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Spatial and Temporal Extent of a Subsurface Hydrocarbon Intrusion Following the Deepwater Horizon Blowout

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Spatial and Temporal Extent of a Subsurface Hydrocarbon Intrusion Following the *Deepwater Horizon* Blowout

by

Kathleen Murray Watson

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science College of Marine Science University of South Florida

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Keywords: Gulf of Mexico, Oil Spill, PAHs, BTEX

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Dedication

This thesis is dedicated to the families of the 11 men who were victims of the Deepwater Horizon explosion on April 20, 2010, with the hope that such a preventable tragedy will never happen again.
Acknowledgments

This research was made possible in part by a grant from BP/The Gulf of Mexico Research Initiative, \textit{C-IMAGE}, and in part by the von Rosenstiel endowed fellowship through the University of South Florida College of Marine Science.

I thank my committee members, Dr. Isabel Romero, Dr. David Hollander, Dr. Steve Murawski and Dr. Bob Weisberg. Each of you brought a unique perspective that helped shape this research into the project it became. Special thanks are due to my major professor, David Hollander, for his scientific vision and for his realistic but high expectations. Isabel, I owe you a special thank-you for your encouragement, patience, and reassurance that all the hard work would be worth it. I thank the thousands of responders, including employees and volunteers with NOAA, the US EPA, and BP, who were responsible for the collection and analyses of the samples that provided the data for this research. I thank Ben Shorr and Ann Jones at NOAA for their assistance with the NRDA dataset, and Luke McEachron at Florida Fish and Wildlife Research Institute for ArcGIS Spatial Analyst support. I would also like to thank the members of the USF Paleoceanography and Population and Marine Ecosystems labs, for supporting all of my endeavors, both academic and otherwise. Finally, thank you to my parents for instilling in me a love of learning and a drive to succeed.
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Abstract

The Deepwater Horizon (DWH) oil spill in the Gulf of Mexico (GoM) released an estimated 4.9 million barrels of oil between April 20, 2010 and July 15, 2010. An estimated 36% of the oil formed a neutrally buoyant intrusion, containing both dissolved compounds and oil microdroplets, between 1000 and 1300 m depth. This study used geographic information systems software, and data from water samples that were collected as part of the National Resource Damage Assessment (NRDA), to determine that an area of at least 1,600 km² was exposed to DWH oil. Toxic BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds and polycyclic aromatic hydrocarbons (PAHs) reached concentrations 950 and 50 times higher than maximum background concentrations, respectively. BTEX and n-alkane concentrations above pre-2010 values were present through late August, more than a month after the wellhead was capped. This study is the first to examine the DWH intrusion over such a large temporal and spatial extent.

We further estimated that an area between 500 and 1000 km² may have been exposed to harmful PAH concentrations, based on studies of PAH toxicity and U.S. Environmental Protection Agency (EPA) guidelines. We also found evidence of aggregation and deposition of oil near the DWH wellhead, as well as an area of 400 km² where the intrusion may have impinged on the seafloor. While relative rates of dilution, degradation, and deposition in the intrusion are unknown, we have shown evidence that supports two previously proposed processes that may have deposited DWH oil from this deep intrusion onto sediments, where toxic compounds could be resuspended and continue to be bioavailable to benthic organisms.
Introduction

Background on the Deepwater Horizon Blowout

On April 20, 2010, an explosion on the Deepwater Horizon (DWH) drilling rig resulted in a broken riser pipe at a depth of 1520 m, and the release of an estimated 4.9 million barrels (780 million liters) of oil over the next 87 days. Of these, 0.8 million barrels were recovered at the wellhead and 4.1 million barrels were released into the water column. The DWH blowout was unlike other oil spills because an estimated 36% of the oil dissolved or formed microdroplets (<50-90 µm diameter) that were incorporated into the water column, forming a neutrally buoyant subsurface intrusion at 1000–1300 m depth. This hydrocarbon intrusion was identified shortly after the DWH wellhead began leaking, and was estimated to be comprised of 70% dissolved compounds and 30% microdroplets. Hydrocarbons that were not entrained in this intrusion rose to the surface, where they evaporated, remained part of the surface slick, or washed onshore. It is likely that oil was also aggregated into flocculent material at the surface and throughout the water column. This oil-contaminated flocculent material containing planktonic, microbial, and clay particles sank to the seafloor, causing a widespread marine snow event.

Despite many studies confirming the existence of a subsurface intrusion during the spill, limited spatial and temporal information regarding the dynamics of this intrusion have been published to date. Compounds such as low molecular weight alkanes (methane, ethane, propane) and monoaromatics (benzene, toluene, ethylbenzene and total xylenes; collectively known as BTEX), which were 100% entrapped in the intrusion, were observed up to 12.5 and 35 km from...
the wellhead, respectively.\textsuperscript{11–14} Polycyclic aromatic hydrocarbons (PAHs) at toxic concentrations (up to 189 $\mu$g/L) were observed 13 km from the wellhead.\textsuperscript{15} Additionally, oil consumption by petroleum-degrading bacteria resulted in relative oxygen minimum zones in the water column up to 10 km from the wellhead.\textsuperscript{11,12,14,16,17} Other biological impacts were also observed; deep-water coral communities 11 km southwest of the wellhead were covered with a brown flocculent material in December 2010, and benthic faunal abundance and diversity was decreased over an area of 172 km$^2$ around the \textit{DWH} wellhead.\textsuperscript{18,19} Schwing et al. (2013) found a decline in benthic foraminifera density at sites as far as 60 km northeast of the wellhead in 2010. As of 2011, some of these areas had not recovered.\textsuperscript{20}

**Objectives**

The objective of our study was to better define the spatial and temporal chemical composition and fate of the deep subsurface hydrocarbon intrusion (1000–1300 m) that was formed during the \textit{DWH} oil spill. While previous studies showed the existence of the deep subsurface intrusion during 2010, they generally followed a single transect and were limited in spatial and temporal resolution.\textsuperscript{6,11–15,21,22} Our data analysis highlights the areas that were contaminated by elevated BTEX and PAH concentrations during the \textit{DWH} oil spill, using samples collected over an area of 70,000 km$^2$ in the Gulf of Mexico (GoM). This study has examined data collected in every direction from the wellhead, which enabled the estimation of the entire extent of the intrusion. Furthermore, this is the first study to examine water column data collected after July 15, 2010, in order to determine how long elevated hydrocarbon concentrations were detected in the GoM. Results also show which areas were exposed to oil,
including areas where hydrocarbons in the intrusion may have impinged on, or been deposited on, the seafloor and could continue to be bioavailable to benthic organisms.
Methods

Study Site and the Environmental Response Management Application Database

As part of both the Unified Area Command’s response to and the National Resource Damage Assessment (NRDA) of DWH, the U.S. National Oceanic and Atmospheric Administration (NOAA), in collaboration with the U.S. Environmental Protection Agency (EPA), U.S. Coast Guard, the U.S. Department of the Interior, and state agencies, organized and implemented the collection and analysis of GoM water column samples from May through December 2010. Water samples were analyzed for a large suite of oil-related compounds, including PAHs, BTEX, and n-alkanes, and data was uploaded to the Environmental Response Management Application (ERMA) website (http://gomex.erma.noaa.gov/erma.html#x=-88.25810&y=27.03211&z=6&layers). For this study, data was only used from samples that were collected where the water column depth was greater than 1000 m. A total of 590 profiles and 3800 water samples covered approximately 70,000 km$^2$ in the GoM (Figure 1).

