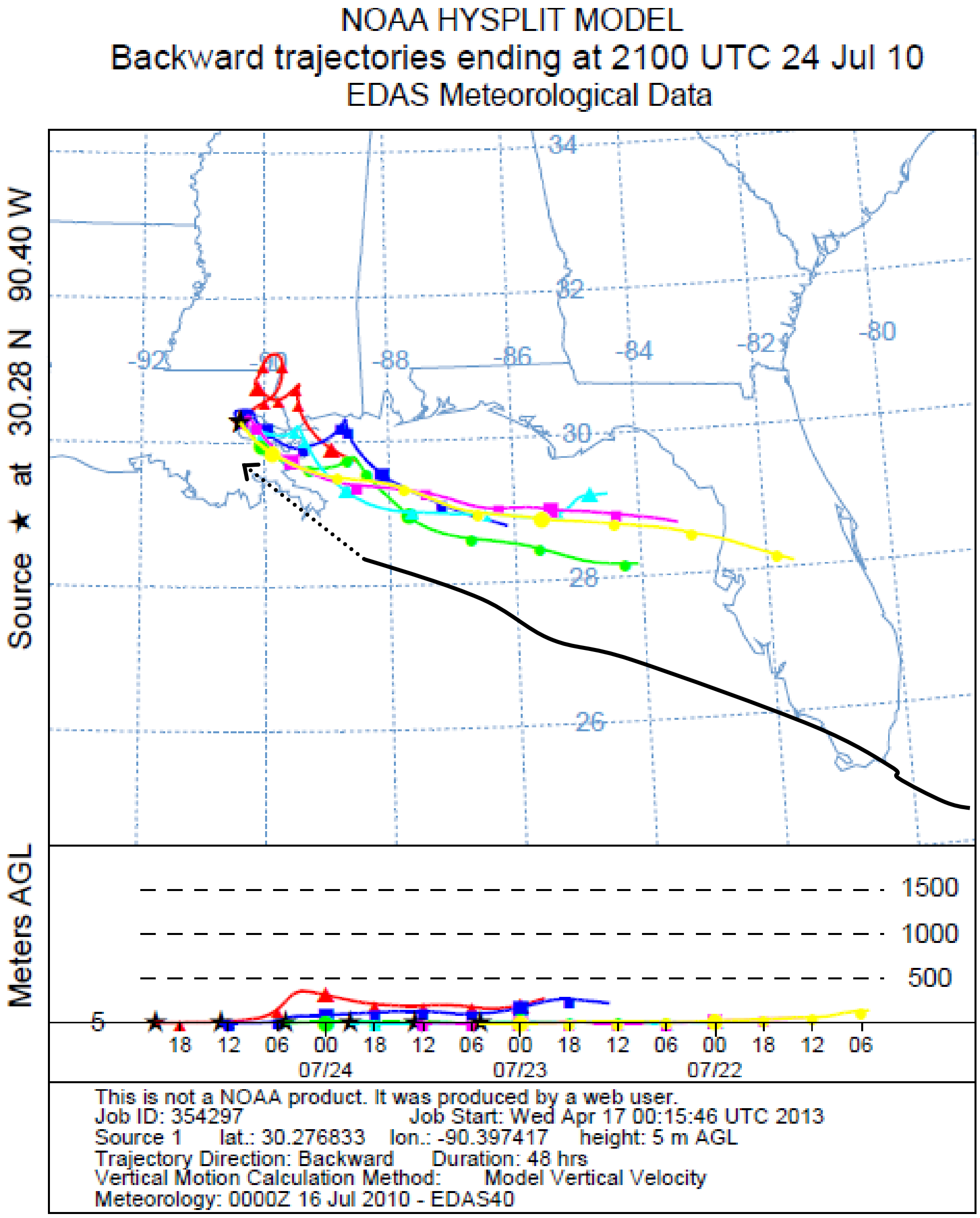

Figure 3.2. Particle back trajectories were calculated using the NOAA HYSPLIT Model (Draxler and Rolph, 2003) for air arriving at the sampling site at every 6 hour time point from the end of the sampling period to 48 h previous. Each trajectory for a given sampling date is denoted by a different color. The bottom panels of each map mark the height in meters above ground level (AGL) of the airmass during its path to the study site. The black line is the track of the eye of *TS Bonnie* west to southern Louisiana (Stewart, 2010) pushing nGOM atmospheric particles onshore.

Carbon sampling and analysis

Rainwater associated with *TS Bonnie* was collected (60 mL) beginning on July 23rd at ~18:00:00 h at the Turtle Cove station and then at 20:00:00h at a hotel parking lot adjacent to the southern side of Lake Pontchartrain. On the morning of July 24th, the samples were retrieved and combined to yield a spatially and temporally-integrated rainwater sample. Rainwater was collected using clean pressure vessels as described previously in Chapter 2.

Rainwater was vacuum filtered through pre-muffled GFFs (42 mm dia., 0.7 μm GFF) placed on top of 47 mm diameter muffled glass filter heads. The filtrate was kept frozen at -20°C until it was shipped on dry ice in a cooler to the Keck Carbon Cycle AMS Facility of the Earth System Science Department, UC Irvine for radiocarbon analysis. Radiocarbon abundances are reported as $\Delta^{14}C$ and conventional radiocarbon age, following the conventions of Stuiver and Polach (1977). Corrections for the mass and $\Delta^{14}C$ value for extraneous carbon were applied. The $\delta^{13}C$ values were measured using light isotope mass spectrometry.

PAH Extraction

All samples were processed for PAHs in the Organic Geochemistry laboratory at East Carolina University, as previously discussed in Chapters 1 and 2. Kimwipes^{TM}, GFFs, and PUF plugs were extracted for PAHs using a Dionex Accelerated Solvent Extractor 350 (ASE-350). Samples were placed in 66 mL or 100 mL sample cells and spiked with 1 mL of deuterated PAH surrogate standard (in acetone). Heated solvent [acetone:hexane cocktail (2:1 v:v)] at 100 ^{o}C was purged through the sample cell over three static cycles of three minutes each and 40% by volume rinse between each static cycle. Polyurethane foam plugs from the air sampler were extracted using a Soxhlet apparatus by refluxing with acetone, DCM, and hexane for 24h each.

The solvent extracts were purified using silica open-column fractionation (Dickhut and Gustafson, 1995) and concentrated by evaporation after adding 1 mL of deuterated PAH internal standard (in hexane). All samples were injected on a Shimadzu QP-2010-S operated in selected ion monitoring (SIM) mode for PAH identification by gas chromatography-mass spectrometry (GC/MS).

Quality Control

All samples were run in batches, with each batch including a lab blank and National Institute of Standards and Technology (NIST) Standard Reference Material (SRM)1941b (Marine Sediment), following the PAH extraction procedures as described above. Data were considered not quantifiable (NQ) if the PAH abundance in a sample was less than twice the abundance in a lab blank, if the recovery of the deuterated surrogate standard compared to the deuterated internal standard was less than 50%, or if PAH concentrations deviated by more than 10% from certified values in the SRM.

Statistical comparisons of PAH distributions were conducted either by linear regression using Sigmaplot© (Systat Software, Inc., San Jose, CA) or by hierarchical cluster analysis using R statistical software version 2.14.0 (©R Foundation for Statistical Computing, 2011). For hierarchical cluster analysis, the matrix of distances was calculated using the dist.prop function in the R library ade4 (Dray and Dufour, 2007); cluster analysis was conducted using the hclust function using Ward's linkage).

RESULTS AND DISCUSSION

Concentrations of PAHs (Figure 3.3) and their relative distributions on window film (Table 3.1) at Turtle Cove vary between pre- and post-*TS Bonnie* window film, with little statistical correlation in PAH distributions (Figure 3.4, r^2=0.20). The pre-*TS Bonnie* window film distribution is enriched in low-molecular weight PAH up to pyrene, but depleted in high molecular weight PAHs (Figure 3.3). In contrast, the post-*TS Bonnie* window film shows a higher abundance of total PAHs with less variation in relative abundance of any of the 34 PAHs extracted (Figure 3.3). The total PAH loading to the window film increased from 181.17 ng m^{-2} before *TS Bonnie* to 9638.12 ng m^{-2} less than 12h after the passage of the storm (Table 3.1). The amount of naphthalene extracted from window film samples from before and after the storm increased from 47.67 ng m^{-2} to 584.90 ng m^{-2}. Similarly, all of the other PAHs in the post-*TS Bonnie* window film are elevated by at least one order of magnitude compared to those measured prior to the storm, with total PAH concentration on the window film at Turtle Cove after passage of *TS Bonnie* as fifty times more abundant than that detected on pre-storm window film.

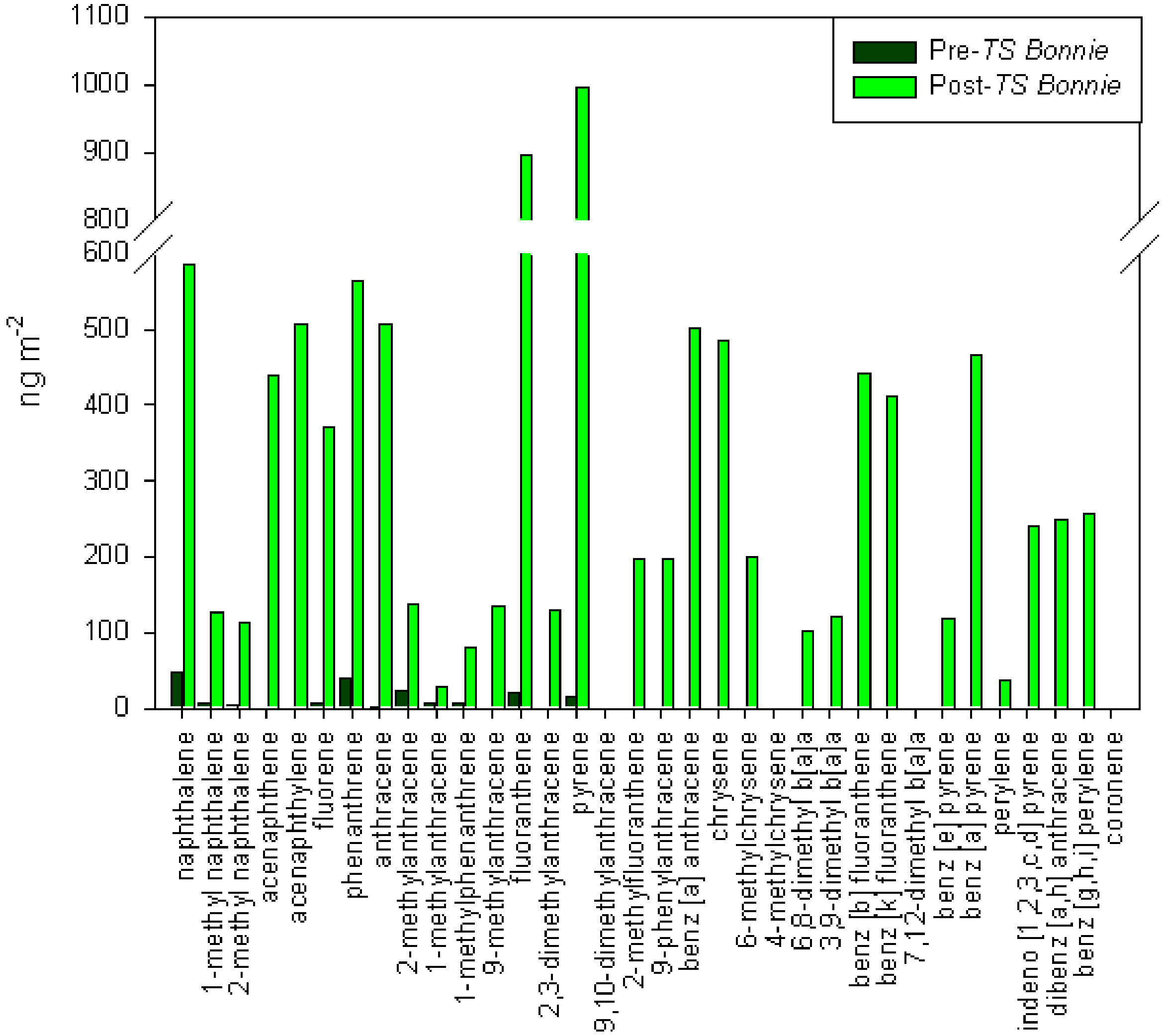

Figure 3.3. Concentrations of PAHs (ng m^{-2}) on window films at the Turtle Cove field station pre-*TS Bonnie* (dark green bars) and post-*TS Bonnie* (light green bars) within 12h of passage. Proceeding left to right, PAHs are listed in order of increasing molecular weight and decreasing vapor pressure.