The spatial coverage of sampling varied monthly, limiting the temporal resolution of our data analysis. Initial sampling in May–July 2010 was concentrated within a 50 km radius of the wellhead (Figure 1). In August 2010 sampling was broadened to within about 150 km of the wellhead, along with more extensive sampling up to 500 km to the southwest (Figure 1). In October–December 2010, samples were collected near the wellhead and up to 400 km southwest of the wellhead.
Water samples were collected with Go-Flo® or Niskin bottles, and aliquots of 1 to 3.5 L were poured into separate containers for each analytical method. The U.S. EPA analytical methods used were 8015 (Nonhalogenated Organics Using GC/FID Following Solvent Extraction, modified), 8260 (Volatile Organic Compounds by GC/MS, modified), and 8270 (Semivolatile Organic Compounds by GC/MS, modified). Consistent analytical methods, a strict chain of custody, calibration check samples, method blanks, and matrix spike samples assured reliable results. A more detailed explanation of QA/QC protocol can be found in a 2010 Joint Analysis Group report. Study notes for all cruises and analyses are also available on the ERMA website (http://gomex.erca.noaa.gov).

**Figure 1**: Locations of samples collected between 1000 and 1300 m depth from May through December 2010.
Data Analysis

The data used for this study was downloaded on April 24, 2013 and consisted of hydrocarbon (PAH, BTEX, n-alkane) concentrations from all water profiles located in areas where water column depth was greater than 1000 m. Total PAH concentrations were the sum of the following 44 PAHs: Naphthalene, C1-Naphthalenes, C2-Naphthalenes, C3-Naphthalenes, C4-Naphthalenes, Acenaphthylene, Acenaphthene, Fluorene, C1-Fluorenes, C2-Fluorenes, C3-Fluorenes, Anthracene, Phenanthrene, C1-Phenanthrenes/anthracenes, C2-Phenanthrenes/anthracenes, C3-Phenanthrenes/anthracenes, C4-Phenanthrenes/anthracenes, Dibenzothiophene, C1-Dibenzothiophenes, C2-Dibenzothiophenes, C3-Dibenzothiophenes, C4-Dibenzothiophenes, Benzo(b)fluorene, Fluoranthene, Pyrene, C1-Fluoranthenes/pyrenes, C2-Fluoranthenes/pyrenes, C3-Fluoranthenes/pyrenes, C4-Fluoranthenes/pyrenes, Benzo(a)anthracene, Chrysene, C1-Chrysenes, C2-Chrysenes, C3-Chrysenes, C4-Chrysenes, Benzo(b)fluoranthene, Benzo(j+k)fluoranthene, Benzo(a)fluoranthene, Benzo(e)pyrene, Benzo(a)pyrene, Perylene, Indeno(1,2,3-c,d)pyrene, Dibenzo(a,h)anthracene, Benzo(g,h,i)perylene. The compounds used to measure total n-alkane concentrations were C9-40, pristane, phytane, 2,6,10 trimethyldodecane, 2,6,10 trimethyltridecane, and norpristane. Data that was flagged as being contaminated or unusable was removed, and undetected compounds were treated as zeros for the purpose of this study. Most detection limits were between 0.001 and 0.1 µg/L for each compound, and any data with a detection limit greater than 0.1 µg/L that did not have detected hydrocarbon concentrations was excluded in order to avoid showing false negatives. Analytical replicates were averaged, unless one of the results was designated as being unreliable. Only data with a matrix of “whole water” was used—results with any other matrix (e.g., sediment, oil, dissolved fraction, particulate fraction) were excluded.
We used samples that were collected between 1000–1300 m, between May and July, to investigate the spatial distribution of hydrocarbons in the intrusion. Water column spatial visualization was performed with ArcGIS 10.0 Spatial Analyst (ESRI®, Redlands, CA), using BTEX concentrations from water samples to generate an interpolated surface. A kernel density interpolation, which is a type of spline interpolation, was used to determine areas of elevated concentrations relative to background concentrations. The interpolated value for each cell was based on the concentration at nearby sample points, and the default ArcGIS search parameters were used.\textsuperscript{28,29} The 1000 m bathymetric contour line was used as an interpolation boundary, because results for this study are contained within 1000–1300 m depth. Previous studies have shown the spline interpolation method, which fits a smooth surface exactly through each input point, to be appropriate for estimating areas of contamination from pollution.\textsuperscript{30}

**Evaluating Toxicity**

Potential toxicity during the sampling period was assessed using the EPA’s PAH/BTEX benchmark calculation methods.\textsuperscript{31} Based on 96-hour toxicology studies with marine organisms, the EPA has determined an effect concentration (EC\textsubscript{50}; the concentration at which half of the observed organisms exhibit decreased mobility or death) for each PAH and BTEX compound.\textsuperscript{32} Each compound has been assigned a Chronic Potency Divisor (CPD), based on the EC\textsubscript{50} of that compound.\textsuperscript{32} For each compound, the Chronic Potency Ratio (CPR) was calculated by dividing the concentration of that compound by the its CPD. The toxicity of a sample is determined by adding the contribution from each compound (sum of all CPRs in a sample). By definition, samples with a total CPR greater than 1 were above the acceptable EPA limit, meaning that the concentrations were above the 4-day EC\textsubscript{50} for any species.\textsuperscript{31} Because this did not necessarily
address possible chronic, sublethal effects, we also used PAH toxicity data from other studies\textsuperscript{32–36} to predict which areas of the GoM may have been impacted by sublethal PAH exposure. A kernel density (spline) interpolation was used to estimate the total area that may have been exposed to harmful PAH concentrations.

**Calculation of Biodegradation and Source Ratios**

Selected ratios of $n$-alkanes and PAHs were calculated in order to assess the degree of weathering in the intrusion and to compare the hydrocarbon composition to the source oil. We calculated the Carbon Preference Index (CPI; sum of odd $n$-alkanes/sum of even $n$-alkanes) for C\textsubscript{14-35}, C\textsubscript{14-25}, and C\textsubscript{26-35}, because DWH source oil contains abundant $n$-alkanes in the C\textsubscript{14-35} range.\textsuperscript{21} Furthermore, the ratios C17/pristane and C18/phytane were examined as indicators of biodegradation. Weathering of PAHs was investigated using the ratio of low molecular weight (LMW; 2–3 rings) PAHs to high molecular weight (HMW; 4–6 rings) PAHs, as LMW PAHs degrade more quickly than HMW PAHs.\textsuperscript{37–39} PAH weathering was calculated using the conservative biomarker 17\alpha(H),21\beta(H)-Hopane, a molecule that does not typically degrade. Because soluble PAHs such as naphthalenes were preferentially incorporated into the intrusion, samples collected between 1 and 2 km from the wellhead were considered the “source” for hydrocarbons in the intrusion. The following equation, where [PAH\textsubscript{water}] and [Hopane\textsubscript{water}] are the concentrations of those constituents in a sample, and [PAH\textsubscript{source}] and [Hopane\textsubscript{source}] are the average concentrations from samples collected between 1 and 2 km from the wellhead, was used:

$$\% \text{ weathering} = \left(1 - \frac{[\text{PAH}]_{\text{water}}}{[\text{PAH}]_{\text{source}}} * \frac{[\text{Hopane}]_{\text{source}}}{[\text{Hopane}]_{\text{water}}} \right) * 100$$

The PAH source was evaluated by looking at three diagnostic ratios: (1) anthracene / (phenanthrene + anthracene), (2) Parental / Alkylated PAHs, and (3) Pyrogenic Index (PI):
\[ \sum(\text{other 3-6 ring EPA priority PAHs}) / \sum(5 \text{ alkylated PAHs}) \] \textsuperscript{40,41} The five alkylated PAHs are the alkylated compounds of: naphthalene, phenanthrene, dibenzothiophene, fluorene, and chrysene. The “other” 3-6 ring EPA priority PAHs are: biphenyl, acenaphthylene, acenaphthene, anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, and benzo(ghi)perylen. The hydrocarbon composition of the source oil (MC252) was obtained from the BP Gulf Coast Restoration Organization (https://gratis.cloudapp.net; data can also be found at https://gulfsciencedata.bp.com).
Results/Discussion

Temporal Variability of the Intrusion

Monthly water column profiles of BTEX, PAHs, and \( n \)-alkanes revealed the formation and persistence of a deep intrusion at 1000–1300 m depth, as well as increased concentrations in surface waters and throughout the water column (Figure 2). The BTEX compounds were especially concentrated in the intrusion, even though they only made up approximately 4% (by mass) of the liquid source oil, versus \( n \)-alkanes and PAHs, which comprised about 16% and 4%, respectively.\(^{21}\) The preferential incorporation of BTEX into the moving intrusion, which is also evidenced by lower surface concentrations of BTEX compared to PAHs and \( n \)-alkanes (Figure 2), was due to their high aqueous solubility.\(^{21}\)

Of the 708 samples collected between May and August 2010, and between 1000 and 1300 m, 266 contained elevated BTEX concentrations, 90 contained elevated PAH concentrations, and 66 contained elevated \( n \)-alkane concentrations (Figure 2). Large variations were observed among all 708 samples for BTEX (average ± standard deviation: 22.7 ± 50.8 \( \mu g/L \); max: 442.8 \( \mu g/L \)), PAHs (average ± stdev: 2.0 ± 7.1 \( \mu g/L \); max: 70.0 \( \mu g/L \)), and \( n \)-alkanes (average ± stdev: 6.5 ± 24.0 \( \mu g/L \); max: 310.8 \( \mu g/L \)). Within the 266 samples that had elevated BTEX concentrations, the average concentrations for BTEX, PAHs and \( n \)-alkanes were 51.8 ± 66 \( \mu g/L \), 4.0 ± 9.3 \( \mu g/L \), and 11.6 ± 30.6 \( \mu g/L \), respectively. These averages and ranges are comparable to values reported in previous studies. Hazen et al. (2010) found that samples within
10 km of the wellhead had an average BTEX concentration of 139 µg/L, and Camilli et al. (2010) found that samples within 16 km of the wellhead had BTEX concentrations up to 54 µg/L. Diercks et al. (2010) found total PAH concentrations up to 189 µg/L within 13 km of the wellhead.

**Figure 2**: Profiles of all water samples collected within 50 km of the wellhead, where the water depth was ≥ 1000 m, from May–December 2010 (N=2485). Note the break on the x-axis.
Temporal changes in intrusion concentrations and ratios were examined using the sites located within 50 km of the wellhead (Figure 1; N=2485). Large temporal changes in hydrocarbon concentrations were observed in the water column during the studied period (May to December 2010; Figure 2). Elevated BTEX and n-alkane concentrations were present in the water column in August 2010; however, the intrusion was less well-defined, as high BTEX concentrations were present at various depths, not just between 1000 and 1300 m (Figure 2). Ten samples collected between 1000 and 1300 m in August 2010, weeks after the wellhead had been capped, contained elevated BTEX concentrations. These data are summarized in Table 1. Notably, one sample collected 300 km SW of the wellhead on August 21, 2010 had BTEX concentrations of 14.4 µg/L, which is 30 times greater than pre-2010 levels (0.48 µg/L, Table 1). None of the samples collected in August 2010 had elevated PAH or n-alkane concentrations, which may be due to the fact that BTEX compounds were preferentially incorporated into the intrusion, and were therefore present at higher concentrations that took longer to be dispersed.\textsuperscript{21} Furthermore, it is likely that the BTEX compounds were slower to be degraded, and therefore had longer half-lives than the insoluble petroleum hydrocarbons.\textsuperscript{21}

\textbf{Table 1}: 10 samples collected between 1000 and 1300 m in August 2010 contained elevated BTEX concentrations. BDL=below detection limit, N/A=not available.