Table 3.1. Atmospheric and window film PAH concentrations measured at the Turtle Cove Boat Shed and Classroom Facility (Southeastern Louisiana University). The relative abundance ratios are calculated as the measured concentration of the individual PAH to the total PAH per sample (PAH_i/PAH_t).

PAH	Pre-*TS Bonnie* Window Film		Post-*TS Bonnie* Window Film		2010 Aerosol Phase		2011 Aerosol Phase	
	ng m^{-2}	PAH_i/ PAH_t	ng m^{-2}	PAH_i/ PAH_t	ng m^{-3}	PAH_i/ PAH_t	ng m^{-3}	PAH_i/ PAH_t
naphthalene	47.7	0.26	585	0.06	0.05	0.19	0.04	0.14
1-methyl naphthalene	6.53	0.04	126	0.01	0.01	0.04	0.01	0.03
2-methyl naphthalene	4.38	0.02	114	0.01	0.01	0.03	0.00	0.02
acenaphthene	0.00	0.00	440	0.05	0.00	0.00	0.00	0.00
acenaphthylene	0.00	0.00	506	0.05	0.00	0.02	0.00	0.01
fluorene	6.92	0.04	372	0.04	0.01	0.05	0.01	0.03
phenanthrene	39.0	0.22	563	0.06	0.06	0.24	0.04	0.17
anthracene	2.56	0.01	506	0.05	0.00	0.01	0.00	0.01
2-methylanthracene	23.6	0.13	138	0.01	0.02	0.08	0.01	0.04
1-methylanthracene	6.91	0.04	28.9	0.00	0.01	0.02	0.00	0.01
1-methylphenanthrene	7.42	0.04	81.1	0.01	0.01	0.02	0.00	0.01
9-methylanthracene	0.00	0.00	135	0.01	0.00	0.00	0.00	0.00
fluoranthene	20.0	0.11	896	0.09	0.02	0.09	0.04	0.14
2,3-dimethylanthracene	0.00	0.00	128	0.01	0.00	0.00	0.00	0.00
pyrene	16.2	0.09	995	0.10	0.02	0.09	0.03	0.13
9,10-dimethylanthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.03
2-methylfluoranthene	0.00	0.00	197	0.02	0.00	0.00	0.00	0.00
9-phenylanthracene	0.00	0.00	198	0.02	0.00	0.00	0.00	0.00
benz [*a*] anthracene	0.00	0.00	501	0.05	0.00	0.02	0.01	0.02
chrysene	0.00	0.00	486	0.05	0.01	0.03	0.02	0.08
6-methylchrysene	0.00	0.00	199	0.02	0.00	0.00	0.00	0.00
4-methylchrysene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6,8-dimethyl benz [*a*] anthracene	0.00	0.00	102	0.01	0.00	0.00	0.00	0.00
3,9-dimethyl benz [*a*] anthracene	0.00	0.00	122	0.01	0.00	0.00	0.00	0.00
benz [*b*] fluoranthene	0.00	0.00	443	0.05	0.01	0.03	0.01	0.03
benz [*k*] fluoranthene	0.00	0.00	411	0.04	0.00	0.01	0.00	0.01
7,12-dimethyl benz [*a*] anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
benz [*e*] pyrene	0.00	0.00	119	0.01	0.00	0.01	0.00	0.02
benz [*a*] pyrene	0.00	0.00	465	0.05	0.00	0.01	0.00	0.01
perylene	0.00	0.00	36.1	0.00	0.00	0.00	0.00	0.00
indeno (1,2,3-cd) pyrene	0.00	0.00	239	0.02	0.00	0.00	0.00	0.01
dibenz [*a*,*h*] anthracene	0.00	0.00	248	0.03	0.00	0.00	0.00	0.00
benz [*g*,*h*,*i*] perylene	0.00	0.00	256	0.03	0.00	0.00	0.01	0.04
coronene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
∑PAH (calc) ->	181		9630		0.25		0.26	