<table>
<thead>
<tr>
<th>Latitude</th>
<th>Longitude</th>
<th>Date</th>
<th>Depth (m)</th>
<th>Distance/direction from wellhead</th>
<th>BTEX (µg/L)</th>
<th>PAH (µg/L)</th>
<th>n-alkanes (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28°43'24&quot;N</td>
<td>88°19'24&quot;W</td>
<td>8/3/10</td>
<td>1088</td>
<td>5 km E</td>
<td>2.7</td>
<td>0.003</td>
<td>1.3</td>
</tr>
<tr>
<td>28°43'24&quot;N</td>
<td>88°19'24&quot;W</td>
<td>8/3/10</td>
<td>1121</td>
<td>5 km E</td>
<td>3.5</td>
<td>0.03</td>
<td>0.9</td>
</tr>
<tr>
<td>28°43'24&quot;N</td>
<td>88°19'24&quot;W</td>
<td>8/3/10</td>
<td>1297</td>
<td>5 km E</td>
<td>0.8</td>
<td>0.03</td>
<td>1.4</td>
</tr>
<tr>
<td>28°41'49&quot;N</td>
<td>88°13'24&quot;W</td>
<td>8/4/10</td>
<td>1100</td>
<td>17 km ESE</td>
<td>1.4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>28°41'49&quot;N</td>
<td>88°13'24&quot;W</td>
<td>8/4/10</td>
<td>1200</td>
<td>17 km ESE</td>
<td>2.1</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>28°33'5&quot;N</td>
<td>88°35'6&quot;W</td>
<td>8/5/10</td>
<td>1021</td>
<td>34 km SW</td>
<td>0.7</td>
<td>BDL</td>
<td>0.7</td>
</tr>
<tr>
<td>27°26'16&quot;N</td>
<td>90°39'32&quot;W</td>
<td>8/21/10</td>
<td>1119</td>
<td>303 km SW</td>
<td>14.4</td>
<td>0.002</td>
<td>0.8</td>
</tr>
<tr>
<td>27°26'16&quot;N</td>
<td>90°39'32&quot;W</td>
<td>8/21/10</td>
<td>1298</td>
<td>303 km SW</td>
<td>2.5</td>
<td>0.005</td>
<td>0.1</td>
</tr>
<tr>
<td>27°47'28&quot;N</td>
<td>88°55'40&quot;W</td>
<td>8/22/10</td>
<td>1062</td>
<td>135 km SSW</td>
<td>0.5</td>
<td>0.02</td>
<td>0.3</td>
</tr>
<tr>
<td>27°47'28&quot;N</td>
<td>88°55'40&quot;W</td>
<td>8/22/10</td>
<td>1268</td>
<td>135 km SSW</td>
<td>0.8</td>
<td>BDL</td>
<td>0.5</td>
</tr>
</tbody>
</table>
There was no clear intrusion detected during or after September. However, there were elevated concentrations of PAHs and \(n\)-alkanes southwest of the wellhead, but between 1350 and 1600 m depth, just above the seafloor. As these sites are not located by any known seeps (Figure 3), it is possible that the elevated concentrations near the seafloor are a result of oil that was deposited during the \textit{DWH} event and had been resuspended into the water column.

\textbf{Figure 3}: Locations of GoM seeps and sites that had elevated PAH concentrations above the sediment-water interface. Yellow circles are naturally occurring oil seeps (MacDonald et al., http://www.sarsea.org/natural_seapage.html) and red circles are samples that had elevated PAH concentrations between October and December 2010.

Background concentrations of BTEX, PAHs, and \(n\)-alkanes were defined by samples that were collected between October and December 2010 (Figure 1). Between 1000 and 1300 m depth, the mean concentrations of PAHs and BTEX were 0.02 \(\mu\)g/L and 0.01 \(\mu\)g/L, respectively. The maximum concentrations of these compounds were 1.40 \(\mu\)g/L and 0.48 \(\mu\)g/L (Table 2). Gulf
of Mexico hydrocarbon concentrations at other depths, as well as from other references, are also given for comparison.42–46

Table 2: Background mean hydrocarbon concentrations in seawater in the GoM; concentrations in µg/L.

<table>
<thead>
<tr>
<th>Citation</th>
<th>Description</th>
<th>PAHs</th>
<th>BTEX</th>
<th>Alkanes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allan et al., 2012</td>
<td>Bioavailable (dissolved) on LA coast&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mitra et al., 2003</td>
<td>Surface near Mississippi River delta&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom near Mississippi River delta&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wade et al., 1989</td>
<td>570 m depth, near natural seep&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sauer et al., 1978</td>
<td>Surface coastal water&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.020 - 0.45</td>
<td>0.01 - 0.05</td>
<td></td>
</tr>
<tr>
<td>Sauer, 1980</td>
<td>Open ocean—unpolluted&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.02 - 0.07</td>
<td>0.05 - 0.13</td>
<td></td>
</tr>
<tr>
<td>Open ocean—anthropogenic influence&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.04 - 0.13</td>
<td>0.002 - 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coast—unpolluted&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.03</td>
<td></td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Coastal—anthropogenic influence&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.14 - 0.36</td>
<td></td>
<td>0.04 - 0.10</td>
<td></td>
</tr>
<tr>
<td>This study (Oct-Dec 2010)</td>
<td>See Figure 1 for sample locations</td>
<td>mean (max)</td>
<td>mean (max)</td>
<td>mean (max)</td>
</tr>
<tr>
<td>0-100 m depth (N=92)&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>0.02 (1.0)</td>
<td>0.09 (0.25)</td>
<td>0.70 (26)</td>
<td></td>
</tr>
<tr>
<td>100-399 m depth (N=8)&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>0.01 (0.03)</td>
<td>BDL (BDL)</td>
<td>0.87 (4.7)</td>
<td></td>
</tr>
<tr>
<td>400-699 m depth (N=22)&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>0.01 (0.11)</td>
<td>0.045 (0.10)</td>
<td>0.74 (5.5)</td>
<td></td>
</tr>
<tr>
<td>700-999 m depth (N=64)&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>0.02 (0.97)</td>
<td>0.056 (0.21)</td>
<td>0.39 (25)</td>
<td></td>
</tr>
<tr>
<td>1000-1299 m depth (N=110)&lt;sup&gt;e,f&lt;/sup&gt;</td>
<td>0.02 (1.4)</td>
<td>0.060 (0.48)</td>
<td>0.65 (22)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>33 PAHs (including methylated homologs, listed in citation)
<sup>b</sup>17 PAHs (including methylated homologs, listed in citation)
<sup>c</sup>18 PAHs (including methylated homologs, listed in citation)
<sup>d</sup>C<sub>6</sub>-C<sub>14</sub> n-alkanes
<sup>e</sup>44 PAHs (including methylated homologs, listed in Methods section)
<sup>f</sup>37 alkanes (C9-40, pristane, phytane, 2,6,10 trimethyldecane, 2,6,10 trimethyltridecane, norpristane)

The average concentrations of BTEX, PAHs, and n-alkanes in the intrusion were considerably lower in June and July than in May. This may because the Lower Marine Riser Package, which was placed over the wellhead to collect oil, was used from June 3–July 10, 2010.47 All but 11 water samples were collected after the subsurface application of dispersants.
had started on May 17, 2010,\textsuperscript{47} so dispersant use is not an explanation for temporal variability in this dataset.

**Examination of Biodegradation and Source Ratios**

There were also monthly variations in the ratios of PAHs and \textit{n}-alkanes that were used to examine hydrocarbon sources and weathering of the oil in the intrusion (Table 3). Ratios that are traditionally used in spills to confirm the oil source, including An/(An+Phen), Parental PAHs/Alkylated PAHs, and the Pyrogenic Index,\textsuperscript{40} were calculated to investigate their applicability to a deepwater spill. In the 266 samples that had elevated BTEX concentrations, the averages and standard deviations for An/(An+Phen), Parental PAHs/Alkylated PAHs, and the Pyrogenic Index were 0.20 ± 0.36, 0.49 ± 2.5, and 0.07 ± 0.12. The respective values for the source oil were 0.03, 0.13, and 0.02 (Table 3). The large standard deviation for each parameter is a result of the right-skewed data distribution, because the measured range of concentrations included many very small values and relatively few large values. The source oil value of each parameter was within one standard deviation of the values in the intrusion, but the large standard deviations make the values difficult to compare.

It is possible that the ratios were impacted by the presence of terrestrial or marine organic matter, if particles did indeed aggregate and sink through the water column. Furthermore, compounds from pyrogenic oil could have reached surface waters by land runoff from the Mississippi Delta, from emissions from the thousands\textsuperscript{47} of ships in the vicinity of the \textit{DWH} well, or from the hundreds of thousands of barrels of oil that were burned on the surface. These compounds could have sank from surface waters after aggregation with bacteria, phytoplankton, and/or suspended matter.\textsuperscript{9,10} The presence of pyrogenic PAHs would explain the increase in all
three ratios. In addition, these three ratios could each have been affected by the solubilities of individual compounds and by complexation with suspended and dissolved particles in the water column. Finally, it is possible that complex processes that affected the partitioning of oil into the intrusion, including ejection from the wellhead and the formation of microdroplets, altered ratios in the intrusion in a way that is not well-understood.

Indicators of biodegradation, including C17/pristane, C18/phytane, and HMW/LMW PAHs, did show evidence of biodegradation in the intrusion. For each month, the average C17/pristane and C18/phytane values were lower than in the source oil, and HMW PAH/LMW PAH values were higher than in the source oil (Table 3). This supports other studies that have shown the microbial degradation of oil in the GoM during the DWH spill. An increase in the ratio of HMW/LMW PAHs could also be explained by the input of pyrogenic PAHs.

Weathering percentages were calculated for naphthalene and for total PAHs relative to 17α(H),21β(H)-Hopane, a molecule that does not typically biodegrade. The average percent degradation for PAHs and naphthalene was 22.5 ± 98.5 % and -6.8 ± 191 %, respectively. The negative percent degradation for naphthalene suggests that the dissolved, soluble compounds in the intrusion behaved differently than the whole oil microdroplets that contained insoluble compounds such as 17α(H),21β(H)-Hopane. These results suggest that insoluble compounds in microdroplets were depleted faster than the soluble, dissolved compounds. This agrees with the findings of Reddy et al. (2011).
Table 3: Selected concentrations, in µg/L, and ratios of compounds in samples collected within 50 km of the wellhead, between 1000 and 1300 m depth (mean ± standard deviation; N, range).

<table>
<thead>
<tr>
<th>Source Oil</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTEX</td>
<td>99 ± 95</td>
<td>37 ± 46</td>
<td>43 ± 49</td>
<td>1.9 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>61,440</td>
<td>132,233</td>
<td>66,176</td>
<td>6,2.8</td>
</tr>
<tr>
<td>PAH</td>
<td>10.3 ± 14.6</td>
<td>2.0 ± 6.3</td>
<td>2.6 ± 5.1</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>61,70</td>
<td>132,42</td>
<td>66,21</td>
<td>6,0.03</td>
</tr>
<tr>
<td>n-alkanes</td>
<td>27 ± 55</td>
<td>8.1,17.9</td>
<td>5.2 ± 6.9</td>
<td>0.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>61,311</td>
<td>132,124</td>
<td>66,32</td>
<td>6,0.7</td>
</tr>
<tr>
<td>CPI_{14-23}</td>
<td>0.91</td>
<td>1.1 ± 0.3</td>
<td>1.3 ± 0.8</td>
<td>1.4 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>54,2.3</td>
<td>122,4.9</td>
<td>60,4.9</td>
<td>4,4.7</td>
</tr>
<tr>
<td>CPI_{24-35}</td>
<td>0.86</td>
<td>1.0 ± 0.5</td>
<td>1.5 ± 2.9</td>
<td>0.8 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>54,2.6</td>
<td>111,27</td>
<td>60,46</td>
<td>3,1.5</td>
</tr>
<tr>
<td>CPI_{14-35}</td>
<td>0.90</td>
<td>1.0 ± 0.3</td>
<td>1.3 ± 1.3</td>
<td>1.0 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>55,1.8</td>
<td>123,13.4</td>
<td>63,3.5</td>
<td>4,77.4</td>
</tr>
<tr>
<td>CPI_{9-40}</td>
<td>1.1</td>
<td>1.2 ± 0.5</td>
<td>1.9 ± 2.5</td>
<td>1.4 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>55,2.9</td>
<td>124,21</td>
<td>62,4.5</td>
<td>4,27.6</td>
</tr>
<tr>
<td>C17/pristane</td>
<td>1.6</td>
<td>1.0 ± 0.4</td>
<td>0.9 ± 0.5</td>
<td>1.0 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>50,2.2</td>
<td>110,3.5</td>
<td>58,2.4</td>
<td>1,0</td>
</tr>
<tr>
<td>C18/phytane</td>
<td>2.3</td>
<td>1.6 ± 0.5</td>
<td>1.7 ± 0.9</td>
<td>1.7 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>52,2.7</td>
<td>110,7.8</td>
<td>54,3.4</td>
<td>1,0</td>
</tr>
<tr>
<td>HMW/LMW PAH</td>
<td>13.3</td>
<td>29 ± 40</td>
<td>13 ± 38</td>
<td>48 ± 92</td>
</tr>
<tr>
<td></td>
<td>55,240</td>
<td>122,295</td>
<td>63,493</td>
<td>2,115</td>
</tr>
<tr>
<td>An/(An+Phen)</td>
<td>0.03</td>
<td>0.01 ± 0.02</td>
<td>0.4 ± 0.5</td>
<td>0.1 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>45,0.1</td>
<td>58,1</td>
<td>33,1</td>
<td>0</td>
</tr>
<tr>
<td>Parental/alkylated</td>
<td>0.13</td>
<td>0.3 ± 0.5</td>
<td>0.5 ± 3.3</td>
<td>0.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>55,3.8</td>
<td>120,35.9</td>
<td>61,0.8</td>
<td>3,10.9</td>
</tr>
<tr>
<td>PI</td>
<td>0.02</td>
<td>0.06 ± 0.2</td>
<td>0.09 ± 0.1</td>
<td>0.06 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>55,1.2</td>
<td>124,0.9</td>
<td>64,0.5</td>
<td>3,0.2</td>
</tr>
<tr>
<td>% PAH Degradation</td>
<td>-22.6 ± 121</td>
<td>68.1 ± 41.7</td>
<td>6.5 ± 98.6</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>44,557</td>
<td>49,166</td>
<td>25,315</td>
<td>1,0</td>
</tr>
<tr>
<td>% Naphthalene Degradation</td>
<td>-87.5 ± 243</td>
<td>91.7 ± 27</td>
<td>-66.6 ± 190</td>
<td>100</td>
</tr>
</tbody>
</table>