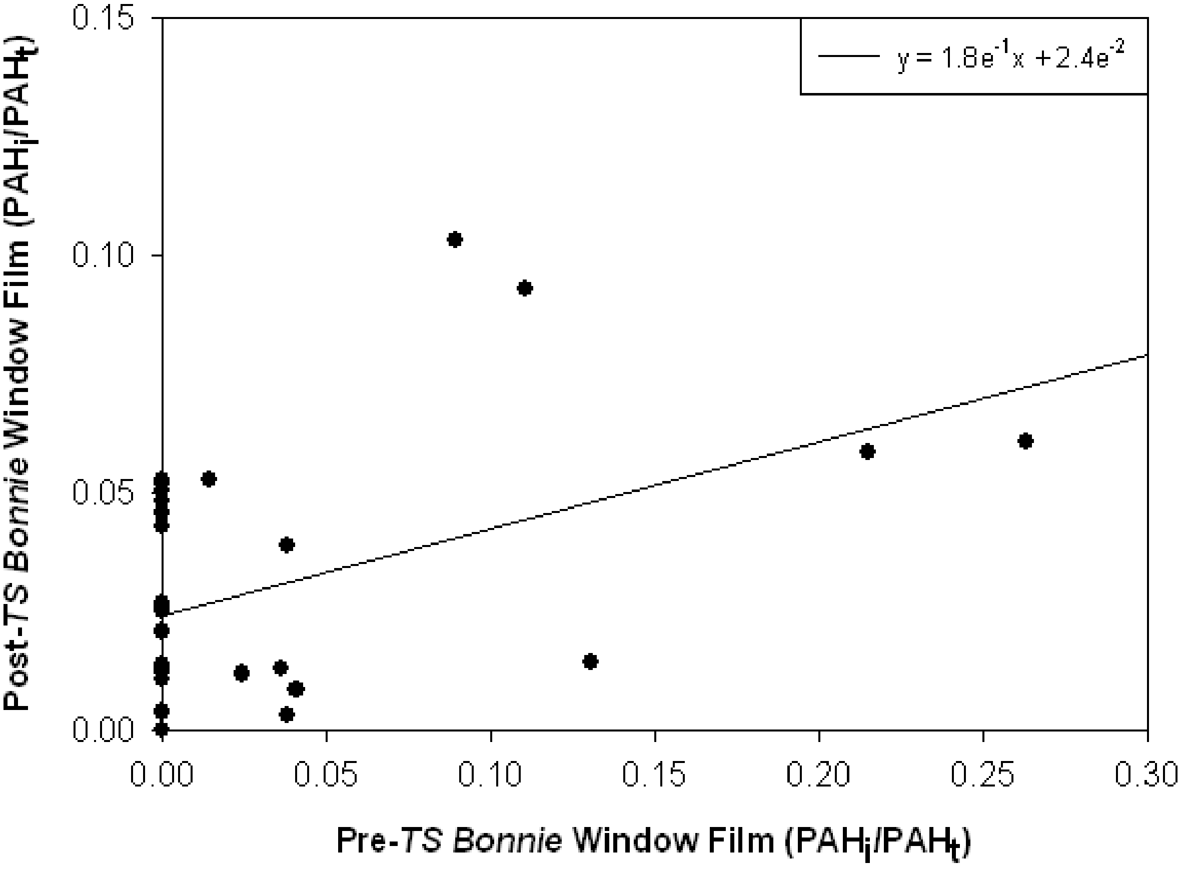

Figure 3.4. The simple linear regression between the relative abundance ratios (PAH_i/PAH_t) of the individual PAH (PAH_i) to the total PAH (PAH_t) of the PAH distributions measured on pre- and post-*TS Bonnie* window film (x-axis and y-axis, respectively) shows a poor correlation ($r^2 = 0.20$).

The uniform PAH distributions on the post-*TS Bonnie* window film appears to be independent of PAH molecular weight and merits further discussion. Window films tend to act as passive samplers by scavenging low molecular weight and high vapor pressure compounds from the vapor phase (Diamond et al., 2000). In general, PAHs in the vapor-phase of the ambient atmosphere are relatively enriched in low-to-mid molecular weight hydrophobic organic compounds and characteristically bereft of high molecular weight compounds (Gustafson and Dickhut, 1997). Distributions of so many PAHs, irrespective of molecular weight as observed after passage of *TS Bonnie*, suggest that these compounds did not exclusively sorb onto the window film from the vapor phase. In order for high molecular weight PAHs to sorb onto window film, the flux of PAHs to the windows must be driven by turbulent processes that are independent of diffusive vapor-phase scavenging by direct aerosol impact onto window films. This would occur through dry or wet deposition and accounts for why the concentrations are so high for the entire suite of extracted PAHs from post-*TS Bonnie* window film.

The radiocarbon content of rainwater collected at Turtle Cove (Δ^{14}C of -629 ± 6 ‰ and -695 ± 25 ‰; Table 3.2) suggests that dissolved organic carbon (DOC) in *TS Bonnie* was radiocarbon depleted, with an age of 7960 ± 130 and 9530 ± 660 years before present. Two other studies have noted that marine rainwater DOC contains fossil carbon, presumably resulting from desorption of aged material from fossil-fuel derived aerosols or scavenging of fossil-fuel derived vapors (Raymond, 2005, Avery et al., 2006). Certainly urban fossil fuel aerosols from the New Orleans area could have been blown onto the windows as urban aerosols have been shown to be fossil in age (Masiello et al., 2002). Although aerosol PAHs in urban areas may be sufficiently enriched (Simcik et al., 1998) and lead to the observed loading on window films post-*TS Bonnie*, leaching of radiocarbon-dead, water-soluble organic carbon from such aerosols into rainwater could have been ultimately responsible for our observed fossil radiocarbon values in the *TS Bonnie* rainwater (Wozniak et al., 2012).

Table 3.2. Isotopic carbon analyses of *Tropical Storm* (*TS*) *Bonnie* rainwater DOC and hydrocarbons from the *Deepwater Horizon* (*DWH*) oil release.

	DOC (μM)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	^{14}C age (y BP)
TS Bonnie Rainwater (Rep 1)	2,180 ± 270	-25.7	-629 ± 6	7,960 ± 130
TS Bonnie Rainwater (Rep 2)	1,250 ± 300	-23.5	-695 ± 25	9,530 ± 660
Saturated hydrocarbons*		-27.9		
Aromatic hydrocarbons*		-26.5		

*Reddy et al., 2011

Unfortunately we have no actively-collected air samples from during *TS Bonnie* due to potential water damage to the high volume air sampler should it be deployed during a storm surge. However, distributions of PAHs associated with aerosols collected at non-storm times in 2010 as well as 2011 are similar to each other throughout the nGOM coast and on an oceanic transect in the GOM (Figure 3.5), providing a PAH fingerprint of a typical summertime ambient environment. Non-storm aerosol samples are enriched in the lower molecular PAHs, primarily naphthalene, phenanthrene, fluoranthene and pyrene and are relatively depleted in the higher molecular weight PAHs. In contrast, the vapor phase PAH distribution at Turtle Cove prior to *TS Bonnie* was relatively enriched in mid-molecular weight PAHs of phenanthrene through pyrene (Figure 3.5), an observation consistent with other studies of vapor phase PAHs in coastal environments (Gustafson and Dickhut, 1997, Cortes et al., 1999). The consistency in the relatively high abundance of low molecular weight PAHs on aerosols irrespective of sampling locations suggests a uniform source of these background levels of PAHs. Furthermore, ambient aerosol distributions correlate with their distributions on window films isolated at all the locations sampled in the U.S. Gulf Coast during non-storm periods ($r^2 = 0.63$, Figure 3.6). Thus, it is reasonable to assume that the contrasting PAH distributions in the post-*TS Bonnie* window film (Figure 3.2) is representative of the aerosols and air quality associated with a discrete event, such as passage of a storm.