Spatial Extent of the Intrusion

A spatial interpolation of BTEX data from samples collected at the intrusion depth (1000–1300 m) during the spill (through July 15, 2010) indicates a contaminated area of approximately 1600 km², based on background BTEX concentrations (N=548; Table 2, Figure 3). BTEX were used to estimate the total spatial extent of the intrusion because they were the
most concentrated compounds in the intrusion. Insoluble compounds such as PAHs and \( n \)-alkanes were present in the intrusion in lower initial concentrations, and were therefore harder to detect after being diluted. The dissolved BTEX compounds were also more slowly degraded.\textsuperscript{21}

During the spill, elevated concentrations of BTEX compounds were generally predicted anywhere within 10 km of the wellhead, and up to 50 km southwest of and 18 km northeast of the wellhead (Figure 3). However, because more extensive sampling was not done until after the wellhead had stopped leaking, it is difficult to estimate the full extent of the intrusion in the southwest direction. Our results support and expand upon previous studies that documented elevated hydrocarbon concentrations near the DWH wellhead (Table 4). The data confirm that the intrusion was mostly southwest of the wellhead, and that soluble compounds were present in relatively higher concentrations compared to insoluble compounds.\textsuperscript{13,21} This supports the finding that the intrusion was a mixture of both dissolved, soluble hydrocarbons and microdroplets containing soluble and insoluble compounds.\textsuperscript{6} This also agrees with models that showed Gulf of Mexico currents during the spill moving mostly in the southwest and northeast directions.\textsuperscript{53,54} It appears that movement of the oil away from the wellhead was primarily due to advection, as the oil was entrained in moving water.\textsuperscript{21}

![Figure 4: Interpolated surfaces showing predicted BTEX concentrations at 1000–1300 m depth, using data collected from May 10–July 15, 2010.](image)
Table 4: Summary of findings about the *DWH* intrusion between 1000 and 1300 m depth.

<table>
<thead>
<tr>
<th>Date</th>
<th>Methods</th>
<th>BTEX</th>
<th>PAHs</th>
<th>n-alkanes</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>May-December 2010</td>
<td>Water samples analyzed for hydrocarbons using modified EPA methods 8015, 8260, 8270</td>
<td>Concentrations up to 443 µg/L; interpolated area covering 1600 km²</td>
<td>Concentrations up to 70 µg/L; interpolated area covering 800 km²</td>
<td>Concentrations up to 359 µg/L; interpolated area covering 800 km²</td>
</tr>
<tr>
<td>Camilli et al. (2010)</td>
<td>Late May/Early June 2010</td>
<td>Water samples analyzed using gas chromatography</td>
<td>Concentrations above 50 µg/L detected 16 km from wellhead</td>
<td></td>
<td>11 samples with a chronic toxicity ratio &gt; 1</td>
</tr>
<tr>
<td>Diercks et al. (2010)</td>
<td>May 9-16, 2010</td>
<td>In situ profiles of fluorescence and beam attenuation; water samples analyzed for PAHs using GC/MS</td>
<td></td>
<td>Elevated concentrations 13 km SW of wellhead; concentrations up to 189 µg/L</td>
<td></td>
</tr>
<tr>
<td>Hazen et al. (2010)</td>
<td>May 25-June 2, 2010</td>
<td>Collected and analyzed water samples collected within 10 km of wellhead; measured fluorescence (<em>in situ</em>), hydrocarbon concentrations, hydrocarbon concentrations (GC/MS), bacterial richness</td>
<td>Concentrations significantly higher (mean 139 µg/L) than in non-plume samples (mean 0.5 µg/L)</td>
<td>Significantly elevated concentrations of octadecane and <em>n</em>-docosane</td>
<td>Identified 951 bacterial taxa; only 16 γ-Proteobacteria were enriched in the intrusion</td>
</tr>
<tr>
<td>Joye et al. (2011)</td>
<td>May/June 2010</td>
<td>Depth profiles for dissolved oxygen and CDOM; volatile alkanes with head space extraction followed by GC/MS</td>
<td>Concentrations up 78 µg/L detected up to 27 km from wellhead</td>
<td></td>
<td>Methane concentrations 20 km from wellhead were 10-10⁴ times greater than naturally observed</td>
</tr>
<tr>
<td>Reddy et al. (2011)</td>
<td>June 21, 2010</td>
<td>Water samples analyzed using GC/MS</td>
<td>Mass balance of compounds that evaporated (~5%), were in surface slick (~10%), or were incorporated into intrusion (~35%)</td>
<td></td>
<td>CDOM maximum and relative oxygen minimum between 1000-1300 m depth</td>
</tr>
<tr>
<td>Valentine et al. (2010)</td>
<td>June 11-21, 2010</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Potential Toxicity of the Intrusion**

PAHs, which made up 4% (by mass) of the Macondo Well oil,²¹ are environmentally persistent and harmful to organisms via ingestion and absorption through the skin.⁵⁵–⁵⁷
concentrations of PAHs in water can cause accumulation of PAHs in the organism’s hydrophobic phase (lipids), resulting in a disruption of cell membrane function, divergence in gene expression, endocrine disruption, growth inhibition, and shifts in population and ecosystem dynamics.\textsuperscript{57–63} Furthermore, complex indirect effects from oil exposure can cause changes in nutrient and ecosystem dynamics. In a review of 150 papers, trophic cascades were found in 60% of studies that manipulated the abundance of an organism (e.g., phytoplankton, zooplankton, amphipods).\textsuperscript{64}

The EPA method of evaluating toxicity takes into account the toxicity of individual compounds, which is based on the effect concentration (EC50) for the most sensitive marine organisms.\textsuperscript{32} Between May and July 2010, 11 of the 551 collected samples had a CPR>1, thereby exceeding the EPA threshold for a chronic exposure time of 4 days. However, because the wellhead was leaking for 87 days, it is possible that a CPR below the threshold was still harmful, as a result of the long exposure time. Multiple studies have documented the mortality of and significant sublethal effects on marine organisms after long-term PAH exposure (Table 5).\textsuperscript{33–36}

Using data from references that examined effects of low-level PAH exposure, we estimated that PAH concentrations above 0.3 µg/L could have impacted marine life in the GoM, and we classified these sites as “potentially impacted” (N=100; Table 5). Using the same interpolation method that was used for BTEX concentrations, we approximated this “potentially impacted” area to be 1000 km\textsuperscript{2} (Figure 5). However, half of this area was due to high concentrations at one site. Therefore, an estimated impacted area range is between 500 and 1000 km\textsuperscript{2}. 