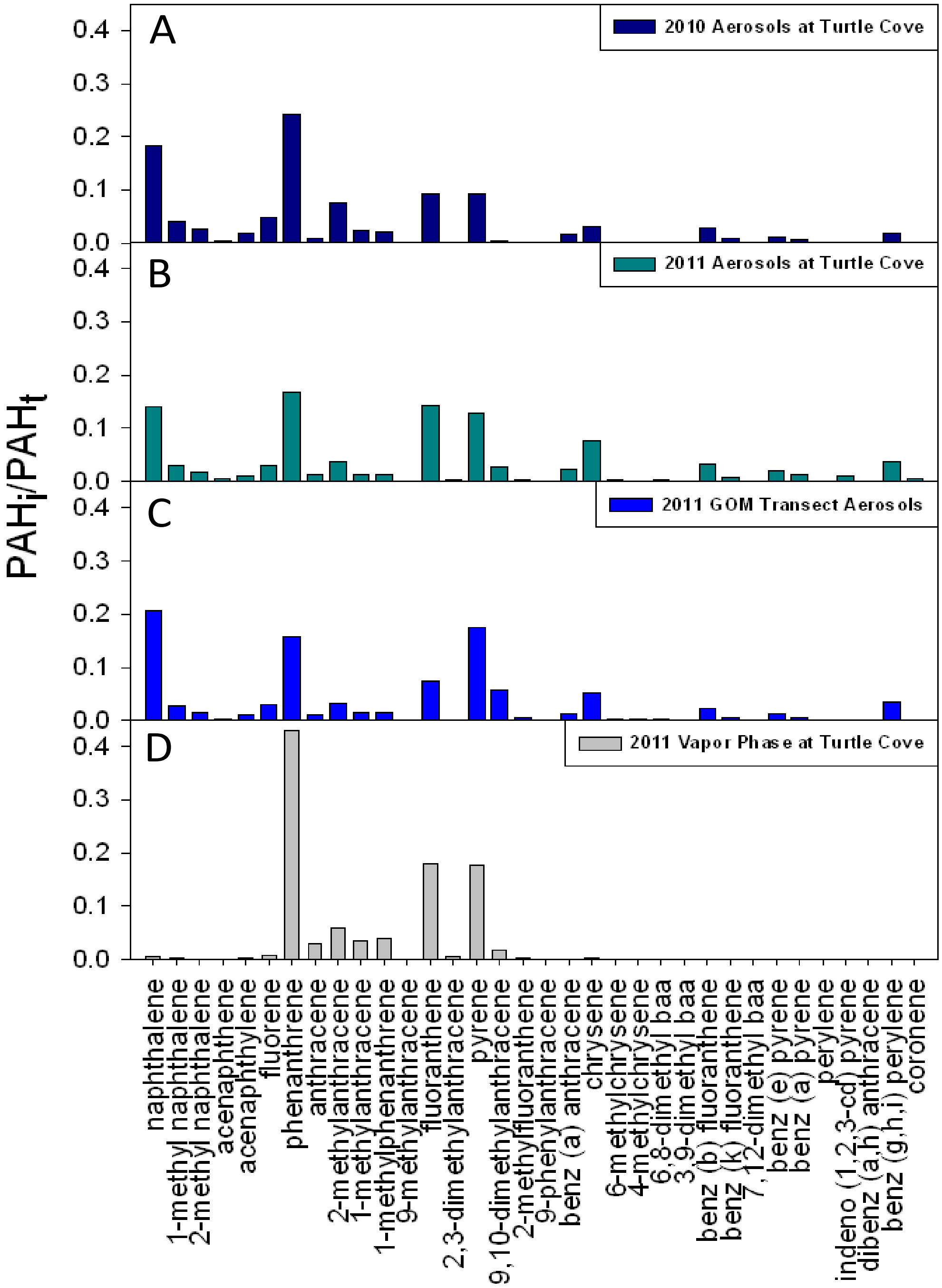

Figure 3.5. Plotted in these histograms are the relative abundance ratios (PAH$_i$/PAH$_t$) of the PAH distributions for A) aerosols collected in July 2010 at the Turtle Cove sampling site prior to *TS Bonnie*, B) aerosols collected in July 2011at the same location at Turtle Cove when there was not the *DWH* oil slick present in the nGOM nor the passage of a storm, C) aerosols collected on a shipboard transect along the nGOM in August 2011, and D) in the vapor phase at Turtle Cove, collected in July 2011. Compound molecular weight increases proceeding from left to right.

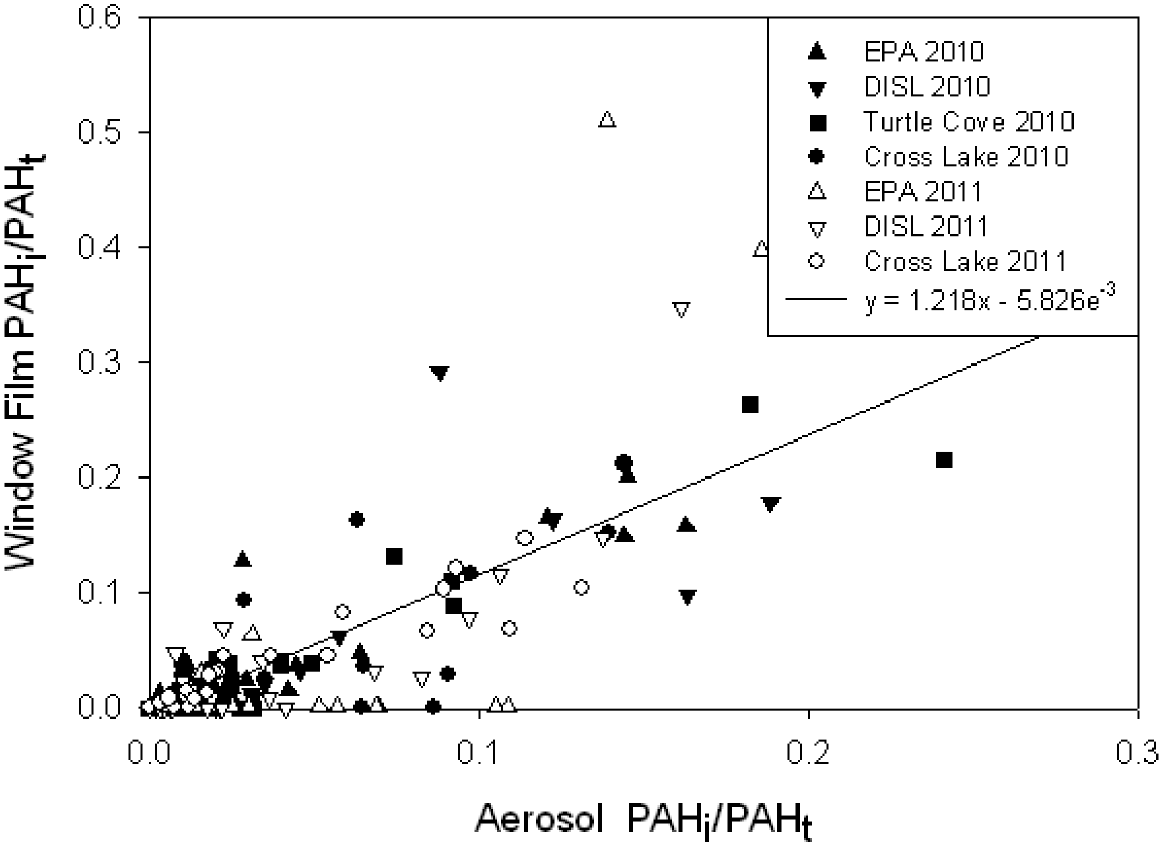

Figure 3.6. A linear relationship between ($r^2 = 0.63$) between the relative abundance ratios (PAH_i/PAH_t) of the individual PAH (PAH_i) to the total PAH (PAH_t) of the distributions measured on aerosols from the high volume air sampler (x-axis) and the corresponding window film samples from each sampling site (y-axis) shows the window film PAH distributions can be a good representative of the aerosol PAH distributions.

It is appears that our observed PAH distributions coupled with fossil radiocarbon values of rainwater DOC, both associated with the passage of *TS Bonnie*, are the result of the surface slick of *DWH* oil from the accident in the GOM. The distance between the slick and Turtle Cove (~250 km) is short enough to allow for the transport of lower molecular weight *DWH*-derived hydrocarbons to be transported (Ryerson et al., 2011). This explanation is plausible for several reasons. First, the average $\delta^{13}C_{DOC}$ for *TS Bonni*e rainwater (-24.6 ‰) was within 2 ‰ of the $\delta^{13}C$ of the aromatic hydrocarbons in the *DWH* riser oil leaking in the GOM (Reddy et al., 2011).

The mass transfer of oil-derived hydrocarbons from water to air during spills is directly related to wind speed (Sebastiao and Soares, 1995). Although *TS Bonnie* was degraded to a tropical depression by the 23rd of July, its wind speeds across the nGOM were documented to have been greater than 74 km h^{-1} (Stewart, 2010) and wind vectors were from the east-southeast (over the *DWH* oil slick) to make landfall in southern Louisiana (Weather Prediction Center, 2013). Wind speeds of this magnitude are sufficient to cause enough turbulence in the water column of the GOM such that oil droplets could become entrained in the atmosphere above the ocean (Fingas, 1998).

Second, PAH isomer (different structural compounds with the same molecular formula) ratios on the window film after passage of *TS Bonnie* may be petrogenic. Ratios of fluoranthene/(fluoranthene+pyrene) [flu/flu+pyr] in the window film samples prior to *TS Bonnie* were 0.56 while post-*TS Bonnie* window film ratios of the same isomers were 0.47; a value of [flu/flu+pyr] less than 0.5 is associated with PAH distributions originating from a petrogenic source (Yunker et al., 2002). Furthermore, the ratio of phenanthrene:anthracene on window film changes from 15.2 to 1.11 after passage of *TS Bonnie* (Table 3.1). Anthracene, a more photoreactive isomer compared to phenanthrene (Mackay et al., 1992), would decrease in relative abundance compared to phenanthrene with greater exposure to sunlight. Thus, a ratio of phenanthrene:anthracene close to unity suggests minimal photolytic transformation as expected for a fairly rapid aerosol transit time with minimal exposure to sunlight. Lastly, the post-*TS Bonnie* window film sample contains a relatively greater abundance of alkylated PAHs, commonly associated with petrogenic processes (Mai et al., 2003; Khairy and Lohmann, 2012). These observations, coupled with the hydrocarbon loading and overall PAH distribution patterns to the Turtle Cove window, suggest that *TS Bonnie* may have enhanced the potential marine-to-land transport of nGOM-derived fossil carbon and PAHs, likely including *DWH*-derived PAHs to the nGOM coast.