Table 5: Proposed PAH concentrations (µg/L) that may impact marine organisms. Numbers in parentheses are corresponding CPR values.

<table>
<thead>
<tr>
<th>Description</th>
<th>No Impact</th>
<th>Low Impact</th>
<th>High Impact</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proposed PAH range categories (this study)</td>
<td>&lt; 0.3 (0 - 0.2) N=409</td>
<td>0.3 - 17.9 (0 - 0.7) N=100</td>
<td>17.9 - 70 (0.7 - 3.5) N=42</td>
<td></td>
</tr>
<tr>
<td>Current EPA Criteria (this study)</td>
<td>nd - 28.5 (&lt; 1) N=540</td>
<td>17.9 - 70.0 (1 - 3.5) N=11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aas et al., 2000</td>
<td>N/A</td>
<td>0.3 - 7.8</td>
<td>&gt; 7.8 (0.24)</td>
<td></td>
</tr>
<tr>
<td>Carls et al., 1999</td>
<td>N/A</td>
<td>0.4 - 0.7</td>
<td>&gt; 0.7</td>
<td></td>
</tr>
<tr>
<td>Heintz et al., 1999</td>
<td>N/A</td>
<td>0.7 - 18</td>
<td>&gt; 18</td>
<td></td>
</tr>
<tr>
<td>Heintz et al., 2000</td>
<td>N/A</td>
<td>5.2 - 19.4 (0.2)</td>
<td>&gt; 19.4 (0.4)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5: Interpolated surface showing “potentially impacted” and “impacted” areas at 1000–1300 m depth, using data collected from May 10–July 15, 2010.
Fate of the Subsurface Oil

Following the DWH blowout in the GoM, Montagna et al. (2013) found severely decreased benthic invertebrate diversity and abundance in the sediments extending 3 km from the wellhead, and a moderate decrease up to 17 km from the wellhead. These effects were correlated with PAH concentrations, as well as distance from the wellhead.19 The 170 km² impacted area found by Montagna et al. (2013) is entirely encompassed by the intrusion area estimated by this study. Evidence for sediment contamination is also seen in our study, with high concentrations found just above the sediment-water interface between October and December 2010 (Figures 2 and 3).

If PAHs were deposited in sediments, they could continue to be resuspended into the water column, becoming repeatedly bioavailable to organisms.65 Re-suspension has been observed in multiple study areas, including San Francisco Bay, the Mediterranean Sea, and the Saudi Arabian coast.66–68 Engraff et al. (2011) showed that lethality from exposure to the PAHs phenanthrene, fluoranthene, and pyrene continuously increased over of a period of 9 days for two benthic amphipod species.69

A second mechanism for sediment exposure is the direct contact of the intrusion with the sediment surface. Locations to the north and west of the wellhead, where the sediment depth was between 1000 and 1300 m, may have seen direct contact with the intrusion. Assuming that this was the case, we assumed that the intrusion area (Figure 3) where the depth was between 1000 and 1300 m depth may have been exposed to hydrocarbons in the intrusion. This corresponded to a sediment area of 400 km².
Conclusions

This study expanded on previous knowledge regarding the subsurface intrusion that formed during the DWH oil spill. Using data from 590 water column profiles, we showed a well-defined intrusion between 1000 and 1300 m depth. Using a spline interpolation, and BTEX concentrations measured in 551 water samples that were collected between May and July 2010, we estimated that the overall extent of the intrusion was 1600 km$^2$. Furthermore, we showed that, while the amount of oil in the intrusion decreased slightly from May to June/July, elevated hydrocarbon concentrations were still present in late August, weeks after the wellhead had been capped.

We used ratios that are typically used to identify an oil source, such as the Pyrogenic Index and An/(Phen+An), to show that pyrogenic PAHs may have reached the intrusion between 1000 and 1300 m. The ratios C17/pristane and C18/phytane showed evidence of degradation in the intrusion, and depletion ratios relative to $^{17}$α(H),$^{21}$β(H)-Hopane show that soluble, dissolved compounds were present for longer than insoluble microdroplets. There were considerable differences in these ratios between May, June, and July 2010, and we hypothesize that those differences may be due to the use of the Lower Marine Riser Package (LMRP) that was placed over the wellhead and used to collect oil from June 3, 2010 through July 10, 2010.

We also suggested that using the standard EPA method for determining toxicity may underestimate the overall impact area, based on long-term PAH exposure studies that were done in light of the Exxon Valdez oil spill in 1989. In this dataset, water column samples with a CPR
greater than 1 corresponded to samples with a total PAH concentration greater than 28 µg/L. However, Aas et al. (2000) exposed Atlantic Cod (Gadus morhua) to oil for 30 days and showed that PAH concentrations as low as 0.3 µg/L caused the formation of DNA adducts and the induction of the gene CYP1A. These are both biomarkers for PAH exposure, and have been correlated with more negative effects. Given the findings of these studies, the EPA’s current toxicity thresholds may be too high. This is especially true because GoM organisms may have been exposed to elevated PAHs and BTEX for up to 120 days, but EPA chronic toxicity criteria are based on an exposure time of 4 days. Therefore, we classified sites with a PAH concentration greater than 0.3 µg/L as “potentially toxic”. This total area was estimated to be between 500 and 1000 km².

Finally, we hypothesized that the hydrocarbon intrusion may have reached the GoM sediments by two different mechanisms, the first being the aggregation and sinking of oil and other organic particles, and the second being direct impingement where the water depth was less than 1300 m. Benthic organisms in sediments impacted by either or both of these processes could have experienced adverse effects from both acute and chronic PAH exposure.
References


(2) Oil Budget Calculator Science and Engineering Team Oil Budget Calculator: Deepwater Horizon; 2010; pp. 1–217.


(24) Joint Analysis Group (JAG) _Initial Quality Control of Analytical Chemistry Data from Water Samples Taken in the Vicinity of MC252#1_; 2010; pp. 1–65.


(47) National Response Team *On Scene Coordinator Report Deepwater Horizon*; 2011.


(56) Souza-Bastos, L. R.; Freire, C. a Osmoregulation of the Resident Estuarine Fish Atherinella Brasiliensis Was Still Affected by an Oil Spill (Vicuña Tanker, Paranaguá Bay, Brazil), 7 Months after the Accident. *The Science of the total environment 2011*, 409, 1229–34.


Appendix A:

Changes in PAH Distributions with Distance

In an effort to investigate weathering rates, and changes over distance, all water samples (between 1000 and 1300 m) with elevated PAH concentrations were grouped into the following distances from the wellhead: 0-2 km (N=68), 5-10 km (N=44), 10-15 km (N=20), 15-20 km (N=20), 43 km (N=1), and 160 km (N=1). The ratios investigated were LMW (2-3 rings)/HMW (4-5 rings) PAHs, N3/P2 (C3-naphthalenes/C2-phenanthrenes; an appropriate weathering ratio),\(^{39}\) and overall PAH distributions.