Consequently, some studies have been performed to examine and quantify the gas flux of volatile hydrocarbon (C1-C6) compounds to the atmosphere above the nGOM in comparison to the abundance of those hydrocarbons in the *DWH* oil slick (de Gouw et al., 2011; Middlebrook et al., 2011; Ryerson et al., 2011). In this study, the PAH concentrations of the *DWH* subsurface oil extract (Chapter 1, Table 1.1) and of the coastal air samples we collected both show abundant amounts of low molecular PAHs up to pyrene in contrast to higher molecular weight PAHs. In an effort to quantify the volatilization flux of these low molecular weight PAHs from the oil slick, a simple two-film model for air-water partition of PAHs (i.e. Henry's Law) was applied. The PAH concentrations within an air mass residing over the oil slick, taking into account two-phase partitioning are in a different hierarchical cluster from the PAH distributions on the window film after passage of *TS Bonnie* (Figure 3.7). This may be why the PAH distributions patterns of the coastal air samples and *DWH* oil extracts do not match. However, this is not surprising as the application of a two-phase partitioning model to explain air-water partitioning assumes a steady-state and calm meteorological regime. Of course, this was not the case for *TS Bonnie*, in which wind speeds exceeding 74 km h^{-1} can result in whitecaps and moderate wave activity (Stewart, 2010). Due to turbulence of the sea surface, particles could easily be picked up, transported to, and deposited on windows along the nGOM coast.

Isomer-air partition and air-film coefficients of PAHs are comparable to one another (Diamond et al., 2000) therefore, window film is an accurate representation of the gas-phase concentrations in an air mass. Window films are in a dynamic equilibrium with constant volatilization and deposition of high vapor pressure compounds distributing between the film and gas-phase in the air. The post-*TS Bonnie* window film may have lost low molecular weight gas-phase PAH to the atmosphere due to diffusion and/or wash-off during the time between the passage of the storm and our window sampling (~ 12h). Thus, despite the results of the hierarchical cluster analysis, the window film at Turtle Cove may still have been influenced by PAHs from the *DWH* oil slick.

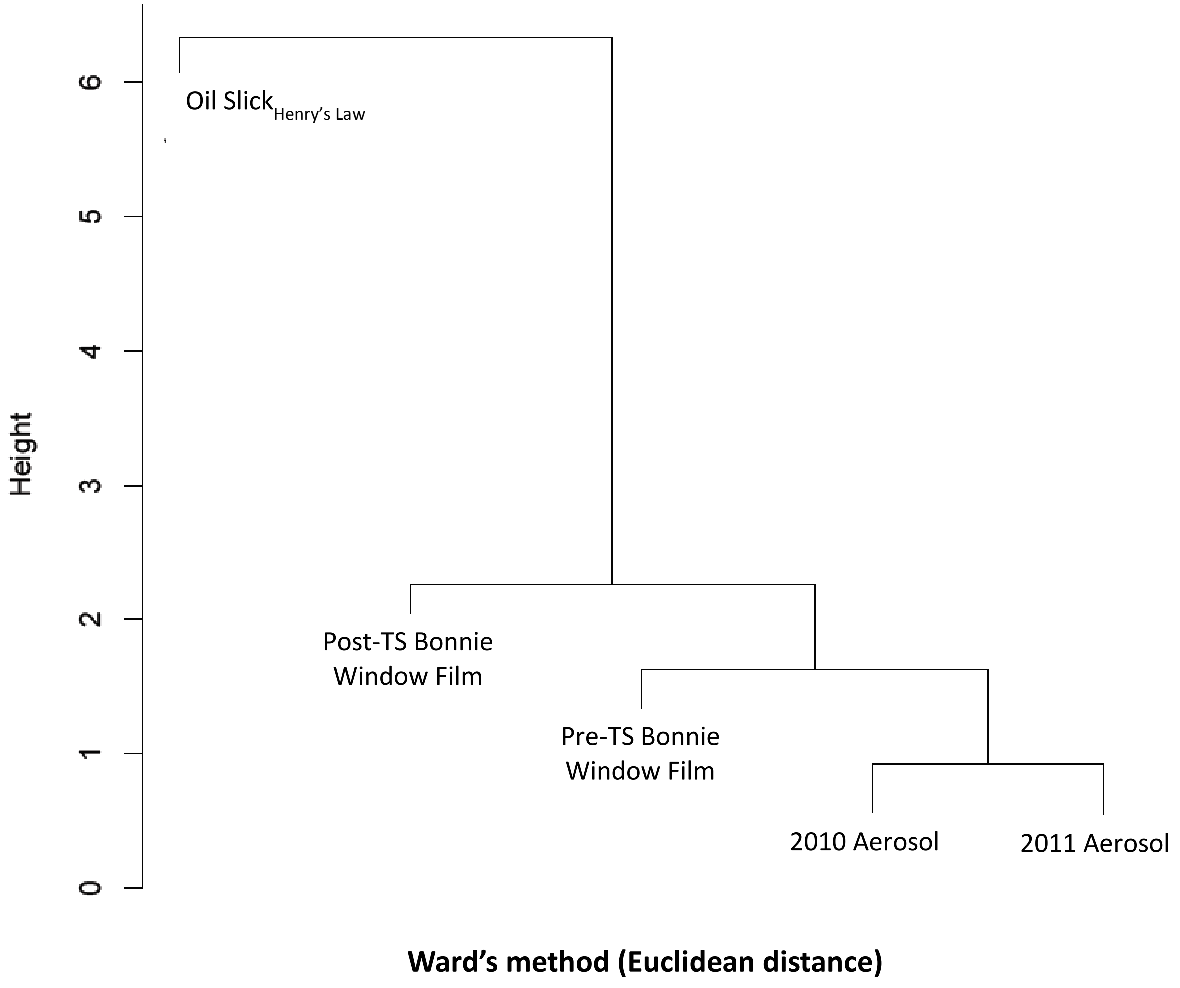

Figure 3.7. In the hierarchical cluster analysis the PAH distributions from the 2010 and 2011 sampling campaigns at Turtle Cove cluster together and are most similar to pre-*TS Bonnie* window film at the same site. The PAH distribution pattern from atmosphere above oil slick calculated with respect to Henry's Law is the most dissimilar from the aerosol PAHs at Turtle Cove.