The % depletion for each PAH was calculated relative to samples collected within 2 km of the wellhead. The samples collected within 2 km wellhead with elevated PAH concentrations were assumed to be in the intrusion (and therefore had already undergone the soluble-dependent fractionation described in Reddy et al., 2011). They were also assumed to contain oil that had been recently released from the wellhead, and was therefore not weathered. The following equation, where \([\text{PAH}]_{\text{water}}\) and \([\text{Hopane}]_{\text{water}}\) are the concentrations of those constituents in a sample, and \([\text{PAH}]_{\text{source}}\) and \([\text{Hopane}]_{\text{source}}\) are the averages concentrations from samples collected between 0 and 2 km from the wellhead, was used:

\[
\% \text{ weathering} = \left( 1 - \frac{[\text{PAH}]_{\text{water}}}{[\text{PAH}]_{\text{source}}} \times \frac{[\text{Hopane}]_{\text{source}}}{[\text{Hopane}]_{\text{water}}} \right) \times 100
\]
**Figure 6:** Changes in ratios of LMW to HMW PAHs with distance from wellhead.

**Figure 7:** The average percent depletion for all PAHs in all samples (N=68) collected between 2 and 5 km from the wellhead.
Figure 8: The average percent depletion for all PAHs in all samples (N=44) collected between 5 and 10 km from the wellhead.

Figure 9: The average percent depletion for all PAHs in all samples (N=20) collected between 10 and 15 km from the wellhead.
Figure 10: The average percent depletion for all PAHs in all samples (N=20) collected between 15 and 20 km from the wellhead.

Figure 11: The average percent depletion for all PAHs in a sample collected 43 km from the wellhead.
**Figure 12:** The average percent depletion for all PAHs in a sample collected 160 km from the wellhead.

**Figure 13:** The weathering ratio $N_3/P_2$ versus distance from wellhead. Points represent the following groups of samples: 0-2 km ($N=68$), 5-10 km ($N=44$), 10-15 km ($N=20$), 15-20 km ($N=20$), 43 km ($N=1$), and 160 km ($N=1$).
We also selected a single transect with samples that were collected at roughly the same
time (between May 31 and June 3), but at different distances from the wellhead. PAH
distributions were examined because parental PAHs degrade faster than alkylated PAHs.
Degradation will also cause an increase in relative amounts of HMW PAHs.\footnote{40,52}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14}
\caption{Transect of samples collected between May 31 and June 3, between 1000 and 1300 m depth. These samples were used to investigate distance as a variable.}
\end{figure}
Figure 15: The average concentration (µg/L) for all PAHs the sample collected 2.3 km from the wellhead (Figure 6).
Figure 16: The average concentration (µg/L) for all PAHs the sample collected 5.8 km from the wellhead (Figure 6).
Figure 17: The average concentration (µg/L) for all PAHs the sample collected 9.5 km from the wellhead (Figure 6).
Figure 18: The average concentration (µg/L) for all PAHs the sample collected 11.5 km from the wellhead (Figure 6).
Figure 19: The average concentration (µg/L) for all PAHs the sample collected 14.3 km from the wellhead (Figure 6).
Figure 20: The average concentration (µg/L) for all PAHs the sample collected 15.5 km from the wellhead (Figure 6).
The same data from Figures 15–20 is represented below in Figures 21–27, with PAH distributions shown in percentages rather than absolute values.

**Figure 21**: The average composition (% of total PAHs) for each PAH in the sample collected 2.3 km from the wellhead (Figure 6).
Figure 22: The average composition (% of total PAHs) for each PAH in the sample collected 5.8 km from the wellhead (Figure 6).
Figure 23: The average composition (% of total PAHs) for each PAH in the sample collected 9.5 km from the wellhead (Figure 6).
Figure 24: The average composition (% of total PAHs) for each PAH in the sample collected 11.5 km from the wellhead (Figure 6).
Figure 25: The average composition (% of total PAHs) for each PAH in the sample collected 12.1 km from the wellhead (Figure 6).
Figure 26: The average composition (% of total PAHs) for each PAH in the sample collected 14.3 km from the wellhead (Figure 6).
Figure 27: The average composition (% of total PAHs) for each PAH in the sample collected 15.5 km from the wellhead (Figure 6).
Figure 28: The ratio N3/P2 versus distance from the wellhead, using samples shown in Figure 6.

Figure 29: The ratio D3/C3 versus distance from the wellhead, using samples shown in Figure 6.
Figure 30: The % of 2-ring PAHs relative to total PAH concentrations versus distance from the wellhead, using samples shown in Figure 6.

Figure 31: The ratio of benzene to toluene versus distance from the wellhead, using samples shown in Figure 6.
Figure 32: The ratio of benzene to ethylbenzene versus distance from the wellhead, using samples shown in Figure 6.
Appendix B:

Changes in PAH Distributions with Time

We also chose a site 2 km from the wellhead (28.732022, -88.376802) that had samples collected on different dates, to look for changes over time. All samples used for this were collected between 1000 and 1300 m depth.

Figure 33: Fractionation of selected PAHs relative to benzene versus date collected.
**Figure 34:** Concentration (µg/L) of naphthalenes versus date collected.

**Figure 35:** Ratio N3/P2 versus date collected.
Figure 36: Ratio D3/C3 versus date collected.

Figure 37: The % of 2-ring PAHs relative to total PAH concentrations versus date collected.
Figure 38: Ratio of benzene/toluene versus date collected.

Figure 39: Concentration (µg/L) of each PAH in the sample collected on 05/15/10 at 28.732022, -88.376802.
**Figure 40:** Concentration (µg/L) of each PAH in the sample collected on 05/16/10 at 28.732022, -88.376802.

**Figure 41:** Concentration (µg/L) of each PAH in the sample collected on 05/17/10 at 28.732022, -88.376802.
**Figure 42:** Concentration (µg/L) of each PAH in the sample collected on 05/20/10 at 28.732022, -88.376802.

**Figure 43:** Concentration (µg/L) of each PAH in the sample collected on 05/23/10 at 28.732022, -88.376802.
Figure 44: Concentration (µg/L) of each PAH in the sample collected on 05/25/10 at 28.732022, -88.376802.

Figure 45: Concentration (µg/L) of each PAH in the sample collected on 05/30/10 at 28.732022, -88.376802.
Figure 46: Concentration (µg/L) of each PAH in the sample collected on 06/05/10 at 28.732022, -88.376802.

Figure 47: Concentration (µg/L) of each PAH in the sample collected on 06/25/10 at 28.732022, -88.376802.