Nevertheless, window film sampling for trace organic compounds is a research practice used to compare rural and urban gradients in air quality (Gingrich et al., 2001; Butt et al., 2004). The levels of PAHs associated with the window film at Turtle Cove (a rural setting) after the passage of *TS Bonnie* are comparable to those measured on window film in urban Baltimore, MD (Liu et al., 2003). For example, loadings of ΣPAH to window films in inner-city Baltimore, MD were ~4270 ng m^{-2} and 9453 ng m^{-2} (Liu et al., 2003). The post-*TS Bonnie* window film ΣPAH loading was ~8000 ng m^{-2} in our study, although our ΣPAH comprised only 18 of the 20 PAHs noted in Liu et al. (2003). This suggests that a disruption in the wind regime can drastically alter air quality in a coastal area. In comparison to minimum exposure limits set by the EPA, these values are not an acute health concern to the average person. For example, extrapolation of air volume results to window films suggests that the concentration of anthracene would have to be two orders of magnitude greater (from 506 ng m^{-2} to 0.03 mg m^{-2}) in order to place an individual at risk for adverse health effects from acute exposure (Agency for Toxic Substances and Disease Registry, 1995). However, that is not to say there is no health risk from enhanced PAH exposure at these levels for longer duration.

SUMMARY

Ambient PAH concentrations along the nGOM coastal region are seasonally consistent but influenced by distinct shifts in air mass origin. Specifically in 2010, there was a significant difference in PAH loading to the ambient air composition between before and after the passage of *TS Bonnie*. This was demonstrated by our window film sampling, a method that is an excellent marker of ambient PAH and passive sampler meteorological events. Moreover, these window film results are relevant for public health, as PAHs in the extracts of the natural window film formed in urban areas (via vapor phase exchanges with the atmosphere) have been shown to exert teratogenic effects and alter gene expression in vertebrate organisms (Diamond et al., 2000; Hodge et al., 2003). In light of the increasing trends in offshore oil exploration, the toxic and carcinogenic PAHs that originate from potential oil spills (National Research Council, 2003; Reddy et al., 2011), and the seasonally-driven winds in temperate coastal areas, we suggest that air quality in coastal areas be monitored at more frequent time intervals, especially associated with hurricanes and other coastal storms.

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OVERALL SUMMARY

This study focuses on the *Deepwater Horizon* (*DWH*) oil spill of 2010, the largest accidental oil spill in United States history, which caused widespread damage to the coastal habitat of the northern Gulf of Mexico (nGOM) coast of the United States. It is important to identify *DWH*-specific products distributed throughout the nGOM resulting from the spill for an accurate assessment of environmental consequences for the region.

The fate of oil transported in the marine environment depends on factors including composition, source, depth of release to the water column and weathering. One group of chemicals found in oil, polycyclic aromatic hydrocarbons (PAHs), has been used to fingerprint oil and subsequently trace its path through the environment. I analyzed a suite of 34 PAHs in various oil samples, including the *DWH* subsurface riser, the *DWH* surface slick, GOM natural seep oil, and various oils from the Santa Barbara Channel, CA to establish a unique PAH fingerprint of the DWH oil by chromatographic data processing and multivariate data analysis. The results of the PAH extraction for chemical fingerprinting revealed that the abundance of the low-molecular weight compounds within the *DWH* oil is much lower in samples from the surface slick in the nGOM compared with the *DWH* subsurface oil obtained from the riser. A hierarchical cluster analysis showed that the PAH distributions for the *DWH* oil was dissimilar from the oil samples of other origin, suggesting a unique *DWH* PAH fingerprint.

The next step was to make an assessment of the nGOM coast air composition to determine what effect, if any the *DWH* oil spill had on the air composition of the region. I hypothesized that the concentration of PAHs in the atmosphere in coastal nGOM, U.S. was higher in 2010 versus 2011, due to volatilization and transport of these compounds from the *DWH* oil spill by way of southerly air masses. Active and passive air samples were collected using a high volume air sampler and organic films on south-facing windows in the coastal states of the nGOM in July 2010 while the *DWH* oil slick was present and again in July 2011 when the oil slick was no longer present. Bulk carbon and PAHs were quantified in aerosols at each of the five sampling locations: Gulf Breeze, FL, Dauphin Island, AL, Turtle Cove, LA, Cross Lake, LA, and Lake Okatibbee, MS. In general, the actively collected aerosols were more enriched in organic carbon (OC) and black carbon (BC) in 2010 than in 2011 and were enriched in low molecular weight, high vapor pressure PAHs at all sampling locations during both weeks of sampling.

In contrast, the PAHs extracted from window films showed a slightly different PAH distribution from the aerosols in that the higher molecular weight PAHs were less abundant on window films, likely due to the weathering of PAHs through rapid photooxidation. Regardless, organic films on windows are an easy and excellent marker of ambient air composition. Coupled with the PAH distributions extracted from aerosols sampled with the high volume air sampler, the window film PAH distributions between the two summers suggests a uniform source for background levels of PAHs across the nGOM coast. While this conclusion does not fully support the hypothesis that the *DWH* oil slick influenced air masses in 2010, three pieces of evidence suggest a regular marine influence (which would be inclusive of the *DWH* oil slick) on the coastal air quality: the C-enriched aerosols, particle back-trajectory analyses that traced over the nGOM, and the abundance of oil-derived (lower molecular weight) PAHs in aerosols and on window films. Thus, our sampled aerosols could easily have traveled from the nGOM and to be deposited along the U.S. Gulf Coast.

Lastly, I report on the marine-to-land atmospheric transport of PAHs to coastal states of the nGOM before and after passage of *Tropical Storm Bonnie* (*TS Bonnie*) in July 2010. Although ambient PAH concentrations along the nGOM coastal region are seasonally consistent, using the results from sampling of GOM-facing windows, high volume air sampling, and measurements of fossil carbon in rainwater, I conclude the marine-to-land transport vector was facilitated by passage of *TS Bonnie* across the *DWH* oil slick. There was a significant difference in PAH loading to the ambient air composition from before and after the passage of *TS Bonnie*. Specifically, total atmospheric PAH loading to window film at the rural sampling station of Turtle Cove increased by a factor-of-fifty post-storm. These tropical storm-enhanced levels of PAHs were comparable to typical PAH levels detected in urban settings on windows sampled in inner-city Baltimore, MD, suggesting that marine-to-land transport through the atmosphere may be an important transport vector for carbon and chemical contaminant loading in coastal locations.